PROCEEDINGS OF THE INTERNATIONAL SYMPOSIUM
ON RADIATION VULCANIZATION OF NATURAL
RUBBER LATEX

January 1990

(Ed.) Sueo MACHI
JAERI-Mレポートは、日本原子力研究所が不定期に公刊している研究報告書です。
入手の問い合わせは、日本原子力研究所技術情報部情報資料課（〒319-11茨城県取手郡東
海村）あて、お申しこしください。なお、このほかに財団法人原子力弘済会資料センター
（〒319-11茨城県取手郡東海村日本原子力研究所内）で複写による実費領布をおこなって
おります。

JAERI-M reports are issued irregularly.
Inquiries about availability of the reports should be addressed to Information Division
Department of Technical Information, Japan Atomic Energy Research Institute, Tokai-
mura, Naka-gun, Ibaraki-ken 319-11, Japan.

© Japan Atomic Energy Research Institute, 1990

発行 部 日本原子力研究所
印刷 いばらき印刷㈱
Proceedings of the International Symposium on
Radiation Vulcanization of Natural Rubber Latex

(Ed.) Sueo MACHI

Takasaki Radiation Chemistry Research Establishment
Japan Atomic Energy Research Institute
Watanuki-cho, Takasaki-shi, Gunma-ken
(Received December 23, 1989)

The First International Symposium on Radiation Vulcanization of
Natural Rubber Latex (RVNRL) was held from 26 to 28 July 1989 at Tokyo
and Takasaki. In these proceedings, thirty six papers presented at
the Symposium are compiled. Main topics are commercial application of
RVNRL, characterization of NR latex and vulcanization, properties of
radiation vulcanized NR latex, development of sensitizers, mechanism
of RVNRL, RVNR with electron beams, and new Co-60 irradiator for RVNRL.
Absence of nitrosamines and low cytotoxicity of radiation vulcanized NR
latex are recognized as the remarkable advantages of RVNRL. The radia-
tion vulcanization process for the production of protective rubber
gloves for radioactive contamination was presented as the first
commercial success in RVNRL. It was reported that various kinds of
rubber articles for medical uses have being developed in West Germany.
A sensitizer system consisting of n-butyl acrylate and t-butyl
hydroperoxide was found to reduce the vulcanization dose to 8 kGy.

Keywords: Radiation Vulcanization, Natural Rubber, Latex, Proceedings,
Symposium
EDITOR

Editor-in-Chief

S. MACHI
Japan Atomic Energy Research Institute
Japan

Editors

F.R. AL-SIDDIQUE
Bangladesh Atomic Energy Commission
Bangladesh

E.V. THOMAS
Rubber Board
India

F. SUNDARDI
National Atomic Energy Agency
Indonesia

K. MAKUUCHI
Japan Atomic Energy Research Institute
Japan

SIDEK DULNGALI
Rubber Research Institute of Malaysia
Malaysia

S.W. KARUNARATNE
Rubber Research Institute of Sri Lanka
Sri Lanka

CHYAGRIT S.
Chulalongkorn University
Thailand
Organizing Committee

Chairman
S. Machi

Manoon A.
V. Markovic
Y. Tabata
T. Yoshimoto
K. Kokubu
K. Yokokawa
W. Kawakami

Japan Atomic Energy Research Institute
International Atomic Energy Agency
International Atomic Energy Agency
Japanese Society of Radiation Chemistry
Society of Rubber Industry, Japan
Japan Atomic Industry Forum
Japan Atomic Energy Research Institute
Japan Atomic Energy Research Institute

Secretariat

Secretary General
W. Kawakami

M. Washino
I. Shigaki
K. Makuuchi
T. Sasaki

Japan Atomic Energy Research Institute
Japan Atomic Energy Research Institute
Japan Atomic Energy Research Institute
Japan Atomic Energy Research Institute
Japan Atomic Energy Research Institute

天然ゴムラテックスの放射線加硫に関する
国際シンポジウム論文集

日本原子力研究所高崎研究所
（編）町 未男

（1989年12月25日受理）

平成元年7月に開催された天然ゴムラテックスの放射線加硫に関する国際シンポジウムのブローディングである。口答で発表された招待講演3，特別講演6，一般講演27の計36報を編集し掲載した。主な内容は以下のとおりである。1）放射線で加硫した天然ラテックスゴムは、細胞毒性が低く、発癌性物質であるエトロソアミンも含まない。2）また、放射線加硫天然ラテックスゴムは硫黄と酸化亜鉛を含まないため、焼却時に亜硫酸ガスが発生せず、灰も残らない。さらにこのゴムは柔らかく、透明性が高いという特長もある。3）この特長を活用し、放射線加硫天然ラテックスからの放射性汚染防護用ゴム手袋が日本で実用化された。これは、世界で初めての実用化例である。4）また、電子線で加硫した天然ラテックスを用いて、医療用や玩具向け製品など、さまざまな用途でゴム製品が開発されつつある。5）電子線による加硫には経済性があり、r線よりも加硫線量が高くなる。6）天然ゴムラテックスを8kGyのr線で加硫する促進剤が開発された。7）千トン/年以上の加硫施設の概念設計が完成した。
CONTENTS

PREFACE ................................................................................................................. 1

1. ADDRESS OF WELCOME .................................................................................. 3
   1.1 Address of Welcome 1 ................................................................. 5
       MASAKO KOBAYASHI, Ministry of Foreign Affairs, Japan
   1.2 Address of Welcome 2 ................................................................. 7
       HIROSHI FUJITA, Science and Technology Agency, Japan
   1.3 Address of Welcome 3 ................................................................. 9
       MANOON ARAMRATTANA, IAEA

2. OPENING ADDRESS ......................................................................................... 13
   2.1 Opening Address .................................................................................. 15
       MASAJI YOSHIKAWA, JAERI

3. INVITED PAPER ............................................................................................... 17
   3.1 New Trends in Radiation Processing Application in Japan ..................... 19
       SUEO MACHI
   3.2 The Natural Latex Industry and Its Future Prospects ......................... 27
       T. D. PENDLE
   3.3 Characteristic Elastomers Derived from Functional Substances ........... 42
       SHINZO YAMASHITA

4. SPECIAL PAPER ............................................................................................... 77
   4.1 Radiation Vulcanized Natural Rubber Latex is Not Cytotoxic .............. 79
       AKITADA NAKAMURA, Y. Ikarashi, T. Tsuchiya, and M. Kaniwa
   4.2 Development of Optical Laser Balloon and Drainage from Radiation Vulcanized Natural Rubber Latex .......... 88
       YOSHIYUKI SHIMAMURA
   4.3 Progress in Radiation Vulcanization of Natural Rubber Latex through International Cooperation .................. 91
       KEIZO MAKUUCHI
   4.4 Latex Industry and RVNRL Development in Malaysia ....................... 100
       SIDEK BIN DULNGALI
   4.5 RVNRL in Europe .................................................................................... 111
       HARALD NIEPEL
4.6 Use of Radiation Vulcanized Natural Rubber Latex in Small and Mediu... 118
    Medium Scale Industries in Sri Lanka
S. W. KARUNARATNE

5. CONTRIBUTED PAPER ...................................................... 125

COMMERCIAL APPLICATION OF RVNRL .................................. 127

5.1 Commercialization of Protective Rubber Gloves by Radiation
        Vulcanization ....................................................... 127
        KYOGO TSUSHIMA, K. Makuuchi, F. Yoshii, and I. Ishigaki

5.2 Development of Condom and Gloves from Radiation
        Vulcanized Natural Rubber Latex .................................. 132
        F. SUNDARDI, Marga Utama, S. Iskandar, and Herwinarni

5.3 Commercial Irradiation of Natural Rubber Latex ................. 146
        T. Saito, G. Koike, Y. Sato, and MASAAKI TAKEHISA

CHARACTERIZATION OF NR LATEX AND VULCANIZATION ........ 157

5.4 Effect of Non-Rubber Components on Sensitized RVNRL .... 157
        NORJANAH MOHID, K. Makuuchi, F. Yoshii and I. Ishigaki

5.5 Selection of Thai Latex for Radiation Vulcanization .... 164
        CHYAGRIT SIRI–UPATHUM, Krisda Suchiva, and Jindarom
        Chwajarenpun

5.6 Characteristics of Natural Rubber Latex from Indonesia . 169
        MARGA UTAMA, F. Sundardi, Herwinarni, M. Sumarti,
        S. Iskandar, D. Irmanani, K. Makuuchi and F. Yoshii

5.7 Effect of Non-Rubber Solids and Stabilizing Agents on Radiation
        Vulcanization of Natural Rubber Latex ......................... 178
        E.V. THOMAS

PROPERTIES OF RADIATION BULCANAIZED NR LATEX ............ 189

5.8 Technological Evaluation of Radiation Pre-Cured NR Latex .... 189
        K.F. Gazeley and T.D. PENDLE

5.9 Thermoplastic Elasomers by Radiation Grafting on NR Latex
        and Its Extrusion molding ...................................... 198
        SEIJI ONO, F. Yoshii, K. Makuuchi and I. Ishigaki

5.10 Effect of Coagulant on Mechanical Properties of Radiation
        Vulcanized NR Latex Film ........................................ 207
        T. Saito, FUMIO YOSHII, K. Makuuchi and I. Ishigaki

5.11 Effect of Heating and Leaching on Mechanical Properties of
        Radiation Vulcanized Natural Rubber Latex Film ............ 216
        SHUKRI BIN HJ. AB. WAHAB, K. Makuuchi, R. Devendra
5.12 Standardization of Radiation Vulcanized Natural Rubber Latex .......... 225
   S.W. KARUNARATNE

5.13 Effect of Antioxidant on the Aging Property of Rubber Film
   Prepared from Radiation Vulcanized Natural Rubber Latex .......... 234
   Dedik Eko Sumbogo, F. SUNDARDI and Marga Utama

5.14 Stabilization of Radiation Vulcanized Natural Rubber Latex Film .......... 245
   SHUKRI BIN HJ. AB. WAHAB and Siti S.B. Sulaiman,
   K. Makuuchi, R. Devendra and Pansa Chuoy-Plong

5.15 Development of Surgical Gloves from Radiation Vulcanized
   Natural Rubber Latex ........................................ 260
   NGUYEN QUOC HIEN, Doan Binh, Vo Tan Thien,
   Le Hai, Nguyen Tan Man and Vo Thi Thanh

5.16 Sensitization in Radiation Grafting, Curing and Vulcanization
   Processes ......................................................... 268
   J.L. GARNETT, P.A. Dworjanyn, S.J. Bett, and H.P. Dang

DEVELOPMENT OF SENSITIZER AND VULCANIZATION MECHANISM

5.17 Combination Effect of Carbon Tetrachloride with 2-Ethylhexyl
   Acrylate as a Sensitizer for Radiation Vulcanization of Natural
   Rubber Latex .................................................. 290
   RANSI DEVENDRA and K. Makuuchi

5.18 Selection of Hydroperoxides as Co-Sensitizer for n-Butyl Acrylate .......... 305
   PARINYA AROONVISOOT and K. Makuuchi

5.19 Effect of Hydrogen Peroxide on the Radiation Vulcanization
   of Natural Rubber Latex Sensitized with Carbon Tetrachloride
   and n-Butyl Acrylate ......................................... 319
   YANTI S. SOEBIANTO and F. Sundardi

5.20 n-Butyl Acrylate as a Sensitizer for Radiation Vulcanization
   of Natural Rubber Latex ....................................... 326
   CHEN ZHONGHAI and K. Makuuchi

5.21 Radiation Vulcanization Mechanism of Liquid Isoprene with
   2-Ethylhexyl Acrylate ......................................... 336
   CHYAGRIT SIRI-UPATHUM, K. Makuuchi and I. Ishigaki

RVNRL WITH ELECTRON BEAMS AND NEW IRRADIATOR FOR RVNRL

5.22 Radiation Vulcanization of Natural Rubber Latex Using 300 keV
   Electron Beam Machine ....................................... 350
W. Sofiarti, F. Sundardi and MARGA UTAMA

5.23 Radiation Vulcanization of Natural Rubber Latex with 3 MeV
Electron Beams (Part 1) ........................................ 358
CHEN ZHONGHAI and K. Makuuchi

5.24 Radiation Vulcanization of Natural Rubber Latex with 3 MeV
Electron Beams (Part 2) ........................................ 368
SAMANTHA S. SOORIYAAARACHCHI K. Makuuchi, F. Yoshii
and I. Ishigaki

5.25 Application of RVNRL in Europe ............................. 378
WILLFRIED BEZ

5.26 An Alternative Option Study of Malaysian Latex Irradiator ............ 383
MUHD. NOOR BIN MUHD. YUNUS

5.27 Improved Dry Type Irradiator .................................. 395
Workshop for Uses of Radiation, Japan Atomin Industrial Forum

6. SUMMING-UP ADDRESS ........................................... 405

6.1 Summing-up Address .............................................. 407
VITOMIR MARKOVIC, IAEA

AUTHOR INDEX ...................................................... 411

(Note: Name typed in block letters indicates speaker.)
目 次

序 言 ........................................................................................................................................ 1

1. 歓迎の辞 .................................................................................................................................. 3
   1.1 歓迎の辞・1 .......................................................................................................................... 5
       小林 政子（外務省国際連合局）
   1.2 歓迎の辞・2 .......................................................................................................................... 7
       藤田 浩（科学技術庁）
   1.3 歓迎の辞・3 .......................................................................................................................... 9
       MANOON ARAMRATTANA（国際原子力機関）

2. 開会の辞 .................................................................................................................................. 13
   2.1 開会の辞 ................................................................................................................................ 15
       吉川 允二

3. 招待講演 .................................................................................................................................. 17
   3.1 これからの放射線プロセス ..................................................................................................... 19
       町 未男
   3.2 天然ゴムラテックス工業の将来 ............................................................................................... 27
       T. D. PENDLE
   3.3 高機能性エラストマー ......................................................................................................... 42
       山下 聡三

4. 特別講演 .................................................................................................................................. 77
   4.1 放射線加硫ラテックスは細胞毒性がない ................................................................................... 79
       中村 晃一，五十嵐良行，土屋 利江，鶴庭 正昭
   4.2 放射線加硫ラテックスを用いたレーザーバルーン及びドレナージの開発 ............................ 88
       島村 善行
   4.3 国際協力による天然ゴムラテックスの放射線加硫の進歩 ..................................................... 91
       潤内 恵三
   4.4 マレーシアにおける天然ゴムラテックス工業と放射線加硫 ................................................ 100
       SIDEK BIN DULNGALI
   4.5 ヨーロッパにおける放射線加硫への期待 ............................................................................... 111
       HARALD NIEPEL
5. 一般論
放射線加硫ラテックスの実用化
5.1 放射線加硫による防護用ゴム手袋の実用化
対馬 恭吾, 關内 恵三, 吉井 文男

放射線加硫ラテックスからのコンドームと手術用手袋の開発
F. SUNDARDI, Marga Utama, S. Iskandar, Herwinarni

5.2 天然ゴムラテックスの商業的照射

天然ゴムラテックスのキャラクタリゼーションと放射線加硫特性
5.4 増感放射線加硫における非ゴム成分の影響
NORJANAH MOHID, 闕内 恵三, 吉井 文男

放射線加硫用タイラテックスの選定
CHYAGRIT SIRI-UPATHUM, Krisda Suchiva, Jindarom
Chwajarenpun

5.5 インドネシア産天然ゴムラテックスの特性
MARGA UTAMA, F. Sundardi, Herwinarni, M. Sumarti,
S. Iskandar, D. Iramani, 闕内 恵三, 吉井 文男

5.6 天然ゴムラテックスの放射線加硫に対する非ゴム成分及び安定剤の影響
E. V. THOMAS

放射線加硫ラテックスの性質
5.8 放射線加硫天然ゴムラテックスの技術的評価
K. F. Gazeley, T. D. PENDLE

放射線加硫天然ラテックスゴムの熟可塑性の性質
小野 清治, 吉井 文男, 闕内 恵三, 石垣 功

放射線加硫天然ゴムラテックスフィルムの機械的性質に対する凝固剤の影響
斎藤 敏夫, 吉井 文男, 闕内 恵三, 石垣 功

放射線加硫天然ゴムラテックスフィルムの安定化
SHUKRI BIN HJ. AB. WAHAB, Siti S. B. Sulaiman,
闕內 恵三, R. Devendra, Pansa C-P.

放射線加硫天然ゴムラテックスの標準化
S. W. KARUNARATNE

放射線加硫天然ゴムラテックスフィルムの老化に及ぼす老化防止剤の影響
Dedik Eko Sumbogo, F. SUNDARDI, Marga Utama

放射線加硫天然ゴムラテックスフィルムの機械的性質に対する加熱及び
水洗の影響
SHUKRI BIN HJ. AB. WAHAB, 闕内 恵三, R. Devendra,
Pansa C-P.

5.15 放射線加硫ラテックスからの手術用ゴム手袋の開発 ............................... 260
NGUYEN QUOC HIEN, Doan Binh, Vo Tan Thien, Le Hai,
Nguyen Tan Man, Vo Thi Thanh

5.16 放射線グラフト、キュアリング、加硫における増感 .................................. 268
J. L. GARNETT, P. A. Dworjanyn, S. J. Bett, H. P. Dang

放射線加硫促進剤の開発と加硫機構  ............................................................. 290

5.17 天然ゴムラテックスの放射線加硫における四塩化炭素とアクリル酸 2
- エチルヘキシルの併用効果 ................................................................. 290
RANSI DEVENDRA, 壁内 恵三

5.18 アクリル酸n-プチルの助促進剤としてハイドロバーキサイドの選定 .............. 305
PARINYA AROONVISOOT, 壁内 恵三

5.19 四塩化炭素とアクリル酸n-プチルで増感された天然ゴムラテックスの
放射線加硫における過酸化水素の影響 ...................................................... 319
YANTI S. SOEBIANTO, F. Sundardi

5.20 天然ゴムラテックスの放射線加硫促進剤としてのアクリル酸n-プチル .......... 326
陳 忠海，壁内 恵三

5.21 液状ポリイソブレンのアクリル酸2-エチルヘキシルによる放射線加硫機構 ....... 336
CHYAGRIT SIRI-UPATHUM, 壁内 恵三，石垣 功

電子線による加硫及び新しい照射施設 ......................................................... 350

5.22 300 keV 電子加速器による天然ゴムラテックスの加硫 ......................... 350
W. Sofiarti, F. Sundardi, MARGA UTAMA

5.23 3 MeV 電子線による天然ゴムラテックスの加硫（第1部） ......................... 358
陳 忠海，壁内 恵三

5.24 3 MeV 電子線による天然ゴムラテックスの加硫（第2部） ......................... 368
SAMANTHA S., 壁内 恵三，吉井 文男，石垣 功

5.25 放射線加硫天然ゴムラテックスのヨーロッパにおける応用 ......................... 378
WILLFRIED BEZ

5.26 マレインシアにおける天然ゴムラテックス照射施設 ................................ 383
MUHD NOOR BIN MUHD YUNUS

5.27 乾式照射施設の改良 ........................................................................... 395
原産会議照射利用研究会ワーキンググループ

6. 発表の要約 ......................................................................................... 405

6.1 要約報告 .......................................................................................... 407

VITOMIR MARKOVIC（国際原子力機関）

発表者索引 .................................................................................................. 411
PREFACE

Radiation vulcanization of natural rubber latex (RVNRL) is the technology of radiation-induced crosslinking of cis-polyisoprene in an aqueous dispersed phase. Evaporation of water from the irradiated latex brings about the adhesion of rubber particles and consequently the formation of homogeneously crosslinked rubber films. The mechanisms of radiation-induced crosslinking in the dispersed phase and the structure of crosslinks are further subjects of the fundamental research of RVNRL. Technology of RVNRL includes techniques of latex irradiation and utilization of RVNRL.

The research on RVNRL was began in 1966 in Japan and the RVNRL technology had been studied later in French and other countries. The RVNRL technology has been developed as the Regional UNDP project of RCA/IAEA for the Application of Isotopes and Radiation technology. The Project aims at producing economical and social benefits of the participating countries by the use of isotopes and radiation technology. The Japan Atomic Energy Research Institute (JAERI) has been contributed to the project since the beginning of the Project in 1981. Countries participating RVNRL Project are Peoples' Republic of China, Malaysia, Indonesia, Thailand, Bangladesh, India, Sri Lanka, Vietnam, and Japan. Remarkable progress in the RVNRL technology has been achieved in the reduction of irradiation cost and improving the quality of manufactured products from radiation vulcanized NR latex. The IAEA and JAERI therefore organized an International Symposium on RVNRL to review the progress and to exchange the information. The Symposium was held in Tokyo and Takasaki from 26 to 28 July 1989. About 120 participants from 16 countries attended the Symposium and presented 36 papers which are complied in these Proceedings.

Several aspects of RVNRL were discussed from view points of new trends in radiation processing and the future prospects of natural rubber latex industry at the Symposium. The main topics of the Symposium were:

Commercial application of RVNRL,
Characterization of NR latex and RVNRL,
Properties of radiation vulcanized NR latex,
Mechanisms of RVNRL,
RVNRL by electron beams, and
New irradiator for RVNRL.

Intensive research to bring forth new economical application was also reported by participants from several countries. It was clearly shown that absence of nitrosamines, sulfur and zinc oxide and extremely low cytotoxicity are noticeable advantages of RVNRL. Many NR latex products produced from the radiation vulcanized NR latex were presented at the Symposium. Those are optical laser balloon, drainage, surgical gloves and condom. The production of protective rubber gloves for radioactive contamination in Japan was reported as the first success in commercial use of RVNRL in the world. Further development of RVNRL will be actively made aiming at its industrial use.

The JAERI and the IAEA gratefully acknowledge the active contribution of all participants to the Symposium as well as the cooperation of the Japanese Government, the Japan Atomic Energy Industrial Forum, the Society of Rubber Industry, Japan, and Japanese Society of Radiation Chemistry.

October 20, 1989

S. Machi
Takasaki Radiation Chemistry Research Establishment
JAERI
1. ADDRESS OF WELCOME
1.1 Address of Welcome

MASAKO KOBAYASHI, Ministry of Foreign Affairs, Japan

Distinguished experts, Ladies and Gentlemen

On behalf of the Government of Japan, I would like to express my heartfelt welcome to all the experts from RCA member countries and guest experts from United Kingdom and Germany participating the International Symposium on Radiation Vulcanization of Natural Rubber Latex.

I also wish to express my deepest gratitude to the Japan Atomic Energy Research Institute, the organizer of this symposium and to Dr. Manoon, the UNDP Industrial Project Coordinator for having kindly spared his time to attend this meeting and to deliver the opening remarks on behalf of the Agency.

My country has strongly supported this RCA sub-project of the UNDP Industrial Project since its participation in the agreement in 1978. Takasaki Institute, JAERI has largely contributed in promoting the implementation of this project. Particularly Dr. Makuuchi has been playing an active role in the development of the program activities and helped to ensure a fruitful outcome in various member countries. In this opportunity, I would like to express my sincere thanks for his continuous effort and devotion to this project and for his spirit of cooperation.

Production of a commercial product using radiation vulcanized rubber latex is one of the principal targets of the project RVNRL in the second phase. A remarkable results of the project were reported by Indonesia, Vietnam and Japan in the latest Working Group Meeting of RCA member countries held in Sydney last March. It was reported that a medical product had been produced and used in the family planning in Indonesia and that Japanese industry was producing surgical gloves. A delegate from Vietnam announced that his country had irradiated 400 kg latex which was being used in production runs. The current symposium not only provides us with an opportunity to exchange the latest
informations on research and development in the field but also offer an occasion to discuss the aspect on the commercial benefits and strategy in promoting the promulgation in industrial scene, for the technology developed by the experts should be well applied in industries and contributed to the economic development in the region.

Hoping that the symposium will be a momentum to enhance the possibilities of each participating expert, I expect it will result in the further prosperous activities in this sub-project in the future.

RCA is a valuable instrument shared by the IAEA and the member states to assist the transfer of modern technology in areas of common interest to member states, bringing greater scientific and social benefits to the region. Japan, therefore, intends to expand as much as possible its cooperation in the framework of the RCA.

With these words, in opening the symposium, I take pleasure in wishing you success in your discussion.
1.2 Address of Welcome 2

HIROSHI FUJITA, Science and Technology Agency, Japan

Distinguished participants, ladies and gentlemen

On behalf of the Science and Technology Agency, I would like to welcome distinguished delegates from many states attending this "International Symposium on Radiation Vulcanization of Natural Rubber Latex".

Our government has been a member state of RCA since 1978 and actively participated to the RCA projects, such as UNDP Industrial Project, medical applications and radiation protection. STA has supported and contributed these activities in cooperation with the Ministry of Foreign Affairs. Also, STA has been satisfied with excellent achievements of the RCA projects for technology transfer to many states.

In this respect, I would like to express our sincere thanks to the International Atomic Energy Agency for its efforts to guide the RCA activities.

Radiation technology in Japan is well accepted in industry and future growing in new applications. Radiation technology on vulcanization of natural rubber latex is one of very important applications closely related to our lines.

In Japan, research and development of radiation chemistry of natural rubber latex is implemented by JAERI, private industries, universities and national institutes. These organizations have actively contributed to RCA and will expand their contribution in future with the endorsement of the Japanese Government.

Invited participants, I hope that RCA is efficient vehicle for technology transfer and that this symposium will be fruitful and useful for planning of R&D programs in radiation vulcanization of natural rubber latex and future activities of RCA/UNDP Industrial Project.
Before closing my remarks, I sincerely hope that you will enjoy staying in Japan.

Thank you very much for your kind attention.
1.3 Address of Welcome 3

MANOON ARAMRATTANA, IAEA

Representative of Ministry of Foreign Affairs, 
Representative of Science and Technology Agency, 
Executive Director of Japan Atomic Energy Research Institute, 
Distinguished Invited Lecturers, 
Distinguished National Research Group Leaders on RVNRL, 
Distinguished Participants, and 
Ladies and Gentlemen:

Applications of isotopes and radiation for developments of health, agriculture, industry and environmental well beings have been one of the main policies of the International Atomic Energy Agency (IAEA) since its establishment over 30 years ago. Any development and achievement under the policy guidelines are in the great interest of the IAEA and its Board of Governors. The achievements of the Technology Development Programme on Radiation Vulcanization of Natural Rubber Latex or RVNRL of this Project have been well recognized with great appreciation in the IAEA's Technical Cooperation Programme. On behalf of the Director General of the IAEA, I wish to express my cordial congratulations on the achievements of the Technology Development Programme. Particularly, I wish to express my gratitude to the Government of Japan for her leading role in the programme and for hosting this important seminar.

A new dimension of regional cooperation has been established once again within RCA where a new technology is jointly developed and shared by the participating countries. The role of National Research Groups and their leaders have been noted with respect of their endeavours, and their contributions to the current achievements of the Technology Development Programme have been praised of their great spirit of cooperation. In this respect, the Deputy Director General of Department of Technical Cooperation, Dr. Noramly bin Muslim, Director of Technical Assistance and Cooperation Division, Dr. Mohammad Ridwan, and the RCA Coordinator, Dr. P. Airey, wish to convey their cordial congratulations on the achievements of the Programme and their gratefulness to the contributions of the National Research Groups. Particularly, they wish to convey their gratitudes for the support of the Science and Technology
Agency through the Japan Atomic Energy Research Institute and its Takasaki Radiation Chemistry Research Establishment.

Ladies and Gentlemen, as a search for new material continues in hygienic product manufacturings worldwide, RWNRL has already found its way in protective glove manufacturing and is likely to find its way to a new plateau of applications in the near future. It was made known to us last May that the RWNRL is a prime candidate for a new material to revolutionize hygienic product standards and their manufacturing processes. I am sure you will hear more of its new properties leading to new applications in the course of this symposium. So, please make best use of your time here, make your views known to us, and enjoy your old and new friendships.

The Project is pleased and proud of the achievement of the Technology Development Programme on RWNRL so far. I would like, on behalf of the IAEA and my own behalf, to thank all the NRC leaders and Dr. K. Makuuchi, in particular, for the achievements. Their continued contributions will only assure of a successful technology transfer of the RWNRL to the developing participating countries and strengthening the overall regional cooperation under the RCA.

In this symposium, we recognize the value of views and suggestions from our invited lecturers and participants. With the same representation, I would like to thank them for their cooperation with the IAEA, and for their sharing of valuable experience.

Ladies and Gentlemen, organization of this symposium requires substantial planning and collaboration as well as cooperation among all parties concerned. On behalf of the IAEA and my own behalf, I would like to thank the staff of the Takasaki Radiation Chemistry Research Establishment for their initiatives as well as endeavors to make this symposium a successful one. Especially, I would like to cordially thank Dr. S. Machi, the Director General of the Takasaki Radiation Chemistry Research Establishment, for his support and without whom this symposium would not have been realized.

Finally, on behalf of the IAEA, I welcome you all to this
Symposium. The IAEA trusts and believes this meeting will mark a milestone in the development of RVNRL technology.

Thank you.
2. OPENING ADDRESS
2.1 Opening Address

MASAJI YOSHIKAWA, JAERI

Ladies and gentlemen

It is a great pleasure for the Japan Atomic Energy Research Institute (JAERI) and the International Atomic Energy Agency (IAEA) to open this International Symposium on Radiation Vulcanization of Natural Rubber Latex here in Japan today. This symposium is also supported by the Society of Rubber Industry, Japan, the Japan Atomic Industrial Forum, and the Japanese Society of Radiation Chemistry. We at JAERI, as the local organizer, would like to thank all those societies for their invaluable assistance in organizing this symposium. In particular, we would like to express our deepest appreciation to the IAEA for providing us with guidances and inspirations which are so much needed in organizing this kind of symposium with a wide scope of very interesting areas.

Ladies and gentlemen, I was told that this year marks the 150th anniversary of the invention of vulcanization of natural rubber by a use of sulphur. I think that it is quite fitting and appropriate to hold this symposium on a newer method of vulcanization of latex through a use of radiations, looking back those many years through which we have progressed in vulcanization technology.

Radiation vulcanization of natural rubber latex has been nominated by the IAEA as one of its research and development programs (UNDP/RCA program) for industrial utilization of radiations and isotopes, and since then active efforts have been pursued in this area in many Asean countries. Our country has been collaborating in this program from its early stage by sending experts and by inviting researchers from abroad. I am pleased here to inform you that, as a result of the efforts, test production of latex articles was started in Indonesia at a factory scale and basic research and product development studies are being made in Malaysia, Thailand, Bangladesh, India, Sri Lanka, People's Republic of China and Vietnam.
Now, what is the benefit which would result from radiation vulcanization? Since the vulcanization does not involve sulfur and zinc oxide, no ashes and sulfur dioxide gases are expected to result when the rubber is incinerated at the time of its disposal. The rubber is low in nitrosoamine and cytotoxicity and superior in softness and transparency. The latter characteristics are being exploited in medical applications for optical laser balloons, drinages and surgical gloves. I hear that Indonesia is developing such applications for medical and hygiene purposes and European countries such as West Germany have also a strong interest in these areas. I would like to note lastly that since this spring a Japanese company has started producing special gloves to be used in a radioactive environment such nuclear power plants, taking its previously mentioned advantage at the time of disposal.

During the present symposium there will be a number of papers, invited papers and special lectures on the radiation vulcanization of natural rubber latex and related areas. I expect, and indeed believe, that, when the symposium is over, you will go home richer in scientific understanding and technical knowledge. I would also hope that you will do so even richer in friendship, goodwill and collaborating spirit for the future of this program.

I now declare open the International Symposium on Radiation Vulcanization of Natural Rubber Latex.
3. INVITED PAPER
3.1 New Trends in Radiation Processing Application in Japan

SUEO MACHI

Japan Atomic Energy Research Institute
Takasaki Radiation Chemistry Research Establishment
Takasaki, Japan

1. Introduction

Research and development of radiation processing applications have been carried out for more than 30 years resulting industrial applications in new polymeric materials, surface conversion, medical products sterilization and food irradiation. Nowadays, about 180 electron beam machines and 10 Cobalt-60 facilities are used for radiation processing as shown in Table 1. Research and development have been carried out in Governmental institutes such as JAERI and private companies.

Environmental conservation is important task in Japan. Radiation processing for this purpose has been conducted. Radiation chemistry will provide fundamental theory to estimate the life time of organic materials used in nuclear plants under radiation. This paper reports the overview of up-to-date radiation applications and its future trends in Japan.

2. New Polymer Applications

2.1 New Drug Delivery System

Since radiation induced polymerization can be carried out even at very low temperature, drugs can be capsuled in polymer matrix by radiation induced polymerization without their thermal degradation. This gives new process to prepare drug delivery system. Slow release anti-cancer drugs prepared by radiation polymerization have been successfully tested in clinical use. Recently new drug delivery system containing insulin sensible to temperature was developed by our Institute. Scheme of the preparation is shown in Fig. 1. This polymer of proline methyl ester swells at 4°C and insulin release rate increases while at 35°C it shrinks and the release rate decreases as shown in Fig. 2. Morphology change is well demonstrated in picture of micrograph shown in Fig. 3. Release rate can be, then, controlled by temperature change.
2.2 Battery Separator

Graft polymerization by pre-irradiation method has been used for battery separator manufacturing in acrylic acid grafted polyethylene. This technology was developed by our Institute and transferred to industry. The separator is used for silver oxide battery and other secondary batteries and shows excellent life time, and its commercial production is increasing.

2.3 New Deodorant

New deodorant has been developed by our Institute by using radiation grafting of syrene and chloromethyl styrene onto polypropylene fiber followed by sulfonation and quaternization. These products have much higher capacity of deodorizing and adsorbs acidic and alkaline pollutants. Commercial production will be started in 1989 in Japan.

2.4 Crosslinked Polymers

Radiation crosslinking is widely used for polyethylene for wire insulation, heat shrinkable materials and foamed polyethylene. New products of radiation crosslinked materials have been developed by the Sumitomo Electric Industries, which are crosslinked polyurathane and nylon. Figure 4 shows excellent hot water resistance of the radiation crosslinked polyurathane used for cable of antilock brake sensor of automobile.

Radiation crosslinking of natural rubber latex has been studied in a project of Asian regional cooperation of IAEA. Better qualities of manufactured products in terms of transparency, less amount of ash and sulfur dioxide formation at insineration and less hazard to skin are produced by this process.

2.5 Curing of Surface Coating

This application is most widely used and still expanding in industries. Major applications are listed in Table 2. Further development of new applications will be expected in finding new formulation of coatings and substrates.
3. Environmental Conservation

3.1 SO$_2$ and NOx Removals from Stack Gases

Stack gas treatment to remove SO$_2$ and NOx by electron beams was first studied by the joint research of JAERI and Ebara Mfg. 17 years ago. Based on this research US Department of Energy had carried out pilot scale experiments to study commercial feasibility of this technology for coal combustion gases. The results indicate technology reliability and economic merit in comparison with conventional chemical treatment.

JAERI group has been studying basic research to support US DOE Project and further elucidate detail mechanism of reactions. Recently it was found that NOx is partially reduced to nitrogen in addition to the conversion to nitric acid. Reaction mechanism so far elucidated is summarized in Fig. 5.

A demonstration plant of commercial scale should be operated to study engineering terms and to show long time operation reliability.

3.2 Waste Water and Water Treatment

Waste water containing pollutants not degradable by biological treatment can be treated by radiation to reduce its COD. Chlorinated organic compounds polluting water can be efficiently removed by radiation in the presence of ozone. This technology can be used for treatment of raw drinking water and waste water. Extensive studies are conducted in JAERI Takasaki in this important field.

3.3 Sewage Sludge Treatment and Its Composting

In Japan more than 200 million tons of sludge is disposed from sewage treatment plants per year to land and ocean or incinerated to bring about environmental pollutions. Only 20% of sludge is used for farming land. Our group has studied the technology to disinfect sludge by electron beams and compost it efficiently. Pilot experiment has been carried out to show technical and economical feasibility of the technology.
4. Ion Beam Applications

A new project of ion beam applications and chemistry has been initiated in JAERI and four ion beam accelerators including AVF cyclotron will be installed in three years as shown in Fig. 6. Major research projects are (1) material science under space environment, (2) material science for nuclear fusion environment, (3) biotechnology application, (4) development of new functional materials and (5) new materials by ion implantation.
Table 1 Number of Electron Accelerator in Japan

<table>
<thead>
<tr>
<th>Application Field</th>
<th>Number</th>
<th>Energy (MeV)</th>
<th>Current (mA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Research &amp; Development</td>
<td>64</td>
<td>0.175 - 3.0</td>
<td>100</td>
</tr>
<tr>
<td>Curing</td>
<td>50</td>
<td>0.2 - 0.3</td>
<td>600</td>
</tr>
<tr>
<td>Wire &amp; Cable Insulation</td>
<td>38</td>
<td>0.3 - 2.0</td>
<td>100</td>
</tr>
<tr>
<td>Pre-Curing of Tire Rubber</td>
<td>9</td>
<td>0.5 - 0.8</td>
<td>220</td>
</tr>
<tr>
<td>Shrinkable Tube &amp; Sheet</td>
<td>8</td>
<td>0.3 - 3.0</td>
<td>100</td>
</tr>
<tr>
<td>Polyolefin Foam</td>
<td>6</td>
<td>0.5 - 1.0</td>
<td>100</td>
</tr>
<tr>
<td>Others</td>
<td>5</td>
<td>0.5 - 2.0</td>
<td>60</td>
</tr>
<tr>
<td>Total</td>
<td>180</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 2 EB Curing Processes in Japan

<table>
<thead>
<tr>
<th>Year</th>
<th>Product</th>
<th>Company</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1988/89</td>
<td>Precoated Steel PVC-Laminated</td>
<td>Nisshin Steel</td>
<td></td>
</tr>
<tr>
<td>1987/88</td>
<td>PCB (electro-conductive)</td>
<td>CMK</td>
<td></td>
</tr>
<tr>
<td>1986</td>
<td>Micro Floppy Discs</td>
<td>TDK</td>
<td></td>
</tr>
<tr>
<td>1986</td>
<td>Plastic Sheet Printing</td>
<td>Mitsumura Printing</td>
<td>175 keV, 300 mA</td>
</tr>
<tr>
<td>1985</td>
<td>Juice Carton Printing</td>
<td>Tetra Pak Japan</td>
<td>2 lines</td>
</tr>
<tr>
<td>1984</td>
<td>Gypsum Tile</td>
<td>Achilles</td>
<td>280 keV, 40 mA</td>
</tr>
<tr>
<td>1982</td>
<td>Precoated Steel</td>
<td>Dai-Nippon Ptg. Ellio</td>
<td>300 keV, 80 mA 2 lines</td>
</tr>
<tr>
<td>1979</td>
<td>Cement Roof Tile</td>
<td>Nakazato Sangyo</td>
<td>300 keV, 100 mA</td>
</tr>
<tr>
<td>1973-80</td>
<td>Motorcycle Parts (steel, ABS, PP)</td>
<td>Suzuki Motor</td>
<td>300 keV, 100 mA (2 heads)</td>
</tr>
</tbody>
</table>
Fig. 1 Model scheme for preparation of temperature-activated mechanochemical polymer formulations containing insulin for drug delivery systems.

Fig. 2 In vivo release profile of insulin from a poly (acryloyl-L-proline methyl ester) formulation between 4°C and 37°C at 24-hour intervals.
Fig. 3  Morphology change of proline methyl ester by temperature

Fig. 4  Hot water resistance of new radiation crosslinked polyurethane
Fig. 5 Reaction scheme of stack gas treatment by electron beams

Fig. 6 Ion beam facilities under construction at TRCRE of JAERI
3.2 The Natural Latex Industry and Its Future Prospects

T. D. PENDLE

Malaysian Rubber Producers' Research Association
Tun Abdul Razak Laboratory,
Brickendonbury,
Hertford SG13 8NL
England

Abstract

The natural latex concentrate industry currently produces about half a million tonnes (dry weight) per annum and this quantity is likely to increase in the future. The bulk (ca 60%) of this latex is used for the production of dipped goods of which the various kinds of rubber gloves are the largest item. Other important uses of natural latex include adhesives and extruded thread for clothing applications.

At the present time the future of natural latex concentrate seems assured because of the strong upward trend in demand for rubber gloves. The excess capacity for gloves which currently exists is expected to disappear as more stringent demands for quality and reliability produce their inevitable effects. Only efficient manufacturers of high quality gloves will be able to compete for the markets in developed countries in the future.

To ensure as far as possible a good future, latex concentrate producers need to improve the consistency of their product in certain respects, particularly in the reproducibility of processing behaviour. The ability to do this depends on further research work and more concentrated studies of the relation between latex properties and processing performance.

Other factors affecting the future prospects for natural latex include such matters as the cytotoxicity and dermatitic nature of latex products, their effects upon the environment and the presence of nitrosamines. Latex producers and latex product manufacturers must consider all of these aspects if they are to ensure a good future for their companies. New developments, such as radiation cross-linked latex are to be welcomed in so far as they offer the possibility of solving at least some of these problems.
1. Introduction

The natural latex concentrates used for the manufacture of dipped goods, such as gloves, are products both of nature and technology. They are made using the "field" latex obtained from the tree species "Hevea Brasiliensis" of the Euphorbiaceae family. As the name implies this tree originates from Brazil but is today most intensively cultivated in the far east (Malaysia, Indonesia, etc.) and in parts of Africa. Nature provides the raw material, field latex, which is then modified, preserved, concentrated and tested by scientifically developed methods to produce the commercial concentrates.

About 500,000 tonnes, dry rubber weight, of natural latex concentrates are produced annually at present and this quantity is expected to increase steadily in the future. Field latex can be concentrated by creaming, evaporation and centrifugation but the latter method predominates and this paper will be confined to concentrates obtained by this process.

2. Testing of Concentrates

Some 13 characteristics of natural latex concentrates are described in ISO specification, 2004\(^1\). These characteristics are measured by long-established and reliable test methods. The requirements of ISO 2004 and the test methods used to determine them are listed in Table 1. The ISO specification and test methods are virtually identical to the American (ASTM.D-1076) and British (BS 4355) requirements. Malaysian latex producers regularly test for all of these properties and often make additional non-specified, measurements e.g. of magnesium contents or viscosity values.

The testing of concentrates is carried out immediately after preparation but certain properties, i.e. those liable to change, are retested at intervals up to the time of shipment. The properties liable to change are mechanical stability and the VFA and KOH numbers. In a well prepared latex the VFA and KOH numbers should change very slowly, if at all, but the mechanical stability changes rapidly in a freshly made concentrate. Fresh concentrate has a mechanical stability (MST) of less than 100s but this should rise, by natural processes, to exceed the ISO minimum value (650s) by the time of shipment. The typical change in mechanical stability values of a natural latex
concentrate during storage is depicted in Fig. 1. Since the mechanical stability of a latex is a measure of its resistance to mechanical shear and agitation it is vital that the MST increases adequately prior to shipment or the latex may be destabilized during pumping into the ship's tank.

In order to minimise batch to batch variations in properties Malaysian latex producers carry out extensive blending of the bulk production lots prior to shipment. Supplies of field latex are blended prior to concentration; batches of concentrate are blended in factory storage tanks; factory batches are blended in the large port-installation tanks; installation batches are blended in a ship's tank. A schematic illustration of these procedures is shown in Fig. 2 with respect to the effect upon mechanical stability values. Once a latex concentrate is about 60 days old it becomes quite stable in all properties and little change is evident over the next 6 months - under good conditions of storage. If the latex is subjected to excessive heat or if it is frozen substantial changes in properties may occur, however.

Recent publications\textsuperscript{2,3} have given details of the average properties exhibited by a large number of shipments of HA and LATZ lattices imported into Western Europe. A summary of this data is presented in Table 2. It will be seen that the properties of the two types of concentrate are very similar although the LATZ type tends to exhibit lower VFA and ROH numbers.

From the data in the above papers the degree of between-batch variation of natural latex concentrates has been derived. This data is shown in Table 3. The coefficients of variation shown in this Table are the mean values divided by the 'population standard deviation' and expressed as a percentage. In general, coefficients of variation of less than 10% represent quite small variability, whereas values of 30% or more represent high variability. It will be seen from Table 3 that in most cases the variability of the properties of both types of latex is less than 20% which shows an excellent level of consistency for a natural product. The only property exhibiting very high variability is the VFA number, which is more variable in HA lattices than it is in the LATZ type. Some of this high variability, however, is regarded as artificial in so far as it arises from the fact that many VFA measurements are made at, or near, the limit of accuracy of the test method.
In general, one must conclude that Malaysian latex producers do a good job of ensuring consistency in a product which must necessarily reflect the unavoidable variables of soil type, clone and climate.

3. Natural Latex Applications

Natural latices are produced by a large number of countries, see Table 4, but Malaysia dominates with a 75% share. The increase in latex production in recent years has been greater than the increase in total natural rubber production and this is shown very clearly by the Malaysian production figures (Table 5).

Although the locus of production of latex articles has been moving from west to east in the past decade the majority of latex concentrate is still exported from the countries of origin. A list of the main consuming areas for NRL is given in Table 6. The anticipated growth rates in these countries (Table 7) suggest that this situation will remain unchanged for the next few years although the greatest rates of growth will occur in the producing countries.

Natural latices, despite representing a single type of polymer, have a surprisingly wide range of uses. A summary of the main areas of use is shown in Table 8. It is obvious that the "dipped goods" area accounts for some 60% of all NRL usage, this sector has been the major consumer for many years but has recently increased further in importance due to the upsurge in glove production. A detailed breakdown of the dipped goods industry is shown in Table 9. From this it is clearly seen that gloves, particularly examination and household gloves, are the most important products but it is also obvious that rubber balloons are a significant item. The huge increase in demand for examination gloves which occurred in 1988 is now over as supply has caught up with demand. It is firmly believed, however, that a basic upward trend in examination glove usage still exists - Europe, for example, has yet to catch up with the USA in consumption of these products - and future growth, at a much lower rate than in 1988, is confidently expected. In the highly developed countries current attitudes stress the importance of the safety of workers and of patients/consumers and this attitude virtually guarantees a further expansion in the use of protective gloves. However, the same attitude also demands that the gloves are effective, i.e. that they should be free of defects that impair user safety. This undoubtedly means that glove manufacturers will experience
increasing pressure to meet more stringent quality standards and those unable to do so will not stay in business for long.

The current world consumption of examination gloves is estimated to be $12 \times 10^9$, of which some $8 \times 10^9$ are used in the USA. This product is therefore the largest single item, in tonnage terms, made from natural latex, although household gloves are not far behind. The growth rate estimates in Table 9 suggest an overall growth for the dipped goods sector of some 6% per annum. This consumption sector is obviously highly important to natural latex but future prospects look good, especially in the areas of medical/surgical gloves, condoms and balloons.

The other areas of importance to NRL are adhesives and extruded thread. Natural latex has a unique place in the adhesives industry because of its combination of high self-tack and high cohesive strength, and these characteristics render it highly suitable in the 'cold-seal' or 'self-seal' type of adhesive for packagings, envelopes etc. The growth in this area is strong and natural latex should have a good future. Latex thread, too, shows a good level of increasing uptake and, despite competition from polyurethane thread, is widely used in clothing applications.

4. Factors affecting future growth

4.1 Processability

The increasing level of automation, particularly in the dipping industry, and the need for high-volume output of guaranteed quality places increasing pressure on producers of latex to ensure uniformity of behaviour of their product. As described earlier, natural latex concentrates from Malaysia show a fairly high level of consistency in most properties. Nonetheless, some variation does exist and this is most likely to be observed in the form of variable behaviour on an automatic dipping machine. The elimination of this variability is a difficult task and it depends upon obtaining a much more detailed understanding of the factors that control the colloidal stability of the latex.

The factors controlling, for example, the mechanical stability of the raw latex are not properly understood at present and the role of particle charge in determining stability is in doubt. Recent work at
the MRPRA Laboratories has confirmed the lack of apparent relation between particle charge (zeta potential) and mechanical stability. In Table 10 are shown the electrophoretic mobility and MST values for a number of lattices treated with proteolytic enzymes. In a given system the electrophoretic mobility is directly related to the zeta potential of the particles which is in turn related to the electrical potential at the particle surface. The results show relatively little change in mobility for very large changes in MST and the small changes that were observed are in the reverse of the anticipated direction. The apparent inverse relation between mobility and MST is attributable to the increase in charge due to enzyme addition probably arising from adsorption of the enzyme.

Similarly, the addition of zinc ammine acetate solution to latex, which greatly reduces mechanical stability, has very little effect upon electrophoretic mobility (Table 11).

The consequence of these results is to raise doubts about the relation of particle charge to mechanical stability in NR lattices and also about the importance of the fatty acid soaps in determining that stability. Much more detailed work will be required before a complete understanding of the mechanical stability behaviour of natural rubber latex is attained. This work is part of a current research project at MRPRA directed to providing a better understanding of latex stability with the ultimate objective of ensuring supplies of natural latex of predictable processing behaviour to meet the needs of product manufacturers.

4.2 Medical Gloves

One of the most important areas of use of latex products is in medical/surgical applications and in this field the safety of the user (surgeon, doctor, nurse etc.) and the safety of the patient are the pre-eminent concerns. Concern for safety of the patient was the original reason for the use of operating gloves but this concern is now matched by the fear that doctors and nurses handling patients face a significant risk of being infected by AIDS, hepatitis or other viruses. The integrity of rubber gloves is therefore a major factor which will determine future growth. Medical personnel must have confidence that the gloves they use provide an effective barrier against the transmission of viruses and bacteria. Despite claims to the
contrary there is ample evidence that latex films are an effective barrier to bacteria and viruses provided that they contain no defects. It is the assurance of freedom from defects - pin-holes, thin areas or flaws - that will be the most important factor in determining future glove sales. Manufacturers whose products contain any of these faults - other than on extremely rare occasions - will have great difficulty in selling their products in the future. Guarantees of quality control throughout the factory operation, including taking action on customer complaints, will increasingly be required. The terms 'Good Manufacturing Practice' (GMP) or 'Total Quality Management' (TQM) will increasingly be heard as buyers of gloves inspect supplying factories.

These factors will place increasing pressure on glove manufacturers to revise and improve their operations or to go out of business. However, if the manufacturing industry can guarantee supplies of gloves of consistently fault-free quality there is no doubt that a strong and growing market for their products will exist and that they will get a satisfactory return for their investment. The 'Rubber Consultants' service of the Malaysian Rubber Research & Development Board is able to advise manufacturers on improving quality control procedures.

4.3 Catheters/Tubing

In this area another aspect of 'safety' becomes important, that is the absence of harm to the patient from contact with the products. These articles are often placed inside the body, in contact with body tissue, for relatively long periods and it is important to the patient's health that no adverse tissue reactions occur. It is unfortunately the case that natural latex catheters and tubes tend to give more tissue reactions than products from certain synthetic polymers (eg. silicones or polyurethanes). Considerable improvements in the cytotoxicity of natural latex products need to be made if the production of these articles is to grow substantially in the future. The reason for the poor cytotoxic performance of latex products is not known with certainty but it seems likely that the vulcanization system may be responsible, at least in part. If this is true then a vulcanize free of accelerators and sulphur would be expected to show much improved cytotoxic performance, and radiation vulcanized natural rubber latex would seem to be an ideal candidate for this type of application in the future. Radiation vulcanized latex, if it demonstrates a superior
cytotoxic performance to conventional pre-vulcanized latices, should have a strong future in this sector of the market.

4.4 Balloons

The balloon market has been growing strongly for many years and future prospects look good. However, there are two factors which may affect future growth in this area, these are:

(a) nitrosoamines

(b) environmental considerations

The presence of nitrosoamines or nitrosatable-amines in latex balloons is currently being considered in Germany where balloons are being subjected to the same restrictions as are presently applied to babies teats and soothers i.e. a maximum of ten parts of nitrosoamines and 200 parts of nitrosatable amines in 10^9 parts of rubber. The reason for this proposed restriction is that toy balloons, like teats and soothers, are put in children's mouths and the ingestion of nitrosoamines is considered to be a possible cause of cancers. It is clearly possible to re-formulate balloon mixes to comply with these regulations, as has already been done with teats and soothers, but the required formulations do not process in the same way as conventional ones and this may represent another opportunity for radiation vulcanized latex which has been shown^5 to be free of nitrosoamines and substantially free of nitrosatable amines.

Environmental considerations may become an important factor affecting the growth of balloon usage. Concern is currently being expressed at the possible effect of large balloon releases, eg. on sporting occasions etc., on the environment. In the USA, where large-scale balloon releases are common several state legislatures are currently considering regulations to limit the number of balloons that can be released at one time. This has happened because of fears, largely unfounded, that balloons are not bio-degradable and, further, may be harmful to animals. In fact thin latex rubber films are biodegradable, unless especially protected, and no evidence exists that rubber balloons have harmed any animal. (In the case of plastic balloons, also widely used in the west these statements may not be true.) However, the undoubted biodegradation of conventional rubber balloon formulations may not occur sufficiently rapidly to satisfy the environmental lobby and a more rapid level of degradability may be required.
In this connection the work being done by the Japanese Fermentation Research Institute to degrade rubber gloves bacteriologically is of great interest. Radiation prevulcanized latex is a potentially attractive material for balloon production as it is free of nitro-soxamines and may be capable of ready biological/chemical degradation.

4.5 Radiation-prevulcanized Latex (RVNRL)

This relatively new form of pre-vulcanized latex has considerable future potential for the reasons mentioned above. Although it is still in the development stage it has been shown\(^5\) that it can be used satisfactorily in coagulant dipping processes. The physical properties of coagulant dipped RVNRL films are quite satisfactory (Table 12) and the ageing resistance is reasonably good and probably capable of further improvement. Its coagulant dipping behaviour is quite acceptable (Fig. 3) and its films contain no nitrosoamines and very little nitrosatable amines (Table 13).

5. Summary

The future prospects for natural latex concentrate look very good with increased demand for many significant latex products. Further success however, is dependent upon the industry satisfying consumer demands for consistency of quality and for appropriate product properties. It appears to this author that the latex producing and product manufacturing industries are well aware of these demands and should be in a good position to satisfy all of them in the near future.

References


4. Davies, R.T. (MRPRA) unpublished

Table 1  ISO 2004 (1974) Requirements for centrifuged Natural Latex Concentrates

<table>
<thead>
<tr>
<th></th>
<th>HA</th>
<th>LA</th>
<th>ISO Test Method No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Solids content, min., (%)</td>
<td>61.5</td>
<td>61.5</td>
<td>124</td>
</tr>
<tr>
<td>Dry Rubber content, min., (%)</td>
<td>60.0</td>
<td>60.0</td>
<td>126</td>
</tr>
<tr>
<td>Non Rubber solids (max) (%)</td>
<td>2.0</td>
<td>2.0</td>
<td>125</td>
</tr>
<tr>
<td>Alkalinity, as NH₃ on latex weight (%)</td>
<td>0.6(min)</td>
<td>0.29(max)</td>
<td></td>
</tr>
<tr>
<td>Mechanical Stability, min. (s)</td>
<td>650</td>
<td>650</td>
<td>35</td>
</tr>
<tr>
<td>Coagulum Content, max., (%)</td>
<td>0.05</td>
<td>0.05</td>
<td>706</td>
</tr>
<tr>
<td>Volatile Fatty Acid number, max.</td>
<td>0.20</td>
<td>0.20</td>
<td>506</td>
</tr>
<tr>
<td>Potassium Hydroxide number, max.</td>
<td>0.0</td>
<td>1.0</td>
<td>127</td>
</tr>
<tr>
<td>Copper Content, max., (mg/kg solids)</td>
<td>8</td>
<td>8</td>
<td>1654</td>
</tr>
<tr>
<td>Manganese Content, max., (mg/kg solids)</td>
<td>8</td>
<td>8</td>
<td>1655</td>
</tr>
<tr>
<td>Sludge Content, max., (%)</td>
<td>0.1</td>
<td>0.1</td>
<td>2005</td>
</tr>
<tr>
<td>Colour</td>
<td>no blue or grey</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Odour²</td>
<td>no putrefactive odour</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1 The difference between the total solids and dry rubber contents
2 After neutralization of ammonia with boric acid

Table 2  Typical Properties of Centrifuged Natural Latex Concentrates

<table>
<thead>
<tr>
<th></th>
<th>HA</th>
<th>LATZ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Solids content (%)</td>
<td>61.4</td>
<td>61.3</td>
</tr>
<tr>
<td>Dry Rubber content (%)</td>
<td>59.7</td>
<td>59.6</td>
</tr>
<tr>
<td>Non Rubber solids (%)</td>
<td>1.6</td>
<td>1.6</td>
</tr>
<tr>
<td>Alkalinity (NH₃) (%)</td>
<td>1.76</td>
<td>0.21</td>
</tr>
<tr>
<td>Mechanical stability (s)</td>
<td>1,020</td>
<td>1,130</td>
</tr>
<tr>
<td>Volatile Fatty acid number</td>
<td>0.07</td>
<td>0.05</td>
</tr>
<tr>
<td>Potassium Hydroxide number</td>
<td>0.63</td>
<td>0.58</td>
</tr>
<tr>
<td>Coagulum content (%)</td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td>Copper content (mg/kg solids)</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Manganese content (mg/kg solids)</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Viscosity, Brookfield, 60 rpm</td>
<td>77</td>
<td>70</td>
</tr>
<tr>
<td>23°C (MPa.s)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 3 Variability of Properties\(^{(a)}\)

<table>
<thead>
<tr>
<th></th>
<th>HA</th>
<th>LATZ</th>
</tr>
</thead>
<tbody>
<tr>
<td>TSC</td>
<td>0.47</td>
<td>1.58</td>
</tr>
<tr>
<td>DRC</td>
<td>0.53</td>
<td>1.54</td>
</tr>
<tr>
<td>Non-Rubber Solids</td>
<td>14.3</td>
<td>13.5</td>
</tr>
<tr>
<td>Alkalinity</td>
<td>13.4</td>
<td>12.2</td>
</tr>
<tr>
<td>MST</td>
<td>21.3</td>
<td>17.4</td>
</tr>
<tr>
<td>VFA</td>
<td>57.7</td>
<td>38.2</td>
</tr>
<tr>
<td>KOH</td>
<td>12.3</td>
<td>8.9</td>
</tr>
<tr>
<td>pH</td>
<td>2.2</td>
<td>2.2</td>
</tr>
</tbody>
</table>

\(^{(a)}\) Data from 20 HA concentrates and 21 LATZ concentrates

Table 4 Production of NR Latex by Country (1,000 tonnes)

<table>
<thead>
<tr>
<th></th>
<th>1986</th>
<th>1987</th>
<th>1988(^{(\text{Est.})})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Malaysia</td>
<td>241</td>
<td>272.5</td>
<td>379.4</td>
</tr>
<tr>
<td>Indonesia</td>
<td>44</td>
<td>45</td>
<td>43</td>
</tr>
<tr>
<td>Liberia</td>
<td>29</td>
<td>32</td>
<td>24</td>
</tr>
<tr>
<td>India</td>
<td>10</td>
<td>24.5</td>
<td>25</td>
</tr>
<tr>
<td>China</td>
<td>23</td>
<td>19</td>
<td>5</td>
</tr>
<tr>
<td>Thailand</td>
<td>5</td>
<td>6</td>
<td>8</td>
</tr>
<tr>
<td>Sri Lanka</td>
<td>4</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>Brazil</td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Other Latin America</td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Total</td>
<td>362</td>
<td>411</td>
<td>496.4</td>
</tr>
</tbody>
</table>

Table 5 Malaysian Production

<table>
<thead>
<tr>
<th></th>
<th>1000 tonnes</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Dry NR</td>
</tr>
<tr>
<td>1986</td>
<td>1,298</td>
</tr>
<tr>
<td>1987</td>
<td>1,308</td>
</tr>
<tr>
<td>1988</td>
<td>1,405</td>
</tr>
<tr>
<td>Growth (% pa)</td>
<td>4</td>
</tr>
</tbody>
</table>
Table 6  The Major Consumers of NR Latex  
(1,000 tonnes)

<table>
<thead>
<tr>
<th></th>
<th>1986</th>
<th>1987</th>
<th>1988 (Est.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EEC</td>
<td>85.3</td>
<td>87.4</td>
<td>95</td>
</tr>
<tr>
<td>USA</td>
<td>63.8</td>
<td>71.1</td>
<td>74</td>
</tr>
<tr>
<td>USSR</td>
<td>52.5</td>
<td>50.0</td>
<td>49</td>
</tr>
<tr>
<td>China</td>
<td>34.0</td>
<td>43.0</td>
<td>50</td>
</tr>
<tr>
<td>Malaysia</td>
<td>27.0</td>
<td>35.3</td>
<td>50</td>
</tr>
<tr>
<td>Korea</td>
<td>22.3</td>
<td>25.7</td>
<td>28</td>
</tr>
<tr>
<td>India</td>
<td>-</td>
<td>25.7</td>
<td>26</td>
</tr>
</tbody>
</table>

Table 7  Possible Future Growth Rates of Major Consumers of Natural Latex

<table>
<thead>
<tr>
<th></th>
<th>Possible Growth (% pa)</th>
<th>Projected Consumption in 1992 (1,000 tonnes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EEC</td>
<td>2</td>
<td>97</td>
</tr>
<tr>
<td>USA</td>
<td>3</td>
<td>82</td>
</tr>
<tr>
<td>USSR</td>
<td>2</td>
<td>54</td>
</tr>
<tr>
<td>CHINA</td>
<td>8</td>
<td>68</td>
</tr>
<tr>
<td>MALAYSIA</td>
<td>15</td>
<td>87</td>
</tr>
<tr>
<td>KOREA</td>
<td>5</td>
<td>34</td>
</tr>
</tbody>
</table>

Table 8  Consumption of NR Latex Concentrates

<table>
<thead>
<tr>
<th>Product Area</th>
<th>1988 Consumption (1,000 tonnes)</th>
<th>Estimated Current Growth Rate (%)</th>
<th>Estimated Consumption in 1992 (1,000 tonnes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dipped goods</td>
<td>330</td>
<td>6</td>
<td>417</td>
</tr>
<tr>
<td>Adhesives/Binders etc.</td>
<td>60</td>
<td>2</td>
<td>65</td>
</tr>
<tr>
<td>Thread</td>
<td>45</td>
<td>3</td>
<td>57</td>
</tr>
<tr>
<td>Carpets/Rugs</td>
<td>25</td>
<td>1</td>
<td>26</td>
</tr>
<tr>
<td>Moulded Foam</td>
<td>34</td>
<td>1</td>
<td>35</td>
</tr>
<tr>
<td>Total</td>
<td>494</td>
<td>4.9</td>
<td>600</td>
</tr>
</tbody>
</table>
Table 9 NRL Dipping Industry

<table>
<thead>
<tr>
<th>Product</th>
<th>1988 Tonnage (1,000t)</th>
<th>Est. Growth Rate pa. (%)</th>
<th>Est. tonnage 1992 (1,000 tonnes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Examination Gloves</td>
<td>135</td>
<td>7</td>
<td>177</td>
</tr>
<tr>
<td>Household Gloves</td>
<td>120</td>
<td>3</td>
<td>140</td>
</tr>
<tr>
<td>Surgeons Gloves</td>
<td>25</td>
<td>4</td>
<td>41.0</td>
</tr>
<tr>
<td>Balloons</td>
<td>35</td>
<td>4</td>
<td>41</td>
</tr>
<tr>
<td>Condoms</td>
<td>11</td>
<td>4</td>
<td>13</td>
</tr>
<tr>
<td>Bladders</td>
<td>1.8</td>
<td>0</td>
<td>1.8</td>
</tr>
<tr>
<td>Catheters</td>
<td>1.5</td>
<td>1</td>
<td>1.6</td>
</tr>
<tr>
<td>Others</td>
<td>2.0</td>
<td>0</td>
<td>2.0</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>331</strong></td>
<td><strong>6.0</strong></td>
<td><strong>417</strong></td>
</tr>
</tbody>
</table>

Table 10 Electrophoretic Mobility and MST

<table>
<thead>
<tr>
<th>Latex</th>
<th>Electrophoretic Mobility (a) (10^{-8} \text{m}^2 \text{v}^{-1} \text{s}^{-1})</th>
<th>Mechanical Stability (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HA A</td>
<td>6.88</td>
<td>435</td>
</tr>
<tr>
<td>HA B</td>
<td>6.44</td>
<td>870</td>
</tr>
<tr>
<td>LA C</td>
<td>6.37</td>
<td>900</td>
</tr>
<tr>
<td>LA D</td>
<td>6.17</td>
<td>960</td>
</tr>
<tr>
<td>LA E</td>
<td>6.40</td>
<td>1245</td>
</tr>
<tr>
<td>HA F</td>
<td>6.24</td>
<td>1935</td>
</tr>
<tr>
<td>HA G</td>
<td>6.29</td>
<td>1988</td>
</tr>
<tr>
<td>HA H</td>
<td>5.93</td>
<td>2070</td>
</tr>
</tbody>
</table>

(a) Moving boundary method

\[ K = -0.75 \]
\[ R^2 = 0.56 \]

Table 11 Effect of Zn Ammine Acetate on Electrophoretic Mobility

<table>
<thead>
<tr>
<th>Latex</th>
<th>Added Zn Ammine Acetate (mmol Zn/100gR)</th>
<th>Electrophoretic Mobility (10^{-8} \text{m}^2 \text{v}^{-1} \text{s}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>HA (1)</td>
<td>0</td>
<td>6.1</td>
</tr>
<tr>
<td>HA (1)</td>
<td>0.252</td>
<td>5.8</td>
</tr>
<tr>
<td>LA</td>
<td>0</td>
<td>6.0</td>
</tr>
<tr>
<td>LA</td>
<td>2.54</td>
<td>6.3</td>
</tr>
<tr>
<td>HA (2)</td>
<td>0</td>
<td>6.0</td>
</tr>
<tr>
<td>HA (2)</td>
<td>0.71</td>
<td>6.0</td>
</tr>
<tr>
<td>HA (3)</td>
<td>1.71</td>
<td>5.7</td>
</tr>
</tbody>
</table>
Table 12 Physical Tests on Coagulant Dipped Film from Coagulant-dipped Film and from RVNRL

<table>
<thead>
<tr>
<th></th>
<th>TS (MPa)</th>
<th>EBZ (MPa)</th>
<th>M300 (MPa)</th>
<th>M500 (MPa)</th>
<th>T. set(a) (%)</th>
<th>Tear str (N/mm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unaged</td>
<td>22.0</td>
<td>820</td>
<td>1.00</td>
<td>2.7</td>
<td>0.8</td>
<td>23.3</td>
</tr>
<tr>
<td>Aged 7d/70°C</td>
<td>22.1</td>
<td>900</td>
<td>1.11</td>
<td>2.4</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Aged 14d/70°C</td>
<td>19.8</td>
<td>875</td>
<td>1.09</td>
<td>2.1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Aged 1d/100°C</td>
<td>18.5</td>
<td>915</td>
<td>0.67</td>
<td>1.5</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

(a) Tension set measurements were made at 400% extension for 22 hrs and after 30 mins relaxation.

Table 13 RVNRL: Determination of Nitrosoamines (BGA Procedure)

<table>
<thead>
<tr>
<th></th>
<th>Found</th>
<th>Permitted</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrosoamines</td>
<td>nil</td>
<td>&gt;3×10⁻⁸</td>
</tr>
<tr>
<td>Nitrosatable Materials</td>
<td>1×10⁻⁸</td>
<td>&gt;5×10⁻⁷</td>
</tr>
</tbody>
</table>

Fig. 1 Effect of Age on MST
Fig. 2 Effect of Blending during Production on Mechanical Stability Time Values

Fig. 3 Coagulant dipping, Dry film thickness
3.3 Characteristic Elastomers Derived from Functional Substances

SHINZO YAMASHITA

Department of Chemistry and Materials Technology
Faculty of Engineering and Design
Kyoto Institute of Technology
Matsugasaki, Sakyo
Kyoto 606, JAPAN

Abstract

High performance and novel functionality in diene or olefin rubber could be obtained by various chemical reactions through suitable functional groups attached to the rubber. Here, I would like to talk about these possibilities along our experiences in 1-chloro-1,3-butadiene--1,3-butadiene rubber (CB-BR), viologen elastomers and ABA type liquid crystalline elastomers, focusing on their chemical reactions and applications, and then discuss about some chemical improvements of natural rubber (NR) to point out some possibilities that high performance NR and functionalized NR are obtained effectively by blending with these synthetic polymers.

(1) 1-Chloro-1,3-butadiene--1,3-Butadiene Rubber (CB-BR)

1-Chloro-1,3-butadiene obtained as a by-product in the course of chloroprene production is copolymerizable with 1,3-butadiene by emulsion process and affords a novel rubber, CB-BR, having hydroxyl groups and chlorine atoms. Thus, various chemical modifications and non-sulfur vulcanizations were found to be possible, i.e., moisture-, isocyanate-, diamine-, and epoxide-curable rubber and lignin-reinforced rubber with good processability etc.

(2) Ionene-type Viologen Elastomers

We have reported the synthesis and properties of an ionene-type elastomer consisting of poly (oxytetramethylene) units and viologen units (PTV), and clarified that PTV behaves as a typical photochromic and photomechanical material. The ionene-type viologen elastomers (NBV) having poly (butadiene-co-acrylonitrile) were obtained by the reaction of \( \alpha,\alpha'-\)dichloro-\( p \)-xylene (DCX), 4,4'-bipyridine (BP) and dimethylamine-terminated liquid nitrile rubber (AT-NBR). We synthesized two sorts of
NBV by using variable quantities of AT-NBR, DCX and BP as well as NBR ionene (NBI). The tensile properties of these elastomers were found to depend upon the number of cation-site in a structural unit of the ionene, and to attain about 450 kgf/cm² in tensile strength at break and 400% in elongation at break without any reinforcement and vulcanization.

(3) ABA Type Liquid Crystalline Elastomers

Two sorts of ABA type liquid crystalline elastomers terminated with mesogenic groups were synthesized to clarify the correlation between their structure and properties. The polymeric segment of B is polyolefin with molecular weight of about 2000. Mesogenic groups of A carrying two or three phenylene groups combined by ester linkage, were prepared by the reaction of terephthalic acid and p-hydroxybenzoic acid. Thermal properties, mechanical properties and morphology were investigated on two kinds of ABA type liquid crystalline elastomers: one was polyolefin terminated with p-carboxybenzoyloxybenzoyl esters (LP-PC-1), and the other was polyolefin terminated with p-caboxybenzoyl-oxybenzoyloxybenzoyl esters (LC-PO-2). Both LC-PO-1 and LC-PO-02 were liquid crystalline and could be formed into elastic films.
1. Introduction

High performance and novel functionality in diene or olefin rubber could be obtained by various chemical reactions through suitable functional groups attached to their polymeric chains. Along our studies, this review describes 1-chloro-1,3-butadiene--1,3-butadiene rubber (CB-BR), viologen elastomers and ABA type liquid crystalline elastomers, focusing on their chemical reactions and applications, and then discusses about chemical improvements of natural rubber (NR) to point out some possibilities that high performance NR and functionalized NR may be obtained by blending with these synthetic polymers.

The reason why I take up these polymers in this review is that (1) CB-BR is a cure type solid rubber carrying OH groups and Cl atoms besides double bonds, (2) viologen elastomers are thermoplastic elastomers (TPE) derived from liquid rubber, indicating some characteristic behaviors, i.e., high tensile properties and special functions, and (3) ABA type liquid crystalline elastomers are also new TPE at room temperature, but behave as liquid rubber at high temperature.

2. 1-Chloro-1,3-butadiene--1,3-Butadiene Rubber (CB-BR)

1-Chloro-1,3-butadiene (CB) obtained as a by-product in the course of chloroprene production is copolymerizable with 1,3-butadiene by emulsion process and affords a novel rubber, CB-BR, having chlorine atoms and hydroxy groups derived by hydrolysis of some of chlorine atoms attached to 1,4-butadiene units (Fig. 1)\(^1\),\(^2\).

In Table 1 is shown its representative structure. These moieties in CB-BR enable us to perform a variety of chemical reactions with vulcanizers of new types, reactive softeners, reactive antioxidants, and reactive reinforcing fillers like silica or lignin. Some of the results are given in Fig. 2\(^3\). These results may be taken to indicate that a large variety of applications is possible in CB-BR, i.e., grafting reaction with many kinds of monomers and oligomers, IPN formation, blend with the other polymers, covulcanization, and production of highly functionalized elastomers.

Here is concerned with development of lignin-reinforced CB-BR and moisture curing of CB-BR.
2.1 Modified Lignin-Reinforced CB-BR\textsuperscript{4,5} 

A large amount of fuel oil or electric power has to be consumed when carbon black is manufactured\textsuperscript{6}. From the points of saving energy and an effective use of natural resource, much attention has been attracted to utilizing lignin from the pulp wastes as a substitute for carbon black\textsuperscript{7,8}.

A rubber/lignin compound, which is usually given by coprecipitated from a rubber latex, shows large strength and a high heat resistant power in its vulcanizate. However, the rubber/lignin compound has a big problem for a practical use, that is, an extremely high viscosity or a low processability in the unvulcanized state.

To improve the processability of the rubber/lignin compound without losing the good mechanical and heat-resistant properties, we used 1-chlorobutadiene-butadiene rubber, which has hydroxyl groups to make chemical bond with lignin (Fig. 3), and a chemically modified lignin whose phenolic hydroxyl groups were converted into aliphatic hydroxides (Fig. 4).

The preparation method of the modified lignin-reinforced CB-BR vulcanizate is schematically shown in Fig. 5. The compounding recipes illustrated in Table 2 were used for preparing five sorts of CB-BR vulcanizates, i.e., the modified or unmodified lignin (ML or L) - reinforced CB-BR cured by sulfur with or without a blocked triisocyanate (designated as IS or S, respectively) and HAF-loaded CB-BR cured by sulfur (sample C). This sample C was used as a control one.

Table 3 shows the Wallace plasticities of these compounds and the tensile properties of the vulcanizates cured at the optimum conditions. From this table, the sample IS-ML showed the best tensile strength at break, $T_B$, and modulus at 100% elongation, $M_{100}$ in all lignin-loaded CB-BR vulcanizates, and its $M_{100}$ is higher than that of HAF black-loaded stock, sample C, in spite of the lowest Wallace plasticity, i.e., the lowest viscosity, of the uncured stock. These results indicate that the chemical modification of lignin by ethylene chlorohydrin resulted in recognizable good effects for improving processability and reinforcing CB-BR. High moduli of IS samples, especially IS-ML, were concluded to be due to the increase of chemical crosslinks as shown in Fig. 6.

To mention other characteristic properties of samples IS-L and IS-ML, it should be pointed out that these samples have good heat-resistance as given in Fig. 7. This result seems to be due to high heat
stability of urethane crosslinks. Lower heat stability of the sulfur vulcanize of the modified lignin-reinforced CB-BR (S-ML) compared with that of unmodified lignin-reinforced CB-BR (S-L) may depend upon the decrease of the concentration of phenolic hydroxide by the reaction of ethylenechlorohydrin.

It is well known that the aging properties of rubber vulcanizates are strongly influenced by chemical structure of sulfur crosslinks. Table 4 gives the crosslink densities of polysulfide ($v_\beta$), disulfide ($v_\gamma$) and monosulfide plus C-C linkage ($v_{1,0}$) in IS and S vulcanizates loaded with reinforcing fillers, L, ML and C determined by the thiol-amine method developed by Campbell.

It will be seen from Table 4: (1) poor aging properties of the sulfur vulcanizates, S-L and S-ML, may be due to higher values in $v_\beta$ and lower values in $v_{1,0}$ compared with those of the carbon black stock vulcanize, S-C, and (2) good aging properties of sulfur / triisocyanate vulcanizates, IS-L and IS-ML, may depend on higher values in $v_{1,0}$ compared with those of S-L and S-ML due to the presence of heat-stable urethane crosslinks, though it is not clear why IS samples indicated good heat resistance in spite of having high values of $v_\beta$. Experiments to elucidate the reason must be the subject of future research.

In conclusion, the results of the study of the modified lignin-reinforced CB-BR on characteristic properties are of interest in three points, i.e., good processability, high tensile properties and good aging properties. Of course, the present method for producing lignin-reinforced elastomer is valuable from the point of useful utilization of natural resources and low energy processing.

It is quite possible that blending of CB-BR latex with NR latex in the presence or absence of the modified lignin yields some mutual benefits, i.e., improvements of NR in rebound, abrasion resistance, compression set, low temperature properties, aging properties etc., and those of CB-BR in processability, green strength, tear resistance, and tensile properties et al. The investigations of these possibilities must be the subjects of future research.

2.2 Moisture-Cure of CB-BR

Silane coupling agents having hydrolyzable alkoxyisilyl groups have been used for surface treatment of inorganic fillers to reinforce rubber and plastic composites. When the silane coupling agents have
functional groups which can react with a polymer, they can be used as cross-linking agents for the polymer in the presence of water. This type of cross-linking reaction is the so-called moisture-cure.

Moisture-curable polymers were prepared from the following combinations: halogenated butyl rubber/3-aminopropyltriethoxysilane (APS)$^{11,12}$, poly(acrylate)s/APS$^{13}$, polyethylene (PE)/vinyltrimethoxysilane (VTMS)$^{14}$, ethylene-propylene-diene rubber (EPDM)/VTMS$^{15}$ etc. Moisture-curable PE is now commercialized. These moisture-curable compounds are useful for cables, pipes, sealants, liners, adhesives, etc.

We reported that CB-BR having active chlorine atoms attached to 1,4-butadiene units, is moisture-curable after grafting it with APS$^{16}$. The cross-linking reaction is composed of two steps, that is, the replacement reaction of the chlorine atoms of CB-BR by APS, followed by the condensation of the silanol groups which are produced by the hydrolysis of ethoxysilyl groups, as shown in Fig. 8 (with only one condensation for simplicity, which does not mean that only one ethoxy group is reactive).

It has already been reported that halogenated butyl rubbers are moisture-curable with APS$^{11,12}$. The details of the cure system, however, have not been studied. Therefore, we studied and reported on the moisture-cure of halogenated rubbers: 1-chlorobutadiene-butadiene rubber$^{16}$, halogenated butyl rubbers$^{17,18}$, chlorosulfonated polyethylene and chloroprene rubber.

The moisture-cure of halogenated rubber by APS has a shortcoming of relatively lower reactivity of APS toward active halogen atoms attached to rubber molecules compared with the rate of condensation reaction between triethoxysilane groups in APSs under usual vulcanization conditions. This tendency produces poor processability.

Thus we developed a novel moisture cure of CB-BR by using 4-trimethoxysilyl-1,2,3,6-tetrahydrophthalic anhydride (MSTP)$^{19}$. In Figs. 9 and 10 are shown the reaction mechanism of the moisture cure of CB-BR by MSTP and the preparation method of moisture-cured film by casting, respectively. Dibutyltin dilaurate (DBTDL) was used as a catalyst for silanol condensation reaction.

Figure 11 illustrates time-conversion curves of the reaction of CB-BR with MSTP in toluene solution, showing that the consumed amount of hydroxyl groups in CB-BR attains about 70mol-% at 50°C for several hours. Table 5 shows the kinetic data including our previous
experiments carried out by using 3-aminopropyltriethoxysilane (APS), indicating that the addition reaction of MSTP with CB-BR is faster than that of APS toward chlorinated rubbers including CB-BR.

The CB-BR films obtained at 60°C for 24h by the method described above were soaked in hot water at prescribed conditions. Figure 12 indicates the relationship between the network-chain density calculated from the swelling data and the soaking time in hot water.

The ratio of observed network-chain density, $v_{\text{s,obs}}$, to the calculated one, $v_{\text{s,cal}}$, is indicated by $R$, then $R = v_{\text{s,obs}}/v_{\text{s,cal}}$. Here, the value of $v_{\text{s,cal}}$ (mol/cc) is presumed to be equal to the amount of MSTP (mol/cc) attached to CB-BR, although there remain some theoretical problems. The results are shown in Table 6, indicating that the value of $R$ increases with the increase of temperature. However, these values are very small, probably due to higher steric hindrance of MSTP attached to CB-BR molecule. A high frequency factor in the kinetic data of the moisture cure of CB-BR by MSTP as shown in Table 7 may support this presumption.

The moisture-curable CB-BR is also made by usual rubber processing. Table 8 gives a typical compounding recipe with or without hydrated silica. In Fig. 13 is shown the preparation method of the moisture-cured film by using a two-roll mill.

Table 9 includes $R$ values of the samples listed in Table 8. From the data given in Table 9, what is evident on comparing with the data in Table 6 is that $R$ values of the samples prepared by using a two-roll mill are larger than those obtained by casting. Especially, compounding of the silica enables us to increase $R$ value.

From these facts, we may conclude that the moisture-cure of CB-BR by MSTP is more favorable than that by APS from the viewpoint of a higher reactivity of MSTP toward CB-BR.

Moisture-cure of NR appears to be an attractive possibility through the graft reaction of trialkoxyvinylsilane to NR under radiation as shown in Fig. 14. This method may be useful not only for lowering the radiation dose to curing NR but also for covulcanization of NR with synthetic polymers, i.e., general purpose rubber (GP-rubber), special purpose rubber (SP-rubber) and general purpose resin (GP-resin) through modifications of these polymers by suitable silane coupling agents as shown in Fig. 15.
3. Viologen Elastomers

Viologen has been known as a reduction-oxidation-type organic dye. Recently, viologen derivatives attract interests among researchers owing to their special functions such as photochromism\textsuperscript{20,21}, electrochromism\textsuperscript{22-24} and thermochromism\textsuperscript{25,26}. In order to use in practical applications, it would be much more convenient if the material be obtained in thin flexible form, e.g., elastomeric polymer film.

The present studies are concerned with some characteristic ionene-type elastomers (PTV and NBV) consisting of viologen moieties and poly(oxytetramethylene) or poly(butadiene-co-acrylonitrile) as shown in Fig. 16.

3.1 PTV\textsuperscript{27,28}

The ionene-type viologen elastomer having CF\textsubscript{3}SO\textsubscript{3} \textsuperscript{-} as a counter anion was successfully synthesized by the reaction of living dicationic poly(tetrahydrofuran) with 4,4\textsuperscript{\prime}-bipyridine (BP) at \(-70^\circ\text{C}\) as shown in Fig. 17\textsuperscript{27}. Lately, there appeared presentations on synthesis and characterization of such viologen elastomers\textsuperscript{29,30} according to our method\textsuperscript{27}. Figure 18 illustrates a stress-strain curve of the elastomeric cast PTV film, showing 30 MPa in tensile strength at break and 620\% in elongation at break without vulcanization.

The PTV film behaves as a typical photochromic material. By irradiation from a 150-W Halogen Lamp without any filters, a peak of visible light absorption of PTV film appeared and increased (Fig. 19). A shoulder was recognized at 610 nm, which was assigned to usual monomeric viologen cation-radical. The observed blue shift was explained by an agglomeration of viologen units in solid state.

The PTV film also behaves as a photomechanical material\textsuperscript{31}. Light onto the film caused the change in tensile stress-strain curve, i.e., a lowering of the tensile modulus as shown in Fig. 20. It seems that photo-irradiation reduces the viologen dication into viologen cation-radical to induce the stress relaxation due to the change of ion clustering.

3.2 NBV\textsuperscript{32}

The ionene-type viologen elastomer having poly-(butadiene-co-acrylonitrile) was obtained by the reaction of \(\alpha,\alpha\textsuperscript{\prime}\)-dichloro-p-xylene (DCX), 4,4\textsuperscript{\prime}-bipyridine (BP) and dimethylamine-terminated liquid
nitrile rubber (AT-NBR). We synthesized two sorts of NBV (a=1 and 2) by using variable quantities of AT-NBR, DCX and BP as well as NBR ionene, NBI (a=0 in NBV) as shown in Fig. 21.

The synthetic method is as follows: The prescribed amounts of DCX and BP illustrated in Table 10 were dissolved in 10% THF solution of AT-NBR. The solution was cast on a glass plate and was heated at 100°C for 1 hr after removing THF.

AT-NBR was obtained by the reaction of carboxy-terminated liquid nitrile rubber (CT-NBR) and N,N-dimethyl-1,3-propanediamine (DMPDA) as given in Fig. 22.

The tensile properties of sulfur-cured nitrile rubber having 29wt% acrylonitrile (NBR-S) and the ionenes of NBI, NBV-1 and NBV-2 are given in Table 11, and these stress-strain curves are shown in Fig. 23. In Table 11, R indicates number of cation site per ionene structural unit. From this table it is to be noted that tensile strength, T_B, and tensile modulus at 100% elongation, M_{100}, depend strongly on the number of cation-site, R, in a structural unit of ionene as shown in Fig. 24.

Functionalization of NBV is of attractive interest. However, it is still being studied and is not yet a stage of reporting.

In conclusion, viologen elastomers derived from the reaction of telechelic liquid rubber with viologen moiety have the following characteristic properties;

1) high tensile properties,
2) high oil resistance,
3) good adhesion properties,
4) reinforcement and vulcanization are unnecessary,
5) dipping or casting process is available,
6) many sorts of functionalized elastomers are anticipated.

The solution of viologen elastomer is favorable to use for coating on NR products, because of the improvements of oil resistance, abrasion resistance, tear strength, adhesion, aging resistance, and so on. These possibilities must be the subjects of future researches.

4. ABA Type Liquid Crystalline Elastomers

Teleblock copolymers of ABA type (A: hard block, B: soft block) are widely used as thermoplastic elastomers (TPEs), i.e., SBS, SIS, SEBS etc. The average molecular weights of A block and B block are usually higher than 5,000 and 50,000, respectively. On the other hand,
ABA type teleblock copolymers, carrying mesogenic groups to each end of soft blocks, are expected to be a new type of TPE whose molecular weight in hard block is relatively low compared with usual TPE (Fig. 25). Thus, it is of interest to pursue the possibility of the realization of new elastomer having a characteristic property of reversible phenomenon, i.e.,

\[
\text{Elastomer} \xrightarrow{\text{high temp.}} \text{liquid rubber.} \xrightarrow{\text{low temp.}}
\]

Lenz and his coworkers\textsuperscript{35} have prepared some thermotropic liquid crystalline elastomers (TLCE) having mesogenic groups at terminal chain ends in oligomers having average molecular weight of several thousand. However, no experiment has been made to elucidate their phase structure and mechanical properties.

An ABA type TLCE derived from telechelic polytetrahydrofuran and 4-[(4'-alkoxybenzoyl)oxy]benzoyl compound was synthesized, and its phase transitions were determined by measurements of linear viscoelastic properties\textsuperscript{36}. However, the mesogen-induced cross-linking showed little resistance to large amplitude shearing.

Here, an attempt was made to elucidate the structure-properties relationship of ABA type TLCE in order to develop high performance TLCE.

4.1 Preparation of ABA type TLCE

We synthesized two ABA type liquid crystalline elastomers terminated with two kinds of mesogenic groups (A segments) (Fig. 26). One was a polyolefin terminated with p-carboxybenzoyloxybenzoyl esters (LCPO-1), and the other was terminated with p-carboxybenzoyloxybenzoyl esters (LCPO-2). B segments in both LCPO-1 and LCPO-2 were polyolefin (HT-PO) having molecular weight of 2,000. Mesogenic groups were synthesized from p-hydroxybenzoic acid and terephthalic acid.

The synthetic routes of LCPO-1 and LCPO-2 are shown in Fig. 27. The properties of HT-PO, LCPO-1 and LCPO-2 are given in Table 12.

4.2 Physical Properties of ABA type TLCE

Both LCPO-1 and LCPO-2 were found to be liquid crystalline and could be formed into elastic films. Phase transition temperatures of these polymers illustrated in Table 13 show that mesomorphic
temperature range (M.R.) of LCPO-2 (78-150°C) is higher and broader than that of LCPO-1 (65-90°C) due to the increase of aromatic groups in the mesogenic groups.

Temperature dispersions of mechanical damping index, $\Delta$, and relative rigidity, $G_r$, for LCPO-1 and LCPO-2 measured by torsional braid analysis (TBA) method showed two peaks corresponding to the glass transition and melting temperatures as shown in Fig. 28 and Table 14, suggesting the presence of microphase separation in both polymers. Fig. 29 shows the result of tensile test, and indicates that mechanical properties, especially tensile strength, $T_B$, increased with the increase of the rigidity of mesogenic groups (LCPO-1, $T_B=0.77$MPa; LCPO-2, $T_B=2.10$MPa).

SAXS measurements provided us with the informations on phase structures: Bragg spacings were 73 Å for LCPO-1 and 83 Å for LCPO-2, which confirmed the microphase separation in these polymers (Fig. 31(B)). The SAXS pattern of LCPO-2 at 100°C (liquid crystalline state) shows three well-defined peaks which appeared at $q$ (scattering vector) = 0.09, 0.16, and 0.18 as shown in Fig. 30. The results of the SAXS measurement of LCPO-2 are listed in Table 15. From the ratio of $q(1:\sqrt{3}:2)$, a cylindrical domain structure based on the aggregation of the mesogenic groups in non-polar polymer matrix was proposed as illustrated in Fig. 31 (A).

The tensile properties of LCPO-2 are not so good as shown in Fig. 29 in spite of its good phase separation as indicated in Fig. 28 and Table 15. The reason is not clear, but it seems that the mesogens are held together in domains by relatively weak forces, i.e., the cross-linking due to clustering of mesogenic groups did not show so large resistance to tensile deformation, and or that there are some polymers whose hard segments enter the same cylinder domain as shown in Fig. 31 (C).

Further experiments on clarification of these presumptions are being carried out.

5. Conclusion

Recently, functionalized rubbers come up as important elastic materials not only to improve in performances but also to afford various functions. I took up typical novel three elastomers and reviewed their syntheses, structures, properties and applications. The
conclusions are as follows:

(1) 1-Chloro-1,3-butadiene--1,3-Butadiene Rubber (CB-BR)

1-Chloro-1,3-butadiene obtained as a by-product in the course of chloroprene production is copolymerizable with 1,3-butadiene by emulsion process and affords a novel rubber, CB-BR, having hydroxyl groups and chlorine atoms. Thus, various chemical modifications and non-sulfur Vulcanizations were found to be possible, i.e., moisture-, isocyanate-, diamine-, and epoxide-curable rubber and lignin-reinforced rubber with good processability etc. Especially, ethylene chlorohydrin-modified lignin-reinforced CB-BR indicated good processability, high tensile properties and good aging properties. The moisture-cure of CB-BR by MSTP was found to be more favorable than that by usual APS from the view point of a higher reactivity of MSTP toward CB-BR.

(2) Ionene-type Viologen Elastomers

We have reported the synthesis and properties of an ionene-type elastomer consisting of poly(oxetetramethylene) units and viologen units (PTV), and clarified that PTV behaves as a typical photochromic and photomechanical material. The tensile properties of PTV obtained by casting method attain about 30 MPa in tensile strength at break and 620% in elongation at break without Vulcanization. The ionene-type viologen elastomers (NBV) having poly(butadiene-co-acrylonitrile) were obtained by the reaction of a,a'-dichloro-p-xylene (DCX), 4,4'-bipyridine (BP) and dimethylamine-terminated liquid nitrile rubber (AT-NBR). We synthesized two sorts of NBV by using variable quantities of AT-NBR, DCX and BP as well as NBR ionene (NBI). The tensile properties of these elastomers were found to depend upon the number of cation-site in a structural unit of the ionene, and to attain about 45 MPa in tensile strength at break and 400% in elongation at break without any reinforcement and vulcanization.

(3) ABA Type Liquid Crystalline Elastomers

Two sorts of ABA type liquid crystalline elastomers terminated with mesogenic groups were synthesized to clarify the correlation between their structures and properties. The polymeric segment of B is polyolefin with molecular weight of about 2000. Mesogenic groups of A carrying two or three phenylene groups combined by ester linkage, were prepared
by the reaction of terephthalic acid and p-hydroxybenzoic acid.
Thermal properties, mechanical properties and morphology were investi-
gated on two kinds of ABA type liquid crystalline elastomers: one was
polyolefin terminated with p-carboxybenzoyloxycarboxyl esters (LC-PO-1),
and the other was polyolefin terminated with p-carboxy-benzoyloxycarboxyl-
oxybenzoyl esters (LC-PO-2). Both LC-PO-1 and LC-PO-2 were liquid
crystalline and could be formed into elastic films. Tensile strengths
at break of LCPO-1 and LCPO-2 were 0.77 MPa and 2.10 MPa, respectively.
From SAXS measurements a cylindrical domain structure based on the
aggregation of the mesogenic groups in non-polar matrix was proposed.

References
Technol., 50, 364 (1977)
4. S. Yamashita, Research on Effective Use of Energy in Chemical
Process, Reports of Special Project Research on Energy, Oct. 1987,
pp. 109-110, and pp. 117-122
Oct. 12, Sydney, 1988
    F.P. Baldwin, A. Malatesta; Chem. Abstr., 68, 60386u (1968)
12. S.-Yamashita, T. Matsumoto, M. Kakehi, S. Ikeda, Technical Polymer-
    Research Group (Japan) 4th Meeting, Kobe Japan, November 1981
13. O.A. Govorova, F.A. Galyl-Ogly, M.A. Zakirova, Int. Rubber Conf.,
    San Francisco, Oct. 1976, Paper No. 52
    Chem. Abstr. 95, 116814j (1981)
    104636u (1981)

- 55 -
Table 1 Typical cold CB-BR

\[
\begin{align*}
\text{CL} & \quad \text{OH} \\
\text{CH} & \quad \text{CH} = \text{CH} = \text{CH}_2 \\
\text{1.0} & \\
\text{CH} & \quad \text{CH} = \text{CH} = \text{CH}_2 \\
\text{0.8} & \\
\text{CH} & \quad \text{CH}_2 = \text{CH} = \text{CH}_2 \\
\text{97.0} & \\
\text{CH} & \quad \text{CH} = \text{CH} - \text{Cl} \\
\text{1.2} & \\
\end{align*}
\]

Properties

\[
\begin{align*}
\eta^a & \quad 2.75 \\
M_H & \quad 8.8 \times 10^4 \\
M_n & \quad 53.8 \times 10^4 \\
\text{Cl (10}^{-4} \text{ mol/g)}^b & \quad 4.0 \\
\text{OH (10}^{-4} \text{ mol/g)}^c & \quad 1.4 \\
\end{align*}
\]

a) Toluene at 25.9°C
b) Elemental analysis
c) UV method

Table 2 Compounding recipes (phr)

<table>
<thead>
<tr>
<th></th>
<th>IS</th>
<th>S</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>CB-BR\textsuperscript{a) }</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Lignin\textsuperscript{b) }</td>
<td>60</td>
<td>60</td>
<td>-</td>
</tr>
<tr>
<td>Carbon black</td>
<td>-</td>
<td>-</td>
<td>45</td>
</tr>
<tr>
<td>ZnO</td>
<td>5.0</td>
<td>5.0</td>
<td>5.0</td>
</tr>
<tr>
<td>Sulfur</td>
<td>2.2</td>
<td>2.2</td>
<td>2.2</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>DM\textsuperscript{c) }</td>
<td>1.7</td>
<td>1.7</td>
<td>1.7</td>
</tr>
<tr>
<td>m-HMDI\textsuperscript{c) }</td>
<td>26.3</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>DBU\textsuperscript{d) }</td>
<td>0.3</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Process oil</td>
<td>-</td>
<td>-</td>
<td>5.0</td>
</tr>
</tbody>
</table>

\textsuperscript{a) }[\text{OH}] = 1.6 \times 10^{-4} \text{ mol/g}
\textsuperscript{b) }[\text{OH}] = 9.27 \times 10^{-4} \text{ mol/g}
\textsuperscript{c) }[\text{NCO}] / ([\text{OH}]_{\text{rubber}} + [\text{phenolic [OH]}}) = 1
\textsuperscript{d) }1,8-Diaza[bicyclo[5,4,0]undecene-7]
\textsuperscript{e) }Dibenzothiazyl disulfide
Table 3 Physical properties of lignin- or carbon black-loaded CB-BRs

| Cure | Filler | W.P. a) | M_{100} b)(MPa) | T_{B} c)(MPa) | E_{B} d)(%)
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>IS e)</td>
<td>L g)</td>
<td>64</td>
<td>5.8</td>
<td>9.5</td>
<td>160</td>
</tr>
<tr>
<td></td>
<td>ML h)</td>
<td>50</td>
<td>6.1</td>
<td>12.3</td>
<td>220</td>
</tr>
<tr>
<td>SF f)</td>
<td>L</td>
<td>74</td>
<td>4.2</td>
<td>10.0</td>
<td>290</td>
</tr>
<tr>
<td></td>
<td>ML</td>
<td>61</td>
<td>4.8</td>
<td>9.0</td>
<td>250</td>
</tr>
<tr>
<td>S i)</td>
<td>C j)</td>
<td>86</td>
<td>5.4</td>
<td>12.9</td>
<td>190</td>
</tr>
</tbody>
</table>

a) Wallace plasticity  
b) Tensile modulus at 100% elongation  
c) Tensile strength  
d) Elongation at break  
e) Isocyanate-sulfur cure  
f) Sulfur cure  
g) Unmodified lignin  
h) Modified lignin  
i) Carbon black

Table 4 Characterization of sulfur crosslinks

<table>
<thead>
<tr>
<th>Cure</th>
<th>Filler</th>
<th>Network-chain density (10^{-4} mol/cm^{3})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>v_p</td>
</tr>
<tr>
<td>IS</td>
<td>L</td>
<td>1.82</td>
</tr>
<tr>
<td></td>
<td>ML</td>
<td>1.77</td>
</tr>
<tr>
<td>S</td>
<td>L</td>
<td>0.47</td>
</tr>
<tr>
<td></td>
<td>ML</td>
<td>0.84</td>
</tr>
<tr>
<td>S</td>
<td>C</td>
<td>0.33</td>
</tr>
</tbody>
</table>
### Table 5 Kinetic data of polymer/silane coupling agent reaction system

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Temp. (°C)</th>
<th>Final conv. (%)</th>
<th>k x 10^4 (1/mol·sec)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>B-IIRa)</td>
<td>90</td>
<td>69</td>
<td>13</td>
<td>(1)</td>
</tr>
<tr>
<td>C-IIRa)</td>
<td>90</td>
<td>40</td>
<td>0.44</td>
<td>(1)</td>
</tr>
<tr>
<td>CRa)</td>
<td>90</td>
<td>37</td>
<td>1.4</td>
<td>(2)</td>
</tr>
<tr>
<td>CB-BRa)</td>
<td>90</td>
<td>-</td>
<td>31.0</td>
<td>(3)</td>
</tr>
<tr>
<td>CB-BRb)</td>
<td>50</td>
<td>70</td>
<td>195</td>
<td>this work</td>
</tr>
</tbody>
</table>

a) APS reaction system  
b) MSTP reaction system

(2) S. Yamashita et al., ibid., 188, 2553 (1987)  
(3) C.S. Yoo et al., 34th Ann. Meeting of Polym. Sci., Jpn, Kobe, July 8, 1988

### Table 6 Calculated and observed network-chain densities

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Soaking Time (h)</th>
<th>v_s,cal a) x 10^5 (mol/cm³)</th>
<th>v_s,obs x 10^5 (mol/cm³)</th>
<th>R b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>24</td>
<td>10.53</td>
<td>0.62</td>
<td>0.06</td>
</tr>
<tr>
<td>70</td>
<td>24</td>
<td>10.53</td>
<td>0.97</td>
<td>0.09</td>
</tr>
<tr>
<td>90</td>
<td>24</td>
<td>10.53</td>
<td>1.61</td>
<td>0.15</td>
</tr>
</tbody>
</table>

a) v_s,cal = ρ x C  
C: MSTR (mol/g rubber)  
ρ: density of CB-BR (0.917 g/cm³)  
b) R = v_s,obs/v_s,cal
Table 7 Kinetic data of moisture-curable CB-BR

<table>
<thead>
<tr>
<th>Soaking Temp. (°C)</th>
<th>k×10^5 (S^-1)</th>
<th>Ea (kJ/mol)</th>
<th>A×10^-2 (S^-1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>1.22</td>
<td></td>
<td></td>
</tr>
<tr>
<td>70</td>
<td>5.39</td>
<td>53.6</td>
<td>64.9</td>
</tr>
<tr>
<td>90</td>
<td>11.61</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 8 Compounding recipe of moisture-curable CB-BR (phr)

<table>
<thead>
<tr>
<th>CB-BR</th>
<th>MSTP a)</th>
<th>DBTDL b)</th>
<th>Silica</th>
</tr>
</thead>
<tbody>
<tr>
<td>MSF 100</td>
<td>4.4</td>
<td>1.02</td>
<td>40</td>
</tr>
<tr>
<td>MS 100</td>
<td>4.4</td>
<td>1.02</td>
<td>-</td>
</tr>
</tbody>
</table>

a) molar ratio, [MSTP]/[OH] = 1.0
b) molar ratio, [DBTDL]/[MSTP] = 0.1

Table 9 Calculated and observed network-chain densities

<table>
<thead>
<tr>
<th>Sample</th>
<th>Soaking Temp. (°C)</th>
<th>Soaking Time (h)</th>
<th>(v_s, \text{cal}^a) \times 10^5) (mol/cm³)</th>
<th>(v_s, \text{obs} \times 10^5) (mol/cm³)</th>
<th>(R^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MS</td>
<td>50</td>
<td>24</td>
<td>14.83</td>
<td>2.09</td>
<td>0.14</td>
</tr>
<tr>
<td>MS</td>
<td>70</td>
<td>24</td>
<td>14.83</td>
<td>2.22</td>
<td>0.15</td>
</tr>
<tr>
<td>MS</td>
<td>90</td>
<td>24</td>
<td>14.83</td>
<td>3.13</td>
<td>0.21</td>
</tr>
<tr>
<td>MSF</td>
<td>50</td>
<td>24</td>
<td>14.83</td>
<td>10.85</td>
<td>0.73</td>
</tr>
<tr>
<td>MSF</td>
<td>70</td>
<td>24</td>
<td>14.83</td>
<td>10.42</td>
<td>0.70</td>
</tr>
<tr>
<td>MSF</td>
<td>90</td>
<td>24</td>
<td>14.83</td>
<td>13.96</td>
<td>0.94</td>
</tr>
</tbody>
</table>
Table 10 Compounding Recipes for Ionomers

<table>
<thead>
<tr>
<th>Sample</th>
<th>AT-NBR</th>
<th>DCX</th>
<th>BP</th>
<th>M.R. a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NBV-1</td>
<td>100</td>
<td>9.7</td>
<td>4.3</td>
<td>1:2:1</td>
</tr>
<tr>
<td>NBV-2</td>
<td>100</td>
<td>14.7</td>
<td>8.7</td>
<td>1:3:2</td>
</tr>
<tr>
<td>NBI</td>
<td>100</td>
<td>4.8</td>
<td>-</td>
<td>1:1</td>
</tr>
</tbody>
</table>

a) Molar ratio, AT-NBR:DCX:BP

Table 11 Tensile Properties of Ionomers

<table>
<thead>
<tr>
<th>Sample</th>
<th>R a)</th>
<th>M100 b) (MPa)</th>
<th>Tσ c) (MPa)</th>
<th>Eσ d) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NBR-S</td>
<td>0</td>
<td>0.9</td>
<td>3.0</td>
<td>490</td>
</tr>
<tr>
<td>NBI</td>
<td>2</td>
<td>2.6</td>
<td>8.6</td>
<td>380</td>
</tr>
<tr>
<td>NBV-1</td>
<td>4</td>
<td>4.4</td>
<td>32.4</td>
<td>390</td>
</tr>
<tr>
<td>NBV-2</td>
<td>6</td>
<td>5.1</td>
<td>45.4</td>
<td>400</td>
</tr>
</tbody>
</table>

a) Number of cation site per ionene unit
b) Tensile modulus at 100% elongation
c) Tensile strength
d) Elongation at break

Table 12 Properties of HT-PO, LC-PO-1 and LC-PO-2

|        | Yield (%) | M a)   | Molar Ratio b)
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Mn</td>
<td>of LC Block</td>
</tr>
<tr>
<td>HT-PO</td>
<td>—</td>
<td>2470</td>
<td>—</td>
</tr>
<tr>
<td>LC-PO-1 c)</td>
<td>57.5</td>
<td>3560</td>
<td>1.98</td>
</tr>
<tr>
<td>LC-PO-2</td>
<td>20.8</td>
<td>3650</td>
<td>2.10</td>
</tr>
</tbody>
</table>

a) By VP0
b) Calculated from Mn and liquid crystalline block concentration
c) Y. Nakae et al.
### Table 13 Phase transition temperatures of HT-PO, LC-PO-1 and LC-PO-2

<table>
<thead>
<tr>
<th></th>
<th>$T_g$ ($^\circ$C)</th>
<th>$T_m$ ($^\circ$C)</th>
<th>$T_c$ ($^\circ$C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HT-PO</td>
<td>-40</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>LC-PO-1</td>
<td>-32</td>
<td>65 (68&lt;sup&gt;e&lt;/sup&gt;)</td>
<td>90 (87&lt;sup&gt;e&lt;/sup&gt;)</td>
</tr>
<tr>
<td>LC-PO-2</td>
<td>-32</td>
<td>78 (84&lt;sup&gt;e&lt;/sup&gt;)</td>
<td>150 (157&lt;sup&gt;e&lt;/sup&gt;)</td>
</tr>
</tbody>
</table>

a) Glass transition temperature  
b) Melting or softening temperature  
c) Clearing temperature  
d) Y. Nakae et al.  
e) Visual observation

### Table 14 Results of TBA and DSC

<table>
<thead>
<tr>
<th></th>
<th>$T_g$ ($^\circ$C)</th>
<th>$T_m$ ($^\circ$C)</th>
<th>$T_c$ ($^\circ$C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LC-PO-1</td>
<td>-28(-32&lt;sup&gt;a&lt;/sup&gt;)</td>
<td>42 (65&lt;sup&gt;a&lt;/sup&gt;)</td>
<td>95 (90&lt;sup&gt;a&lt;/sup&gt;)</td>
</tr>
<tr>
<td>LC-PO-2</td>
<td>-25(-32&lt;sup&gt;a&lt;/sup&gt;)</td>
<td>98 (84&lt;sup&gt;a&lt;/sup&gt;)</td>
<td>155 (157&lt;sup&gt;a&lt;/sup&gt;)</td>
</tr>
</tbody>
</table>

a) By DSC

### Table 15 Results of SAXS measurement of LC-PO-2

<table>
<thead>
<tr>
<th>Temp. ($^\circ$C)</th>
<th>$q (\AA^{-1})$&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Ratio of $q$</th>
<th>$d (\AA)$&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>First peak</td>
<td>Second peak</td>
<td>Third peak</td>
</tr>
<tr>
<td>25</td>
<td>0.076</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>100</td>
<td>0.090</td>
<td>0.156</td>
<td>0.180</td>
</tr>
<tr>
<td>145</td>
<td>0.093</td>
<td>0.161</td>
<td>0.186</td>
</tr>
<tr>
<td>160</td>
<td>0.095</td>
<td>0.163</td>
<td>-</td>
</tr>
</tbody>
</table>

a) $q = 4\pi \sin \theta / 2$  
b) $d = 2\pi / q$
Fig. 1 Copolymerization of 1-chlorobutadiene and butadiene

Fig. 2 Chemical reactions of CB-BR
Fig. 3 Schematic curing mechanism of novel rubber compound

Fig. 4 Reaction scheme of lignin and ethylene chlorohydrin

Fig. 5 Preparation of CB-BR/lignin vulcanizate
Fig. 6 Relationship between $M_{100}$ and $v_s$ of lignin- or carbon black-loaded CB-BRs.
$M_{100}$: Tensile modulus at 100% elongation
$v_s$: Network-chain density by swelling in benzene

Fig. 7 Heat-resistant properties of lignin- or carbon black-loaded CB-BRs. (Aging conditions, temp. 100°C, time 48 hrs)
Retention = \[\frac{\text{property after aging}}{\text{property before aging}}\]
Fig. 8 Reaction mechanism of moisture cure by CB-BR/APS reaction system

Fig. 9 Reaction mechanism of moisture cure by CB-BR/MSTP reaction system
Fig. 10 Preparation of crosslinked film

Fig. 11 Time-conversion curves for the reaction of CB-BR with MSTP
Fig. 12  Relationship between network-chain density of MS CB-BR and soaking time  
(Sample size: 11.36mm in diameter, 3.07mm in thickness)

Fig. 13  Preparation of crosslinked film
Fig. 14 Moisture cure of NR

Fig. 15 Covulcanization of NR with synthetic polymers
\[
\left\{ \frac{(\text{CH}_2\text{Br}_2)_n}{(\text{CH}_2\text{Br}_2)_n} \text{N}^+\text{N}^- \right\}
\]

PTV

poly(oxytetramethylene)/ viologen moiety

\[
\text{CH}_3\text{Cl}^- \\
\text{N}^+\text{C-N-C-N}^-\text{N}\text{CH}_2\text{CH}_2\text{CH}_2\text{N}^+\text{N}\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}^- \\
\text{CH}_3\text{Cl}^- \quad \text{Cl}^- \quad \text{Cl}^- \\
\text{CH}_3
\]

NBV (a=1 and 2, NBI: a=0)

poly(butadiene-co-acrylonitrile)/ viologen moiety

**Fig. 16** Ionene-type viologen elastomers

\[
\text{O} \quad (\text{CF}_3\text{SO}_2)_2\text{O} \quad \text{bulk, 2 °C} \quad \text{O} \quad 2\text{CF}_3\text{SO}_3^- \quad -70 ^\circ\text{C} \\
\text{NaBr aqueous solution} \quad \text{PTV}
\]

**Fig. 17** Synthetic route of PTV
Fig. 18 Tensile properties of PTV film
$M_{100}$: Stress at 100-% elongation
$T_B$: Tensile strength
$E_B$: Elongation at break

Fig. 19 Photo-reduction of PTV(Cl⁻) film (thickness, 50 μm)
at room temperature under vacuum. The time elapsed from the start of irradiation is indicated.
Fig. 20 Photomechanical effect on PTV at room temperature under vacuum; Elongation at 70%
\[
\text{HOOC-NBR-COOH} + 2 \text{H}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{NCH}_2\text{CH}_3 \\
\text{CT-NBR} \quad \text{DMPDA} \\
\text{Mn 3500} \\
\text{AN 27 \%} \\
\text{Functionality 1.85} \\
\begin{array}{c}
\text{H}_2\text{O} \\
\text{at } 130^\circ\text{C for 100h under } \text{N}_2
\end{array} \\
\longrightarrow \text{NBR-CONHCH}_2\text{CH}_2\text{NCH}_2\text{CH}_3 \\
\text{AT-NBR}
\]

Fig. 22 Synthesis of AT-NBR

![Graph showing stress-strain behaviors of ionenes](image)

Fig. 23 Stress-strain behaviors of ionenes
Fig. 24 Relationship between $T_b$, $M_{100}$, $E_b$ and $R$

ABA type LCE

ABA type TPE

Fig. 25 ABA type liquid crystalline elastomer (LCE) and TPE
ABA Type Liquid Crystalline Elastomers (LCE)

Mesogen Long Spacer Mesogen

Mesogen: \( \text{HO}-\text{C}-\text{CO}-\text{O}-\text{C} \), \( \text{HO}-\text{C}-\text{CO}-\text{O}-\text{C} \)

Long Spacer: Polyolefin \( (\text{CH}_2\text{CH}_2)_m(\text{CH}_2\text{CH}_2)_n \)
(\( M_n = 2470 \))

Fig. 26 ABA type liquid crystalline elastomers (LCE)

\[
\begin{align*}
2 \text{CH}_2\text{OC} \text{CO} \text{Cl} + \text{HO}(\text{CH}_2\text{CH}_2)_m(\text{CH}_2\text{CH}_2)_n \text{OH} & \rightarrow \text{PBTBC or PBTB}_2\text{C} \\
\text{HT-PO} & \rightarrow 80^\circ\text{C} \ 24 \text{ or } 96 \text{ hr} \\
-2\text{HCl}
\end{align*}
\]

Fig. 27 Syntheses of LC-PO-1 and LC-PO-2
Fig. 28 Effect of temperature on mechanical damping index $\Delta$ and relative rigidity $Gr$ for LC-PO-1 and LC-PO-2.

Fig. 29 Stress-elongation curves of LC-PO-1 and LC-PO-2.
Fig. 30 Small angle X-ray scattering curve of LC-PO-2 at 100°C

Fig. 31 Structure in LC-PO representing aggregation of mesogenic groups (A), tie molecule (B), and reentry molecules (C)
4. SPECIAL PAPER
4.1 Radiation Vulcanized Natural Rubber Latex is Not Cytotoxic

AKITADA NAKAMURA, Y. Ikarashi, T. Tsuchiya and M. Kaniwa

Division of Medical Devices, National Institute of Hygienic Sciences, Kamiyogo 1-18-1, Setagaya-ku, Tokyo, Japan

Abstract

It has been reported that urethritis and/or urethral strictures caused by urinary catheters relates to cytotoxicities of their materials, and that natural rubber latex (NRL) materials often show the strong cytotoxicities. This paper reports the cytotoxicity testing method using Chinese hamster V79 cultured cells, clarifies that the toxicities of NRLs vulcanized by the conventional processes are due mainly to the contents of zinc dialkyldithiocarbamates in the materials, and that the cytotoxicity of radiation vulcanized NRL (RVNRL) is very weak.

1. Introduction

It has been reported that urethritis and/or urethral strictures caused by urinary catheters relates to cytotoxicities of their materials, and that natural rubber latex (NRL) materials often show the strong cytotoxicities. These toxicities are thought due to leaching toxic substances from the materials to the body fluid. As a result of the clinical complaints in Australia and on the basis of the examination by Graham et al., the cytotoxicity titration assay has been included as a safety test for urinary catheters in the Australian Standard for Foley catheters. However, there is no standard for urinary catheters in Japan yet.

This paper describes the colony suppression assay method for evaluating cytotoxicities of rubber materials using Chinese hamster V79 cultured cells. The method is so convenient and quantitative that it is useful for a routine testing method as an alternative to Graham's method. By the method and the analyses of rubber chemicals, we have clarified that the cytotoxicities of NRLs vulcanized by the conventional processes are due mainly to the contents of zinc dialkyldithiocarbamates in the NRLs, and that the cytotoxicities of radiation vulcanized NRLs (RVNRLs)
are very weak as compared with those of NRLs produced by the conventional processes.

2. Materials and Analytical Method

Chemicals - The accelerators and antioxidants analyzed and their abbreviations were listed in Table 1.

Rubber Materials - The rubber materials cut from the various commercial surgical gloves and urinary catheters and the RNWRC materials made by Dr. Makuuchi, Japan Atomic Energy Research Institute, were used for the experiments. n-Butyl acrylate was used as a sensitizer for radiation vulcanization.

Analytical methods - The accelerators and antioxidants in the rubber materials were analyzed by the methods previously reported.²⁻⁷

3. Cytotoxicity Testing Method

Preparation of extracts - Approximately 1 g of materials was cut into pieces and placed in a screw capped glass bottle of approximately 100 ml capacity. The sample was sterilized by autoclaving at 121°C for 20 min. For each sample, 20 ml of culture medium consisting of Eagle's minimum essential medium supplemented with 10% fetal calf serum and kanamycin (60 μg/ml) (MEM-FCS) was added per gram of test materials. The bottle was shaken, and incubated stationary at 37°C for 24 hours. After incubation, the material pieces was discarded and the extract was diluted with culture medium serially.

Cytotoxicity titration - Chinese hamster V79 cells were obtained from Japanese Cancer Research Resources Bank, and were grown in MEM-FCS. The cells were grown in plastic tissue culture flask in an atmosphere of 5% CO₂ and 95% air at 37°C.

Then, the culture medium was removed and growing cells were washed with calcium- and magnesium-free medium (CMF). After trypsinization, the cells were transferred to a screw capped plastic centrifuge tube and washed twice with CMF. The cells were resuspended in MEM-FCS, adjusted to give 1 x 10² cells/ml. Two milliliter of this cell suspension was seeded into a 60 mm diameter culture dish, and incubated to attach for 4hr.

The medium was then removed, and the cells were replaced with 5 ml of fresh medium as control, undiluted or serial diluted extracts of
are very weak as compared with those of NRLs produced by the conventional processes.

2. Materials and Analytical Method

Chemicals - The accelerators and antioxidants analyzed and their abbreviations were listed in Table 1.

Rubber Materials - The rubber materials cut from the various commercial surgical gloves and urinary catheters and the NVWRL materials made by Dr. Makuuchi, Japan Atomic Energy Research Institute, were used for the experiments. n-Butyl acrylate was used as a sensitizer for radiation vulcanization.

Analytical methods - The accelerators and antioxidants in the rubber materials were analyzed by the methods previously reported4-7.

3. Cytotoxicity Testing Method

Preparation of extracts - Approximately 1 g of materials was cut into pieces and placed in a screw capped glass bottle of approximately 100 ml capacity. The sample was sterilized by autoclaving at 121°C for 20 min. For each sample, 20 ml of culture medium consisting of Eagle's minimum essential medium supplemented with 10% fetal calf serum and kanamycin (60 μg/ml) (MEM-FCS) was added per gram of test materials. The bottle was shaken, and incubated stationary at 37°C for 24 hours. After incubation, the material pieces was discarded and the extract was diluted with culture medium serially.

Cytotoxicity titration - Chinese hamster V79 cells were obtained from Japanese Cancer Research Resources Bank, and were grown in MEM-FCS. The cells were grown in plastic tissue culture flask in an atmosphere of 5% CO2 and 95% air at 37°C.

Then, the culture medium was removed and growing cells were washed with calcium- and magnesium-free medium (CMF). After trypsinization, the cells were transferred to a screw capped plastic centrifuge tube and washed twice with CMF. The cells were resuspended in MEM-FCS, adjusted to give $1 \times 10^2$ cells/ml. Two milliliter of this cell suspension was seeded into a 60 mm diameter culture dish, and incubated to attach for 4 hr.

The medium was then removed, and the cells were replaced with 5 ml of fresh medium as control, undiluted or serial diluted extracts of
test materials. Each concentration of extract was tested in triplicate. The cells were incubated in a humidified 5% CO₂ atmosphere at 37°C for colony formation. After 7 days the medium or extracts was removed from the dishes, colonies were fixed with 10% formalin in 0.9% saline, and stained with Giemsa. Excess stain was washed off with water and the dishes were allowed to dry. The number of visible colonies on each dish was counted. Relative percentage of colony number as control were plotted on semilogarithmic graph paper against the extract concentration expressed percentage. The cytotoxic potential of the materials was expressed in terms of extract concentration that suppress colony formation to 50% of the control value; IC₅₀(%).

4. Results and Discussion

The test methods were compared on the basis of their sensitivity and relative accuracy. Though cytotoxicity test is most sensitive among the various toxicity tests for biomaterials, its sensitivity depends on cell line, application technique of materials to the test, and interpretation of cell response. The method described in this paper for cytotoxicity by comparing colony forming ability (colony suppression assay) is simple and inexpensive. It is superior to Graham's method because the cell response can be easily defined as a number of colonies (see Fig. 1), whereas in Graham's method the cell response is evaluated by looking for morphological changes in the cell monolayer. Judging with morphological changes requires much experiences.

Cytotoxicity potential can be quantitatively expressed as IC₅₀(%) which is easily determined from the colony formation - extract concentration curve as shown in Fig. 2. In the case of S-2, the colony formation was completely suppressed even at 10% dilution of the extract and increased with further dilution and reached to the same level with the control level at 2% dilution. From these data, IC₅₀(%) was determined as 4.7.

We tested the cytotoxicities and determined the contents of the accelerators and antioxidants in the rubber materials cut from 17 surgical gloves, 23 rubber gloves for domestic use, 8 urinary catheters and 5 RVNRLs. As a matter of fact, we have concluded that the cytotoxicities of rubber materials are related mainly to the contents of dialkylidithiocarbamates by multivariable analysis of all data. These analytical results will be reported in the other journal, while Table 2
shows the limited data. Even with the limited data shown in Table 2, we can understand the relation between the toxicity and the contents.

The NRRLs contained large amounts of plural DTCs such as S-2, S-3, S-19, C-1 and C-2 showed strong cytotoxicities, while S-24 and C-3 containing no DTCs showed relatively weak cytotoxicities. Despite of the large ZDBC content, C-4 gave the relatively low toxicity. It should be due to Teflon-coating and/or to the fact that the cytotoxicity of ZDBC is less than one-tenth of those of ZDMC, ZDEC and ZPC as shown in Table 3.

C-3 contained another type of accelerators, MBT and MBTS, showed the weak toxicity which is easily explained by the weak cytotoxicities of MBT and MBTS as shown in Table 3. On the other hand, Petersen et al. have reported that MBT reacts with ethylene oxide to give 2-(2-hydroxyethylmercapto)benothiazole (HMBT) during ethylene oxide sterilization. Guess and O'Leary have reported that MBT and HMBT is rated as highly toxic in mice and that HMBT is more toxic than MBT. Moreover, MBT and MBTS are known as strong sensitizers. Care must be taken accordingly in using MBT-type accelerators.

The cytotoxicities of RVNRRLs were very low as shown in Table 2 and Fig. 2. IC_{50}(%) increased, thus the toxicity decreased with increasing washing period with aqueous sodium hydroxide solution at room temperature. It means that the substances of low toxicities should still remain in RVNRRLs and they could be removed by the simple treatment with aqueous alkaline solution. We applied the same treatment on S-2 to decrease its toxicity, but the cytotoxicity did not significantly decrease even by treatment for 4 hr. Namely, IC_{50}(%) at 0 hr was 2.7 while 4.6 at 4 hr.

There must be several ways to let materials for urinary catheters be safe: i.e., using silicone rubber, coating with silicone or Teflon on NRL, adopting the other vulcanizing processes such as peroxide vulcanization, and using RVNRRL. Whichever way is adopted, the toxicities of the products must be evaluated and the colony suppression assay is useful for the evaluation.

Consequently, the results described in this paper strongly suggest the possibility to use RVNRRLs as the likeliest alternative to sulfur-vulcanized NRLs for catheter material.
References

Table 1  Accelerators and Antioxidants Analyzed in the Experiment

<table>
<thead>
<tr>
<th>Compound</th>
<th>Abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Dithiocarbamate-type accelerator</strong></td>
<td></td>
</tr>
<tr>
<td>Zinc dimethyldithiocarbamate</td>
<td>ZDMC</td>
</tr>
<tr>
<td>Zinc diethyldithiocarbamate</td>
<td>ZDEC</td>
</tr>
<tr>
<td>Zinc dibutylidithiocarbamate</td>
<td>ZDBC</td>
</tr>
<tr>
<td>Zinc ethylphenyldithiocarbamate</td>
<td>ZEPC</td>
</tr>
<tr>
<td>Zinc pentamethylenedithiocarbamate</td>
<td>ZPC</td>
</tr>
<tr>
<td><strong>Mercaptobenzothiazole-type accelerator</strong></td>
<td></td>
</tr>
<tr>
<td>2-Mercaptobenzothiazole</td>
<td>MBT</td>
</tr>
<tr>
<td>Dibenzothiazyl disulfide</td>
<td>MBTS</td>
</tr>
<tr>
<td><strong>Antioxidant</strong></td>
<td></td>
</tr>
<tr>
<td>Styrenated phenol</td>
<td>SP</td>
</tr>
<tr>
<td>2,2'-Isobutylidene-bis(4,6-dimethylphenol)</td>
<td>IBBDMP</td>
</tr>
<tr>
<td>2,6-Di-tert-butyl-4-methylphenol</td>
<td>BHT</td>
</tr>
<tr>
<td>2,2'-Methylene-bis(4-methyl-6-tert-butylphenol)</td>
<td>MBMMP</td>
</tr>
<tr>
<td>4,4'-Thio-bis(3-methyl-6-tert-butylphenol)</td>
<td>TEMBP</td>
</tr>
<tr>
<td>4,4'-Butylidene-bis(3-methyl-6-tert-butylphenol)</td>
<td>BBMBP</td>
</tr>
</tbody>
</table>
Table 2 Results on Analysis and Cytotoxic Test

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Material</th>
<th>Accelerators (ppm)</th>
<th>IC50(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>ZDMC</td>
<td>ZDEC</td>
</tr>
<tr>
<td>surgical gloves</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S-2</td>
<td>NURL</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>S-3</td>
<td>NRL</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>S-19</td>
<td>NRL</td>
<td>-</td>
<td>510</td>
</tr>
<tr>
<td>S-24</td>
<td>NRL</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>urinary catheters</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C-1</td>
<td>NRL</td>
<td>-</td>
<td>452</td>
</tr>
<tr>
<td>C-2</td>
<td>NRL</td>
<td>-</td>
<td>474</td>
</tr>
<tr>
<td>C-3</td>
<td>NRL</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C-4</td>
<td>NRL*2</td>
<td>-</td>
<td>3720</td>
</tr>
<tr>
<td>C-7</td>
<td>NRL</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C-8</td>
<td>silicone</td>
<td></td>
<td></td>
</tr>
<tr>
<td>radiation vulcanized NRLs</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R-1*3</td>
<td>RVNRL</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>R-2</td>
<td>RVNRL</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>R-3</td>
<td>RVNRL</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>R-4</td>
<td>RVNRL</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>R-5</td>
<td>RVNRL</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

*1 not detected  
*2 Teflon coated  
*3 The materials R-1 to R-5 differ from one another in washing period with 1% aqueous sodium hydroxide solution: R-1, 0 hr; R-2, 0.5 hr; R-3, 1 hr; R-4, 4 hr; R-5, 24 hr.
Table 3  Cytotoxicities of Rubber Chemicals

<table>
<thead>
<tr>
<th>Accelerator Chemicals</th>
<th>IC₅₀ (µg/ml)</th>
<th>Antioxidant Chemicals</th>
<th>IC₅₀ (µg/ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZDMC</td>
<td>0.24</td>
<td>SP</td>
<td>17</td>
</tr>
<tr>
<td>ZDEC</td>
<td>0.40</td>
<td>IBRDMP</td>
<td>11</td>
</tr>
<tr>
<td>ZDBC</td>
<td>5.4</td>
<td>BHT</td>
<td>58</td>
</tr>
<tr>
<td>ZEPC</td>
<td>1.6</td>
<td>MBMBP</td>
<td>19</td>
</tr>
<tr>
<td>ZPC</td>
<td>0.41</td>
<td>TBMBP</td>
<td>1.3</td>
</tr>
<tr>
<td>MBT</td>
<td>49</td>
<td>BMEMBP</td>
<td>16</td>
</tr>
<tr>
<td>MBTS</td>
<td>&gt;200</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Fig. 1 Colonies observed at various extract concentrations in the case of S-20

Fig. 2 Colony suppression curves of NRL materials; S, surgical gloves; C, urinary catheters; R, RVNRLs
4.2 Development of Optical Laser Balloon and Drainage from Radiation Vulcanized Natural Rubber Latex

YOSHIYUKI SHIMAMURA

Department of Surgery, National Matsudo Hospital
123-1 Takatsuka-Shinden, Matsudo, Chiba, 217 Japan

Extended Abstract

Rubber film made of the radiation vulcanized natural rubber latex (RVNRL) has better transparency and lower toxicity compared with sulfur-vulcanized latex film. These characteristics of RVNRL suggest wide applications of RVNRL in medical field. With this advantage in mind, we developed an optical laser balloon (optical endoscopical balloon) and a drainage from RVNRL.

Figure 1 presents several types of endoscopic balloons which will be used widely for the diagnosis and treatment of internal organs. The balloon which is attached and sealed to the top of an endoscope by ligature is filled with saline through the transport channel when the endoscope is inserted. The balloon is thin and transparent enough to perform endoscopic examination and laser treatment through it. The transmission of Nd-Yag laser through the balloon is 98%, higher than the sulfur-vulcanized latex rubber (65%) as shown in Fig. 2. The accuracy of the examination is improved by the balloon method in blood vessel including portal vein, digestive tract such as stomach and bile duct and urinary bladder. The high transparency of the balloon is also favorable for the laser treatment, preventing incidental burning and destruction of the optical laser fiber tip and ensuring exact laser irradiation to the affected part. Figure 3 illustrates the laser treatment against gastric cancer.

A drainage bag used conventionally to collect discharged fluids as post-operative measure often causes restriction of mobility of the patient due to its bulkiness. The drainage bag made of RVNRL is compact in size as shown in Fig. 4. The remarkable advantage of the bag is the less irritation to the attached skin because of the low toxicity. The high transparency of the bag facilitates the easy observation of discharged fluids without detaching the bag from the tube.
Fig. 1 Endoscopic balloons made of RVNRL

Fig. 2 Transmission of Nd-Yag laser through balloon made of RVNRL figures in parenthesis: sulfur-vulcanized latex balloon
Fig. 3 Schematic diagram of balloon method
※ compressed contents of stomach
by balloon

Fig. 4 Drainage bag made of RVNRL
4.3 Progress in Radiation Vulcanization of Natural Rubber Latex through International Cooperation

KEIZO MAKUUCHI

Japan Atomic Energy Research Institute
Takasaki Radiation Chemistry Research Establishment
1233 Watanuki, Takasaki, Gunma, 370-12 Japan

Abstract

In 1982 IAEA implemented a regional Project of RVNRL as a part of Cooperation Program for Asia and the Pacific region. Bangladesh, China, India, Indonesia, Japan, Malaysia, Sri Lanka, Thailand and Vietnam are now participating in the Project. The work plan of the Project consists of a R&D program, products development program and cost estimation of RVNRL. The main achievement of the R&D program are 1) reduction in vulcanization dose from 40 kGy to 8 kGy and 2) improvement in the quality of products. The advantages of RV NR latex rubbers over NR latex rubbers vulcanized using sulfur are 1) absence of nitrosoamine, 2) low cytotoxicity, 3) absence of sulfur and zinc oxide, 4) transparency, and 5) softness. Test production of various rubber products such as condom, surgical gloves are being carrying out in each participating country. In March 1989 rubber gloves for workers in nuclear power plants have been commercialized in Japan. Optical laser balloon for diagnosis and treatment of gastric cancer and drainage are also developed in Japan. Three types of irradiators were designed for the cost estimation of RVNRL.

1. Introduction

Radiation vulcanization of natural rubber (NR) latex (RVNRL) has been investigated for a long time. The first paper\(^1\) appeared as a patent which claimed to irradiated NR latex more than 300 kGy. In 1961 Asao et al.\(^2\) reported that carbon tetrachloride reduces the dose for vulcanization (vulcanization dose). Since then researches on RVNRL were carried out in France\(^3\), USSR\(^4\), China\(^5\), Poland\(^6\), India\(^7\), and Indonesia\(^8\). Among them, France was very eager to commercialize the process\(^9\). The RVNRL technique, however, has not been used in industries. The high cost of irradiation of vulcanization and low quality of products from the radia-
tion vulcanized (RV) NR latex are believed to be the main reasons for the lack of interest from the industry.

In 1982 IAEA implemented a regional Project of RVNRL as a part of Cooperation Program for Asia and the Pacific region (RCA Program) funded by UNDP. A pilot plant of RVNRL was installed in the Center for Application of Isotopes and Radiation, the National Atomic Energy Agency, Jakarta, Indonesia in 1983. This pilot plant has been used for the Training and Demonstration of the RVNRL.

Parallel to the Training and Demonstration activities in Jakarta, TRCRE made a research on development of new sensitizer to reduce the vulcanization dose and to replace toxic carbon tetrachloride. Sensitizing effect of polyfunctional monomers for RVNRL was studied\textsuperscript{10-12}. Monofunctional acrylates such as 2-ethylhexyl acrylate (ZHEA) were found to reduce the vulcanization dose to 30 kGy\textsuperscript{13}. The advantage of acrylates as sensitizers for RVNRL is also studied\textsuperscript{14-15}.

In 1985 IAEA convened a meeting of the Expert Advisory Group (EAG) on RVNRL to assess the present status of RVNRL and to prepare the main guidelines for long term programming for the development, promotion, and transfer of this technology to the industry in the region. The meeting made a work plan on RVNRL. The work plan consisted of following programs.

1) R&D program
2) Products development program
3) Cost estimation of RVNRL

This paper reviews the progress in RVNRL achieved by the international cooperation through the RCA project. Since the main parts of the achievement will be presented at this Symposium by scientists participated the program, only small part of the work plan will be reviewed here.

2. R&D Program

Purpose of the R&D program is to reduce the irradiation cost and to increase the quality of rubber products. The actual work of the R&D program has been carried out at JAERI from 1986 by scientists from China, Indonesia, Japan, Malaysia, Sri Lanka and Thailand. The results were presented at 2nd and 3rd meetings of EAG (in 1986 at Takasaki and in 1987 at Jakarta) and meeting of National Research Group (NRG) leaders (in 1988 at Kunming, China and in 1989 at Takasaki) to review
the progress and renew the program.

2.1 Selection of NR latex

The suitable NR latex for RV is the NR latex of which vulcanization dose is low and tensile strength (Tb) is high. Conclusion obtained by a evaluation of fifteen NR latex are summarized as follows:

1) Tb of HA is higher than those of LA-TZ and LA-SPP.
2) Reduction in the protein content reduces Tb.
3) Vulcanization dose decreases with increasing green strength of rubber.
4) Green strength increases with increasing microgel content.
5) Microgel increases with increasing nitrogen contents.

It was concluded that the NR latex suitable for RVNRL is the HA latex having high green Tb. The selection of NR latex brought about the reduction in vulcanization dose and the improvement in quality of RV NR latex rubber.

2.2 Process factors

The Tb increases quite sharply on heating. The Tb also increases substantially upon leaching. It was concluded that the physical properties of RV NR latex rubber can be improved by controlled heating and leaching.

2.3 Sensitizer

The R&D program was aimed at to find out sensitizer system reduce the vulcanization dose below 30 kGy. It was found that carbon tetrachloride enhances the sensitizing effect of 2EHA. For example, the vulcanization dose is reduced from 30 kGy to 15 kGy by the addition of 1 phr of carbon tetrachloride to 5 phr of 2EHA. However, carbon tetrachloride is toxic to human beings and environments.

Vapor pressure of 2EHA is rather high and smell of 2EHA is not good. It is difficult to remove trace amount of 2EHA which is remaining rubber products prepared from RVNRL. The vapor pressure of n-butyl acrylate (n-BA) is higher than that of 2EHA. However, n-BA tends to reduce the stability of NR latex. Therefore a research work has been carried out to increase the stability of NR latex containing n-BA. It was found that the addition of KOH can stabilize NR latex sufficient to withstand against the addition of n-BA (19). The
vulcanization dose of this NR latex with 5 phr of n-BA is around 12 kGy without coaddition of carbon tetrachloride.

It was often observed that NR latex kept for a long time shows higher efficiency of radiation vulcanization than a new NR latex. It was also found that the vulcanization dose decreases by oxygen bubbling or the addition of hydrogen peroxide (H₂O₂) before irradiation as shown in Fig. 120. These facts suggest that NR latex contains naturally occurred radical scavengers which prevents radiation vulcanization and oxidizing agent decomposes the radical scavengers. Concerning the effect of oxidizing agents, several hydroperoxides were investigated and found that the addition of 0.1 phr of t-butylhydroperoxide can reduce the vulcanization dose from 12 kGy to 8 kGy with 5 phr of n-BA21. The Tb is higher than 30 MPa.

2.4 Advantages of RVNRL

The R&D Program revealed advantages of the RV NR latex over the conventionally vulcanized NR latex with sulfur. Those advantages are summarized as follows.

1) Absence of N-nitrosoamines22
The RV NR latex contains no detectable nitrosoamines because RV does not use dithiocarbamates. Nitrosoamines regarded as strong carcinogen are formed from dithiocarbamates used as accelerators for a sulfur vulcanization.

2) Low cytotoxicity23
The RV NR latex shows very low cytotoxicity because of the absence of dithiocarbamates.

3) Absence of sulfur and zinc oxide

4) Transparency
The absence of sulfur and zinc oxide is favorable for transparency of rubber films.

5) Softness (low modulus)
The C-C direct bonds are formed by RV. This crosslink structure results in lower modulus compared with C-S-C and C-S-S-C bonds.

3. Products Development Program

Rubber products for medical and health field are the most promising products because the absence of nitrosoamine and low cytotoxicity are strongly requested in these products. Test production of various rub-
ber products such as condom, surgical gloves are now being carrying out in each NRG. Test production of condoms started from 1987 using a existing condom factory in Indonesia\(^\text{24}\). Few private companies in Indonesia intend to build a factory for producing surgical glove using RV NR latex. In Japan in March 1989 rubber gloves for workers in nuclear power plants have been commercialized\(^\text{25}\). The balloon for optical laser endoscope and drainages have been developed using the RV NR latex in Japan\(^\text{26}\).

4. Cost Estimation

Reliable cost estimation is essential to transfer RVNRL technology to industry. Irradiators were designed by an expert to make proper cost analysis of RVNRL\(^\text{27}\). Following three types of irradiator having different capacities were designed.

1) Small irradiator
   dry source storage, laboratory scale
   150 ton/y at 10 kCi Co-60
2) Middle scale irradiator
   dry source storage
   500 ton/y at 100 kCi Co-60
3) Commercial irradiator
   pool type Panoramic Irradiator
   1,000 ton/y at 500 kCi Co-60

NRG carried out cost analysis of investment and operation costs of all the three irradiators in each country conditions. Comparative cost analysis data for irradiation of one kg of NR latex in the three irradiators is given Table 1. The irradiation cost is acceptable in most participating countries.

5. Conclusion

Remarkable progress has been achieved in RVNRL. The mechanism for the progress can be summarized as follows:

1) IAEA set up EAC in a good time.
2) EAC made a reasonable work plan.
3) The work plan was fully supported by IAEA and participating countries.
4) The work plan was put into practice by excellent scientists
and engineers from the participating countries.

5) The achievement of the work plan were reviewed and renewed by EAG and NRG in every year.

The main achievement of R&D program are as follows:

1) Reduction of the vulcanization dose
2) Improvement of the quality of RV NR latex
3) Elucidation of the advantages of RV NR latex

The advantages of RV latex rubber are

1) Absence of nitrosoamine
2) Low cytotoxicity
3) Absence of sulfur and zinc oxide
4) Transparency
5) Softness

Commercial production of rubber gloves from the RV NR latex began in March 1989, using the merit of the absence of sulfur and zinc oxide. Medical devices such as optical laser balloon, drainages, and surgical gloves have been developed.

References

1. POUNDER, D.W., "Curing of rubber latex and the production of articles therefrom", BS Patent 853, 926 (1956)
2. ASAO, M., KUNISAWA, S., MINOURA, Y., Gamma-ray vulcanization of natural rubber latex, Kogyo Kagaku Zasshi, 64, 2066-2071 (1961)
5. LI ZHENGGUI, HU YOUNU, Radiation vulcanization of natural rubber latex, Atomic Energy, 7, 618-627 (1964)


17. SHUKRI, A.W., PANSA, C.P., DEVENDRA, R., MAKUUCHI, K., Effect of heating and leaching on mechanical properties of radiation vulcanized natural rubber latex, in this Proceedings.

18. DEVENDRA, R., MAKUUCHI, K., Combination effect of carbon tetra-chloride with 2-ethylhexyl acrylate as a sensitizer for radiation vulcanization of natural rubber latex, in this Proceedings.

19. CHEN, Z.H., MAKUUCHI, K., n-Butyl acrylate as a sensitizer for RVNRL, in this Proceedings.
21. PARINYA, A., MAKUUCHI, K., Selection of hydroperoxides as co-sensitizer for n-butyl acrylate, in this Proceedings.
23. NAKAMURA, Y., Ikarashi, T., Kanimi, M., Radiation vulcanized natural rubber latex is not cytotoxic, in this Proceedings.
24. TSUSHIMA, K., MAKUUCHI, K., YOSHII, F., ISHIGAKI, I., Commercialization of protective rubber gloves by radiation vulcanization, in this Proceedings.
25. SUNDARDI, F., Development of condom and surgical gloves, in this Proceedings.
Table 1 Comparative cost analysis data for irradiation of one kg of NR latex

<table>
<thead>
<tr>
<th>Country</th>
<th>Portable Irradiator</th>
<th>Dry Storage Irradiator</th>
<th>Wet Storage Irradiator</th>
</tr>
</thead>
<tbody>
<tr>
<td>China</td>
<td>0.239-0.254</td>
<td>0.160-0.180</td>
<td>0.134-0.142</td>
</tr>
<tr>
<td>India</td>
<td>0.42</td>
<td>0.2</td>
<td>0.1</td>
</tr>
<tr>
<td>Indonesia</td>
<td>0.51</td>
<td>0.074</td>
<td>0.04</td>
</tr>
<tr>
<td>Malaysia</td>
<td>0.41</td>
<td>0.17</td>
<td>0.215</td>
</tr>
<tr>
<td>Thailand</td>
<td>0.265</td>
<td>0.137</td>
<td>0.094</td>
</tr>
<tr>
<td>Sri Lanka</td>
<td>0.22</td>
<td>0.18</td>
<td>0.09</td>
</tr>
<tr>
<td>Japan</td>
<td>1.32-1.4</td>
<td>1.82-0.8</td>
<td>0.48-0.16</td>
</tr>
</tbody>
</table>

Fig. 1 Effect of oxygen bubbling and addition of hydrogenperoxide and cymenhydroperoxide on RVNRL (○) control, (□) O₂ bubbling, (△) 0.15 phr of cumen hydroperoxide, (○) 0.15 phr of hydrogen peroxide (30%)
4.4 Latex Industry and RVNRL Development in Malaysia

SIDEK BIN DULNGALI

Rubber Research Institute of Malaysia, P. O. Box 10150,
40908 Kuala Lumpur, Malaysia

Abstract

Malaysia, as the largest producer of NR, exported 72.9% of World's total export of 455,000 tonnes NR latex in 1987. In 1988, it has also become one of the largest consumers of NR latex, consuming 61,063 tonnes and producing 1.34 billion pairs of gloves, 45.5 million units of catheters and other latex products.

Malaysia began active research and development of RVNRL only recently and much of which is through its participation in the UNDP/RCA project on RVNRL.

Commercialization of RVNRL in Malaysia is expected to begin once its technical and economic merits and market potential have been established and demonstrated. It is suggested that a world-wide marketing study be undertaken to access the actual market potential of RVNRL. Companies intending to commercialize RVNRL may collaborate with UTN and RRIM to develop the commercial process for RVNRL.

1. Introduction

The rubber industry is one of the twelve industrial areas identified in the Malaysian Industrial Master Plan (IMP) which has been implemented since 1986\(^1\). Within the rubber industry, the tire sector as well as the latex product sector have been given top priority for greatest expansion. The latex product sector has since performed remarkably well in comparison with the IMP target and has out-performed the tire sector. This paper describes the present status of the Malaysian latex industry. The development of radiation vulcanized natural rubber latex (RVNRL) is also discussed to assess its potential for commercialization.

2. Production and Exports of Natural Rubber

Malaysia is renowned world-wide as the largest producer of natural
rubber (NR). In 1988, Malaysia produced 33.1% of the world's total production of NR of 5.01 million tonnes\(^2\). Indonesia and Thailand contributed 24.0% and 19.2% of this total respectively (Table 1). All the major NR producers registered increase in NR production in 1988 over 1987, ranging from 0.5% for Sri Lanka to 12.0% for India, with Malaysia (86,646 tonnes or 5.2%) providing the largest absolute production increase.

Malaysia's production of 1,660,315 tonnes in 1988 was an all-time record despite reduction in area planted with rubber\(^2,3\). In fact, the area under rubber has decreased by 143,900 hectares or 7.2% from 1980 to 1988 (Table 2). The future share of NR production by Malaysia is likely to decrease while those of Indonesia and Thailand are expected to increase as the last two countries have increasing planted area, and as their yields per hectare are relatively lower, more scope of yield improvement is possible.

Malaysia exported 1,617,226 tonnes of NR in 1988. This represented a drop of 0.19% or 3,028 tonnes over 1987 export.

3. Exports and Consumption of NR Latex

Table 3 shows the world's exports of NR latex from 1986 to 1988. The major exporters in 1987 were Malaysia (72.9%), Indonesia (13.0%), Liberia (8.7%) and Thailand (3.0%). Because of very high demand for latex in 1988, Malaysia's export of NR latex increased by 23.5% to 301,664 tonnes. The other producing countries were also reported to have increased exports, but their export figures are not yet available.

The consumption figures of NR latex by the major consuming countries are shown in Table 4. In 1988, the top four consumers were USA (77,900 tonnes, an increase of 13.6% over 1987), Malaysia (61,063 tonnes, 73.1%), Taiwan (42,000 tonnes, 133.3%) and China which consumed 40,500 tonnes up to September.

4. Latex Product Sector in Malaysia

The latex product manufacturing sector in Malaysia performed remarkably well in 1988. It consumed 57,713 tonnes of latex or 48.0% of total rubber usage of 120,379 tonnes. (The remaining 3,350 tonnes were consumed by the other rubber product sectors namely the industrial and general rubber goods and footwear.) The 1988 consumption figure
represented an unprecedented 81.0% increase over 1987. As a result, the latex product sector becomes the largest sector in the Malaysian rubber product industry.

In 1988, the Malaysian output of rubber gloves amounted to 1.34 billion pairs to record an increase of 237.4% over 1987. This was the result of the great eagerness of local and foreign entrepreneurs to cash in on the burgeoning world demand for examination gloves. There were 98 gloves plants in operation during the year, of which 80 were making examination gloves, while 15 were engaged in the production of household and industrial gloves, and three in the production of surgical gloves. The potential for higher output of gloves, especially examination gloves, is reported to be tremendous but the realities of the market may not allow it to be reached fully. Catheters have also recorded a steady rise in output. Production in 1988 was 45.5 million units, an increase of 42.1% over 1987.

The export values of latex products by Malaysia in 1987 and 1988 are shown in Table 5. The total value of exports of latex products in 1988 was MYR 790.9 million, an increase of 109% over 1987. Gloves, latex thread and catheters were the major items, earning MYR 588.2 million, MYR 121.3 million and MYR 32.0 million respectively. Within the glove category, surgical gloves accounted for MYR 147.2 million, while other gloves, the bulk of which were examination gloves, contributed MYR 440.9 million.

In reference to the Malaysian Industrial Master Plan (IMP) the performance of the latex product sector has indeed augured well with the master plan (Table 6) where actual export values have exceeded the targets in all the three years it has been implemented. In fact, in 1988 the actual exports exceeded the IMP target by 174.8% (at 1978 constant prices)².

5. Development of RVNRL in Malaysia

Although Malaysia is the largest producer as well as one of the largest consumers of NR latex, her involvement in RVNRL development began only recently. This is because of several factors. Firstly, radiation processing of latex was not given significant priority in its R&D activities as RVNRL was regarded to be expensive and the strength properties of RVNRL were reported to be inferior to those of sulfur pre-vulcanized latex (SPVL). Secondly, radiation facility of
significant size was not available for R&D until early 1989.

Malaysia has however been involved in the regional UNDP/RCA project on RVNRL since its inception in 1980 by participating in the test-evaluation programmes, training and demonstration programmes, accelerated R&D activities at Takasaki Radiation Chemistry Research Establishment, experts group meetings and leaders of national research group meetings.

The introduction of strict specification requirements in some countries on toxicity of rubber products in health applications particularly on limits of nitrosoamine and nitrosatable contents has necessitated alternative formulations and methods for the processing of natural rubber and especially latex. The use of RVNRL is an obvious alternative method to achieve this target. Hence, there is greater interest on RVNRL in Malaysia now than previously.

Realizing the potential of RVNRL, Malaysia is now committed to the R&D of RVNRL by forming a national research group (NRG) on the radiation processing of natural rubber with government funding. The group comprises researchers from the Nuclear Energy Unit (UTN), the Rubber Research Institute of Malaysia (RRIM) and the National University.

A radiation facility with 200,000 Ci Cobalt-60 source has been set up and commissioned in January 1989 at the Nuclear Energy Unit in Bangi. Although the facility is primarily designed for the sterilization of medical products, it can also be used for the irradiation of latex. Our researchers have just started working on the testing of various commercial grades of latex to determine their optimum conditions for irradiation. This is done on small samples of latex. A facility for the irradiation of larger quantities (up to 480 liters per batch) of latex has been designed and fabricated. In the meanwhile, the NRG on the Radiation Processing of NR has requested UTN for a pilot radiation facility dedicated to RVNRL be established to speed up the development of RVNRL for commercialization. The design of such radiation facility is discussed elsewhere.

6. Commercialization of RVNRL

In Malaysia, as in any other country, new processes or new materials from NR would be commercialized by the private sector once the technical and economic merits of the new materials or process are established and demonstrated. A recent example of such new materials is
the commercialization of epoxidised NR which is developed by the research institutes of the Malaysian Rubber Research and Development Board. Such commercialization would be given the strong support of these research institutes i.e. the RRIM and the Malaysian Rubber Producers' Research Association in United Kingdom. In the case of RVNRL, UTN would also provide such support.

RVNRL has been shown to possess some advantages over SPVL. These include:

* Better toxicity aspects
* Lower modulus
* Better clarity of film products by virtue of reduced levels of chemical additives
* Lower latex viscosity
* Better latex stability
* Lower ash contents

Although the strength and aging properties of RVNRL have been reported to be inferior to those of SPVL, recent work has shown that these can be improved by proper process control techniques and by the addition of suitable antioxidants respectively. R&D works carried out at TRCRE have also shown that the irradiation dose required for optimum tensile properties of RVNRL films can be lowered from 30 - 50 kGy to about 10 kGy by the proper selection of irradiation sensitizer or combination of sensitizers. The irradiation costs of producing RVNRL at various levels of production in some countries have been estimated and are given in Table 7. For example, at the production scale of 1,000 tonnes per year, the cost estimated on wet weight basis varied from US$0.04/kg in Indonesia to US$0.48/kg in Japan. The cost in Malaysia was estimated to be US$0.215/kg. In addition, the costs of chemicals including sensitizer(s) and antioxidant(s) will have to be added on. As a comparison, the price of SPVL in Malaysia used to be at a premium of MYR 1.00 (∼ US$0.475) to MYR 1.50 (∼ US$0.562) over the price of RSS 1 per kg dry. However, the current premium is said to be only at MYR 0.50 to MYR 0.75 per kg dry. It is thus left to the prospective producer of RVNRL to assess the techno-economic viability of the product.

The added technical advantages of RVNRL however could be exploited for use in premium products such as surgical gloves, baby teats, catheters and condoms. If the health authorities such as the FDA in the US imposed strict toxicity limits for examination gloves, then
RVNRL will have even brighter future. It is estimated that in 1989 the total world consumption of NR latex concentrate will be about 500,000 tonnes and of these 50% is used for dipped latex products\(^{13}\). Even if RVNRL can capture only 10% of these products, this would mean 25,000 tonnes.

Hence, to assess the potential demands for RVNRL for such products it is essential that a world-wide market study be undertaken. Perhaps this can be carried out under the purview of the UNDP/RCA project on RVNRL. An example of such survey which has been carried out is on the liquid rubber project under UNIDO. The results from this survey would give very useful indicators for the commercialization of RVNRL.

In the case of Malaysia, an interested company intending to commercialize RVNRL will first have to develop the commercial process using the latex the company is intending to use as different latex source is known to behave differently on radiation\(^{14}\). This can be done in collaboration with UTN and RRIM. Alternatively, if the company prefers absolute confidentiality, it can develop individually using its own facilities or elsewhere.

The prospect of commercializing RVNRL in Malaysia for the manufacture of high-value added products is considered bright because of the following reasons:

- The technical merits of RVNRL appeared overwhelming even if the cost seemed to be more expensive.
- The possibility of further reduction in irradiation cost at higher irradiation scale.
- The demand for clean and health hazard free latex products.
- The availability of high quality latex required for RVNRL
- The strong R&D support by RRIM and UTN.

Acknowledgements

The writer thanks the Director of the Rubber Research Institute of Malaysia for permission to present this paper and to the Assistant Director (Department of Chemistry and Technology) of RRIM for useful comments. Thanks are also expressed to the Organizers of this International Symposium on RVNRL for the invitation to participate and to the International Atomic Energy Agency for the travel support.
References

3. IRSG Rubber Statistical Bulletin, Vol. 43, No. 8, May 1989
### Table 1 Natural Rubber Production

<table>
<thead>
<tr>
<th>Country</th>
<th>1987 '000 tonnes</th>
<th>% Share</th>
<th>1988 '000 tonnes</th>
<th>% Share</th>
<th>% Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>MALAYSIA</td>
<td>1,578.7</td>
<td>33.1</td>
<td>1,660.3</td>
<td>33.1</td>
<td>5.2</td>
</tr>
<tr>
<td>INDONESIA</td>
<td>1,190.0</td>
<td>24.9</td>
<td>1,200.0</td>
<td>24.0</td>
<td>.8</td>
</tr>
<tr>
<td>THAILAND</td>
<td>933.2</td>
<td>19.5</td>
<td>960.0</td>
<td>19.2</td>
<td>2.9</td>
</tr>
<tr>
<td>CHINA</td>
<td>237.6</td>
<td>5.0</td>
<td>240.0</td>
<td>4.8</td>
<td>1.0</td>
</tr>
<tr>
<td>INDIA</td>
<td>227.4</td>
<td>4.8</td>
<td>254.8</td>
<td>5.1</td>
<td>12.0</td>
</tr>
<tr>
<td>SRI LANKA</td>
<td>121.8</td>
<td>2.6</td>
<td>122.4</td>
<td>2.4</td>
<td>.5</td>
</tr>
<tr>
<td>Rest of World</td>
<td>486.3</td>
<td>10.2</td>
<td>572.5</td>
<td>11.4</td>
<td>17.7</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>4,775.0</strong></td>
<td><strong>100.0</strong></td>
<td><strong>5,010.0</strong></td>
<td><strong>100.0</strong></td>
<td><strong>4.9</strong></td>
</tr>
</tbody>
</table>


### Table 2 Area Planted under Rubber ('000 Hectares)

<table>
<thead>
<tr>
<th>Year</th>
<th>MALAYSIA</th>
<th>INDONESIA</th>
<th>THAILAND</th>
<th>SRI LANKA</th>
<th>INDIA</th>
</tr>
</thead>
<tbody>
<tr>
<td>1975</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>227.6</td>
</tr>
<tr>
<td>1977</td>
<td>1,999.0</td>
<td>2,327.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1979</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1,518.0</td>
</tr>
<tr>
<td>1980</td>
<td>2,004.6</td>
<td></td>
<td></td>
<td></td>
<td>241.5</td>
</tr>
<tr>
<td>1987</td>
<td>1,903.5</td>
<td>3,007.0</td>
<td>1,717.0</td>
<td>205.1</td>
<td>394.0</td>
</tr>
<tr>
<td>1988</td>
<td>1,860.7</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3 NR Latex Exports

<table>
<thead>
<tr>
<th></th>
<th>1986</th>
<th></th>
<th>1987</th>
<th></th>
<th>1988</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>'000 tonnes</td>
<td>% Share</td>
<td>'000 tonnes</td>
<td>% Share</td>
<td>'000 tonnes</td>
</tr>
<tr>
<td>MALAYSIA</td>
<td>244.5</td>
<td>76.4</td>
<td>244.3</td>
<td>72.9</td>
<td>301.7</td>
</tr>
<tr>
<td>INDONESIA</td>
<td>43.8</td>
<td>13.7</td>
<td>43.6</td>
<td>13.0</td>
<td>na</td>
</tr>
<tr>
<td>LIBERIA</td>
<td>29.0</td>
<td>9.1</td>
<td>29.2</td>
<td>8.7</td>
<td>na</td>
</tr>
<tr>
<td>THAILAND</td>
<td>1.9</td>
<td>.6</td>
<td>10.1</td>
<td>3.0</td>
<td>na</td>
</tr>
<tr>
<td>SRI LANKA</td>
<td>.3</td>
<td>.1</td>
<td>.5</td>
<td>.1</td>
<td>na</td>
</tr>
</tbody>
</table>


Table 4 Consumption of NR Latex ('000 Tonnes)

<table>
<thead>
<tr>
<th></th>
<th>1987</th>
<th>1988</th>
<th>% Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>USA</td>
<td>68.6</td>
<td>77.9</td>
<td>13.6</td>
</tr>
<tr>
<td>MALAYSIA</td>
<td>35.3</td>
<td>61.1</td>
<td>73.1</td>
</tr>
<tr>
<td>CHINA</td>
<td>43.0</td>
<td>40.5*</td>
<td>-</td>
</tr>
<tr>
<td>TAIWAN</td>
<td>18.0</td>
<td>42.0</td>
<td>133.3</td>
</tr>
<tr>
<td>INDIA</td>
<td>25.7</td>
<td>27.3</td>
<td>6.2</td>
</tr>
<tr>
<td>SOUTH KOREA</td>
<td>26.0</td>
<td>21.5*</td>
<td>-</td>
</tr>
<tr>
<td>F. R. GERMANY</td>
<td>16.8</td>
<td>22.4</td>
<td>33.3</td>
</tr>
<tr>
<td>JAPAN</td>
<td>17.2</td>
<td>16.9</td>
<td>-1.7</td>
</tr>
<tr>
<td>Other NRPC**</td>
<td>22.0</td>
<td>22.5*</td>
<td>-</td>
</tr>
<tr>
<td>Rest of World</td>
<td>167.3</td>
<td>na</td>
<td>na</td>
</tr>
</tbody>
</table>

455.0  na  na

* Jan. - Sep. 1988
** Excluding Malaysia

Table 5  Exports of Latex Products from Peninsular Malaysia  
(Values in MYR Million)

<table>
<thead>
<tr>
<th></th>
<th>1987</th>
<th>1988</th>
<th>% Change</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surgical gloves</td>
<td>83.71</td>
<td>147.25</td>
<td>75.9</td>
</tr>
<tr>
<td>Other gloves*</td>
<td>158.88</td>
<td>440.91</td>
<td>177.5</td>
</tr>
<tr>
<td>Balloons</td>
<td>2.56</td>
<td>3.55</td>
<td>38.7</td>
</tr>
<tr>
<td>Latex thread</td>
<td>67.55</td>
<td>121.31</td>
<td>79.6</td>
</tr>
<tr>
<td>Concoms</td>
<td>5.84</td>
<td>8.84</td>
<td>51.4</td>
</tr>
<tr>
<td>Catheters</td>
<td>32.58</td>
<td>31.96</td>
<td>-1.9</td>
</tr>
<tr>
<td>Teats and soothers</td>
<td>3.35</td>
<td>4.55</td>
<td>35.8</td>
</tr>
<tr>
<td>Foam products</td>
<td>13.12</td>
<td>13.96</td>
<td>6.4</td>
</tr>
<tr>
<td>Other latex products</td>
<td>11.1</td>
<td>18.61</td>
<td>67.7</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>378.69</td>
<td>790.94</td>
<td>108.9</td>
</tr>
</tbody>
</table>

* Household, examination and industrial gloves.  
Source: Department of Statistics, Malaysia.

Table 6  Exports of Rubber Products: Actual vs Targets, 1986–1988  
(Values in MYR Million at 1978 constant prices)

<table>
<thead>
<tr>
<th>Year</th>
<th>Latex Products</th>
<th></th>
<th>Total Rubber Products</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Actual</td>
<td>IMP</td>
<td>% Dif.</td>
<td>Actual</td>
</tr>
<tr>
<td>1986</td>
<td>192.4</td>
<td>170.5</td>
<td>12.8</td>
<td>324.4</td>
</tr>
<tr>
<td>1987</td>
<td>281.3</td>
<td>184.2</td>
<td>52.7</td>
<td>442.7</td>
</tr>
<tr>
<td>1988</td>
<td>586.5</td>
<td>213.4</td>
<td>174.8</td>
<td>775.8</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Irradiator Type</th>
<th>Portable 150</th>
<th>Dry Storage 500</th>
<th>Wet Storage 1,000</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHINA</td>
<td>0.239-0.254</td>
<td>0.160-0.180</td>
<td>0.134-0.142</td>
</tr>
<tr>
<td>INDIA</td>
<td>0.41</td>
<td>0.2</td>
<td>0.1</td>
</tr>
<tr>
<td>INDONESIA</td>
<td>0.51</td>
<td>0.074</td>
<td>0.04</td>
</tr>
<tr>
<td>JAPAN</td>
<td>1.32-1.40</td>
<td>0.80-0.82</td>
<td>0.16-0.48</td>
</tr>
<tr>
<td>MALAYSIA</td>
<td>0.41</td>
<td>0.17</td>
<td>0.215</td>
</tr>
<tr>
<td>SRI LANKA</td>
<td>0.22</td>
<td>0.18</td>
<td>0.09</td>
</tr>
<tr>
<td>THAILAND</td>
<td>0.265</td>
<td>0.137</td>
<td>0.094</td>
</tr>
</tbody>
</table>

Source: First Meeting of NRC Leaders on Technology Development of RVNRL, Kunming, P. R. China, 7-9 September 1988.
4.5 RVNRL in Europe

HARALD NIEPEL

MAPA GmbH, Zeven, West Germany

Abstract

Natural rubber latex industry in Europe, especially in West Germany is faced with nitrosamine restriction. Nitrosamines are generated unavoidably by the conventional vulcanization process using dithiocarbamates as vulcanizing agents. There are two aspects of nitrosamine regulation, namely concentrations in environment and rubber products. Radiation vulcanized rubber will be an alternative to conventional basic substances especially for the production of consumer goods being in contact with food and human body. It is desirable to find the most effective irradiation process and to investigate the chemical components of the sensitizer and reaction products after irradiation and processing.

1. Introduction

From the point of view of a plant producing consumer goods based on natural rubber latex a contribution entitled RVNRL in Europe will be given. Especially German aspects will be demonstrated in three parts:

- Present situation of NR latex industry in the Federal Republic of Germany
- Nitrosamine situation - BGA recommendations -
- Opinion on and expectation to RVNRL -

In Europe, particularly in Germany, there is an intensification of health aspects to be seen. Rubber industry in general has to face environmental restrictions and producers of consumer goods are burdened with nitrosamine regulations\(^1\),\(^2\). The conventional procedure of cross-linking NR-latex by means of sulphur and sulphur containing accessory substances preferably Dithiocarbamates and Thiruams may be connected with the generation of nitrosamines. RVNRL does not need such chemicals and therefore should be a suitable basic substance for nitrosamine-free products. A special application of RVNRL might be teats and soothers and medical rubber articles. First results of trials will be shown.
1.1 Present situation of NR latex industry in the Federal Republic of Germany

In Germany there are several medium size plants producing NR latex based goods like adhesives, backside of carpets, medical products, condoms and consumer goods like household gloves, teats, soothers, toys, toy-balloons etc. With exception of the two first mentioned articles all others are typical dipped products which are main products of our company Mapa GmbH. The overall consumption of NR latex amounted to about 30,000 tons in 1988 and is still growing.

The following two aspects have influence upon NR latex industry in Germany and other European countries.

Price fluctuations of NR-Latex, advantages of producing NR-latex based articles in the country of origin might strengthen the tendency to use alternative materials like silicone, synthetic latexes, polyurethane and thermoplastic elastomers.

Beyond it and partly combined with this there is the fact that German health authorities are fixed on environmental aspects and have enacted special regulations or recommendations for consumer goods.

Early this year, a workplace environment guideline TRGS 552 "Nitrosamines" has been published", in a revised and by this time effective version. Besides others, rubber industry has to face 'orientation values' of 2.5 µg of nitrosamines per cubic metre of air decreasing to 1 µg after 3 years. Consequences of this are limitations in working time and prohibition to give work to pregnant and juniors dependent on remaining under or overstepping this value. If there is a detection of volatile nitrosamines in the air of a rubber plant the management has to ask for exemption permit from local authorities.

In addition to that, other reaction products of sulphur vulcanization like COS, mercaptans might cause environmental difficulties.

The usage of RNVR in certain parts of rubber industry would be a real advantage with regard to environmental aspects and an alternative to synthetic basic substances.

1.2 N-nitrosamine situation - BGA recommendations

Nitrosamines have to be seen not only from the point of view of industrial safety but on the contrary they are to be found in conventional vulcanized NR-latex based products.

In Europe several different nitrosamine regulations are effective.
Even in 1981 the West German Health Ministry introduced a nitrosamine regulation for baby bottle teats and soothers including limiting values for the migration of nitrosamines and of nitrosatable substances. Table 1 gives a survey of the current situation.

The German Federal Health Office (BGA) has introduced into recommendation XXI "Natural and Synthetic Rubber-based Consumer Goods" further nitrosamine migration limits for rubber articles being in contact with food. The limit for category 1 - 3 articles is 1 µg nitrosamine per square decimetre (dm²). Testing of consumer goods has to be done in distilled water, 3 weight % acetic acid and 10 vol. % ethanol under following migration conditions: Cat. 1: 10 days, Cat. 2: 24 hours, Cat. 3: 10 minutes. Temperature is 40°C.

Typical NR latex products which are covered by this are household gloves (Cat 3).

Furthermore there is a nitrosamine regulation for consumer goods on NR-latex basis like toy-balloons and toys. The limits are equal to those of teats and soothers (Table 1) - migration time is 1 hour, medium is artificial saliva without NaNO₂.

N-nitrosamines in vulcanizes or in the environment of rubber plants are a consequence of using thiram and dithiocarbamates as accessory substances. In addition to their limitation there will be in the near future a regulation for consumer goods concerning secondary amines, dithiocarbamates, thiazoles and primary aromatic amines.

Against this background RVNRL as new basic substance would be a really good alternative material for consumer goods. In that case it has to be claimed for integration into the basic list of substances used - item 2.1.3 recommendation XXI.

The procedure of application might not be necessary if RVNRL contains up to 15% of free carboxyl groups and if acrylates of monovalent aliphatic alcohols (C₁-C₄) are polymerized into the latex.

However, the application procedure is necessary anyway with regard to goods which are prescribed for use in connection with the oral consumption of food or which are prescribed for placing in the mouth or which could possibly be placed in the mouth e.g. feeding teats, soothers, teething rings, toys, toy-balloons. Approved material for such consumer goods is among others unmodified NR-latex.

The basis for a health review of an applied new substance and its possible reaction products which may migrate into food or which may be
directly absorbed by the human body are chemical, physical, analytical and migration data and results of animal tests which enable to sufficient toxicological characterization. Tests are necessary concerning acute toxicity, carcinogenic and genes modifying properties. Usually a 90 days feeding test on rats has to be conducted. Further tests on carcinogenic, teratogenic, mutagenic activity might be claimed by BGA. These items have to be considered by all means in case of monofunctional acrylates and carbon tetrachloride as sensitizing system of R VNRL are used.

1.3 Opinions about RVNRL and expectations

In addition to the explanations given before there were trials with RVNRL in the laboratory of Mapa on feeding teats and incontinence sheaths. They have been chosen because they represent important products of the plant.

2. Experimental

2.1 Material

As basic substance was used high-ammonia electron beam RVNRL of Kautschuk-Gesellschaft mbH. Details to that type of RVNRL are presented by Dr. Bez.

2.2 Preparation of teats and sheaths

Feeding teats and incontinence sheaths were prepared with a laboratory automatic dipping machine. Aluminum formers were used for heat-sensitive and coagulant dipping. Following processes are stripping, leaching, drying and finishing.

2.3 Test of teats and sheaths

The physical properties were measured in accordance with German Industrial Standard specification for testing of elastomers, determination of tensile strength and elongation at break (DIN 53504).

The migration tests of teats were carried out according to Japanese specification of rubber equipment\textsuperscript{10} - nursing equipment and pacifier 1.2.1.5 residue on evaporation - limit 40 ppm - and to 2.5.2 migration recommendation XXI limiting values for general migration 20 mg/dm\textsuperscript{2}.

- 114 -
Nitrosamine examinations were carried out according to BCA\textsuperscript{1,2} artificial saliva and FDA\textsuperscript{6,9} dichloromethane extraction method. Table 2 shows some physical and chemical properties of RVNRL teats and sheaths in comparison to commercial products.

3. Results and Discussion

RVNRL teats show a good finish and good migration and nitrosamine data. Tensile strength values are rather good for sheaths before aging, for teats they are only sufficient. Tensile strength values concerning both products are not sufficient after aging. There are further trials to improve this parameter.

There are three possibilities of improving the properties of NR latex based goods especially consumer goods and medical products: (i) Conventional vulcanization under usage of nitrogenfree or safamine based vulcanization accelerators. Some developmental work has been done in cooperation with producers of accessory substances. An availability is not foreseeable because of extensive toxicological investigations. (ii) A peroxide cure of NR latex seems to be possible. There is special research at MRPA. Peroxides have been applied for integration into recommendation XXI but there are difficulties regarding residues. (iii) Activities on RVNRL show encouraging results. It has to be checked whether accelerated electrons or gamma-irradiation generate the most suitable basic substance. Some aspects have to be considered: type and quantity of sensitizing chemicals. The quantity seems to exceed the one of additives for conventional vulcanization. Reaction products of irradiation of natural non-rubber components and accessory substances may be present and have to be investigated thoroughly.

4. Conclusion and Outlook

The presentation of environmental aspects in rubber industry and the situation of consumer goods based on NR-latex demand for better basic substances. RVNRL could be this material and should be able to compete with synthetic material. It has advantages with regard to nitrosamines and there are expectations that a decreasing of typical rubber-allergies is possible. Investigations are not yet finished. RVNRL seems to be especially suitable for production of consumer goods
which are intended for or have foreseeable contact with the mouth e.g. teats, soothers, teething rings, toys and balloons. In addition to that German industrial standards (DIN) are in preparation for NR-latex based goods like condoms, surgical gloves and other medical products like internal and external catheters and there are also other standards like BS and AFNOR. RUNRL should be listed as basic substance under any circumstances. Above all it should be proposed for the intended EEC directive "Elastomers and rubber".

References

2. BGesundhBl. 27, 160 (1984)
3. BAarbBl. Heft 3/1989, 84
4. BAarbBl. Heft 9/1988, 61
5. BGesundhBl. 30, 146 (1987)
6. BGesundhBl. 31, 365 (1988)
7. BGesundhBl. 30, 11 (1987)
8. FDA-Compliance Policy Guides 7117, 11; 12/26/84
10. Governmental promulgation No. 85 of the Japanese Ministry of Health of April 1, 1986
Table 1 Nitrosamine limits concerning teats and soothers

<table>
<thead>
<tr>
<th>Limit</th>
<th>Federal Republic of Germany</th>
<th>Netherland</th>
<th>Denmark</th>
<th>United Kingdom</th>
<th>EEC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Preformed</td>
<td>10</td>
<td>1</td>
<td>5</td>
<td>30 total</td>
<td>20 total</td>
</tr>
<tr>
<td>Nitrosamines</td>
<td></td>
<td></td>
<td></td>
<td>15 each</td>
<td>10 each</td>
</tr>
<tr>
<td>Nitrosatable</td>
<td>200</td>
<td>20</td>
<td>50</td>
<td>--</td>
<td>200</td>
</tr>
<tr>
<td>Amines [ppb]</td>
<td></td>
<td></td>
<td></td>
<td>Dichloro methane</td>
<td></td>
</tr>
<tr>
<td>Extraction</td>
<td>artificial saliva</td>
<td>artificial saliva</td>
<td>artificial saliva</td>
<td>not fixed</td>
<td></td>
</tr>
<tr>
<td>Method</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\( ^{a}\) Regulation for soothers only
\( ^{b}\) Draft directive 11/6/87

Table 2 Physical and chemical properties of teats and sheaths

<table>
<thead>
<tr>
<th></th>
<th>Teats</th>
<th>Sheaths</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>RVNRL</td>
<td>Commercial</td>
</tr>
<tr>
<td>Tensile strength (Tb, MPa)</td>
<td>17</td>
<td>31</td>
</tr>
<tr>
<td>Elongation at break (Eb, %)</td>
<td>800</td>
<td>950</td>
</tr>
<tr>
<td>Tb after aging(^{a})</td>
<td>12</td>
<td>25</td>
</tr>
<tr>
<td>Eb after aging(^{a})</td>
<td>700</td>
<td>880</td>
</tr>
<tr>
<td>Residue on evaporation [ppm]</td>
<td>5 - 10</td>
<td>20 - 30</td>
</tr>
<tr>
<td>General migration XXI [mg/dm²]</td>
<td>1 - 1,5</td>
<td>4</td>
</tr>
<tr>
<td>BGA nitrosamines</td>
<td>b</td>
<td>c</td>
</tr>
<tr>
<td></td>
<td>0,5 - 2</td>
<td>5 - 10</td>
</tr>
<tr>
<td></td>
<td>3 - 6</td>
<td>10 - 60</td>
</tr>
<tr>
<td>FDA nitrosamines [ppb]</td>
<td>2</td>
<td>2 - 5</td>
</tr>
</tbody>
</table>

\( ^{a}\) aged at 70°C for 7 days
\( ^{b}\) NDMA
\( ^{c}\) NDMA and other species
4.6 Use of Radiation Vulcanized Natural Rubber Latex in Small and Medium Scale Industries in Sri Lanka

S. W. KARUNARATNE

Rubber Research Institute, Telawala Road, Ratmalana, Sri Lanka

Abstract

The latex based industry is fast growing with the setting up of several units to produce household and examination gloves. Production of rubberised coir using concentrated latex is also growing rapidly while more and more small scale industries have been set up. There is also a growth in the large scale sector in the dipped goods manufacture. Use of irradiated latex in the manufacture of dipped products has good potential as the efficiency of production is enhanced in the case of latex containing less additives.

1. Introduction

The Rubber Industry in Sri Lanka is served mainly by three Institutions viz the Rubber Research Institute (RRI), Ceylon Institute of Scientific and Industrial Research (CISIR) and the Industrial Development Board (IDB). The main function of RRI, Sri Lanka and the CISIR is Research and Development, and the IDB is more concerned with small and medium scale industries and down stream development activities. Apart from these three institutions, the Export Development Board (EDB) plays a major role in the export marketing and market promotion of rubber products. Other organizations such as the Greater Colombo Economic Commission (GCEC) support mainly large scale and sometimes medium scale industries.

RRI also plays a key role in servicing the plantation sector. This is RRI's primary function. RRI has also organized to service the rubber products industry in a big way. It is the intention of the RRI to set up a modern Research and Development Laboratory to serve the polymer industry in the near future. This laboratory will be centrally located in the outskirts of Colombo, the capital city of Sri Lanka. The second phase of the development of this laboratory will include the installation of an electron beam machine mainly to develop RVNRL for industrial use.
2. NR in Sri Lanka

The consumption of Natural Rubber in Sri Lanka for rubber products manufacture is given in Table 1. While the total consumption for the year 1988 stood at approximately 20,000 t the consumption of centrifuged latex was 7620 t (dry). The figures show a steady increase in the consumption of centrifuged latex. The increase was 18% from the previous year (1987).

Distribution of small and medium scale latex based industries in Sri Lanka is given in Table 2. Rubberised coir which is a cushioning material made from two natural products widely available in Sri Lanka, namely Rubber and coconut fibre, is manufactured in small and medium scale industries and it is one of the most popular products manufactured by small industrialists. Of the 73 units that are registered 45 units produce rubberised coir cushions. It will be an asset to such industries if prevulcanized latex is supplied that could be used directly for the manufacture of rubberised coir. RVNRL has vast potential for the development of such industries.

Centrifuged latex is supplied to the industry by two main sources the Janatha Estates Development Board (JEDB) and the Sri Lanka Rubber Manufacturing Company (SRMC). JEDB controls about one half of the state owned rubber plantations and they normally do not depend on other sources for field latex for the purpose of centrifuging. SRMC was set up mainly to assist the small holders and this organization depends mainly on small holders latex for the production of centrifuged latex. Field latex from small holders generally have a low Dry Rubber Content (DRC). This tends to reduce the efficiency of centrifuging. SRMC has proved that small holders latex can be a useful source for the manufacture of centrifuged latex provided the necessary precautions are taken in the handling of latex especially in the initial stages of collection. Incentives are given by the Government for the manufacture of centrifuged latex. These incentives are in the form of 1/3rd subsidy on new equipment and for the processing of skim rubber which is a byproduct of centrifuged latex manufacture. Laboratory equipment, if installed for the analysis of centrifuged latex, is also entitled to a subsidy. It is the policy of the Government of Sri Lanka to give maximum support to the growth of the rubber products industry. Incentives include equity participation and special financial assistance, Income Tax reliefs, a transferable tax credit scheme and assistance in
product development and market development. Other advantages in setting up rubber based industries in Sri Lanka is the availability of Natural Rubber (NR) and NR latex as indigenous raw material at a substantially lower price than the world market price of NR. Labour is cheap in Sri Lanka and the wages are relatively low compared to the wages in other countries in the South East Asian region. It's geographical location which is central to both East and West and its port facilities are other attributes for setting up an industry in Sri Lanka. Sri Lanka enjoys preferential tariff to most developed countries with respect to the sale of certain rubber products.

3. RVNRL in Sri Lanka

There is great potential for the use of RVNRL in cottage scale industries. The Government's poverty alleviation programme referred to as JANASAVIYA will be set in motion to assist poor families in income generating ventures. After a careful screening process the recipients of government assistance under this programme will be helped and trained by Institutions such as the RRI, CISIR and the IDB, to start up rubber based industries. Markets for these rubber products will be identified mainly in the periphery of the location of the industry. For an initial period of two years the Government assistance will be a payment of Rs. 2500 per month to each recipient family. Of this amount, Rs. 1400 will be deposited in a savings account and the balance Rs. 1100 will entitle the recipient to purchase food stuffs, agricultural inputs such as seed paddy, agricultural utensils such as mamboties, stationary and school books and similar items which are considered essential for a living. At the end of two years each recipient family will have a bank balance of Rs. 25 000. Under the training scheme, training and selection will take place depending on the aptitudes of the people. After two years a small business venture can be started utilising the money saved by each family. Several families or individuals can get together to start an industry depending on the requirement of capital to start such an industry. The infra structure will be developed to ensure that proper marketing channels are established. Under the RRI adoptive research programme several adoptive research centres will be established in the rubber growing areas and these centres will be manned by technically qualified personnel who will be available to give assistance to set up rubber based industries. RVNRL is a good material for the
 manufacture of dipped rubber goods such as rubber bands, rubber gloves, rubber balloons and rubber valves, on a cottage scale. As vulcanization is already accomplished by radiation the only major operation after dipping is drying, using solar energy. The process is very simple and the RVNRL prepared at a central location can be distributed through the adoptive research centres or similar centres established by other organizations (Table 3).

Several other products can be developed using RVNRL making use of attributes of RVNRL such as clarity, purity, ability to accept fillers and pigment. Pigment acceptance is found to be exceptionally good with the production of coloured products with a good finish and appearance.

Economies of scale are important in the production of items such as examination gloves. There is a big demand for good quality examination gloves. High through put and efficient production with less than 5% of rejects are the main features of a good production line which takes care of all the steps in the production process with precise control of temperature and viscosity of the latex ensuring correct pick up on the surface of a clean former. Cleanliness of the former is ensured in the production line with a built in cleaning operation. It is also important to feed into the system latex of consistent quality. Prevulcanized latex such RVNRL containing very little powders as additives would behave better with less problems from agglomerated particles if powders are not dispersed in the latex. RVNRL will have the edge over conventional sulphur vulcanized latex in this respect.

A medium scale industry to produce quality dipped products using a well engineered production line would be advised to use RVNRL as an alternative to sulphur prevulcanized latex to achieve a higher and more efficient through put.

Reference

Table 1  Consumption of NR in Sri Lanka for rubber products manufacture (t)

<table>
<thead>
<tr>
<th>Year</th>
<th>Dry Rubber</th>
<th>Conc. Latex (dry)</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>1980</td>
<td>13 499</td>
<td>1 427</td>
<td>14 926</td>
</tr>
<tr>
<td>1981</td>
<td>14 765</td>
<td>1 451</td>
<td>16 216</td>
</tr>
<tr>
<td>1982</td>
<td>14 420</td>
<td>1 949</td>
<td>16 369</td>
</tr>
<tr>
<td>1983</td>
<td>14 630</td>
<td>1 819</td>
<td>16 449</td>
</tr>
<tr>
<td>1984</td>
<td>11 991</td>
<td>3 070</td>
<td>15 061</td>
</tr>
<tr>
<td>1985</td>
<td>9 249</td>
<td>5 840</td>
<td>15 089</td>
</tr>
<tr>
<td>1986</td>
<td>10 909</td>
<td>5 474</td>
<td>16 383</td>
</tr>
<tr>
<td>1987</td>
<td>12 100</td>
<td>5 650</td>
<td>17 750</td>
</tr>
<tr>
<td>1988</td>
<td>13 450</td>
<td>6 720</td>
<td>20 170</td>
</tr>
</tbody>
</table>

Table 2  Distribution of small and medium scale latex based industries in Sri Lanka

<table>
<thead>
<tr>
<th>Product</th>
<th>No of Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rubberised coir</td>
<td>45</td>
</tr>
<tr>
<td>Latex dipped products</td>
<td>17</td>
</tr>
<tr>
<td>Cast products</td>
<td>05</td>
</tr>
<tr>
<td>Foam</td>
<td>02</td>
</tr>
<tr>
<td>Spreading and surface coatings</td>
<td>04</td>
</tr>
</tbody>
</table>
Table 3 Scheme of distribution of RVNRL for the Janasaviya Programme

Field Latex ---- RRI

Centrifuged Latex ---- RRI

IRRADIATION CENTRE ---- RRI (or other organization)

RVNRL ---- RRI (Adoptive Research Centre or other organization)

Dipped products and other rubber products ---- JANASAVIYA

Markets

Markets outside periphery
(through island wide co-operative network)

Markets inside periphery

Co-operative stores

Institutions
eg. schools
hospitals
post offices
banks, etc.
5. CONTRIBUTED PAPER
COMMERCIAL APPLICATION OF RVNRL

5.1 Commercialization of Protective Rubber Gloves by Radiation Vulcanization

KYOGO TSUSHIMA1), K. Makuuchi2), F. Yoshii2) and I. Ishigaki2)

1) Okamoto Industries, Inc., Ibaraki Plant, Ryugasaki, Ibaraki.
2) Takasaki Radiation Chemistry Research Establishment, JAERI, Takasaki, Gunma, 370-12 Japan

Abstract

The processes for radiation vulcanization and production of protective rubber gloves for radioactive contamination are described. A newly developed sensitizing system consisting of 5 phr n-butyl acrylate was used to vulcanize natural rubber latex at 12 kGy. Transparent and soft gloves were obtained from the radiation vulcanized latex by a coagulant dipping process. The mechanical properties of the gloves meet Japanese Industrial Standard specification for protective gloves. Combustion analysis of the gloves revealed that the amount of evolved sulfur oxide and remaining ashes are less than those from sulfur vulcanization gloves. A usage of the gloves in a nuclear power plant showed that the gloves were easy to use in delicate work without undergoing fatigue.

1. Introduction

The vulcanization dose is about 40 kGy when carbon tetrachloride is used as a sensitizer (Minoura et al., 1961). Monofunctional acrylic monomers, such as 2-ethylhexyl acrylate (2-EHA) and n-butyl acrylate (n-BA), can reduce the vulcanization dose to 30 kGy (Makuuchi and Tsushina, 1988). n-BA as a sensitizer was excluded as this monomer reduces stability of NR latex. Devendra and Makuuchi (1988) found that the vulcanization dose can be reduced to 12 kGy by the addition of carbon tetrachloride to 2-EHA.

Test production of protective rubber gloves started in 1987 from RVNRL produced using a sensitizer system consisting of carbon tetrachloride and 2-EHA. The rubber gloves presented two problems, namely, smell of gloves and poor resistance of gloves against acid. The smell
is originating from residual 2-EHA. The vapor pressure of 2-EHA is too low and so it cannot vaporise during glove manufacturing. The residual monomer is a problem that must be solved before commercializing the radiation vulcanization process. Residual monomer also causes skin irritation.

Chen and Makuuchi (1988) found a stabilizing method of NR latex against n-BA, which has higher vapor pressure than 2-EHA. The vulcanization dose for latex with n-BA sensitizer is 12 kGy without co-sensitizer carbon tetrachloride. The amount of residual monomer in rubber gloves is measured with a gas chromatograph. Remaining 2-EHA was 150 ppm, while no n-BA was detected. In addition, the acid resistance of rubber gloves was improved by using n-BA as a sensitizer. Based on this study, a commercial production of protective rubber gloves began in February 1989. In this paper the processes of radiation vulcanization, the production of the protective rubber gloves and the properties of the gloves produced are described.

2. Experimental

2.1 Materials and Methods

A high ammonia type centrifuged NR latex (Dunlop HA) was used. The sensitizer used was 5 phr of n-BA. The chemical was used without further purification. NR latex was diluted with 1% ammonia solution and the sensitizer was added to the diluted latex under stirring. The latex containing sensitizer was divided in leatches of 20 litres and taken in polyethylene containers. The mixed latex was left standing for 16 hours before irradiation. The latex was then irradiated by moving it in computer controlled trolley conveyor, using RIC-2 of radia industries, LTD. Takasaki, Japan. The average dose was 12 kGy.

2.2 Preparation of Gloves

As an antioxidant, 0.5 phr of 2, 2'-methylene-bis-(4-ethyl-6-tert-butylphenol) (Nocrac NS-5, Ouchi Shinko Co., Japan) was added to the latex after irradiation. Rubber gloves were produced in an automatic dipping machine in the Ibaraki plant of Okamoto Industries, Inc.. The main processes for glove production are coagulant dipping, latex dipping, drying, beading, drying, stripping, leaching, cleaning, anti-tack finishing, and drying. These rubber gloves were referred to as RVNRL gloves.
2.3 Test of Gloves

The physical properties of the RVNRL gloves were measured according to the Japanese Industrial Standard specification for protective rubber gloves for radioactive contamination (JIS-Z-4810). The combustion test of the gloves was carried out according to the Japanese Industrial Standard specification for the analytical method of determining gases evolved from burning plastics (JIS-K-7217) by the Chemical Inspection & Testing Institute, Japan. The questionnaires were analyzed after usage in a nuclear power plant and a nuclear research institute. The results of the analysis are given in tables 1 & 2.

3. Results and Discussion

3.1 Physical Properties of the Gloves

Table 1 shows the JIS-Z-4810 specification and the physical properties of both the RVNRL gloves and the gloves from sulfur vulcanized latex. The physical properties of the RVNRL gloves are either comparable or superior to those of sulfur vulcanization gloves. It is concluded that the RVNRL gloves can be used as the protective rubber gloves for radioactive contamination, in terms of mechanical properties.

3.2 Combustion Test

Table 2 shows the results of combustion analysis of the RVNRL gloves and the sulfur vulcanization gloves. The result shows that there was no detectable amount of sulfur oxide, hydrogen chloride and carbon monoxide from the RVNRL gloves. On the other hand, 19 mg/g of sulfur oxide, 0.27 mg/g of hydrogen chloride, and 330 mg/g of carbon monoxide were evolved from the sulfur vulcanization gloves. The ashes should also be as low as possible, because ashes do damage the filters in the incinerator. As shown in Table 2, the amount of ashes from the RVNRL gloves was about one fourth of those from the sulfur vulcanization gloves. The oxygen index of the RVNRL gloves is 15.8. And the value is less than that of the sulfur vulcanization gloves. This means that the combustibility of the gloves is slightly improved. There are no significant differences in ignition temperature and calorific value. It can be concluded that the RVNRL gloves evolve less corrosive gases and produce less ashes than the sulfur vulcanization gloves.
3.3 Practical Test

The questionnaires were analyzed after usage in a nuclear power plant and a nuclear research institute. The results of the analysis clearly establish the advantages of RVNRL gloves compared with the sulfur vulcanization gloves. The features of RVNRL gloves as pointed out by the users are as follows.

1) Suitability for workers' hands.
2) Suitability for fine work.
3) Ease of usage for work requiring a long period.

These are due to the lower modulus of the RVNRL gloves compared with the sulfur vulcanization gloves. The results gave evidence that RVNRL gloves are convenient for use as protective rubber gloves.

4. Conclusion

Protective rubber gloves for radioactive contamination have been developed using RVNRL. The advantages of the gloves compared with the commercially available gloves are the lower level of evolved sulfur oxide and remaining ashes, and the ease of usage in delicate work without undergoing fatigue. The gloves have been produced in Okamoto Industries, Inc. since 1989. Finally I would like to suggest that these rubber gloves can be used as surgical gloves.

References

Table 1  Physical Properties of Gloves

<table>
<thead>
<tr>
<th></th>
<th>JIS Z 4810</th>
<th>RVNRL</th>
<th>Sulfur</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile strength (Tb, MPa)</td>
<td>24.5</td>
<td>33.4</td>
<td>33.4</td>
</tr>
<tr>
<td>Elongation at break (Eb, %)</td>
<td>700</td>
<td>967</td>
<td>798</td>
</tr>
<tr>
<td>Permanent set (%)</td>
<td>10</td>
<td>4.0</td>
<td>2.0</td>
</tr>
<tr>
<td>Tb after aging* (MPa)</td>
<td>19.6</td>
<td>30.2</td>
<td>35.7</td>
</tr>
<tr>
<td>Acid resistance**</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tb (MPa)</td>
<td>19.6</td>
<td>28.3</td>
<td>25.1</td>
</tr>
<tr>
<td>Eb (%)</td>
<td>600</td>
<td>1030</td>
<td>800</td>
</tr>
<tr>
<td>Alkali resistance***</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tb (MPa)</td>
<td>19.6</td>
<td>28.8</td>
<td>23.6</td>
</tr>
<tr>
<td>Eb (%)</td>
<td>600</td>
<td>1020</td>
<td>788</td>
</tr>
</tbody>
</table>

* aged at 70°C for 48 hours  
** immersed in 10% aq. HCl solution for 48 hours  
*** immersed in 10% aq. NaOH solution for 48 hours

Table 2  Results of Combustion Analysis

<table>
<thead>
<tr>
<th></th>
<th>RVNRL</th>
<th>Sulfur</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gases (mg/g)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SO(_x)</td>
<td>less than</td>
<td>1.0</td>
</tr>
<tr>
<td>HCl</td>
<td>less than</td>
<td>0.05</td>
</tr>
<tr>
<td>HCN</td>
<td>0.014</td>
<td>0.015</td>
</tr>
<tr>
<td>CO</td>
<td>less than</td>
<td>0.5</td>
</tr>
<tr>
<td>Ashes (wt %)</td>
<td>0.5</td>
<td>2.2</td>
</tr>
<tr>
<td>Oxygen index</td>
<td>15.8</td>
<td>16.8</td>
</tr>
<tr>
<td>Ignition temp. (°C)</td>
<td>348</td>
<td>333</td>
</tr>
<tr>
<td>Calorific value (kcal/g)</td>
<td>10.3</td>
<td>10.4</td>
</tr>
</tbody>
</table>
5.2 Development of Condom and Gloves from Radiation Vulcanized Natural Rubber Latex

F. SUNDARDI, Marga Utama, Sudrajat Iskandar and Herwinarni

Center for the Application of Isotopes and Radiation,
J. Cinere, Pasar Jumat,
Jakarta Selatan,
Indonesia.

Abstract

Study on radiation vulcanisation of natural rubber (NR) had been carried out since early of 1970. The positive result guided it to the establishment of a latex irradiator in 1983. This installation was designed for studying the economic aspect of radiation vulcanised of natural rubber latex (RVNRL), as well as for training and demonstration. After years of experiences in using that installation, it appeared that a lot of improvement should be done before transferring that technology to industry. Further development being done and a significant success has been achieved: characteristic of NR latex, antioxidant for RVNRL, new sensitizer, and cost analysis of RVNRL. A combination of n-BA and CCl₄ or n-BA alone showing a promising new sensitizer, which will be able in reducing the irradiation cost of NR latex.

In order to introduce this technology to rubber gloves industry, a study of producing rubber gloves from RVNRL, a survey of the consumption of rubber gloves by the Hospital in Indonesia, and personal contact with rubber gloves industries have been done. The physical properties of rubber gloves prepared from RVNRL was reported to meet the Indonesian Standard of Industry. A comparison study with conventional sulfur vulcanisation has been done using the same of NR latex. According to the survey, the consumption of rubber gloves in the Hospital throughout Indonesia was about 3.5 million pairs, in which each pair was used for several times.

A number of new rubber gloves companies which was established in this year (1989) was directed to meet the world consumption of examination rubber gloves. The total estimated capacity was about 1000 million/year. Several of those companies having a formal co-operation with BATAN in the development of the application of RVNRL.
1. Introduction

Study on radiation vulcanisation of natural rubber (NR) latex was started in Indonesia as early as 1970\textsuperscript{1,2,3}. In 1983, under UNDP/IAEA-RCA Project, a latex irradiator of 215 kCi was installed for studying the economic aspect of the production of radiation vulcanised natural rubber latex (RVNRL), and for training and demonstration\textsuperscript{4}. After years of experience in using that installation, it appeared that a lot of improvement is needed before introducing the technology to industry. Recent studies has helped in identifying characteristics of NR latex to be used for production of RVNRL and for selecting sensitizers of techno-economic merits.

Study on production of rubber gloves from RVNRL, survey of the consumption of rubber gloves in hospital throughout Indonesia, and manufacturing process of rubber gloves in local industries had been done in order to introduce this technology to industries. A comparative study of the properties of gloves manufactured from RVNRL was done with those of gloves from conventional sulfur vulcanised latex using the same source of NR latex.

2. Development of RVNRL

2.1 Characteristic of NR latex

Natural rubber latex is a dispersion of NR particles in water, and the diameter of the particle is between 0.2 and 1.0. These particles are coated with a protein layer which will stabilise the dispersion in water by forming an electric charge in the layer. Anything that disturb this layer, will disturb the stability of dispersion. Microorganism attack will disturb the protein layer and consequently the stability of the dispersion. An aggregate of NR particles will form, which can be seen by a Scanning Electron Microscope (Fig. 1). By adding a small amount of NH\textsubscript{3}, the stability of the dispersion can be improved.

Investigation showed that there was a clear relationship between the volatile fatty acid content (VFA, product from microorganism attack on carbohydrate) and the green strength or the physical properties of vulcanised film. Low volatile fatty acid number showing a higher physical strength of the film, both unvulcanised or vulcanised. Scanning Electron micrograph of rubber film cross section showing a porous structure of the film (Fig. 2). It appeared that the structure was
responsible in yielding a good physical property of the film. Condensation of a large number of irregular large aggregates of NR particles cannot be expected to form a fine structure of the film, and consequently a low physical strength of the film was obtained.

A well prepared concentrated NR latex will be able to form a good film of RVNRL. Experiences showed that a concentrated NR latex with VFA number of less than 0.02 will be good for preparing RVNRL. It the VFA number is much higher than 0.02, it indicates that the microorganism attack proceeded too far.

A minimum crosslink density of NR film needed to form a three dimensional network throughout the NR matrix is predicted to be about $3.01 \times 10^{24} \times M_n^{-1}$ crosslink unit/ml. The higher the molecular weight of NR, the lower the crosslink density needed to form a three dimensional network, which means the lower the dose of irradiation needed to vulcanise the latex.

Molecular weight measurement of NR latex coming from different sources had been done. The results showed that the molecular weight of NR varies from one clone to another, such as $M_n$ varies from about 170,000 to about 700,000. In the preparation of concentrated NR latex, all clones of NR latex were blended. In such mixture, the crosslink density of NR film to form a three dimensional network was predicted to be more than $3.01 \times 10^{24} \times 10^{-4}/17 = 17.7 \times 10^{18}$ crosslink unit/ml.

2.2 Aging property of RVNRL

Radiolysis of water forming a number of active species, such as $H^+$ and $OH^-$ radicals. Hydrogen radical is reducing agent, while $OH^-$ radical is an oxidising agent. It means that by radiation on water, anything capable being reduced may be reduced, while anything capable being oxidised may be oxidised.

Natural rubber latex containing a natural antioxidant, which will easily be destroyed by radiation through an oxidation process. So it is necessary to add an antioxidant into the irradiated latex in order to replace the natural antioxidant destroyed by radiation. Study on the selection of antioxidant suitable for that purpose are on going, and Vulcanox appears to be promising.

2.3 New sensitizer

The probable mechanism of radiation crosslink of natural rubber
is as follow:
(a) Cleavage of a C-H bond of one polymer chain by radiation to form one hydrogen radical and one polymeric radical ($R^\cdot$). The mobility of hydrogen radial is very high, while polymeric radical is very low.
(b) Absorption of hydrogen atom from neighbouring polymeric radical by the first hydrogen radical, forming a hydrogen molecule and the second polymeric radical.
(c) The two adjacent polymeric radicals having possibility to combine to form a crosslink through a C-C bond.

Because the mobility of these macroradicals/polymeric radicals are very low or limited, the combination only will occur when the distance between the two adjacent polymeric radicals is in close enough, that is in the order of the distance between C-C bond (1.54 Å). The probability that two adjacent polymeric radicals to be in very close distance is very low, and hence only a small fraction of the polymeric radicals will be able to combine forming a crosslink.

By adding a small amount of monomer which easily diffuse into NR, the polymeric radicals will be able to propagate and then combine with the adjacent polymeric radical (which may be far away from the first polymeric radical) forming a crosslink through a monomeric bridge. In this case the problem of two adjacent polymeric radical which far separated, to combine forming crosslink, can be eliminated. So the rate of crosslink will be much increased by the addition of a suitable monomer.

Study on the use of monofunctional acrylic monomers in radiation vulcanization of NR latex already been done. n-butyl acrylate (n-BA) or a combination of n-BA and CCl$_4$ appear to be the promising sensitizer. Dose of irradiation is about 10 kGy by using 5 phr of n-BA, and about 25 kGy by using a combination of 1 phr of n-BA and 1 phr of CCl$_4$. The mobility of the monomer in polymeric mattrix (poly-isoprene) may be the most important factor in increasing the rate of grafting$^5$.

2.4 Cost of irradiation

The most important component of radiation vulcanization cost (non-profit basis) is irradiation cost and the second is sensitizer cost. Application of a new sensitizer is expected to reduce both the irradiation and sensitizer cost. While the application of EB machine and a new design of Co-60 irradiator are expected to reduce the irradiation cost. Study on the application of a new sensitizer and EB irration
have been done and showing a promising method in reducing the radiation vulcanization cost. Table 1 shows the cost analysis of a Latex Irradiator already installed in Jakarta, under IAEA/UNDP Project. This facility was loaded with 215 kCi of Co-60 in 1983, and the maximum activity of Co-60 that can be loaded is about 600 kCi. The efficiency for irradiation of NR latex is about 0.42, for continuous operation. The capacity of this facility can be calculated using following equation. (base on continuous operation):

\[ Q = 42.6 \times C_1 \times c/D \text{ ton/year} \]

where \( C_1 \) = Co-60 activity in kCi, 
\( D \) = dose of irradiation, in Mrad 
\( c \) = efficiency

It is shown that by using a new sensitizer, n-BA or combination of n-BA and CCl₄, and a higher activity of Co-60, the irradiation cost can be much reduced.

3. Application of RVNRL

3.1 Rubber gloves
3.1.1 Survey on rubber gloves consumption

A survey on the consumption of medical rubber gloves in a number of hospitals in Indonesia had been done. The result showed that the annual consumption of medical rubber gloves in Indonesia was about 3.5 million pairs. The gloves were used several times after sterilisation. The gloves mostly were coming from abroad, and only a small fraction was produced locally. The consumption of rubber gloves for other purposes were not detected. It appears that consumption of rubber glove in Indonesia is still low.

3.1.2 World consumption

Due to AIDS, the world demand of examination rubber gloves increase significantly to about 800%. The estimated present demand is about 10,000 million per year. This is a good market for rubber industries.

3.1.3 Present profile of rubber gloves industry in Indonesia

Before 1986, rubber gloves industries in Indonesia was very weak and not recorded in the Indonesian Statistical Book. The exact number of rubber gloves industries were unknown. Most of the rubber gloves
industries were home industries.

To meet the world demand of examination rubber gloves, about 30 new examination rubber gloves factories had been installed and expected to be in operation by the end of 1989. The total capacity of those factories are about 1,600 million examination rubber gloves per year (Table 2). A number of new rubber gloves factories are being planned or under construction (about 80 factories). The common problem of those industries are production of gloves which meet the consumer's standard.

3.1.4 Application of RVNRL for rubber examination gloves

It has been reported that a private company is showing interest to produce examination rubber gloves using RVNRL. This company has already irradiated about 10 ton of NR latex for gloves production. However due to technical difficulty and marketing situation, the production of gloves was postponed.

Another private company in rubber gloves (from West Java) had already sent their technician for two month to CAIR to study the application of RVNRL for producing rubber gloves. This company has not yet started production.

A rubber glove company which just installed his plant with capacity of about 500 millions per year of examination rubber gloves, had already sent their technical personnel to CAIR-BATAN to study the possibility of using RVNRL for producing examination rubber gloves. The study is ongoing and a comparison has been made between gloves from RVNRL and from convensional sulfur vulcanised latex (Table 3 & 4). It is found that rubber examination gloves prepared from both RVNRL and convensional sulfur vulcanised latex meet the specifications prescribed by the Indonesian Standard of Industry (SII). According to this standard, the minimum tensile strength should be 20.6 MPa, and elongation at break should be 700%. The minimum tensile strength after accelerated aging at 70°C for 166 hours should be 15.7 MPa, and elongation at break should be 500%.

3.1.5 Rubber Surgical Gloves

A surgical gloves plant using RVNRL as raw material was under planning. This plant was proposed by national Family Planning Coordinating Board of Indonesia. Designed capacity of this plant is 4 million pairs/year of surgical gloves and 1.5 million pcs/year of balloon catheter. NR latex requirement is about 145 ton/year for both kinds of products. The products will be sterilised by using gamma radiation.
3.2 Condom

A condom plant installed in Indonesia is in operation since 1987. The designed capacity of this plant was about 900,000 gross, using three lines of moulding systems. Flowsheet of this plant is as following:

A study in using RVNRL for condom production has been done, both in the laboratory scale and in factory scale. Several times of test production in this plant using RVNRL had been done. In this case latex compounding process can be omitted, while the following processes (moulding, leaching, powdering etc.) should be adjusted in order to be compatible with RVNRL.

Test production was done in 1988 and 1989 using two different kinds of RVNRL.

3.2.1 April & May 1988

Test production had been done using RVNRL prepared by using CCl₄ (5 phr) and 45 kGy dose of irradiation. That latex had been stored for about 9 months after irradiation. About 150,000 pcs of condoms with thickness between 0.05-0.06 had been produced in this test production. Technical specification and physical properties of this product is as following:

Technical specification : - thickness 0.05-0.06 mm
- wide 49.3 mm
- length 184 mm
- weight 1.33 g

Physical properties : - tensile strength 23.5 MPa
- modulus 600%, 4.8 MPa
- elongation at break 850%
- bursting volume: 35 liter
Number of leakage : 2.4/100 condom.
Color : lightly brown

These condoms appear to meet both BSI or JIS for rubber condom. According to these standards, the minimum tensile strength should be 19.6 MPa and the elongation at break should be 600% for BSI and 650% for JIS.

Although the products already meet the standard of condom, but this experiment not yet fully successful because still about 20% of the products should be rejected due to some defect. Factory adjustment should be done.

The condoms produced partly being used for further test to study the public acceptance.
3.2.2 July 1989

Test production has been done using RVNRL prepared by using n-BA/CCl₄ sensitizer, with dose of irradiation 25 kGy. About 1000 gross (144,000) condoms already been produced and will be packaged soon. Specification and physical properties of this products is as following:

<table>
<thead>
<tr>
<th>Specification</th>
<th>RVNRL</th>
<th>Sulfur</th>
</tr>
</thead>
<tbody>
<tr>
<td>thickness</td>
<td>0.066 mm</td>
<td>0.061 mm</td>
</tr>
<tr>
<td>Modulus 300%</td>
<td>1.01 MPa</td>
<td>1.64 MPa</td>
</tr>
<tr>
<td>Modulus 600%</td>
<td>2.42 MPa</td>
<td>5.68 MPa</td>
</tr>
<tr>
<td>Tensile strength</td>
<td>22.06 MPa</td>
<td>30.59 MPa</td>
</tr>
<tr>
<td>Elongation at break</td>
<td>970%</td>
<td>840%</td>
</tr>
<tr>
<td>Bursting volume</td>
<td>42 liter</td>
<td>35 liter</td>
</tr>
<tr>
<td>Colour</td>
<td>milky white</td>
<td>milky white</td>
</tr>
</tbody>
</table>

These products, both from RVNRL or sulfur compound, appear to meet both BSI of JIS for rubber condom. The advantage of condom prepared from RVNRL are the low modulus, high elongation at break and high bursting volume. Low modulus means that in order to stretch to a given elongation, requires a low force, which consequently it will be able to follow human pattern easily. High elongation means that it can be stretched easily to to a long extension. The disadvantage is lower in tensile strength compared to that sulfur process, but still meet both BSI and JIS. Factory adjustment should be done, because in this experiment still about 20% of the products should be rejected due to some defects.
References

2. F. Sundardi, Sumarno K., Marga Utama, Majalah BATAN IX, 4 (1976)
4. F. Sundardi, Plastic and Rubber Processing and Application 5 (1985) 119-123
6. Herwinarni S., Made Sumarti, dan Marga Utama,
   - ibid -
7. Marga Utama, Made Sumarti, F. Sunardi,
   - ibid -
Table 1 Cost analysis of Latex Irradiator in Jakarta

<table>
<thead>
<tr>
<th>Cost Items</th>
<th>Loaded with 200 kCi of Co-60</th>
<th>Loaded with 500 kCi of Co-60</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
<td>B</td>
</tr>
<tr>
<td>I. FIXED CAPITAL INVESTMENT, US $</td>
<td></td>
<td></td>
</tr>
<tr>
<td>a) Building</td>
<td>450,000</td>
<td>450,000</td>
</tr>
<tr>
<td>b) Equipments: water treatment system, source handling, reactor etc.</td>
<td>550,000</td>
<td>550,000</td>
</tr>
<tr>
<td>c) Co-60 source</td>
<td>350,000</td>
<td>350,000</td>
</tr>
<tr>
<td>d) Contingency</td>
<td>100,000</td>
<td>100,000</td>
</tr>
<tr>
<td>Total</td>
<td>1,450,000</td>
<td>1,450,000</td>
</tr>
<tr>
<td>II. IRRADIATION COST per YAE, US $</td>
<td></td>
<td></td>
</tr>
<tr>
<td>b) Co-60 replacement, 12.5%</td>
<td>47,750</td>
<td>47,750</td>
</tr>
<tr>
<td>c) Depreciation: building, 20 y</td>
<td>22,500</td>
<td>22,500</td>
</tr>
<tr>
<td>d) Depreciation: equipments, 15 y</td>
<td>36,666</td>
<td>36,666</td>
</tr>
<tr>
<td>e) Maintenance &amp; utility, 2% of fixed cap. invs.</td>
<td>29,000</td>
<td>29,000</td>
</tr>
<tr>
<td>f) Tax, insurance, contingency: 3% of fixed cap. invs</td>
<td>43,500</td>
<td>43,500</td>
</tr>
<tr>
<td>III. CAPACITY, ton/year</td>
<td>800</td>
<td>1,800</td>
</tr>
<tr>
<td>IV. IRRADIATION COST, us 4/4kg</td>
<td>0.253</td>
<td>0.113</td>
</tr>
<tr>
<td>V. Sensitizer cost, US $/kg 0.084</td>
<td>0.034</td>
<td>0.084</td>
</tr>
<tr>
<td>VI. Radiation vulcanisation cost, IV + V, $/kg</td>
<td>0.337</td>
<td>0.147</td>
</tr>
</tbody>
</table>

Note: (A) = Sensitizer, CCl₄, and dose = 45 kGy; (B) = Sensitizer CCl₄, 1 phr and n-BA 1 phr with dose = 20 kGy; (C) = Sensitizer n-BA 5 phr with dose = 10 kGy.
Table 2 New rubber gloves factories expected to be in operation in Indonesia, in 1989

<table>
<thead>
<tr>
<th>Name of company</th>
<th>Estimated capacity/y</th>
<th>Latex consumption, ton/year</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Examination gloves,</td>
<td>Surgical gloves,</td>
</tr>
<tr>
<td></td>
<td>pieces</td>
<td>pair</td>
</tr>
<tr>
<td>1. PT Eka Latexindo</td>
<td>86,400,000</td>
<td>-</td>
</tr>
<tr>
<td>2. PT Latexindo Parana</td>
<td>24,000,000</td>
<td>-</td>
</tr>
<tr>
<td>3. PT Indo Rubber Industries</td>
<td>43,200,000</td>
<td>-</td>
</tr>
<tr>
<td>4. Gumisarta Mutiara (PT)</td>
<td>43,200,000</td>
<td>-</td>
</tr>
<tr>
<td>5. PT. Haluwiko Prati</td>
<td>36,000,000</td>
<td>-</td>
</tr>
<tr>
<td>6. PT. Sarana Indo Protex</td>
<td>43,200,000</td>
<td>-</td>
</tr>
<tr>
<td>7. PT. Trias Ariandini</td>
<td>24,000,000</td>
<td>-</td>
</tr>
<tr>
<td>8. PT. Aneka Variasi Sejahtera</td>
<td>43,200,000</td>
<td>-</td>
</tr>
<tr>
<td>9. PT. Toyotama Prasumya</td>
<td>43,200,000</td>
<td>-</td>
</tr>
<tr>
<td>10. PT. Musi Mas</td>
<td>43,200,000</td>
<td>-</td>
</tr>
<tr>
<td>11. PT. Superindo Melody Pacific</td>
<td>24,000,000</td>
<td>-</td>
</tr>
<tr>
<td>12. PT. Agrindo Wahana</td>
<td>24,000,000</td>
<td>-</td>
</tr>
<tr>
<td>13. PT. Hongkong Prima Tama</td>
<td>30,000,000</td>
<td>-</td>
</tr>
<tr>
<td>14. PT. Latexindo Pratama</td>
<td>30,000,000</td>
<td>-</td>
</tr>
<tr>
<td>15. PT. Latexindo Sejahtera</td>
<td>72,000,000</td>
<td>-</td>
</tr>
<tr>
<td>16. NV. Kalibaru</td>
<td>24,000,000</td>
<td>-</td>
</tr>
<tr>
<td>17. PT. Marga Jaya</td>
<td>15,000,000</td>
<td>7,200,000</td>
</tr>
<tr>
<td>18. PT. Kresasi Bajwangis</td>
<td>86,400,000</td>
<td>-</td>
</tr>
<tr>
<td>19. PT. Perkasa Rubber Industries</td>
<td>197,664,000</td>
<td>-</td>
</tr>
<tr>
<td>20. PT. Latexindo Lestari</td>
<td>60,000,000</td>
<td>-</td>
</tr>
<tr>
<td>21. PT. Bilboordin Abadi</td>
<td>15,000,000</td>
<td>-</td>
</tr>
<tr>
<td>22. PT. Tata Rubberindo Industries</td>
<td>60,000,000</td>
<td>-</td>
</tr>
<tr>
<td>23. PT. Scitech Industries</td>
<td>-</td>
<td>50,000,000</td>
</tr>
<tr>
<td>24. PT. Indo Rama</td>
<td>70,000,000</td>
<td>-</td>
</tr>
<tr>
<td>25. PT. Delta Waru Rubber Industry</td>
<td>43,200,000</td>
<td>-</td>
</tr>
<tr>
<td>26. PT. Giri Nusa Harum</td>
<td>84,000,000</td>
<td>-</td>
</tr>
<tr>
<td>27. UD. Pelangi Industri</td>
<td>-</td>
<td>480,000</td>
</tr>
<tr>
<td>28. PT. Karetindo Marga</td>
<td>43,200,000</td>
<td>-</td>
</tr>
<tr>
<td>Nirmala</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Total capacity</strong></td>
<td><strong>1,608,064,000</strong></td>
<td><strong>57,680,000</strong></td>
</tr>
</tbody>
</table>
Table 3  Physical properties of rubber gloves prepared from RVNRL, using n-BA/CCl₃, sensitizer. Dose of irradiation = 25 kGy.

<table>
<thead>
<tr>
<th>Latex storage time, days</th>
<th>Latex properties</th>
<th>Film properties</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Viscosity, mPa.s</td>
<td>Total solid, %</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>20.21</td>
<td>56.8</td>
</tr>
<tr>
<td>5</td>
<td>20.60</td>
<td>56.9</td>
</tr>
<tr>
<td>10</td>
<td>21.37</td>
<td>56.8</td>
</tr>
<tr>
<td>20</td>
<td>21.12</td>
<td>57.0</td>
</tr>
<tr>
<td>30</td>
<td>28.72</td>
<td>56.7</td>
</tr>
</tbody>
</table>

Note:

(A) Unleached, heated at 100°C for 30 minutes.
(B) Leached for 30 minutes in hot water, heated at 100°C for 30 minutes.
Table 4  Physical properties of rubber gloves prepared from convensional sulfur vulcanised NR latex

<table>
<thead>
<tr>
<th>Latex storage time, days</th>
<th>Latex properties</th>
<th>Film properties</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Viscosity, mPa.s</td>
<td>Total solid, %</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>4.09</td>
<td>35.9</td>
</tr>
<tr>
<td>5</td>
<td>4.22</td>
<td>35.9</td>
</tr>
<tr>
<td>7</td>
<td>4.35</td>
<td>36.5</td>
</tr>
<tr>
<td>10</td>
<td>4.35</td>
<td>36.6</td>
</tr>
<tr>
<td>20</td>
<td>4.22</td>
<td>36.2</td>
</tr>
<tr>
<td>30</td>
<td>4.22</td>
<td>36.1</td>
</tr>
</tbody>
</table>

Note:

(A) Unleached, heated at 100°C for 30 minutes.
(B) Leached for 30 minutes in hot water, heated at 100°C for 30 minutes.
Fig. 1 Scanning Electron Micrograph of NR latex particles.

Fig. 2 Scanning Electron Micrograph of cross section of NR film.
5.3 Commercial Irradiation of Natural Rubber Latex

T. Saito, G. Koike, Y. Sato and Masaaki Takehisa

Radiia Industry Co., Ltd.,
Takasaki, Gunma, 370-12 Japan

Abstract

Cost of irradiation is one of the important factor to expand industrial application of radiation vulcanized natural rubber latex (RVNRL). The irradiation cost was studied under the RCA project, RAS/8/061/1109, and reasonable cost was reported by use of single purpose latex irradiation facility of 1500 ton/year.

For a market development of RVNRL, irradiation of latex of the order of 100 ton/year may be required. Construction of the single purpose pilot plant of this scale is not commercially feasible. In this stage use of contract irradiation facilities which are familiar worldwide gives a solution.

Radiia Industry Co., Ltd. have two irradiation facilities with 1.4 MCl of Co-60, and irradiate natural rubber latex for Okamoto Industries, Inc. with use of the incremental dose irradiator which is commonly used for sterilization of medical supplies.

Natural rubber latex filled in standard 20 liter plastic bags are loaded on the hanger of trolley conveyer, and irradiated without agitation. The dose uniformity was around 2, and properties of the RVNRL was reported satisfactory. The dose uniformity can be improved if special container is applied.

In future it is expected to construct a larger single purpose irradiation plant to provide low cost irradiation for multi-client, or import RVNRL from RCA countries provided transportation test is successful.

We have interest in electron beam vulcanization. Radiia Industry Co., Ltd. put an order 5 MeV, 150 kW electron beam machine and it will be operational in 1990. High penetration of 5 MeV electron beam is useful for radiation processing in the condensed media like natural rubber latex.
1. Introduction

Radiation vulcanized natural rubber latex (RVNRL) has characteristics different from conventional sulfur cured natural rubber latex, and is expected to expand the fields of application of NR latex. One of the key points to develop the commercialization of RVNRL is a competition of RVNRL price to that of conventional vulcanized natural rubber latex (NRL).

Cost of radiation vulcanization for each RCA countries was reported in Sep. 1988 under the RCA project based on a result of RAS/8/061/-1109, "Design of gamma irradiator for radiation vulcanization of natural rubber latex". The reported cost of radiation vulcanization in RCA countries was markedly low to that in Japan. In this case, single purpose facility with a irradiator of production capacity of 1500 ton/year was used as the calculation basis.

2. Scenarios for commercialization

Several scenarios may exist to develop commercialization of the new technology. The first one shown in Table 1 is step by step expansion of commercialization of products with unique characteristics. This is the way taken by Okamoto Industries Inc. It seems too risky to invest the radiation vulcanization facility by a latex processing company at the present moment at least in Japan. In a small scale irradiation of NRL, role of a contract irradiation company is important.

The realistic way in the present stage in Japan is to irradiate an order of 10 to 100 ton/year NRL by use of a contract irradiation company. An in-house single purpose irradiation facility is not feasible in this scale. The use of package irradiation is recommended for the production size.

The radiation vulcanization more than 100 ton/year in a contract irradiation company with use of tank type batch irradiator with an agitator of outer radiation source will be possible. In this case guarantee of stable needs of irradiation service from clients is requisite for contract irradiation company.

In TCRE/JAERI, rotating drum type reactor and cubic tank reactor with agitator were used for preparation of considerable amount of RVNRL. Similar reactors can be used in RIC-1 Co-60 facility in Radia Industry, but it is improbable to settle the reactor in common AECL type package irradiators.
Flow type reactor is also expected to increase the efficiency of irradiation, but so far we know study on sticking of NRL onto the reactor wall is not yet reported. It is expected to test such a basic engineering problem in RCA project of RVNRL in this stage.

3. Commercial irradiators

Radiation Industry Co., Ltd. has two irradiation facilities. RIC-1 can be used for batch tank reactor or flow type reactor for radiation vulcanization. RIC-2, a package irradiator with hanger type conveyer which is mainly used in medical supply sterilization is used for NRL package irradiation for Okamoto Industries, Inc. Following are brief description of irradiation facilities.

RIC-1 with Co-60 of 530 kCi shown in Fig. 1 was commissioned in 1972, later being modified the conveyer system. Products are received on the 2nd floor and charged into radiation room on tilted conveyer by gravity, and irradiated on slat conveyer moving beside Co-60 source mounted in plaque of 0.4 m x 4 m. After the first pass the products are again conveyed to the radiation room and the second irradiation is carried out from the opposite side, then transported to a storage area on the lst. floor. For high dose irradiation or irradiation using a vessel is being carried out on a irradiation table. Characteristics of RIC-1 are summarized in Table 2.

RIC-2, the bird's eye view is in Fig. 2 and the conveyer diagram is in Fig. 3, is an incremental dose irradiator with 870 kCi Co-60 which was commissioned in 1984, and the operation is fully controlled by computers. Four products (standard size of 40 cm x 40 cm x 34 cm) are loaded manually into a stainless steel insert box (86 cm x 86 cm x 38 cm) with registration to computer on product number, and required dose. Then two insert boxes are automatically loaded to one hanger and then conveyed into radiation room by trolley conveyer. After required numbers of turn over determined by the dose, the products are unloaded automatically. To make the dose distribution as homogeneous as possible, position of the insert box is shuffled up and down at half dose of the final dose required. For dose assurance, a piece of PMMA dose meter, Radix NRI5, and biological indicator (for only medical supplies) are kept on the minimum dose point in each hanger. Characteristics of RIC-2 are summarized in Table 3.
4. Commercial irradiation of latex

Irradiation of NRL by RIC-2 was carried out with use of plastic container of 30 cm × 30 cm × 30 cm containing 20 liters of NRL. Loading of the container in cardboard box to the insert box and to the hanger is shown in Fig. 4. Irradiation of NRL of the order of one tonne per day can be carried out without problems for the other clients.

Dose distribution, represented in dose maximum to dose minimum, is important in the package irradiation of condensed media without agitation. Fig. 5 shows calculated dose maximum, average, and minimum as a function of container width after both side irradiation using dose build up factor by S. Tanaka's equation of JAERI. Observed dose with 30 cm width container improve the dose uniformity to NRL.

Fig. 6 demonstrates a relation between dose and tensile strength at break for thin film made from RVNRL with NBS sensitizer. With use of thin width container as irradiation vessel, physical properties of products from RVNRL will be improved.

Fig. 7 also demonstrates an optimization of size of NRL irradiation container for RIC-2. Increase in container width increase an amount of batch irradiation, and due to load limit of the hanger conveyer, 130 kg/insert box, amount of NRL batch is no more increase in the thicker container than 25 cm. Irradiation cost in the contract irradiation facility mainly depend on a volume basis for one hanger (or insert box). The irradiation cost per unit volume is independent from container thickness larger than 25 cm. Considering the increase in dose uniformity in thick container, 25 cm width container is optimum from the radiation processing cost. In between 20 to 25 cm, the radiation cost increase in thin container is not so marked. Again optimum container of NRL irradiation in view of a rubber processing industry have to have a width between 20 and 25 cm, because physical properties of RVNRL will be better by improved dose uniformity with thin irradiation container.

5. Future prospect

Table 4 summarizes scale of RVNRL production and the role of contract irradiation company. The authors believe that in a small scale package irradiation in contract irradiation company gives resonable irradiation cost. Presently price of irradiation service in Japan is higher than that in other countries. This must be understood from the
results of cost calculation in RCA project after RAS/8/061/-1109. So
the package irradiation can also be carried out in RCA countries who have
AECL type package irradiator without additional initial investment for
irradiation facility. Use of batch tank irradiator in contract irradia-
tion company will be realized after guaranantee of stable order of NRL
irradiation from rubber processing company. In both cases, radiation
vulcanization in contract irradiation company will be a transient process
in market development or small scale production of rubber company.

It is hoped that full commercialization of the RVNRL processing is
realized in a not so long future in Japan with use of in-house single
purpose irradiator. From the present consumption of NRL of 17,000 ton/
year in Japan, construction of big irradiation facility by co-operative
of rubber companies is effective means to reduce the RVNRL cost.

The authors have keen interest in electron beam vulcanization of
NRL which is under R/D in a public sector and some industrial sector.
Radia Industry Co., Ltd. have put an order of 5 MeV, 150 kW electron
beam machine, and it will be operational in 1990. High penetration of
5 MeV EB will help a engineering problems of EB processing in the con-
densed media.

An alternative scenarios for full commercialization is shown in
Table 5. The authors do not have much words in the scenarios. From
the cost comparison of irradiation in Japan and in RCA countries. It is
clear that import of RVNRL from NRL producing countries with a radiation
processing potential will be more feasible, provided transportation test
in successful. Production of the final products in the region and import
of it may be yet another option.
Table 1 Scenarios for full commercialization of VNRL

1) COMMERCIALIZATION OF PRODUCTS WHICH CAN NOT BE OBTAINED BY CONVENTIONAL VNRL

SMALL PRODUCTION ~ HIGH IRRADIATION COST

IRRADIATION COST ANALYSIS FOR 1500 T/Y

AFTER (RAS/8/061/-1109)

0.82 ~ 0.8 $/kg (DRY TYPE FACILITY)
0.48 ~ 0.16$/kg (WET TYPE FACILITY)

REDUCTION OF COST ~ BIG RADIATION PLANT

2) ROLE OF CONTRACT IRRADIATION COMPANY

Table 2 Characteristics of batch irradiator (RIC-1)

1) CAPABILITY OF BATCH OPERATION SUITABLE FOR HIGH DOSE IRRADIATION

2) CAPABILITY OF IRRADIATION WITH USE OF SINGLE PURPOSE REACTOR AND EQUIPMENT

3) IRRADIATION OF PRODUCT OR EQUIPMENT UP TO 4 METER LONG

4) HIGH PERFORMANCE VENTILATION PERMIT TO IRRADIATE PRODUCTS EVOLVING GASES

POLYMER MODIFICATION, ANTI-RADIATION TEST

Table 3 Characteristics of package irradiator (RIC-2)

1) PRODUCTS OF MAX. 80 × 80 × 34 CM CAN BE IRRADIATED (STANDARD PACKAGE SIZE IS 40 × 40 × 34 CM)

2) IRRADIATION OF PRODUCTS FOR VARIOUS DOSES CAN BE CARRIED OUT SIMULTANEOUSLY BY INCREMENTAL OPERATION (2 kGy INTERVAL)

3) COMPUTER CONTROLLED OPERATION

STERILIZATION OF MEDICAL SUPPLIES, EXP. ANIMAL FEED, LAB. BOODS, PACKAGE MATERIALS, ETC.
Table 4  Scale of RVNRL production and the role of contract irradiation company

<table>
<thead>
<tr>
<th>SCALE T/Y</th>
<th>TYPE OF FACILITY</th>
<th>LOCATION</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 ~ 100</td>
<td>PACKAGE IRRADIATOR</td>
<td>CIC</td>
</tr>
<tr>
<td>100 ~ 500</td>
<td>BATCH TANK</td>
<td>CIC</td>
</tr>
<tr>
<td>1000 ~ 2000</td>
<td>SINGLE PURPOSE</td>
<td>INHOUSE</td>
</tr>
<tr>
<td>~ 5000</td>
<td>SINGLE PURPOSE</td>
<td>CO-OP.</td>
</tr>
<tr>
<td>~ 2000</td>
<td>EB TANK, FLOW</td>
<td>CIC</td>
</tr>
</tbody>
</table>

Table 5  Scenarios for full commercialization of RVNRL

3) IMPORTATION OF RVNRL FROM RCA COUNTRIES
   IRRADIATION COST ANALYSIS FOR 1500 T/Y
   AFTER (RAS/8/061/-1109)

   RCA  0.2 ~ 0.07 (D), 0.14 ~ 0.04 (W) $/kg
   JAP  0.82 ~ 0.8 (D), 0.48 ~ 0.16 (W) $/kg

   TRANSPORTATION TEST

4) PRODUCTION OF FINAL PRODUCT IN RCA REGION
   TECHNOLOGY TRANSFER
Fig. 3 RIC-2 incremental irradiator

Fig. 4 Package irradiation of natural rubber latex
Fig. 5 Calculated & observed dose/pass vs. container width

Fig. 6 Tb of rubber & dose range of static irradiated
Fig. 7 Optimization of latex container width for package irradiator
CHARACTERIZATION OF NR LATEX AND VULCANIZATION

5.4 Effect of Non-Rubber Components on Sensitized RVNRL

NORJANAH MOHLD\textsuperscript{1}), K. Makuuchi\textsuperscript{2)}, F. Yoshi\textsuperscript{2}) and I. Ishigaki\textsuperscript{2})

\textsuperscript{1}) Nuclear Energy Unit, Kompleks PUSPATI, Bangi, Malaysia
\textsuperscript{2}) JAERI, TRCRE, Takasaki, 1 Gunma, 370-12 Japan

Abstract

Attempts were carried out to establish the actual roles of non-rubber components in NR latex in the efficiency of the radiation vulcanization. Several types of latexes including centrifuged, creamed and deproteinized latexes were used for the work. The effect of varying amounts of nitrogen content of latex, in particular, once-, twice- and triple-centrifuged latexes were observed. The results obtained indicate the presence of inhibitor and accelerator for the radiation vulcanization process.

1. Introduction

In recent year there has been considerable development in radiation vulcanization of natural rubber latex (RVNRL)\textsuperscript{1}. Most of these, however, are associated with development of sensitizer system. Despite these advance a full understanding of RVNRL is still lacking. It has been observed that vulcanization dose is dependent on the green strength which is turn depends on the microgel contents. High microgel contents are associated with high nitrogen contents. This has led to the belief that non-rubbers play a major role in RVNRL\textsuperscript{2}.

In this work investigations were carried out to find out whether decreasing the non-rubber content progressively would show any effect on RVNRL.

2. Experimental

2.1 Materials

Latexes were supplied by Guthrie Research Chemara, Malaysia. The properties of latexes are shown in Table 1. The levels of TMTD/ZnO in
these latexes are not clear. Fieled latex also used and its initial properties are as follows:

preserved in 0.8% NH₃ and 0.03% TMTD/0.03% ZnO
TSC:33.7%, DRC:31.9%, VFA No.:0.020, pH:10.2
Sensitizer used was n-butyl acrylate (n-BA).

The sensitizer, n-BA, was added to latex dropwise whilst stirring using a magnetic stirrer to avoid any clumping of the sensitizer. The latex was diluted to 50% TSC with water. The concentration of sensitizer is 5 phr.

Centrifuging was carried out to collect skim of HA latex with a "SAITO" Super Centrifuge, model SPL 100 made by Saito Separation Limited, Tokyo, Japan.

2.2 Irradiation and Measurements

Irradiation was carried out using Co-60 sources at room temperature. The dose rate was fixed at 10 kGy/hr. The irradiated latex was cast on glass plate at room temperature to obtain rubber films having thickness of 0.7 - 1.2 mm. The films were then leached in deionised water for 24 hours and dried at room temperature. Heat treatment of the films were carried out at 80°C for 30 min. These were then conditioned for at least for 24 hours before testing for tensile properties. Tensile tests of rubber films were done with a Toyo Seiki Strograph Rl machine according to JIS K 6301.

3. Results and Discussion

Field latex was irradiated before and after centrifugation to know the effect of non-rubber components on RVNRL. Figure 1 shows the relation between dose and tensile strength (Tb) of film prepared from the irradiated latex. The definition of samples are as follows:

Sample A : field latex
Sample B : centrifuged then irradiated
Sample C : irradiated then centrifuged

From this figure it is clear that sample A gives lowest Tb among three samples. There is not significant difference between B and C, both give a higher maximum Tb than A. This means that centrifugation of field latex enhances RVNRL. It is supposed that some parts of non-rubber which act as inhibitors for RVNRL are removed by centrifugation. The
non-rubber content in latex could be reduced by centrifuging latex a number of times. The relationship between dose and Tb of once-, twice- and triple-centrifuged NR latexes are presented in Fig. 2. It was expected that maximum Tb will increase with increasing number of centrifugation time. Contrary to expectation, maximum Tb decreased with increasing the number of centrifugation. This suggests that field latex will have both types of non-rubber substances which will accelerate and retard RVNRL. When the field latex is centrifuged once, the inhibitors are almost removed. Hence the efficiency of radiation vulcanization increases. In the second time centrifuging some of the accelerators are removed so that the Tb obtained is lower.

Figure 2 also shows the relation of dose and Tb for deproteinized latex and creamed latex. The Tb of deproteinized latex is extremely low compared with the centrifuged and creamed latexes. This suggests that the non-rubber components which accelerate RVNRL are related with proteins. The proteins which combine NR molecules through hydrogen bonds are supposed to the non-rubber components which accelerate RVNRL. During centrifugation some parts of the proteins are removed from the latex, resulting in lowering in Tb.

The non-rubber components which act as inhibitor for RVNRL are supposed to be water-soluble materials which are removed by centrifugation of field latex and not to be removed by creaming process. This suggests that the serum (skim) of once-centrifuged latex is free from inhibitors.

The fact that twice-centrifuged latex gives lower Tb than once-centrifuged one suggests skim from HA latex contains accelerating component. When the skim from HA latex collected by centrifugation of HA latex was added to HA latex sensitized RVNRL with n-BA is accelerated as shown in Fig. 3. The Tb increased with the addition of skim, which is likely caused by some accelerators present in the skim.

We believe that further investigation to assess the functional roles of the non-rubber components need to be done. The studies using deproteinized latex as the starting materials should be able to shed light on the roles of proteins in RVNRL. Confirmation of the presence of inhibitors and accelerators for RVNRL will require extensive studies. The results obtained here can be used for the basis for further work.
References

1. K. Makuuchi, in this proceedings.
<table>
<thead>
<tr>
<th>Latex Sample</th>
<th>NH (%)</th>
<th>TSC (%)</th>
<th>DRC (%)</th>
<th>VFA No.</th>
<th>MST sec</th>
<th>pH</th>
<th>KOH No.</th>
<th>Viscosity (cP)</th>
<th>Nitrogen in Dry Film (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Once-centrifuged HA</td>
<td>0.81</td>
<td>63.33</td>
<td>61.53</td>
<td>0.014</td>
<td>256</td>
<td>10.32</td>
<td>0.60</td>
<td>64.2*</td>
<td>0.21</td>
</tr>
<tr>
<td>Double-centrifuged</td>
<td>0.83</td>
<td>61.07</td>
<td>60.48</td>
<td>0.006</td>
<td>546</td>
<td>10.50</td>
<td>0.24</td>
<td>62.3*</td>
<td>0.15</td>
</tr>
<tr>
<td>Triple-centrifuged</td>
<td>0.82</td>
<td>61.21</td>
<td>60.98</td>
<td>0.004</td>
<td>942</td>
<td>10.70</td>
<td>0.15</td>
<td>85.9*</td>
<td>0.11</td>
</tr>
<tr>
<td>Deproteinized</td>
<td>0.77</td>
<td>57.62</td>
<td>55.35</td>
<td>0.032</td>
<td>656</td>
<td>10.32</td>
<td>0.87</td>
<td>40.4*</td>
<td>0.19</td>
</tr>
<tr>
<td>Creamed</td>
<td>0.44</td>
<td>63.61</td>
<td>61.56</td>
<td>0.032</td>
<td>1946</td>
<td>10.00</td>
<td>0.67</td>
<td>162***</td>
<td>0.22</td>
</tr>
</tbody>
</table>

* Brookfield Spindle #1, 60 rpm,  ** Spindle #3, 60 rpm,  *** Spindle #1, 30 rpm
Fig. 1 Relation between dose and tensile strength
Sample A: field latex
Sample B: centrifuged then irradiated
Sample C: irradiated then centrifuged

Fig. 2 Relationship between dose and tensile strength of once-, twice- and triple-centrifuged, deproteinized and creamed latexes
5.5 Selection of Thai Latex for Radiation Vulcanization

CHYAGRIT SIRI-UPATHUM\textsuperscript{1)}, Krisda Suchiva\textsuperscript{2)} and Jindarom Chwajarernpun\textsuperscript{3)}

1) Chulalongkorn University, Bangkok, Thailand
2) Mahidol University, Bangkok, Thailand
3) Office of Atomic Energy for Peace, Bangkok, Thailand

Abstract

Radiation vulcanization of 7 different sources of concentrated latex found to give the maximum tensile strengths of the rubber film from 15-26 MPa at vulcanization doses of 10-22 KGY. The sensitizer used was a mixture of 5:1 phr of 2 EHA and CCl\textsubscript{4} at concentration of 6 phr. Attempt was made to correlate protein content in latex with vulcanization dose and with maximum tensile strength of the rubber film obtained. Experimental results showed that rate of vulcanization varied inversely with the protein content. Rough estimation of the optimum protein content for which highest tensile strength of the film might obtain was about 1.0 - 1.2\% on total solid content (TSC).

1. Introduction

Selection and characterization of natural rubber (NR) latex from some producers in Indonesia, Malaysia, Sri Lanka and Thailand has been investigated in order to obtain suitable latices for radiation vulcanization\textsuperscript{1).} Latices with low vulcanization dose were considered as suitable latices and characterised by high nitrogen content at lower vulcanization dose when the vulcanized films were washed in ammonia solution. Lower tensile strength of the films from radiation vulcanization of natural rubber latex (RVNRL) were also observed from deprotenised NR and double centrifuged NR. In earlier work of Puig\textsuperscript{2} the effect of amine compounds in latex to improve cross-linking efficiency was investigated by observing maximum swelling at different protein contents after irradiation to a given dose. It revealed however, that cross-linking was more efficient when proteins were removed. Selection of Thai NR latex for RVNRL is investigated here and the results are presented. An attempt is made to predict the vulcanization dose by using protein content in NR latex as a criterion.
2. Experimental

NR lattices used were commercially available high ammonia (HA) concentrated lattices, meeting the ISO 2004 standard. The lattices were diluted to 55 wt% by 1% ammonia water. 2-ethyl hexyl acrylate(2EHA) and CCl₄, in the ratio of 5:1 was used as sensitisier at concentration of 6 phr. Irradiation by Co-60 source at dose rate of 4.5 KGY/hr was done at the Office of Atomic Energy for Peace. (OAEP). Films of 0.8 - 1.0 mm thickness cut from RVNRL were leached by 1% ammonia solution after drying. The wetfilms were oven dried at 70°C for 1 hr. Protein content in lattices were determined by a macro Kjeldhal method.

3. Results and Discussion

3.1 Tensile Strength of rubber films

Tensile strengths of rubber films from RVNRL of the investigated NR lattices are summarised in Table 1. It is noted that Thaitex(TH) which requires the highest vulcanization dose was randomly selected for comparison with lattices from other countries in the mentioned work of Chauplong and Makuuchi¹. In contrast to TH, latex from Rubber Estate Organization (RE) requires a dose of only 10 kGy for vulcanization. Other lattices require vulcanization doses of about 14-18 kGy with tensile strength registering up to 25 MPa.

3.2 Nitrogen content in latex and vulcanization dose

Relationship between nitrogen content in the lattices and vulcanization dose is shown in Figure 1. It indicates that vulcanization dose of NR latex is likely to depend inversely on protein content. Thus vulcanization efficiency is better in latex with low protein content. This result is in good agreement with the work of Puig². Figure 2 indicates the shift of vulcanization dose to a higher value after the addition of casein in alkaline solution to RE latex to increase the nitrogen content from 0.12% to 0.28% on the TSC.

3.3 Nitrogen content in latex and maximum tensile strength of rubber film

At each vulcanization dose maximum tensile strength of rubber films seems to increase with increasing protein content in NR latex as shown
in Figure 1. However if nitrogen content is higher than about 0.25%, maximum tensile strength of rubber films seem to drop sharply. The decrease of maximum tensile strength is also observed in the previous example shown in Figure 2. Another example which show an increase in the maximum tensile strength if the nitrogen content in latex is raised from 0.12% to 0.18% by adding casein is shown in Figure 2. The reason for the observations that RVNRL with nitrogen content higher than 0.25% show a low tensile strength of the film is still not clear and further investigation is needed.

It should be noted that vulcanization of latex by irradiation can give rise to cross links mainly within individual latex particles (intraparticle cross link)\(^3\). Inter particular cohesion is enhanced during heating after complete leaching and results in high tensile strength of the rubber film. On the other hand some degradation components from excess nitrogeneous compound caused by radiation or active species from water radiolysis are found\(^2\). These components, perhaps unleachable by ammoniated water, become inclusions in the rubber film and thus prevent good interparticular cohesion.

4. Conclusions

Radiation vulcanization of Thai latices require vulcanization doses from 10–22 KGY which give maximum tensile strength of the rubber films from 15–26 MPa. Sensitiser used is 2EHA and CCL\(_4\) at a ratio of 5:1 at concentration of 6 phr. Latices with low nitrogen content require low vulcanization dose. Maximum tensile strength of the films is found to slightly increase with nitrogen content in latex upto about 0.25% on TSC, beyond which there is a sharp decrease.

References

Table 1  Effect of nitrogen content in latex on vulcanization dose and tensile strength of rubber film (ZEH/CCL₄ 5:1 at 6 phr as sensitizer)

<table>
<thead>
<tr>
<th>Latex type</th>
<th>Nitrogen content (%)</th>
<th>Green Strength* (MPa)</th>
<th>Vulcanization dose (KGY)</th>
<th>Max Tb (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RE</td>
<td>0.12</td>
<td>2.4</td>
<td>10</td>
<td>23.1</td>
</tr>
<tr>
<td>OR</td>
<td>0.16</td>
<td>2.7</td>
<td>12</td>
<td>23.8</td>
</tr>
<tr>
<td>PA</td>
<td>0.21</td>
<td>3.2</td>
<td>15</td>
<td>25.5</td>
</tr>
<tr>
<td>KN</td>
<td>0.26</td>
<td>3.5</td>
<td>22</td>
<td>26.1</td>
</tr>
<tr>
<td>SR</td>
<td>0.27</td>
<td>2.3</td>
<td>17</td>
<td>18.9</td>
</tr>
<tr>
<td>YT</td>
<td>-</td>
<td>3.0</td>
<td>20</td>
<td>16.1</td>
</tr>
<tr>
<td>OR/1</td>
<td>0.30</td>
<td>2.8</td>
<td>14</td>
<td>20.9</td>
</tr>
<tr>
<td>SU</td>
<td>0.30</td>
<td>-</td>
<td>18</td>
<td>17.8</td>
</tr>
</tbody>
</table>

* with sensitizer at 0 KGY
Fig. 1 Effect of nitrogen content on vulcanization dose and maximum tensile strength of film

Fig. 2 Effect of adding casein to NRL on vulcanization dose and tensile strength of film
5.6 Characteristic of Natural Rubber Latex from Indonesia

MARGA UTAMA1), F. Sundardi2), Herwinarni2), M. Sumarti2), S. Iskandar2), D. Irhami2), K. Makuuchi2) and Y. Yoshii2)

1) Center for Application of Isotopes and Radiation, BATAN, Jakarta, Indonesia
2) TRC RE, JAERI, Takasaki, Gunma, 370-12 Japan

Abstract

Five field latexes from different clones have been characterized. The total solid content increases and the protein content decreases with increasing the age of rubber trees. The average particle size is between 190 and 234 nm. The number average molecular weight varies from 160,000 to 700,000, while the weight average molecular weight varies from 1,000,000 to 500,000. Negligible difference was observed in the physical properties of rubber films prepared from the irradiated field latexes.

1. Introduction

Latex from Hevea brasiliensis tree is an aqueous dispersion of rubber containing 25 - 40% rubber hydrocarbon, stabilised by a small amount of protein and fatty acid1).

The particle size and molecular weight of rubber form Malaysia have been studied by some authors2), 3), 4), 5). They reported that the particle diameter of rubber is between 0.1 - 3.0 micron, and molecular weight is between 10^3-10^6. Studies on the irradiated latex in Indonesia began in 1972. The natural rubber latex studied was in the concentrated form, (about 60% dry rubber content). The results showed that the mechanical properties of the rubber film were much influenced by the origin of the latex.

This paper presents the characteristics of field latex from West Java before and after irradiation.

2. Experimental

2.1 Materials

The field natural rubber latex was from Pasir Waringin Plantation, Serang, West Java and was used as an ammonia preserved latex. These
field latices were from clones Mix 16/1968, GT 1/1969, GT 1/1974 GT 1/1977, RRIM/1977, PR 300/1977 and PR 28/1974. These latex were from trees tapped in April and July 1985. Tetra hydro furan (THF), K₂SO₄, CUSO₄, NaOH, KOH, H₃PO₃ were supplied from Wako Pure Chemical Industries Ltd, Japan.

2.2 Equipment

Latex irradiator (capacity 1.5 t/20 h), Gel permeation Chromatograph (shimadzu LC-5A), Infra red spectrophotometer (Shimadzu IR-435), Automatic Kjedahl, Viscometer and scanning Electron Microscope (Jeol) were used.

2.3 Method of collection of field latex

Fifty rubber trees from each clone were tapped. Each rubber tree was able to produce 10-30 ml fresh latex, which was directly preserved with 5% ammonia.

After collection the latex was preserved again with ammonia until the concentration of NH₃ in latex was adjusted to between 1.0 - 1.2% by weight.

The fresh latex was stored overnight and the total solids viscosity and other characteristics were measured. The fresh latex was irradiated by co-60 with irradiation dose of 5,10,20 and 30 KCy.

Total solids content, viscosity and mechanical properties of irradiated NR film were determined according to ASTM*.

Protein content was determined by the Kjeldhal method.

Particle diameter of fresh latex was measured after mixed with osmium tetroxide and standing overnight. The fresh latex was diluted until the concentration was 0.01%. One drop of this solution was dried on a plate and coated with Au for Scanning Electron Microscopy.

The molecular weight of NR was determined as follows: NR film (0.1g) was dissolved in THF (100 c.c.). The solution (about 0.1 ml) was injected into GPC column with the flow rate of 15 ml/min. at a pressure of 5 kg/cm². The column temperature was 40°C. Before using, the column was calibrated with linear polystyrene standard. The molecular weight was calculated using equation (1):

\[
\log M_{nr} = 0.185 + 0.950 \log M_s
\]

where : \(M_{nr}\) = molecular weight of natural rubber
Ms = molecular weight of standard polystyrene

The infra red spectrum of NR film was obtained using Shimadzu IR-435 spectrophotometer.

The soluble fractions in acetone and benzene were calculated by measuring the loss in weight of NR film after extraction in the solvent for 48 h.

3. Results and Discussion

3.1 Natural rubber latex from various clones

The characteristics of NR latex and film from various clones are shown in Table 1. It is found that the total solids of natural rubber field latex increases with the increases in the age of rubber trees, e.g. total solids of GT 1/1977 (8 years) is 29.7%; GT 1/1974 (11 years) is 35.2% and total solids of GT 1/1969 (16 years) is 38.2%.

There is a tendency, for the older plants to have a lower protein content than the younger ones, e.g. the protein content of Mix 16/1968 is 1.138%; GT 1/1969 is 1.147%, GT 1/1977 is 1.347%; PR 300/1977 is 1.332% and RRIM/1977 is 1.326%. The decrease in the protein content is due to the effect of proteolitic enzymes in the rubber trees.

Electron micrographs of latex particles for various clones are shown in Fig. 1. It is found that the NR particles formed an aggregate which consist of a number of particles. The average particles size of NR latex is between 190-234 nm.

Table 1 shows that the number average molecular weight M_n varies from 160,000 to 700,000, while the weight average molecular weight M_w varies from 500,000 to 1,000,000. The value of M_w/M_n shows that NR is a highly polydispersed polymer (Fig. 2).

The infra red spectra of the NR field latex is shown in Fig. 3. The spectra of NR latex from five clones are almost the same. The important major absorptions are: C-H stretching vibration from CH_3 at 2960 cm^{-1} and from CH at 2850 cm^{-1}. CH deformation at 1447 cm^{-1} and 1375 cm^{-1}. The C=C stretching vibration at 1660 cm^{-1} and CH out of plane deformation for cis R'C=CHR at 837 cm^{-1}.

3.2 Irradiated NR field latex from various clones

Table 2 shows the properties of irradiated latex and its film. It can be seen that by increasing the irradiation dose, the modulus (at
600% Elongation), gel fraction in benzene and tensile strength increases, while the permanent set decreases. However the viscosity of latex, elongation at break, and gel fraction in acetone remains stable with increasing dose.

4. Conclusion

The characteristics of NR latex from Pasir Waringin Plantation, West Java, were investigated, along with the properties of irradiated NR film. The results show that the fresh latex from old rubber trees have a higher total solid content. The infrared spectra of NR from five clones are quite the same. The diameter of NR particle is between 0.1 - 3.0 micron, the weight average molecular weight is between 160,000 - 700,000, and the number average molecular weight is between 500,000 - 100,000.

References
<table>
<thead>
<tr>
<th>Clone of NR planation</th>
<th>Latex characteristic</th>
<th>Molecular weight of film</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>TS       V  PC  APS</td>
<td>$M_n$         $M_w$  $M_z$  $M_v$</td>
</tr>
<tr>
<td>Mix 16/68</td>
<td>38       5   1.138 198</td>
<td>255,500       575,500 1,081,150 824,000</td>
</tr>
<tr>
<td>GT 1/1969</td>
<td>39       10  1.147 234</td>
<td>177,200       705,000 1,550,700 1,110,740</td>
</tr>
<tr>
<td>GT 1/1974</td>
<td>35       5   1.116 215</td>
<td>653,900       993,150 1,434,450 2,226,320</td>
</tr>
<tr>
<td>PR 28/1974</td>
<td>36       5   1.326 206</td>
<td>699,930       1,087,300 1,700,190 1,406,000</td>
</tr>
<tr>
<td>PR 300/1977</td>
<td>37       4   1.326 204</td>
<td>362,960       747,960 1,293,350 998,450</td>
</tr>
<tr>
<td>GT 1/1977</td>
<td>33       3   1.345 198</td>
<td>708,870       980,130 1,318,290 1,161,630</td>
</tr>
<tr>
<td>PRIM/1977</td>
<td>38       6   1.332 200</td>
<td>166,000       511,800 1,101,920 788,800</td>
</tr>
</tbody>
</table>

TS = total solid, %.
V = Viscosity, m Pa S.
PC = Protein concet, %.
APS = Average particle size, nm.
Table 2  Properties of irradiated NR latex from various clones and its film properties

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>Vis</td>
<td>5</td>
<td>10</td>
<td>5</td>
<td>3</td>
<td>6</td>
<td>4</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>Hard</td>
<td>37</td>
<td>37</td>
<td>37</td>
<td>37</td>
<td>37</td>
<td>37</td>
<td>37</td>
<td>37</td>
</tr>
<tr>
<td></td>
<td>M-600</td>
<td>0.6</td>
<td>0.6</td>
<td>0.6</td>
<td>0.6</td>
<td>0.6</td>
<td>0.6</td>
<td>0.6</td>
<td>0.6</td>
</tr>
<tr>
<td></td>
<td>TB</td>
<td>1.7</td>
<td>1.7</td>
<td>1.6</td>
<td>1.7</td>
<td>1.6</td>
<td>1.6</td>
<td>1.6</td>
<td>1.6</td>
</tr>
<tr>
<td></td>
<td>EB</td>
<td>1800</td>
<td>900</td>
<td>940</td>
<td>990</td>
<td>1000</td>
<td>990</td>
<td>990</td>
<td>990</td>
</tr>
<tr>
<td></td>
<td>PS</td>
<td>54</td>
<td>59</td>
<td>52</td>
<td>59</td>
<td>58</td>
<td>58</td>
<td>58</td>
<td>59</td>
</tr>
<tr>
<td></td>
<td>GFa</td>
<td>7.00</td>
<td>5.39</td>
<td>6.96</td>
<td>6.86</td>
<td>7.15</td>
<td>8.54</td>
<td>8.65</td>
<td>8.65</td>
</tr>
<tr>
<td></td>
<td>Gfb</td>
<td>86.60</td>
<td>87.38</td>
<td>87.88</td>
<td>87.84</td>
<td>89.16</td>
<td>83.65</td>
<td>83.66</td>
<td>83.66</td>
</tr>
<tr>
<td>5</td>
<td>Vis</td>
<td>5</td>
<td>10</td>
<td>6</td>
<td>4</td>
<td>6</td>
<td>5</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>Hard</td>
<td>38</td>
<td>38</td>
<td>40</td>
<td>39</td>
<td>38</td>
<td>40</td>
<td>40</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>M-600</td>
<td>1.4</td>
<td>1.9</td>
<td>1.6</td>
<td>1.6</td>
<td>1.9</td>
<td>2.1</td>
<td>1.7</td>
<td>1.7</td>
</tr>
<tr>
<td></td>
<td>TB</td>
<td>7.7</td>
<td>6.8</td>
<td>6.4</td>
<td>4.8</td>
<td>6.9</td>
<td>6.0</td>
<td>8.8</td>
<td>8.8</td>
</tr>
<tr>
<td></td>
<td>EB</td>
<td>970</td>
<td>980</td>
<td>913</td>
<td>872</td>
<td>920</td>
<td>920</td>
<td>970</td>
<td>970</td>
</tr>
<tr>
<td></td>
<td>PS</td>
<td>26</td>
<td>30</td>
<td>36</td>
<td>34</td>
<td>29</td>
<td>26</td>
<td>28</td>
<td>28</td>
</tr>
<tr>
<td></td>
<td>GFa</td>
<td>6.70</td>
<td>6.09</td>
<td>7.34</td>
<td>6.20</td>
<td>0.13</td>
<td>1.39</td>
<td>6.88</td>
<td>6.88</td>
</tr>
<tr>
<td></td>
<td>Gfb</td>
<td>16.70</td>
<td>16.59</td>
<td>34.32</td>
<td>18.59</td>
<td>20.59</td>
<td>21.06</td>
<td>14.34</td>
<td>14.34</td>
</tr>
<tr>
<td>10</td>
<td>Vis</td>
<td>6</td>
<td>11</td>
<td>7</td>
<td>4</td>
<td>6</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>Hard</td>
<td>42</td>
<td>40</td>
<td>41</td>
<td>40</td>
<td>40</td>
<td>41</td>
<td>41</td>
<td>41</td>
</tr>
<tr>
<td></td>
<td>M-600</td>
<td>2.9</td>
<td>2.4</td>
<td>2.4</td>
<td>2.2</td>
<td>2.7</td>
<td>2.5</td>
<td>3.0</td>
<td>3.0</td>
</tr>
<tr>
<td></td>
<td>TB</td>
<td>12.4</td>
<td>12.2</td>
<td>8.3</td>
<td>7.3</td>
<td>12.0</td>
<td>7.3</td>
<td>14.9</td>
<td>14.9</td>
</tr>
<tr>
<td></td>
<td>EB</td>
<td>960</td>
<td>970</td>
<td>930</td>
<td>930</td>
<td>943</td>
<td>900</td>
<td>980</td>
<td>980</td>
</tr>
<tr>
<td></td>
<td>PS</td>
<td>22</td>
<td>23</td>
<td>31</td>
<td>29</td>
<td>21</td>
<td>23</td>
<td>22</td>
<td>22</td>
</tr>
<tr>
<td></td>
<td>GFa</td>
<td>7.40</td>
<td>15.27</td>
<td>6.33</td>
<td>5.71</td>
<td>8.86</td>
<td>7.11</td>
<td>6.92</td>
<td>6.92</td>
</tr>
<tr>
<td></td>
<td>Gfb</td>
<td>12.09</td>
<td>10.93</td>
<td>14.16</td>
<td>15.60</td>
<td>14.43</td>
<td>14.51</td>
<td>11.18</td>
<td>11.18</td>
</tr>
<tr>
<td>20</td>
<td>Vis</td>
<td>6</td>
<td>10</td>
<td>6</td>
<td>4</td>
<td>5</td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>Hard</td>
<td>43.50</td>
<td>42</td>
<td>44</td>
<td>42</td>
<td>43</td>
<td>43</td>
<td>42</td>
<td>42</td>
</tr>
<tr>
<td></td>
<td>M-600</td>
<td>3.9</td>
<td>3.8</td>
<td>3.6</td>
<td>2.8</td>
<td>3.7</td>
<td>3.6</td>
<td>3.6</td>
<td>3.6</td>
</tr>
<tr>
<td></td>
<td>TB</td>
<td>24.5</td>
<td>18.9</td>
<td>17.6</td>
<td>16.4</td>
<td>22.0</td>
<td>11.2</td>
<td>21.7</td>
<td>21.7</td>
</tr>
<tr>
<td></td>
<td>EB</td>
<td>1000</td>
<td>990</td>
<td>960</td>
<td>910</td>
<td>990</td>
<td>850</td>
<td>990</td>
<td>990</td>
</tr>
<tr>
<td></td>
<td>PS</td>
<td>12</td>
<td>17</td>
<td>18</td>
<td>19</td>
<td>16</td>
<td>18</td>
<td>17</td>
<td>17</td>
</tr>
<tr>
<td></td>
<td>GFa</td>
<td>6.94</td>
<td>5.40</td>
<td>6.15</td>
<td>6.02</td>
<td>9.20</td>
<td>8.05</td>
<td>5.98</td>
<td>5.98</td>
</tr>
<tr>
<td>30</td>
<td>Vis</td>
<td>6</td>
<td>9</td>
<td>6</td>
<td>5</td>
<td>4</td>
<td>4</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>Hard</td>
<td>45.50</td>
<td>45</td>
<td>46</td>
<td>47</td>
<td>44</td>
<td>46</td>
<td>45</td>
<td>45</td>
</tr>
<tr>
<td></td>
<td>M-600</td>
<td>4.8</td>
<td>4.2</td>
<td>4.7</td>
<td>3.9</td>
<td>5.0</td>
<td>4.2</td>
<td>4.2</td>
<td>4.2</td>
</tr>
<tr>
<td></td>
<td>TB</td>
<td>20.8</td>
<td>19.8</td>
<td>20.4</td>
<td>18.4</td>
<td>20.5</td>
<td>19.1</td>
<td>18.7</td>
<td>18.7</td>
</tr>
<tr>
<td></td>
<td>EB</td>
<td>910</td>
<td>940</td>
<td>910</td>
<td>940</td>
<td>920</td>
<td>940</td>
<td>950</td>
<td>950</td>
</tr>
<tr>
<td></td>
<td>PS</td>
<td>9</td>
<td>12</td>
<td>14</td>
<td>15</td>
<td>12</td>
<td>15</td>
<td>13</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td>GFa</td>
<td>7.55</td>
<td>5.96</td>
<td>5.89</td>
<td>6.21</td>
<td>9.58</td>
<td>7.88</td>
<td>6.30</td>
<td>6.30</td>
</tr>
<tr>
<td></td>
<td>Gfb</td>
<td>8.70</td>
<td>8.19</td>
<td>9.50</td>
<td>8.70</td>
<td>11.19</td>
<td>10.01</td>
<td>8.28</td>
<td>8.28</td>
</tr>
</tbody>
</table>

Note: Vis = Viscosity, m Pa S.  
       EB = Elongation at break, %.  
       Hard. = Hardness, shore A.  
       PS = Permanent set, %.  
       M-600 = Modulus 600%, M Pa.  
       GFa = Fraction soluble in acetone, %.  
       TB = Tensile strength, M Pa.  
       Gfb = Fraction soluble in benzene, %.
Fig. 1 Electron micrograph of various latex particle
Fig. 2 Molecular size distribution of various latex particle
Fig. 3 Infrared spectra of NR latex from various clones
5.7 Effect of Non-Rubber Solids and Stabilizing Agents on Radiation Vulcanization of Natural Rubber Latex

E.V. THOMAS

Rubber Board India.
Kottayam 686 009, Kerala, India

Abstract

Natural rubber latex contains non-rubber substances like proteins, resins and carbo-hydrates along with the rubber hydro-carbon. Vulcanization of rubber present in latex is brought about by heating latex with chemicals like sulphur and accelerators. Radiation from γ-source is also used in vulcanizing natural rubber latex. The effect of non-rubber substances on vulcanization by radiation from a γ-source is reported in the paper.

Non-rubber content in latex can be varied by centrifuging it or by mixing pure chemical equivalents of non-rubbers with it. In order to obtain lattices with varying non-rubber contents both procedures were used in the study. Stability of natural latex is controlled within desirable limits by addition of certain colloidal stabilisers. The effect of popular stabilisers on production of RVNRL was also investigated in the paper. Latex was vulcanized by exposing it to radiation source in presence of sensitisers. Dry films were prepared from RVNRL produced under different trials. These films were tested for their tensile strength, modulus and crosslink density.

Results of the study indicate that the non-rubbers present in natural rubber latex have no significant effect on crosslinking by radiation. It was further observed that lattices with comparatively lower non-rubber contents yielded RVNRL of better physical properties.

1. Introduction

The non-rubber solids present in natural rubber latex are proteinaceous materials, higher fatty acid soaps and salts of non-volatile acids\(^1\). The fatty acid soap is derived from naturally occurring phospholipids by alkaline hydrolysis. During concentration by centrifuging or creaming, a part of the non-rubbers are lost in the serum and a latex
with less non-rubbers are obtained as the concentrate. For improving
the stability of concentrated latex different surface active agents such
as lauric acid soap, polyethylene oxide condensate, casein etc. are
added to latex.  
Rubber hydrocarbon which is the dispersed phase in rubber latex, is
a polymer of isoprene. The exact structure of rubber hydrocarbon is cis,
1-4, polyisoprene. This hydrocarbon has novel physical and chemical
properties. Vulcanization is an important chemical reaction of rubber.
This reaction modifies the plastic flow properties of rubber to elastic
properties. In rubber industry usually vulcanization is carried out by
heating rubber with sulphur and accelerators. It is proved that during
vulcanization rubber molecules are interlinked and this crosslink for-
mation is responsible for the change in properties of rubber after
vulcanisation.

High energy radiations like γ-rays and electron beams are also used
in some sectors of industry for modifying properties of polymeric sub-
stances by crosslinking. Studies were undertaken in different countries
for producing crosslinked natural rubber by subjecting rubber latex to
radiation. The bombardment of high energy particles or electrons, makes
rubber molecules ionised and excited. The excited molecules will be
turned to free radicals through energy transfer, thus leading to cross-
linking reaction between molecules. Therefore radiation vulcanisation
will give rubber a satisfactory net-work structure without addition of
radiational crosslinking agents and activators. When rubber or rubber
latex is subjected to radiation the duration of exposure for obtaining
satisfactory level of crosslinking was found to be unusually long.
This is an obstacle for its industrial application on commercially
attractive terms. So different sensitising agents were used to reduce
radiation dose in crosslinking. Some organic compounds can give free
radicals at relatively low radiation dose. The energy transfer between
those radicals and chains of rubber molecules can lead to activation of
rubber molecules so as to increase crosslinking efficiency. Substances
used for this purpose are called sensitising agents.

From the studies already conducted by earlier workers it was shown
that the degree of crosslinking by radiation is influenced by the source
of latex. This would mean that the non-rubber substances present in
latex can either increase or decrease the degree of cross-linking by
radiation. The present study was taken up in this context to investigate
the effect of non-rubber solids and colloidal stabilising agents on vulcanization of latex using $\gamma$-ray radiation. Rubber latex from different clones differ in their rubber to non-rubber ratio. Non-rubber content in latex can be substantially reduced by subjecting the latex to repeated dilution and centrifugation. The final concentrate after three or four cycles will have only 20 to 30 percent of the non-rubbers that may be present in fresh latex.

2. Materials and Methods

2.1 Materials

Lattices used in the study were collected from two different clones, viz., RRII 105 and GI i. Latex was preserved with one percent ammonia and stored for ten days before irradiation. Centrifugally concentrated latex used in the study conformed to specification of Bureau of Indian Standards (BIS) 5430 (1981). Purified latex with low non-rubber solid content required in the experiment was obtained by repeated dilution and concentration of latex by centrifugation. All other raw materials required for the study were collected from established suppliers in the country. Carbon tetrachloride was the sensitiser used in the study. This was added to latex as a 50 percent emulsion. Antioxidants used in the study were also added to latex as dispersions/emulsions.

2.2 Irradiation

The equipment for radiation was an R900 model Co-60 radiation source, supplied by Bhaba Atomic Research Centre, Trombay, India. The dose rate was 0.2 Mrad/hour.

2.3 Measurements

The Total Solids Content (TSC) and Dry Rubber Content (DRC) of lattices were determined as per the procedures formulated by BIS.

Results are given in Table 1. Lattices of different non-rubber contents were treated with 5 phr carbon tetrachloride. This is added as 30 percent emulsion. These were then divided into different parts and each subjected to a specified radiation dose starting from 2.0 Mrad to 6 Mrads. From the radiation vulcanised natural rubber latex (RNNRL) so prepared films of 1 to 1.25 mm thickness were obtained by spreading over glass plates. The film was dried overnight at 30°C and
finally heated at 100°C for 15 minutes to get optimum physical and chemical properties. Total crosslinks formed was estimated by the swelling method. From each sample 0.2 to 0.3 gm vulcanised film was taken and allowed to swell in an excess of benzene containing 0.5 percent N-phenyl \( \beta \) naphthyl amine at 30°C for 48 hours. The swollen sample was weighed, the solvent removed in vacuum and the sample weighed again. Value of \( V_r \), the volume fraction of rubber in the swollen vulcanisate, was calculated from the above data using the method suggested by Ellis and Welding\(^6\). This measured the total amount of crosslinks in the vulcanisate. The tensile properties of the films were determined according to ASTM D-412 using Zwick UTM (Model-1474). The results are given in Table 2 and 3. Different non-rubbers present in rubber latex like carbohydrates and proteins were added to latex in varying concentrations and subjected to radiation in presence of \( \text{CCl}_4 \) sensitiser. The RVNRL obtained from these were also converted to dry films and their physical properties studied. Results are given in Table 4.

2.4 Effect of colloidal stabilising agents on radiation vulcanization

Purified NR latex was divided into three parts. Each part was treated with a selected stabiliser. The stabilisers used in the study were Potassium laurate, ammonium caseinate and vulcastab VL and the concentration was one phr. The samples were then mixed with 5 phr carbon tetrachloride and subjected to a radiation dose of 4 Mrads. RVNRL thus prepared from the individual samples were dried separately for obtaining films and the physical properties and vulcanization characteristics assessed. Results are given in Table 5.

2.5 Effect of antioxidants on the ageing properties of radiation vulcanized latex films

The centrifuged latex was mixed with 5 phr carbon tetrachloride and irradiated to a radiation dose of 4 Mrads. The RVNRL so obtained was then divided into two parts. One part was mixed with 1 phr styrenated phenol and the other with 1 phr ditertiary butyl \( p \)-cresol. Latex films were then prepared from the RVNRL and different properties evaluated, both before and after ageing. Ageing was done at 100°C for 22 hours. Results are given in Table 6.
3. Results and Discussion

Table 1 gives the TSC and DRC of four different lattices with varying non-rubber contents. Samples 1 and 2 represent freshly preserved field latex and so their non-rubber contents are high. Sample 3 is centrifugally concentrated latex and its non-rubber level is lower. Sample 4 is latex purified by repeated dilution and centrifugation. Here the non-rubber content is extremely low. It may be seen from Table 2 that the crosslink density of the latex films with different non-rubber values increases with increasing radiation dose. But the non-rubbers did not show any significant role in controlling the process of crosslinking by radiation. In Table 3, the physical properties of the dried films of RVNRL are given. It is evident from this table that all the samples which gave high crosslink density also gave high modulus values. It may also be seen from the table that the tensile strength values for the latex films from centrifuged lattices were higher than those for the films from field lattices. It may further be seen from Table 3 that when radiation dose exceed 4 Mrad tensile strength decreases slightly. So 4 Mrad dose is taken as the optimum radiation dose in the present study. In Table 4 physical properties of RVNRL films produced from latex containing added non-rubber substances like starch and casein are given. It may be seen from the table that addition of these non-rubber substances to latex has no noticeable effect on crosslinking of rubber hydrocarbon by radiation. A study of the crosslink density values reported in Table 2 and 3 reveals that a radiation dose increases crosslink density also increases. The tensile strength of films was found to decrease when latex was exposed to radiation dose higher than 4 Mrad. This may be attributed to the restricting effect of more random crosslinks on the strain induced crystallisation of natural rubber. The non-rubber substances may affect the inter-particle cohesion of the rubber particles in latex and as the non-rubber increases, the inter-particle fusion decreases and this may lead to decrease of tensile strength. Besides field latex will have a larger number smaller size rubber particles. This may be the reason for the lower tensile strength values of sample 1 and 2 given in Table 3. It is, therefore, advisable to use centrifugally concentrated lattices for producing RVNRL.

The effect of stabilising agents on the radiation crosslinking of latex are given in Table 5. It may be seen from the table that the cross-
linking density and tensile strength of the films produced from latex stabilised with Potassium hydroxide were lower than those for the control sample. The stabilising agents casein and vulcastab VL did not show any effect on crosslinking by radiation.

The type of crosslinks formed in radiation vulcanization process is mostly C-C crosslinks. This type of linkage is known to have high thermal stability. But the tensile strength of RVNRL film was found to decrease substantially after ageing. This may be attributed to the breakage in chain length and the tendency can be reduced by use of antioxidants. In Table 6 the ageing properties of RVNRL films prepared with two different antioxidants are compared with those of a control sample. It may be seen from the results that BHT offers greater protection than anti-oxidant SP. The tendency for degradation during heating in air is more in RVNRL films than what is observed in films of sulphur vulcanized latex films. During ageing in presence of air or oxygen the crosslinked chain breaks and some new chains are reformed in sulphur vulcanized films as the ingredients for such re-vulcanizations are present in the compound. But in RVNRL the chain broken by heating is not reformed as the cross-linking agents are absent in the films. This may be the reason for the poorer ageing properties of RVNRL. If the RVNRL is suitably compounded using good antioxidants the ageing properties can be improved.

4. Summary and Conclusions

The non-rubber substances like proteins and carbohydrates have no significant effect on crosslinking of natural rubber latex by radiation. When the non-rubber content in latex is high, that will reduce the tensile strength of RVNRL films. It is advisable to use centrifugally concentrated lattices for production of RVNRL.

References

3. Lu Li Kang, Study on Radiation Vulcanisation of Rubber and discussion on its industrial applications (Shenyang Industrial Rubber Products
Table 1  Non-rubber solids content

<table>
<thead>
<tr>
<th>Sample type</th>
<th>TS</th>
<th>DRC</th>
<th>TS-DRC (Non-rubber)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Preserved clonal latex, RRII 105</td>
<td>39.39</td>
<td>36.00</td>
<td>3.39</td>
</tr>
<tr>
<td>Preserved clonal latex, G1 l</td>
<td>41.78</td>
<td>38.49</td>
<td>3.29</td>
</tr>
<tr>
<td>Centrifuged latex (60%)</td>
<td>61.33</td>
<td>60.14</td>
<td>1.18</td>
</tr>
<tr>
<td>Purified latex</td>
<td>60.284</td>
<td>60.173</td>
<td>0.111</td>
</tr>
</tbody>
</table>

Table 2  Concentration of chemical crosslinks in RVNRL film, different non-rubber contents (Vr values)

<table>
<thead>
<tr>
<th>Sample type</th>
<th>Vr - Values</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2 Mrad</td>
</tr>
<tr>
<td>Preserved clonal latex RRII 105</td>
<td>0.1240</td>
</tr>
<tr>
<td>Preserved clonal latex G1 l</td>
<td>0.1200</td>
</tr>
<tr>
<td>Centrifuged latex (60%)</td>
<td>0.1230</td>
</tr>
<tr>
<td>Purified latex (60%)</td>
<td>0.1120</td>
</tr>
</tbody>
</table>
Table 3  Tensile properties of RVNRL films with different non-rubber contents

<table>
<thead>
<tr>
<th>Sample type</th>
<th>Non Rubber content</th>
<th>Radiation dose</th>
<th>Tensile properties</th>
<th></th>
<th></th>
<th>E. B. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Modulus 300% (MPa)</td>
<td>Tensile strength (MPa)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Preserved</td>
<td>2</td>
<td>0.55</td>
<td>9.50</td>
<td>908</td>
<td>1100</td>
<td></td>
</tr>
<tr>
<td>Clonal latex</td>
<td>3.39</td>
<td>1.10</td>
<td>13.20</td>
<td>908</td>
<td>1067</td>
<td></td>
</tr>
<tr>
<td>RRII 105</td>
<td>6</td>
<td>1.30</td>
<td>11.50</td>
<td>767</td>
<td>988</td>
<td></td>
</tr>
<tr>
<td>Preserved</td>
<td>2</td>
<td>0.65</td>
<td>9.50</td>
<td>1100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Clonal latex</td>
<td>3.29</td>
<td>0.95</td>
<td>12.75</td>
<td>1067</td>
<td></td>
<td></td>
</tr>
<tr>
<td>GI 1</td>
<td>6</td>
<td>1.10</td>
<td>12.50</td>
<td>988</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Centrifuged latex (60%)</td>
<td>1.18</td>
<td>0.70</td>
<td>12.00</td>
<td>1090</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>0.90</td>
<td>16.50</td>
<td>1028</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>1.10</td>
<td>16.25</td>
<td>1066</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Purified latex (60%)</td>
<td>0.111</td>
<td>0.75</td>
<td>11.50</td>
<td>1100</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>1.1</td>
<td>16.00</td>
<td>1083</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>1.15</td>
<td>16.25</td>
<td>1090</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 4  Vulcanisate properties of RVNR/L films prepared with incorporation of casein and starch

<table>
<thead>
<tr>
<th>Details of the non-rubber ingredient added</th>
<th>Crosslink density Vf</th>
<th>Modulus 300 percent MPa</th>
<th>Tensile strength MPa</th>
<th>Elongation at break percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ordinary centrifuged latex control</td>
<td>0.1508</td>
<td>1.2</td>
<td>16.5</td>
<td>1050</td>
</tr>
<tr>
<td>Starch added to latex at 0.02 percent on weight of latex</td>
<td>0.1527</td>
<td>1.00</td>
<td>15.1</td>
<td>1020</td>
</tr>
<tr>
<td>Starch added to latex at concentration of 0.1 percent on weight of latex</td>
<td>0.1468</td>
<td>1.10</td>
<td>14.79</td>
<td>1010</td>
</tr>
<tr>
<td>Casein added at concentration of 0.02 percent on weight of latex</td>
<td>0.1453</td>
<td>0.94</td>
<td>15.30</td>
<td>1250</td>
</tr>
<tr>
<td>Casein added at 0.1 percent on weight of latex</td>
<td>0.1441</td>
<td>0.94</td>
<td>15.4</td>
<td>1240</td>
</tr>
</tbody>
</table>
Table 5  Vulcanisate properties of RVNRL films containing different stabilisers

<table>
<thead>
<tr>
<th>Stabilising agent</th>
<th>Vr</th>
<th>Modulus 300% MPa</th>
<th>Tensile strength MPa</th>
<th>E. B. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Purified latex</td>
<td>0.1450</td>
<td>1.1</td>
<td>16.00</td>
<td>1100</td>
</tr>
<tr>
<td>Purified latex + 1% Potassium laurate</td>
<td>0.1380</td>
<td>0.90</td>
<td>13.50</td>
<td>1000</td>
</tr>
<tr>
<td>Purified latex + 1% vulcastab VL</td>
<td>0.1500</td>
<td>1.0</td>
<td>15.95</td>
<td>1120</td>
</tr>
<tr>
<td>Purified latex + 1% Casein</td>
<td>0.1540</td>
<td>1.1</td>
<td>15.90</td>
<td>1080</td>
</tr>
</tbody>
</table>

Table 6  Effect of antioxidants on the ageing resistance of RVNRL film

<table>
<thead>
<tr>
<th>Properties</th>
<th>Antioxidants*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Control</td>
</tr>
<tr>
<td>Modulus (MPa) B. A.</td>
<td>1.22</td>
</tr>
<tr>
<td>300% A. A.</td>
<td>0.95</td>
</tr>
<tr>
<td>% Retension</td>
<td>78</td>
</tr>
<tr>
<td>Tensile strength MPa</td>
<td>B. A.</td>
</tr>
<tr>
<td></td>
<td>A. A.</td>
</tr>
<tr>
<td>% Retension</td>
<td>22</td>
</tr>
<tr>
<td>Elongation at break %</td>
<td>B. A.</td>
</tr>
<tr>
<td></td>
<td>A. A.</td>
</tr>
<tr>
<td>% Retension</td>
<td>78</td>
</tr>
</tbody>
</table>

* Ageing 240 hours at 70°C
B. A. - Before Ageing.
A. A. - After Ageing.
PROPERTIES OF RADIATION VULCANIZED NR LATEX

5.8 Technological Evaluation of Radiation Pre-Cured NR Latex

K.F. GAZELEY and T.D. PENDLE

The Malaysian Rubber Producers' Research Association
Tun Abdul Razak Laboratory
Brickendonbury
Hertford SG13 8NL
England

Abstract

This paper describes the evaluation, in technological terms, of a radiation vulcanized natural rubber latex concentrate supplied by the Takasaki Radiation Chemistry Research Establishment. The latex was used to prepare cast films, coagulant dipped and heat-sensitive dipped films. The processing behaviour of the latex in these operations was observed and the tensile properties of the films were determined.

The film-forming behaviour of the latex in film casting was normal and the properties of the cast films, after leaching, were very good. The heat-ageing behaviour at 70°C was inferior to that of sulphur pre-vulcanized films but may be sufficiently good for many applications.

The latex behaved well in the coagulant dipping process and gave films of adequate tensile strength and improved ageing resistance, compared with the cast films. It is believed that the differences observed between the cast and coagulant-dipped films may be artefactual but further work may be required to confirm this idea.

The latex proved difficult to use in a PVME heat-sensitive process due to its colloidal stability characteristics. The physical properties of the films obtained were inferior to those of the cast and coagulant-dipped films.

The latex was found to be free of detectable nitrosoamines and to have only a trace of nitrosatable amines and should therefore be suitable for use in several products where these factors are important.

1. Introduction

A radiation-prevulcanized natural latex (RVNRL) was supplied by the
Takasaki Radiation Chemistry Research Establishment to the Malaysian Rubber Producers Research Association in the UK for evaluation. This latex was examined for its behaviour in coagulant and heat-sensitive dipping processes. The physical properties and heat-ageing behaviour of films, prepared by both casting and dipping, were also determined and the content of nitrosoamines and nitrosatable materials measured.

The report describes the results obtained in this study and makes an assessment of the possible areas of application of RVNRL.

2. Experimental

This latex was supplied by Dr K Makuuchi of the Japan Atomic Energy Research Institute, Takasaki Radiation Chemistry Research Establishment and the following details were given about its preparation:

2.1 Latex

Dunlop HA latex, diluted to 52% DRC with 1% ammonia
Sensitiser: 5 pphr n-butyl acrylate
Stabiliser: 0.2 pphr KOH

Mixed in Stainless steel drum, stored overnight.

Irradiation: Date of irradiation 1st November 1988
γ-ray dose rate: 0.62 kGy
Temperature: ca. 20°C
Irradiation time: 9 hours
Total dose: 11-78 kGy

No antioxidant was added to this latex.

Some of the properties of this latex, as determined at MRPRA, are shown in Table 1.

2.2 Cast films

These were prepared on glass plates, dried at room temperature.
Leaching, where applicable, was done as described in the text.

2.3 Coagulant dipped films

Samples were dipped on aluminium sheet formers using a 40% solution of calcium nitrate in water as coagulant. The dwell time in the latex was one minute. The dipped film was leached as the wet gel for 5 minutes in warm (40°C) water and dried at 70°C, Measurements were made for
tensile strength, tear strength and puncture strength.

2.4 Heat sensitized dipping

The base compound was prepared as follows:

<table>
<thead>
<tr>
<th>Component</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>RVNRL</td>
<td>192</td>
</tr>
<tr>
<td>25% Texofor FN30</td>
<td>2</td>
</tr>
<tr>
<td>40% Formaldehyde solution to pH</td>
<td>8.4</td>
</tr>
<tr>
<td>50% Zinc Oxide</td>
<td>2.0</td>
</tr>
<tr>
<td>10% PVME</td>
<td>10</td>
</tr>
</tbody>
</table>

Leaching was done on the dry film for 20hr at RT (film 1) and on the wet-gel for 30 mins at 40°C (film 2).

3. Results

3.1 Comment on Tensile Strength Measurement

For thin (< 0.5 mm) latex films the measurement of tensile strength values can be difficult. The standard (BS.903) dumbbells do not always give reliable or reproducible results due to a high frequency of grip-breaks or slippage. As a consequence, the MRPRA physical testing laboratory uses a non-standard dumbbell having a narrower stem and larger tab-ends than the BS903, type 2, dumbbell. This procedure ensures much more reproducible, and often higher, tensile strength values and its use may account for any discrepancies observed between the data in this paper and that presented by other authors.

3.2 Cast film Properties

The cast films, approximately 0.5 mm thick, were tested for physical properties both before and after leaching. The results, for the RVNRL films without added antioxidant, are shown in Table 2. It is clear from these results that the films have very good tensile strengths when they have been leached. Two different sets of leaching conditions were used, both more extensive than would normally be used in commercial processes, but there appears to be little to choose between them.

The improvement in tensile strength after leaching is characteristic of pre-vulcanized latex films and is believed to be due to the removal of hydrophilic materials whose presence either hinders particle integration or promotes regain of atmospheric moisture.

Table 3 shows the results of physical tests on cast films containing
added antioxidants. The ageing behaviour of these films is somewhat different from that of sulphur prevulcanized films as it appears to be characterized by a relatively rapid loss of strength in the first seven days but thereafter a slower rate of loss prevails. In broad terms the ageing behaviour is poor in comparison with conventional prevulcanized lattices and needs to be improved, if possible. It is likely that an evaluation of a range of antioxidants would reveal better protective agents for these films than antioxidant 2246.

3.3 Coagulant-dipped films

As one of the possible major outlets for RVNRL is in the dipping industry, it was decided to prepare coagulant-dipped films for evaluation. The response of RVNRL to calcium nitrate coagulant in terms of pick-up versus time of dwell is shown in Fig. 1. The response was qualitatively similar to that of a sulphur-prevulcanized latex but probably a little slower i.e. less pick-up in a given time. The difference is not thought to be of great significance in terms of the commercial utilization of RVNRL.

The physical properties of a coagulant-dipped film are shown in Table 4, together with the ageing results. The initial properties are reasonably good, although the tensile strength is a little lower than those of the cast films, and the ageing behaviour is actually better than was obtained previously. The reasons for the variations in strength properties and ageing behaviour are not known at present but we regard the unaged tensile strength as unusually low and this may be giving a false picture of the ageing resistance. Further work is required to clarify this point.

It was also decided to examine the puncture strength of the coagulant dipped film and this was done by the Australian Consumers Association method¹ described by Gorton². The results are shown in Table 5 and also in Fig 2 where they are compared with those of a sulphur prevulcanized latex. It is clear from Fig. 2 that RVNRL films have a measurably lower puncture strength than sulphur-prevulcanized films. It is considered that the difference may be a consequence of the lower modulus of the RVNRL films. Again, this could readily be checked by a carefully designed study.
3.4 Heat-sensitive dipped films

It was found that RVNRL did not behave in the same way as ordinary latex when used in a heat-sensitive (PVME) dipping compound. It proved difficult to maintain a good balance between stability and gellability. The behaviour of the latex mix appeared very sensitive to pH.

The dipped films were finally prepared using a mix containing 0.1 phr of Texofor FN30 at a pH of 8.0 and with the formers at 70°C.

The tensile properties of the heat-sensitive dipped films are given in Table 6. The tensile strengths obtained were very low even after leaching, the low values are probably the consequence of inadequate extraction of PVME due to the relatively high leaching temperatures. Further work is obviously required if RVNRL is to be used in this type of formulation.

3.5 Nitrosoamine content

An obvious potential area of use for RVNRL is in the medical or food-related products because the absence of sulphur and accelerators should contribute to greater toxicological safety. In the food-contact sector, however, the presence of nitrosoamines in vulcanizates has recently become very important and many countries now have severe restrictions on the amounts of these materials that are permitted in certain products such as babies' teats and soothers. For this reason it decided to determine the nitrosoamine content of RVNRL films according to the German (BGA) procedure. The results of these measurements are shown in Table 7.

No nitrosoamines could be detected in the film. Very low levels of nitrosatable materials were detected — possibly arising from traces of TMTD used as a field preservation — but these were well below the required limits.

It is clear, therefore, that RVNRL has a distinct advantage over sulphur prevulcanized latex in respect of nitrosoamines and nitrosatable products and is potentially useful where these factors are important.

4. Summary

This preliminary evaluation suggests that RVNRL has good potential for use in the manufacture of dipped products by the coagulant process and should be further evaluated for the production of such products as
surgeon's/examination gloves, condoms, teats and soothers, catheters, medical tubing and balloons.

Further development work is required to select the best antioxidant system for this type of latex and to extend its use to heat-sensitive dipping systems.

References

Table 1 RNRL properties

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Solids Content (%)</td>
<td>52.99</td>
</tr>
<tr>
<td>pH</td>
<td>10.0</td>
</tr>
<tr>
<td>MST (s)</td>
<td>1,920</td>
</tr>
<tr>
<td>Viscosity (1)</td>
<td></td>
</tr>
<tr>
<td>3 rpm (cps)</td>
<td>58</td>
</tr>
<tr>
<td>12 rpm (cps)</td>
<td>42</td>
</tr>
<tr>
<td>60 rpm (cps)</td>
<td>30</td>
</tr>
<tr>
<td>Level of Prevulcanization</td>
<td>PRM(2)</td>
</tr>
<tr>
<td></td>
<td>5.5</td>
</tr>
</tbody>
</table>

(1) Brookfield LVT, Spindle 1, 23°C
(2) Prevulcanize relaxed modulus

Table 2 Physical properties of cast films

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Unleached</td>
<td>Leacheda</td>
</tr>
<tr>
<td>TS (MPa)</td>
<td>18.9</td>
<td>27.7</td>
</tr>
<tr>
<td>M300 MPa</td>
<td>0.82</td>
<td>0.92</td>
</tr>
<tr>
<td>M500 MPa</td>
<td>1.58</td>
<td>1.71</td>
</tr>
<tr>
<td>EB (%)</td>
<td>898</td>
<td>956</td>
</tr>
</tbody>
</table>

(a) Leached 24 hrs in 1% ammonia solution, dried at room temperature then heated 1 hr at 70°C
(b) Leached 16 hrs in distilled water and dried at 70°C

Table 3 Properties and ageing behaviour of leached cast filmsa

<table>
<thead>
<tr>
<th></th>
<th>Unaged</th>
<th>Aged</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>TS MPa</td>
<td>M300 MPa</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(MPa)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Film c</td>
<td>28.2</td>
<td>0.69</td>
</tr>
<tr>
<td>Film D</td>
<td>27.2</td>
<td>0.72</td>
</tr>
</tbody>
</table>

a Leached in 1% aqueous ammonia for 24 hrs, dried at room temperature and heated 1 hr at 70°C
b Contains 0.5 phr Antioxidant 2246
c Contains 1.0 phr Antioxidant 2246
Table 4  Physical tests on coagulant dipped films from RVNRL

<table>
<thead>
<tr>
<th></th>
<th>TS (MPa)</th>
<th>EB%</th>
<th>M300 (MPa)</th>
<th>M500 (MPa)</th>
<th>T. set(a) (%)</th>
<th>Tear str (Nmm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unaged</td>
<td>22.0</td>
<td>820</td>
<td>1.00</td>
<td>2.7</td>
<td>0.8</td>
<td>23.3</td>
</tr>
<tr>
<td>Aged 7d/70°C</td>
<td>22.1</td>
<td>900</td>
<td>1.11</td>
<td>2.4</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Aged 14d/70°C</td>
<td>19.8</td>
<td>875</td>
<td>1.09</td>
<td>2.1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Aged 1d/100°C</td>
<td>18.5</td>
<td>915</td>
<td>0.67</td>
<td>1.5</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

(a) Tension set measurements were made at 400% extension for 22 hrs and after 30 mins relaxation

Table 5  Puncture tests on coagulant dipped films from radiation cured latex

<table>
<thead>
<tr>
<th>Thickness (mm)</th>
<th>Force (N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.56</td>
<td>11.1</td>
</tr>
<tr>
<td>0.72</td>
<td>27.6</td>
</tr>
<tr>
<td>0.67</td>
<td>34.5</td>
</tr>
<tr>
<td>0.62</td>
<td>31.4</td>
</tr>
<tr>
<td>0.60</td>
<td>30.9</td>
</tr>
<tr>
<td>0.58</td>
<td>33.4</td>
</tr>
</tbody>
</table>

Table 6  Tensile properties of heat-sensitive dipped films from radiation-cured latex

<table>
<thead>
<tr>
<th>Film</th>
<th>TS (MPa)</th>
<th>EB%</th>
<th>M300 (MPa)</th>
<th>M500 (MPa)</th>
<th>M700 (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1(a)</td>
<td>12.1</td>
<td>815</td>
<td>0.9</td>
<td>1.6</td>
<td>6.2</td>
</tr>
<tr>
<td>2(b)</td>
<td>17.8</td>
<td>940</td>
<td>0.9</td>
<td>1.7</td>
<td>6.4</td>
</tr>
</tbody>
</table>

(a) Dry film leached 20 h/RT
(b) Wet gel leached 30 mins/40°C

Table 7  RVNRL: Determination of Nitrosoamines (BGA Procedure)

<table>
<thead>
<tr>
<th></th>
<th>Found</th>
<th>Permitted</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrosoamines</td>
<td>n11</td>
<td>&gt; 3x10⁻⁸</td>
</tr>
<tr>
<td>Nitrosatable Materials</td>
<td>1x10⁻⁸</td>
<td>&gt; 5x10⁻⁷</td>
</tr>
</tbody>
</table>
Fig. 1 Coapulant dipping. Dryfilm thickness v. Immersion time

Fig. 2 Film puncture strength v. Thickness
5.9 Thermoplastic Elasomers by Radiation Grafting on NR Latex and Its Extrusion molding

SEIJI ONO1), F. Yoshii2), K. Makuuchi2) and I. Ishigaki2)

1) Hiroshima Kasei, Ltd., 2-2-11 Matsuhama-cho, Fukuyama-shi, Hiroshima-ken, 720 Japan
2) Takasaki Radiation Chemistry Research Establishment, JAERI

Abstract

Thermoplastic elastomer (TPE) was synthesized by radiation grafting of methyl methacrylate (MMA) onto radiation vulcanized natural rubber latex (NRL) with n-butyl acrylate (n-BA). The processability test of MMA grafted rubber for TPE was carried out as follows. The MMA grafted rubber was masticated by a two-roll mill to enhance the processability and was then mixed with 0.5 phr of antioxidant and process oil in a kneader. The compound was milled at 150°C to get a sheet. The processability was evaluated by observing the surface flatness of milled sheet. The optimum concentration of MMA for tensile strength was 50 phr. The hardness is increased with increasing MMA concentration and was around 50 (shore A) for the compound with 10 phr of process oil. The tubing was produced from this TPE compound using an extruder with a tube die, 9 mm external diameter and 6 mm internal diameter at 150°C. The melt flow of this compound was good enough to produce a smooth surface. The diameter of the tube produced was almost the same as the die size. From these results, it appears that the MMA grafted rubber becomes a TPE by kneading after mastication and its extrusion molding is possible.

1. Introduction

We have been studying radiation grafting of methyl methacrylate (MMA) onto natural rubber latex (NRL). In the previous studies1, the grafting rate of MMA on NRL under various conditions and the chain lengths of grafted polymer (polymerized MMA) were determined. It was found that latex prepared by radiation grafting of MMA was effective as a material for adhesives2. Adhesion tests of MMA grafted latex for leather and plywood have been carried out. It is known that block copolymer and blend polymer consisting of soft segment and hard segment
are favorable as material for thermoplastic elastomer (TPE). TPE materials can be molded by injection and extrusion with plastic molding machine. Thus, it is expected that the radiation grafted copolymer consisting of soft segment of rubber and hard segment of PMMA will have the properties as a material for TPE.

In this report, the processability test of MMA grafted NR for TPE and its extrusion molding were carried out.

2. Experimental

Dunlop natural rubber latex obtained from Malaysia was mainly used for grafting with MMA. The latex was stabilized by adding 0.2 phr KOH. 5 phr of n-butyl acrylate (n-BA) as the sensitizer was added to the stabilized latex and this was then irradiated with gamma-ray for vulcanization with 15 kGy at the dose rate of 10 kGy/hr. MMA was added to the vulcanized latex and then this mixture was irradiated with gamma-rays with 5 kGy for grafting. After grafting, the latex was cast on glass plate to get the dry rubber. The cast film was immersed in 1.5% aqueous ammonia for 24 hrs to remove the proteins and then, dried at room temperature. Processability test for TPE was carried out as shown in Fig. 1. The grafted NR was masticated on a cold roll-mill to enhance its processability. The masticated rubber was mixed with a process oil, antioxidant and stearic acid in the kneader. In order to evaluate its processability for TPE, a 0.7 mm sheet was formed by passing the compound between two hot rolls. For extrusion molding, the grafted sheet was extruded in to a tube, while for the measurement of physical properties, the sheet was pressed again to 0.5 mm thickness, at 150°C and at 100 kg/cm². The hardness and tensile strength of TPE prepared from grafted NR were measured for evaluation of physical properties.

3. Results and discussion

3.1 Effect of blade revolution rate on tensile strength of MMA grafted NR

In the molding of rubber, some additives such as antioxidant and slip agent are added in the kneader after mastication. Figure 2 shows photograph of kneader; Antioxidant and oil are mixed with grafted NR in the kneader. Mixing time and revolution rate of blade are very important
factors for processability of grafted NR. Figure 3 shows the appearance of MMA grafted NR sheet pressed between two hot mill (150°C) after mixing at 20 rpm. For a shorter revolution time, big cracks are observed at the edges and the surface of the sheet is not flat. On the other hand, for 40 and 60 min mixing times, the edges and surface of grafted NR are clear. From these findings, it was shown that the processability of grafted NR increase with increasing mixing time. Accordingly, the processability of grafted NR for TPE is evaluated by observing the flatness of grafted NR after mixing. Table 1 shows the processability of grafted NR for TPE at various revolution rate of blade in the kneader. At a lower revolution rate of 20 rpm, the mixing time needed to get a flat sheet is 60 min while at higher revolution rate of 40 and 60 rpm, flat sheets are obtained at shorter mixing time of 20 and 10 min, respectively. The tensile strength of grafted NR sheet after mixing are shown in Fig. 4. At higher revolution rates, the tensile strength decrease remarkably with increasing mixing time because of chain scission, while for lower revolution rates such as 20 rpm, the decrease in tensile strength is relatively smaller, even though the mixing time is longer. Thus, a longer mixing time at 20 rpm is favorable for the process of grafted NR for TPE.

3.2 Effect of oil and MMA content on physical properties

Generally, in the molding of an elastomer, process oil is added to the rubber as a softener in order to enhance processability. The effects of oil on the tensile strength and hardness of grafted NR are shown in Fig. 5. The tensile strength and hardness of grafted NR without oil are higher than that with oil. TPE is formed without additives. Thus, it is found that the molding of grafted NR for TPE is possible even without the use of oil.

Figure 6 shows the effect of MMA content on the tensile strength, elongation at break and hardness. For tensile strength, the optimum MMA content is 50 phr and the value is around 100 Kg/cm². The elongation at break decrease and hardness increase linearly with increasing MMA content. These results demonstrates that the physical properties of grafted NR TPE can be controlled by the MMA content.

3.3 Production of the tube by extruder

From the above experimental, the conditions of extrusion molding
for grafted NR TPE are set as follows.

<table>
<thead>
<tr>
<th>Process</th>
<th>Setting</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mixing by roll mills</td>
<td>60 min at 20 rpm</td>
</tr>
<tr>
<td></td>
<td>10 min at 60 rpm</td>
</tr>
<tr>
<td>Process oil</td>
<td>0 and 10 phr</td>
</tr>
<tr>
<td>MMA content</td>
<td>50 phr</td>
</tr>
<tr>
<td>Molding temp.</td>
<td>Cylinder 150°C</td>
</tr>
<tr>
<td></td>
<td>Die head 160°C</td>
</tr>
</tbody>
</table>

Figure 7 shows cross section of cylinder in extruder. The grafted sample is sent from hopper to die by screw. This machine can extrude the polymer at various screw rates or at different temperatures. Fig. 8 shows the production of tube by extruder. The tubes from grafted NR TPE, with and without oil, are produced by an extruder with a tube die, 9 mm external diameter and 6 mm internal diameter at 150°C. The melt flow of this TPE was good for producing a smooth surface. The diameter of the tube produced is almost the same as the die size.

4. Conclusion

Processability test was carried out in order to confirm the thermoplastic properties of MMA grafted NR. The results are as follows. The processability of grafted NR for TPE is enhanced by kneading after mastication. The optimum MMA content for tensile strength is 50 phr to rubber component. The extrusion of grafted NR compound is possible. Thus, it becomes clear that a TPE can be synthesized by radiation grafting of MMA onto radiation vulcanized NRL with monomer.

References

1. Modification of Natural Rubber Latex by Radiation Graft Polymerization, JAERI-memo, may 1988
Table 1 Evaluation of processability for thermoplastic properties

<table>
<thead>
<tr>
<th>Revolution (rpm)</th>
<th>Revolution time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5</td>
</tr>
<tr>
<td>20</td>
<td>x</td>
</tr>
<tr>
<td>40</td>
<td>x</td>
</tr>
<tr>
<td>60</td>
<td>A</td>
</tr>
</tbody>
</table>

x : Big cracks are observed in TPE sheet.
A : Surface of TPE sheet is not flat, although without crack.
o : TPE sheet is very clear.

Fig. 1 Preparation of thermoplastic elastomer
Fig. 2 Cross section of mixer

Fig. 3 Effect of mixing times on thermoplastic elastomer
Fig. 4  Effect of blade revolution rate on tensile strength of MMA grafted Rubber.
(○) 20 rpm, (●) 40 rpm, (△) 60 rpm
MMA content : 50 phr, Process oil : 10 phr, Mixing temp. : 80°C

Fig. 5  Effect of process oil concentration on tensile strength and hardness of MMA grafted rubber.
(○) with oil, (●) without oil.
MMA content : 50 phr, Revolution rate : 20 rpm, Mixing temp. : 80°C
Fig. 6 Effect of MMA content on tensile strength, elongation at break and hardness.
Process oil : 10 phr,
Mixing temp. : 80°C

Fig. 7 Cross section of extruder
T1 - T5 : Barrel Temperature
M : Resin temperature
(a) production of tube and tape

(b) extruded tube and tape

Fig. 8 Production of tube and tape by extruder
5.10 Effect of Coagulant on Mechanical Properties of Radiation Vulcanized NR Latex Film

T. Saito1), FUMIO YOSHII2), K. Makuuchi2) and I. Ishigaki2)

1) Radia Industries, Ltd., 168 Ohoyagi-machi, Takasaki-shi, Gunma-ken, 370-12 Japan
2) Takasaki Radiation Chemistry Research Establishment, JAERI, Watanuki-machi, Takasaki-shi, Gunma-ken, 370-12 Japan

Abstract

We have produced protective rubber gloves for radioactive contamination from vulcanized natural rubber latex with monomer (n-butyl acrylate). Properties of vulcanized NR film cast onto glass plates were lower than that of rubber gloves prepared by coagulant dipping. In order to find out the cause of this difference in physical properties, the effect of coagulant on these properties was investigated. Physical properties of cast film from radiation vulcanized NRL with 5 phr of 2-ethylhexyl acrylate/1 phr CCl4 increased remarkably by immersion in a 10% Ca(NO3)2 solution. The crosslink density of the Ca(NO3)2-treated film was higher than that of the untreated film. From FTIR measurement, it was found that ammonium carboxylate (-COO- -NH4+) in vulcanized NR converted to calcium carboxylate (-COO- -Ca2+- -OC-) by Ca(NO3)2 treatment. Furthermore, from the photographs of the cross section of the treated film by x-ray microanalyzer, calcium was detected. From these results, it is ascertained that the increase in physical properties by coagulant dipping is attributed to the inter particle crosslinking through Ca2+ ion. Thus, it clearly demonstrated that the Ca(NO3)2 leaching is favorable for the enhancement of physical properties of vulcanized NR.

1. Introduction

It was reported that radiation vulcanization of natural rubber latex (NRL) occurs effectively at a lower dose such as 40 kGy in the presence of carbon tetrachloride by Minoura et al1,2. We have been studying radiation vulcanization of NRL with acrylate and methacrylate monomers as sensitizer3,4. Monofunctional monomers such as 2-
ethylhexyl acrylate (2EHA) and n-butyl acrylate (n-BAA) were superior as sensitizers for the vulcanization of NRL and the dose for vulcanization was 10 - 15 kGy. Protective rubber gloves for radioactive contamination have been produced from the vulcanized latex by coagulant dipping. We made cast film from latex to estimate physical properties of NR after radiation vulcanization. Generally, the tensile strength of the cast film was lower than that of rubber gloves. In order to study the cause of this difference, effect of coagulant on the physical properties of NR was investigated.

2. Experimental

NRL was vulcanized with a cosensitizer of 5 phr 2EHA and 1 phr CCl₄ at 11.9 kGy and then, the latex was cast onto glass plate to make a sheet. The case film was immersed in 1% aq. ammonia solution for 48 hr to remove protein and dried. The production of rubber gloves from vulcanized latex was carried out as shown in Fig. 1. Glove former was immersed in 10% aq. calcium nitrate (Ca(NO₃)₂) solution before dipping into latex. Then, by dipping, rubber gloves was made from vulcanized latex. Leaching and drying of the rubber gloves were carried out by the same procedure as the cast film.

The calcium distribution in the vulcanized rubber was observed by x-ray microanalyzer, XMA (JAOL JX1-super-Prove 773). FTIR spectra was obtained by measuring with refraction method using JAOL 100.

3. Results and Discussion

3.1 Effect of coagulant on physical properties of vulcanized NR

Table 1 shows physical properties of cast film and rubber gloves formed from vulcanized latex. It can be seen that tensile strength of rubber gloves is higher than that of cast film. Since the swelling ratio of rubber gloves is lower than that of cast film, the crosslink density is higher in rubber gloves than cast film. In order to elucidate this difference in tensile strength, the effect of coagulant on vulcanized NR are shown in Fig. 2 and 3. In the case of rubber gloves production from vulcanized latex, glove former was dipped in aq. Ca(NO₃)₂ before dipping in latex. When the former was dipped into the latex, Ca(NO₃)₂ acted as a coagulant in latex. As seen in Fig. 2, the tensile strength
of the cast film after immersion in aq. Ca(NO₃)₂ solution is higher than that without immersion in aq. Ca(NO₃)₂ solution. Tensile strength of sample immersed in aq. Ca(NO₃)₂ solution approach that of rubber gloves shown in Table 1. The elongation at break is hardly changed, even after immersion in aq. Ca(NO₃)₂ solution. The effect of coagulant on swelling ratio is shown in Fig. 3. It can be seen that the crosslink density of vulcanized NR increases by immersion in aq. Ca(NO₃)₂ solution. From the results, it was ascertained that the physical properties of cast film can be improved by increasing the crosslink density by immersion in aq. Ca(NO₃)₂ solution.

3.2 Mechanism of crosslinking by aq. Ca(NO₃)₂

Figure 4 shows the distribution of calcium in cross section of the cast film from X-ray microanalyzer (XMA). The calcium intensity in vulcanized NR increases remarkably by immersion in aq. Ca(NO₃)₂ and the intensity is around 3 times of that of the original sample. However, the calcium intensity in vulcanized NR decrease by immersion in aq. hydrochloric acid after aq. calcium treatment. From this finding, it is considered that calcium in vulcanized NR is released when immersed in hydrochloric acid solution.

FTIR spectra of vulcanized NR after immersion in 1.0% aq. ammonia is shown in Fig. 5. Absorption in vulcanized film at 714, 875 and 1411 cm⁻¹ increases by immersion in aq. ammonia. These are characteristic absorbances of ammonium carboxylate. Figure 6 shows FTIR spectra of vulcanized NR after immersion in aq. Ca(NO₃)₂. The absorption at 714 and 875 cm⁻¹ decreases slightly and the peak of 1411 cm⁻¹ shifts to 1440 cm⁻¹ due to conversion from ammonium to calcium carboxylate. Moreover, the absorption at 1440 cm⁻¹ decreases remarkably when it was immersed in aq. hydrochloric acid as shown in Fig. 6. Absorption due to water is observed at 3415 cm⁻¹. Thus, physical properties of vulcanized NR after hydrochloric acid immersion was reduced due to the increase in water content. From these results, the postulated crosslinking mechanism of vulcanized NR by Ca(NO₃)₂ coagulant is shown in Fig. 7. Although the rubber component in latex particles are fused together after evaporation of water from the cast film, ammonium carboxylate still exists on the surface of latex particles. When vulcanized NR is immersed in aq. Ca(NO₃)₂ solution, ammonium carboxylate in the vulcanized NR converts to calcium carboxylate. Since the ionic crosslinking of Ca²⁺ formed in
the vulcanized film, the tensile strength of cast film increases after coagulant treatment. Calcium in the vulcanized NR is released by immersion in hydrochloric acid and the ionic crosslinked structure decomposes.

4. Conclusion

Tensile strength of rubber gloves prepared by coagulant dipping is higher than that of the cast film. In producing rubber gloves from vulcanized latex, the former is first dipped into aq. Ca(NO₃)₂ coagulant before dipping into latex. Tensile strength of the cast film treated with coagulant approaches that of rubber gloves. The increase in tensile strength is found to be due to the ionic crosslinking by Ca²⁺.

References

Table 1 Comparison of physical properties between cast film and gloves
Sensitizer: 5 phr 2-ethylhexyl acrylate/
CCl₄ 1 phr
Dose: 11.9 kGy

<table>
<thead>
<tr>
<th>Physical properties</th>
<th>Cast film</th>
<th>Gloves</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile strength (Kg/cm²)</td>
<td>319</td>
<td>382</td>
</tr>
<tr>
<td>Elongation at break (%)</td>
<td>978</td>
<td>970</td>
</tr>
<tr>
<td>Swelling ratio (%)</td>
<td>99.6</td>
<td>85.2</td>
</tr>
</tbody>
</table>

Fig. 1 Preparation of rubber gloves and cast film
Fig. 2 Effect of coagulant on tensile strength and elongation at break.

(●) treated in aqueous calcium nitrate for 48 hr.
(○) without calcium nitrate treatment.

Fig. 3 Effect of coagulant on swelling ratio.
(●) immersed in aqueous calcium nitrate for 48 hr.
(○) without calcium nitrate treatment.
Fig. 4 Profiles of X-ray microanalyzer
(A) Before calcium nitrate immersion
(B) Immersion in aq. calcium nitrate for 48 hr
(C) Rinsed by aq. hydrochloric acid after aq. calcium nitrate immersion

Fig. 5 FTIR spectra of vulcanized NR with monomer
A: Vulcanized NR
B: Vulcanized NR after immersion in 1% aq. ammonia for 48 hr
Fig. 6 FTIR of vulcanized NR with monomer
A: Vulcanized NR
B: Vulcanized NR after immersion in 10% aq. Ca(NO₃)₂ for 48 hr
C: Vulcanized NR after immersion in 10% hydrochloric acid the sample B for 48 hr
Fig. 7 Scheme of crosslink by coagulant
5.11 Effect of Heating and Leaching on Mechanical Properties of Radiation Vulcanized Natural Rubber Latex Film

SHUKRI BIN HJ. AB WAHAB\textsuperscript{1)}, K. Makuuchi\textsuperscript{2)}, R. Devendra\textsuperscript{3)}
and Pansu C-P.\textsuperscript{4)}

1) Rubber Research Institute of Malaysia, Selangor, Malaysia,
2) JAERI, TRCRE, Takasaki, Gunma, 370-12 Japan
3) Ceylon Institute of Scientific and Industrial Research, Colombo, Sri Lanka
4) Rubber Research Center, Hatyai, Thailand

Abstract

The effect of heating and leaching on the mechanical properties of radiation vulcanized natural rubber latex (RVNRL) film was investigated. It was found that heating and leaching improved tensile strength of film considerably. The tensile strength could increase as high as 25\% upon heating alone and as high as 75\% upon leaching and drying. The increase in the tensile strength was attributed to reduced moisture content, better particle cohesion and improved entanglement of molecular chains. Complete leaching and drying of RVNRL was found to be important to obtain better and consistent results on the mechanical properties of films from RVNRL.

1. Introduction

The radiation vulcanization of natural rubber latex (RVNRL) using gamma-rays has been studied by many workers since the early sixties\textsuperscript{1-14}. One important area which has not been studied was the effect of heating and leaching on the film properties of RVNRL. Large variation was found in the film properties of RVNRL obtained in those studies. Many workers have also reported difficulties in reproducing results obtained by other workers. Various factors, such as variability in the NR latex, latex formulations and other processing factors have been mentioned as factors contributing to the variability and the lack of reproducibility of results found in those studies.

The aim of this study was to investigate in a more systematic way the effect of heating of RVNRL produced using carbon tetrachloride (CCl\textsubscript{4}) as the sensitizer. An attempt was also made to explain the
reasons for the improvement made in the film properties of RVNRL obtained in this study.

2. Experimental

The latex used in this work was FELDA HA, a high ammonia centrifuged NR latex concentrate supplied by Mitsui & Co. Ltd., Japan. Carbon tetrachloride (CCl₄) was supplied by Wako Pure Chemical Industries Ltd., and potassium laurate (used as a stabiliser) by Nippon Oil and Fats Co., Japan.

The latex formulation used for the irradiation is shown below:

<table>
<thead>
<tr>
<th>Parts by weight</th>
<th>Actual Batch Weight (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Latex, 60% drc</td>
<td>167.0</td>
</tr>
<tr>
<td>CCl₄</td>
<td>5.0</td>
</tr>
<tr>
<td>Potassium laurate</td>
<td>0.3</td>
</tr>
<tr>
<td>Water</td>
<td>add to 55% tsc*</td>
</tr>
</tbody>
</table>

* total solids contents

Potassium laurate was dissolved in water to form a soap solution. Approximately one third of the soap solution was added into CCl₄ and the mixture was stirred at high speed for about 30 minutes. The remaining soap solution was added into the latex to enhance the stability of the latex and this was followed by the addition of CCl₄ mixture. The latex mixture was allowed to mature overnight before irradiation. The latex was irradiated under a stream of nitrogen flowing at a rate of 100 ml/minute. The latex was stirred at slow speed throughout the irradiation process. The irradiation of latex was carried out at a fixed dose rate of 0.5 Mrad/hr for 6 hrs (3 Mrad) at room temperature.

Test samples were prepared by casting the latex on glass plates and then drying them at room temperature until they became clear. These were then subjected to further treatments like heating and leaching under various conditions. They were then kept in a desiccator for 20-24 hrs at 22°C and 30-40% relative humidity before subjecting to the various mechanical tests. Tensile properties, tear resistance and permanent set measurements were carried out in accordance to JIS K 6301 - 1975.
3. Results and Discussion

3.1 Film Properties of Irradiated Latex

Excellent films were produced on casting and drying of latex on glass plates. The latex dried within 10-16 hours at room temperature (ca. 23°C) and at 35-45% relative humidity. The tensile strength of the film measured within two days after drying varied between 19.5 MPa to 25.2 MPa. The elongation at break, however, remained steady at around 1000-1030%.

On storage at room temperature, the tensile strength of the films increased quite remarkably as shown in Fig. 1. Initially, it increased quite rapidly and then reached an optimum of about 35.0 MPa after about 40 days. However, thereafter, it showed a slight reduction on further storage. Heating and leaching the films at certain conditions accelerated the rate of moisture removal as shown in curve B of Fig. 1. Hence, further storage of leached and heated films would not improve the tensile strength further.

The change in the moisture content and hence the tensile strength of film occurred during storage had caused some variations in results obtained by various workers depending upon the time and conditions the films were tested after drying. The rapid change in the tensile strength was attributed to a number of factors, namely, a rapid reduction in the moisture content in the film, an increase in the interparticles adhesion of rubber particles and an increase entanglement of molecular chains between particles as further drying and adhesion occurred during storage. On prolonged storage, a slow reduction in the tensile strength was observed probably due to some degradation of molecular chains.

Other properties such as elongation at break (about 1000%), tear resistance (about 40 kg/cm) and permanent set (about 4%) however showed no significant change during the period of storage investigated.

3.2 Effect of Heating

In this experiment, after drying at room temperature, the latex films were heated in an air oven at 100°C for up to 3 hours and the results of the tensile strength measurement are shown in Fig. 2. The tensile strength increased quite rapidly for the first one hour to give a tensile strength of about 25 MPa, but showed no significant increase on further heating. The rapid increase in the tensile strength on heat-
ing was probably due to some reduction in the moisture content and better fusion of latex particles.

3.3 Effect of Leaching

The effect of leaching the dried cast films in cold water (ca. 23°C) for up to 48 hours followed by drying in an air oven at 70°C until the films became clear is shown in Fig. 3. The tensile strength increased very substantially after leaching and drying, reached an optimum of about 35 MPa at 22-24 hours after leaching. (It was not possible to obtain tensile measurements at longer leaching times as the test piece extended beyond the extension limit of the tensile machine). By comparing Fig. 2 and 3, it is seen that leached films had much higher tensile strengths compared to that of heated films. This was attributed to a much lower moisture content in the leached film. This was because leaching would remove most of the soluble hydrophilic materials present in the latex film. Subsequently, a better adhesion of particles and chain entanglement of rubber molecules occurred. The electron micrograph of the unleached film showed a rough and undulating cross-section with many voids whereas that of the leached films showed smooth and even surface. The close association of proteins in NR latex with the NR hydrocarbon chains could perhaps cause some cross-linking due to the formation of hydrogen bonds. On prolonged leaching, these bonds could be broken due to the removal of proteins. This could probably explain the increase in elongation at break of the test piece leached for more than 24 hours.

The effect of leaching the films in hot water (80°C) at various periods of time followed by drying the film at 70°C for 5 hours is shown in Fig. 4. It was observed that at this temperature a much shorter leaching time was required to reach its optimum tensile strength than it was needed at 23°C. A relatively higher optimum tensile strength (ca. 37.0 MPa) was also achieved when compared to that leached at room temperature (34.0 MPa). This is attributed to the efficiency of leaching soluble materials in hot water compared to that in cold water.

The effect of leaching the films at different temperatures for one hour followed by drying at 70°C for 6 hours is shown in Fig. 5. More or less a similar increase in tensile strength could be achieved at other temperatures in the range investigated (25-80°C), except those leached at 40-70°C. The reason for this observation is obscured. These films have long extension and behaved almost similar to those films
leached at room temperature for more than 24 hours.

3.4 Effect of Moisture Content

The level of moisture content present in the latex film depends to a greater extent upon the degree of drying and the concentration of hydrophilic materials left in the film after leaching. It has been mentioned earlier that the moisture content affects the film properties of RVNRL very significantly. Figure 6 shows the relationship between the moisture content, film thickness and the tensile strength of film. It is clear that a higher moisture content resulted in a lower tensile strength. The maximum level of moisture content allowed was 0.5%, above which it will affect the tensile strength adversely. It is also seen that under normal room temperature drying and without leaching thicker film tends to retain higher moisture content.

4. Conclusions

It was found that heating and leaching improved the tensile strength of the RVNRL films considerable. The tensile strength increases with decreasing moisture content. Complete leaching and drying of the latex film to reduce the moisture content to less than 0.5% were necessary in order to get better and consistent results on the mechanical properties of films from RVNRL.

Acknowledgements

The author wishes to thank the Director of the Rubber Research Institute of Malaysia, Dr. Abd. Aziz Bin S.A. Kadir for permission to present this paper. Special acknowledgements are recorded to Dr. Sidek Bin Dulngali of the Rubber Research Institute of Malaysia for useful discussion and comments.

References


Fig. 1 Effect of storage time on tensile strength of irradiated latex films. A: dried and stored; B: dried, heated and stored

Fig. 2 Effect of heating (100°C) on tensile strength of irradiated films
Fig. 3 Effect of leaching in cold water at RT on tensile strength

Fig. 4 Effect of leaching in hot water (80°C) for various times on tensile strength of films
Fig. 5 Effect of leaching at various temperature for 1 hr on tensile strength of films

Fig. 6 Effect of film thickness and moisture content on tensile strength of films
5.12 Standardization of Radiation Vulcanized Natural Rubber Latex

S.W. KARUNARATNE

Rubber Research Institute
Telewala Road, Ratmalana, Sri Lanka

Abstract

Standards for concentrated latex used in the preparation of irradiated latex, standard irradiation conditions, further treatment of irradiated latex, level of prevulcanization and its estimation, film preparation and testing procedures are discussed in this paper.

1. Introduction

Since the beginning of the Regional Cooperative Agreement (RCA) project on radiation processing in 1978 a wealth of information has been accumulated on radiation vulcanization of natural rubber latex. When it comes to technology transfer the process should be supported by quality assurance and it is necessary to formulate standards for testing. This paper attempts to describe standard techniques for the production of radiation vulcanised natural rubber latex (RVNRL).

2. Standard Latex

The general purpose grades of natural latex concentrate are now subject to the requirements of international standards. They have been technically specified for many years in certain countries and the establishment of international standards indicates the substantial measure of agreement that has been achieved on the characteristics which are required of good quality natural rubber latex. International Standards Organisation (ISO) has defined the requirements for both centrifuged and creamed natural rubber lattices1.

3. Sampling

The sampling method is described in an international standard2. Rubber latex may tend to cream on standing. If stratification has occurred, the latex shall be thoroughly agitated to obtain a homogeneous blend suitable for the withdrawal of a representative sample. The pro-
procedure required differs with the type of container. In all cases where samples are drawn from several containers, 10 per cent sampling of latex in drums or in the case of tanks where extractions are made at various depths, such samples should be bulked and stirred. The final average sample shall then be bottled and sealed.

Standard specifications for centrifuged latex, both high ammonia (HA) type and low ammonia (LA) type are given in Table 1. Any additional characteristics of latex such as pH, specific gravity, viscosity, conductivity, particle size and particle size distribution would be useful. In the case of LA latex the type of stabilizer system should be specified.

4. Standard Irradiation Conditions

Standard recommended practice for exposure of polymeric materials to high energy radiation is described in a standard issued by the American Society for testing materials (ASTM). Irradiation conditions should be reported in the following manner:

1. Type of radiation source and kind of radiation
2. Irradiation dose rate, kilo gray per hour
3. Irradiation time
4. Total dose in kilo gray
5. Reference to or description of irradiation dose measurement procedure
6. Dimensional description of test specimen size/size of container. Specify the design/type of container used for irradiation and the design/type of stirrer needed.
7. Description of the type of material tested shall be reported including the nature of additives eg sensitizer, stabilizer, emulsifier and the method of incorporation of the additives into the latex. The total solids level of the latex should be indicated.
8. Description of irradiation conditions such as the nature of the atmosphere in which irradiation is carried out, temperature of irradiation and the speed of stirring if stirring is carried out.

It is necessary to add a sensitizer in a slow stream while the latex is stirred continuously. The sensitizer should get absorbed into the latex particles and at least 16 hours should elapse before the latex is
irradiated. It is necessary to stir the latex at a speed ranging between 20 to 60 rpm during irradiation, especially for large batches.

5. Further Treatment of Irradiated Latex

It is important to add an antioxidant to the irradiated latex at the rate of 1 to 2 parts per 100 parts of rubber. If the antioxidant is not soluble in water it should be added as a 50 to 80% dispersion in water. The recommended antioxidants are the non staining phenolic types given in Table 2. However other antioxidants may be used depending on the type of application for which the irradiated latex is used.

6. Standard Methods of Testing Irradiated Latex

A few methods of testing irradiated latex is described.

1) Shelf life.

The viscosity of irradiated latex should be determined on a monthly basis. Depending on the increase of viscosity with time the storage stability can be graded as Excellent (E) Good (G) or Poor (P). The latex should be stored in well stoppered bottles under controlled temperature and humidity conditions. The viscosity should be measured under controlled conditions using a well known type of a viscometer. eg Brookfield viscometer.

2) Level of prevulcanization
(a) In line quality control test:

The chloroform coagulation test is a simple and rapid means for testing the degree of prevulcanization. It consists of mixing equal parts of prevulcanized latex and chloroform (10 cm³ of each) and stirring with a glass rod until coagulation is complete. The coagulum is allowed to stand 2 to 3 minutes and then numerically rated from 1 to 4. No.1 is judged as uncured and No.4 is precured to an advanced degree. The chloroform coagulation test is subjective and it does not allow for easy comparison of small differences between individual samples.

(b) Swelling test

Solvent swell tests are more quantitative than the chloroform coagulation test.

A quick method has been developed to determine the degree of vulcanization.
A film of latex is formed on a specially treated paper (e.g., mita copy paper). The film 0.125 mm in thickness (after drying) is cut into a circle (a 50 mm diameter) with the paper backing and placed in a medium-size petri dish containing toluene. The film is allowed to swell for 20 minutes (until swelling is maximum) and the swollen diameter is measured. The percentage swelling gives an indication of the degree of vulcanization.

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Unvulcanized</td>
<td>160%</td>
</tr>
<tr>
<td>Lightly vulcanized</td>
<td>100 - 160%</td>
</tr>
<tr>
<td>Moderately vulcanized</td>
<td>80 - 100%</td>
</tr>
<tr>
<td>Fully vulcanized</td>
<td>75%</td>
</tr>
</tbody>
</table>

3 Film formation
   (a) Coagulant dipping
   The following coagulant solution is recommended

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Parts by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcium nitrate</td>
<td>25</td>
</tr>
<tr>
<td>Water</td>
<td>24</td>
</tr>
<tr>
<td>Methylated spirit</td>
<td>50</td>
</tr>
<tr>
<td>Wetting agent</td>
<td>1</td>
</tr>
</tbody>
</table>

A clean dry former is immersed in a coagulant solution and partially dried (at 70°C) to leave a uniform layer of coagulant over its surface. It is then immersed in the latex at a steady rate and allowed to dwell there for an appropriate time to obtain the required thickness. The wet gel deposit is leached in hot water (70°C - 80°C) for about 30 min. It is then dried at 70°C in an air circulating oven until moisture content is reduced to less than 0.5%. This is followed by post-heat treatment at 100°C for 30 min. It is then dusted. The film is then tested for physical properties.

(b) Straight dipping
   In straight dipping a coagulant solution is not used. The rest of the procedure is the same as for coagulant dipping.

In studying the dipping characteristics, the relation between the deposit thickness, dwell time, and number of dips should be studied. The processing characteristics should also be noted from pos-
sible defects such as pin holes, webbing, lamination etc. Other specifications required for specific end products such as the bursting pressure should be met.

7. Testing of Film for Physical Properties

Preparation and pretreatment of film is necessary prior to testing.

1. Preparation of film for testing

Carefully strain the latex through a 180 μm stainless steel sieve with a nominal aperture of 0.180 ± 0.009 mm into a beaker.

Cover the beaker to minimise surface drying and allow it to stand for 5 minutes before pouring the latex into the glass mould.

The irradiated latex is cast on a glass mould (150 mm square or about similar dimension) and dried under normal atmospheric conditions. The thickness of the dried film should be about 0.75 mm. The film is leached for 24 hrs in water at room temperature and subsequently oven dried at 70°C for 4 hours. The film is then given post heat treatment at 100°C for 30 min. The film is then dusted using talc.

2. Pretreatment of film prior to testing

(a) Leaching

The properties of dried films from prevulcanized latex are affected by leaching them in water and by heating. A pronounced effect on leaching is seen, giving rise to increased Tensile Strength and Modulus.

The explanation of the leaching effect is thought to be in the ability of surface active agents and other hydrophilic materials in the compound to hinder the formation of a homogeneous film on drying. Since the molecular mobility is restricted by the crosslinks, particle merging becomes more difficult and is easily hindered by the non rubbers. Leaching removes a large portion of these non rubbers and so facilitate homogeneous film formation. Heating the film will assist the particles to merge but may introduce extra crosslinks or rearrange existing ones.

(b) Heat treatment

A significant improvement in the physical properties of the film derived from irradiated latex is evident after heat treatment of the prevulcanised film for 30 min at 100°C.
Testing of irradiated latex films

The testing procedures are described in the relevant ISO or British Standards (B.S.) and are given in Table 3.

References

1. ISO 2004
2. ISO 123
3. ASTM-D-1672-66 (1971)
6. ISO 124
7. ISO 126
8. ISO 125
9. ISO 35
10. ISO 706
11. ISO/R 1654
12. ISO 1655
13. ISO 2005
14. ISO 506
15. ISO 127
16. ISO 471 - 1977(E)
17. ISO 471 - 1977(C)
18. ISO 37 - 1977(E)
19. ISO 188 - 1982(G)
20. ISO 2285 - 1981(E)
21. ISO 34 - 1975(E)
22. BS 1673 : Part 4, 1953
Table 1  Standard Specification of HA and LA Latex

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>High Ammonia Latex</th>
<th>Low Ammonia Latex</th>
<th>Reference No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total solids content, % m/m, min</td>
<td>61.5</td>
<td>61.5</td>
<td>6</td>
</tr>
<tr>
<td>Dry rubber content, % m/m, min</td>
<td>60.0</td>
<td>60.0</td>
<td>7</td>
</tr>
<tr>
<td>Non-rubber solids, % m/m, max</td>
<td>2.0</td>
<td>2.0</td>
<td></td>
</tr>
<tr>
<td>Alkalinity (as NH₃) % m/m, on latex concentrate</td>
<td>0.60 min</td>
<td>0.29 max</td>
<td>8</td>
</tr>
<tr>
<td>Mechanical stability, seconds, min</td>
<td>650</td>
<td>650</td>
<td>9</td>
</tr>
<tr>
<td>Coagulum content, % m/m, max</td>
<td>0.05</td>
<td>0.05</td>
<td>10</td>
</tr>
<tr>
<td>Copper content, mg/kg of total solids, max</td>
<td>8</td>
<td>8</td>
<td>11</td>
</tr>
<tr>
<td>Manganese content, mg/kg of total solids, max</td>
<td>8</td>
<td>8</td>
<td>12</td>
</tr>
<tr>
<td>Sludge content, % m/m, max</td>
<td>0.10</td>
<td>0.10</td>
<td>13</td>
</tr>
<tr>
<td>Volatile fatty acid No., max</td>
<td>0.20</td>
<td>0.20</td>
<td>14</td>
</tr>
<tr>
<td>KoH number, max</td>
<td>1.0</td>
<td>1.0</td>
<td>15</td>
</tr>
<tr>
<td>Colour on visual inspection</td>
<td>No pronounced blue or grey</td>
<td>No pronounced blue or grey</td>
<td></td>
</tr>
<tr>
<td>Odour after neutralization with boric acid</td>
<td>No pronounced odour or putrefaction</td>
<td>No pronounced odour or putrefaction</td>
<td></td>
</tr>
</tbody>
</table>
Table 2  Some non staining antioxidant types with their trade names

<table>
<thead>
<tr>
<th>Type of Antioxidant</th>
<th>Trade example</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenol alkanes and hindered</td>
<td></td>
</tr>
<tr>
<td>phenols</td>
<td>Antioxidant 2246</td>
</tr>
<tr>
<td></td>
<td>Antioxidant 425</td>
</tr>
<tr>
<td></td>
<td>Nauga white</td>
</tr>
<tr>
<td></td>
<td>Permanax SP</td>
</tr>
<tr>
<td></td>
<td>Permanax WSL</td>
</tr>
<tr>
<td></td>
<td>Permanax WSP</td>
</tr>
<tr>
<td></td>
<td>Santowhite 54</td>
</tr>
<tr>
<td></td>
<td>Vulkanox BKF</td>
</tr>
<tr>
<td></td>
<td>Vulkanox ZKF</td>
</tr>
<tr>
<td></td>
<td>Wingstay L</td>
</tr>
<tr>
<td></td>
<td>Wingstay S</td>
</tr>
<tr>
<td></td>
<td>Wingstay T</td>
</tr>
<tr>
<td>Hydroquinones</td>
<td>Agerite alba</td>
</tr>
<tr>
<td></td>
<td>Santovar A.</td>
</tr>
</tbody>
</table>
Table 3 Testing Procedures for Rubber Films

<table>
<thead>
<tr>
<th>Test method</th>
<th>Reference No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>a) Conditioning of test pieces</td>
<td>16</td>
</tr>
<tr>
<td>b) Methods of testing vulcanized rubber</td>
<td>17</td>
</tr>
<tr>
<td>c) Determination of tensile stress-strain properties</td>
<td>18</td>
</tr>
<tr>
<td>d) Accelerated ageing or heat resistant tests</td>
<td>19</td>
</tr>
<tr>
<td>e) Determination of tension set at normal and high temperature</td>
<td>20</td>
</tr>
<tr>
<td>f) Determination of tear strength</td>
<td>21</td>
</tr>
<tr>
<td>g) Procedure for testing swelling and gel fraction</td>
<td>22</td>
</tr>
<tr>
<td>h) Colour, transparency and clouding effects</td>
<td>-</td>
</tr>
<tr>
<td>i) Toxicity tests</td>
<td>-</td>
</tr>
<tr>
<td>j) Combustion analysis of films (gas evaluation and ash content)</td>
<td>-</td>
</tr>
</tbody>
</table>
5.13 Effect of Antioxidant on the Aging Property of Rubber Film Prepared from Radiation Vulcanized Natural Rubber Latex

Dedik Eko Sumbogo¹, F. SUNDARDI² and Marga Utama²

1) Technical Faculty, University of Gajah Mada, Yogyakarta, Indonesia.

Abstract

A study of the effect of antioxidants on the aging property of film prepared from radiation vulcanised natural rubber latex (RVNRL) has been done. Commercial antioxidants studied were Vulcanox, Ionol and Nonox. Two kinds of RVNRL were studied, those which prepared by using CCl₄ and n-butyl acrylate (n-BA) sensitizers. The antioxidants were in the form of emulsion and dispersion before blending with the latex. The antioxidants were blended with NR latex just after irradiation. It was found that the addition of Vulcanox, Ionol or Nonox, in the form of emulsion or dispersion into RVNRL, would much improve the aging property of the film. Emulsion of Vulcanox (0.5 phr) appeared to be the best antioxidant for RVNRL prepared using CCl₄ sensitizer. Decreasing in tensile strength after 14 days of aging at 70°C was 17.9% compared to 26.5% for film without that antioxidant. Emulsion of Vulcanox also showing the best sensitizer for RVNRL prepared using n-BA sensitizer.

1. Introduction

Natural rubber (NR) latex, which comes from Hevea Brasiliensis plantation, is a dispersion of NR particles in water. The diameter of the particle is between 0.2 μ and 1.0 μ. The dispersion in water is stabilized by a thin layer of protein on the surface of the particle, which containing an electric charge. Anything that is capable to disturb the electric charge in that layer such as pH, will be capable in disturbing the stability of latex. The solid content of field latex (just tapped from the rubber tree) is between 20% and 40%. The solid fraction consists of rubber constituent (polyisoprene) which normally is about 95%, and the rest is non rubber constituent such as protein, fatty acid, antioxidant etc¹.
It has been known that field NR latex containing 60-70% water, while concentrated NR containing about 40% of water. Irradiation of water will produce a number of active species, such as hydrogen radical (H\(^{\cdot}\)) and OH radical (OH\(^{\cdot}\)). This OH radical is an oxidizing agent while hydrogen radical is a strong reducing agent. So anything that can be oxidised will be oxidised by radiation, and also anything that can be reduced will be reduced by radiation. Because NR latex containing a large fraction of water, it can be expected that irradiation of latex may follow the rule of irradiation of water. The non rubber constituent may be oxidised by radiation including natural antioxidant which normally present in latex. This is a drawback of radiation effect on NR latex.

It is clear that the addition of antioxidant is necessary to replace the natural antioxidant already destroyed by radiation. This paper presents the report of the study on the effect of artificial antioxidant on the aging property of film prepared from RVNRL.

2. Experimental

2.1 Materials

Concentrated natural rubber latex was from West Java, with total solid about 60%, and diluted to about 47% for the experiment. Chemicals such as CCl\(_4\) and n-butyl acrylate (n-BA) were of technical grade. Commercial antioxidants studied were Vulcanox, Ionol and Nonox.

2.2 Equipments

A Panoramic Co-60 irradiator was used for irradiation of NR latex. Instron Model 1000 Testing Machine was used for measuring the physical properties of rubber film, while Visconic E-12 was used for measuring the latex viscosity.

2.3 Method

Radiation vulcanised natural rubber latex (RVNRL) was prepared by two different methods\(^{4-6}\)

1. Using CCl\(_4\) sensitizer (4 phr) with irradiation dose of 50 kGy
2. Using n-BA sensitizer (5 phr) with irradiation dose of 10 kGy.

This RVNRL was mixed with a given amount of antioxidants: Vulcanox, Ionol or Nonox. These antioxidants were used in the form of an emulsion and dispersion. Emulsion of antioxidants were prepared by dissolving
those antioxidants in benzene, and then this solution was emulsified with
water using an emulsifying agent. The dispersion of antioxidants were
prepared by grinding with water in a ball mill for at least three days.

Just after irradiation, RVNRL was mixed with 0.5 phr and 1 phr of
antioxidants. Viscosity and pH of this latex after mixing with anti-
oxidants were determined up to four weeks of storage time, in order to
evaluate the stability of this latex.

Rubber film was prepared by casting method: pouring a given quan-
tity of RVNR on a glass plate, drying at room temperature for several
days, leaching the film overnight at room temperature, drying that film
at room temperature, and then heating at 70°C for 3 hours.

Aging of the rubber film was done in a Geer oven at 70°C, for up
to two weeks. The physical properties of that film was determined both
before and after aging in Geer oven.

Crosslink density of that film was determined by swelling ratio
method, based on FLORY & REHNER equation as follows:

\[ \nu_o = K \times Q^{-5/3} \]

where \( \nu_o \) = crosslink density, c.1/ml
\( K = 4.71 \times 10^{20} \), for a system of benzene-natural rubber,
\( Q = \text{volumetric swelling ratio} \).

3. Results and Discussion

Table 1 and 2 show that pH of latex decreases with increasing in
storage time, for both latex with or without antioxidant. A decrease in
pH may disturb the electrical charge in the surface layer of NR particles,
and consequently will be able to increase latex viscosity. Decreasing
in electrical charge means decreasing in repulsion forces between par-
ticles, which consequently will be able to increase the friction forces,
and so the viscosity. Table 1 and 2 show that latex viscosity increases
with storage time.

The decrease of latex viscosity with the addition of antioxidant
(emulsion & dispersion) may be only due to a small dilution of the
latex, and pH is not much effected by the addition of antioxidants.
Although it has been show the increases of latex viscosity with the
increase of storage time, the increase in viscosity is low and in general
it can be said that the latex still quite in a good condition at least during four weeks of storage.

Table 3 shows that the tensile strength of rubber film (without aging) decreases with the addition of antioxidant into that latex. However the addition of antioxidant into latex showing a better in aging property of the film, compared to that of unadded one. Vulcanox appears to be the best antioxidants among the tested antioxidants. After aging at 70°C for 14 days, the tensile strength of the film still more than 25 MPa, using Vulcanox antioxidant with concentration about 0.5 phr. The tensile strength decreases about 12% for 7 days of aging, and about 18% for 14 days of aging. Elongation at break also decreases with aging time.

Table 4 shows that an emulsion of Vulcanox in concentration of about 0.5 phr appears to be the best antioxidant among the tested antioxidants. The rubber film was from RVNRL prepared using n-BA sensitizer, and 10 kGy dose of irradiation. After aging at 70°C for 14 days, the tensile strength of the film was still more than 20 MPa. Decreasing of tensile strength after 14 days of aging is about 21% using Vulcanox antioxidant (Table 5). The addition of other antioxidants such as Ionol or Nonox also will much improve the aging property of the film, but not as good as Vulcanox.

Table 6 shows that RVNRL prepared by using CCl₄ (4 phr) at irradiation dose of 50 kGy, give a higher crosslink density compared to that of prepared by using n-BA (5 phr). The lower crosslink density causes the higher percentage in decreasing of physical strength after aging, which is in agreement with the experimental results (Table 5). Decreasing of crosslink density by aging time is shown in Table 6, which may be due to oxidation reaction during aging.

Conclusion

Vulcanox appears to be the best antioxidant for RVNRL. The amount of this antioxidant required about 0.5 phr, either in the form of an emulsion or dispersion.
References

<table>
<thead>
<tr>
<th>Antioxidant</th>
<th>Viscosity, mPa.s</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0 week 1 week 2 weeks 3 weeks 4 weeks</td>
<td>0 week 1 week 2 weeks 3 weeks 4 weeks</td>
</tr>
<tr>
<td>1) Without antioxidant</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2) Dispersion of Vulcanox, 0.5 phr</td>
<td>12.12 11.94 13.45 13.95 14.76</td>
<td>0.58 10.56 10.56 10.43 10.13</td>
</tr>
<tr>
<td>3) Dispersion of Ionol, 0.5 phr</td>
<td>11.82 12.28 13.31 14.33 14.63</td>
<td>0.58 10.55 10.53 10.45 10.13</td>
</tr>
<tr>
<td>4) Emulsion of Vulcanox, 0.5 phr</td>
<td>12.63 12.75 13.99 14.76 15.10</td>
<td>0.60 10.58 10.58 10.48 10.17</td>
</tr>
<tr>
<td>5) Emulsion of Ionol, 0.5 phr</td>
<td>12.84 11.94 13.56 14.67 14.53</td>
<td>0.60 10.56 10.56 10.46 10.23</td>
</tr>
<tr>
<td>6) Emulsion of Nonox, 0.5 phr</td>
<td>11.77 11.86 12.54 13.31 13.43</td>
<td>0.58 10.53 10.42 10.37 10.22</td>
</tr>
<tr>
<td>7) Dispersion of Vulcanox, 1 phr</td>
<td>12.24 12.67 13.18 13.86 14.29</td>
<td>0.60 10.53 10.47 10.37 10.02</td>
</tr>
<tr>
<td>8) Dispersion of Ionol, 1 phr</td>
<td>11.59 12.16 13.27 13.74 13.56</td>
<td>0.60 10.53 10.48 10.40 10.13</td>
</tr>
<tr>
<td>9) Emulsion of Vulcanox, 1 phr</td>
<td>12.83 13.82 14.54 14.50 14.93</td>
<td>0.62 10.53 10.46 10.42 10.07</td>
</tr>
<tr>
<td>10) Emulsion of Ionol, 1 phr</td>
<td>12.75 13.95 14.55 14.59 15.06</td>
<td>0.62 10.53 10.48 10.45 10.15</td>
</tr>
<tr>
<td>11) Emulsion of Nonox, 1 phr</td>
<td>11.05 11.47 12.67 12.54 12.58</td>
<td>0.62 10.53 10.52 10.47 10.27</td>
</tr>
<tr>
<td>Antioxidant</td>
<td>Viscosity, mPa·s</td>
<td>pH</td>
</tr>
<tr>
<td>-----------------------------------</td>
<td>------------------</td>
<td>------</td>
</tr>
<tr>
<td></td>
<td>0 week</td>
<td>1 week</td>
</tr>
<tr>
<td>0.5 phr of Nonox 1 phr of Vulcason, 0.5 phr of Ionol</td>
<td>19.11</td>
<td>20.26</td>
</tr>
<tr>
<td>0 phr of Nonox 1 phr of Vulcason, 0.5 phr of Ionol</td>
<td>19.92</td>
<td>20.35</td>
</tr>
<tr>
<td>0.5 phr of Nonox 1 phr of Vulcason, 0.5 phr of Ionol</td>
<td>17.79</td>
<td>18.49</td>
</tr>
<tr>
<td>0 phr of Nonox 1 phr of Vulcason, 0.5 phr of Ionol</td>
<td>18.79</td>
<td>19.49</td>
</tr>
<tr>
<td>0.5 phr of Nonox 1 phr of Vulcason, 0.5 phr of Ionol</td>
<td>18.56</td>
<td>20.26</td>
</tr>
<tr>
<td>0 phr of Nonox 1 phr of Vulcason, 0.5 phr of Ionol</td>
<td>18.3</td>
<td>20.47</td>
</tr>
<tr>
<td>0.5 phr of Nonox 1 phr of Vulcason, 0.5 phr of Ionol</td>
<td>18.54</td>
<td>20.75</td>
</tr>
<tr>
<td>0 phr of Nonox 1 phr of Vulcason, 0.5 phr of Ionol</td>
<td>18.49</td>
<td>20.54</td>
</tr>
<tr>
<td>0.5 phr of Nonox 1 phr of Vulcason, 0.5 phr of Ionol</td>
<td>18.49</td>
<td>20.54</td>
</tr>
<tr>
<td>0 phr of Nonox 1 phr of Vulcason, 0.5 phr of Ionol</td>
<td>18.49</td>
<td>20.54</td>
</tr>
<tr>
<td>0.5 phr of Nonox 1 phr of Vulcason, 0.5 phr of Ionol</td>
<td>18.49</td>
<td>20.54</td>
</tr>
<tr>
<td>0 phr of Nonox 1 phr of Vulcason, 0.5 phr of Ionol</td>
<td>18.49</td>
<td>20.54</td>
</tr>
</tbody>
</table>
Table 3  Physical properties of rubber film prepared from irradiated NR latex, using 4 phr of CCL4, and irradiation dose of 50 kGy. Effect of antioxidants and aging time at 70°C

<table>
<thead>
<tr>
<th>RVNRL treatment</th>
<th>Modulus 600%, MPa</th>
<th>Tensile strength, MPa</th>
<th>Elongation at break, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0 day</td>
<td>7 days</td>
<td>14 days</td>
</tr>
<tr>
<td>1. Without antioxidant</td>
<td>2.31</td>
<td>1.84</td>
<td>1.66</td>
</tr>
<tr>
<td>2. Dispersion of Vulcanox, 0.5 phr</td>
<td>2.37</td>
<td>1.91</td>
<td>1.88</td>
</tr>
<tr>
<td>3. Dispersion of Itonol, 0.5 phr</td>
<td>2.24</td>
<td>1.87</td>
<td>1.75</td>
</tr>
<tr>
<td>4. Emulsion of Vulcanox, 0.5 phr</td>
<td>2.21</td>
<td>1.87</td>
<td>1.82</td>
</tr>
<tr>
<td>5. Emulsion of Itonol, 0.5 phr</td>
<td>2.31</td>
<td>1.97</td>
<td>1.82</td>
</tr>
<tr>
<td>6. Emulsion of Nonox, 0.5 phr</td>
<td>2.21</td>
<td>1.95</td>
<td>1.74</td>
</tr>
<tr>
<td>7. Dispersion of Vulcanox, 1 phr</td>
<td>2.51</td>
<td>2.11</td>
<td>1.98</td>
</tr>
<tr>
<td>8. Dispersion of Itonol, 1 phr</td>
<td>2.35</td>
<td>1.95</td>
<td>1.87</td>
</tr>
<tr>
<td>9. Emulsion of Vulcanox, 1 phr</td>
<td>2.34</td>
<td>2.08</td>
<td>1.97</td>
</tr>
<tr>
<td>10. Emulsion of Itonol, 1 phr</td>
<td>2.45</td>
<td>2.07</td>
<td>1.97</td>
</tr>
<tr>
<td>11. Emulsion of Nonox, 1 phr</td>
<td>2.36</td>
<td>2.01</td>
<td>1.77</td>
</tr>
</tbody>
</table>
Table 4 Physical properties of rubber film prepared from irradiated NR latex, using 5 phr of n-BA, and irradiation dose of 10 kGy. Effect of antioxidants and aging time at 70°C

<table>
<thead>
<tr>
<th>RVNRL treatment</th>
<th>Modulus 600%, MPa</th>
<th>Tensile strength, MPa</th>
<th>Elongation at break, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0 day</td>
<td>7 days</td>
<td>14 days</td>
</tr>
<tr>
<td>1. Without anti-oxidant</td>
<td>1.70</td>
<td>1.50</td>
<td>1.14</td>
</tr>
<tr>
<td>2. Dispersion of Vulcanox, 0.5 phr</td>
<td>1.81</td>
<td>1.68</td>
<td>1.38</td>
</tr>
<tr>
<td>3. Dispersion of Ionol, 0.5 phr</td>
<td>1.89</td>
<td>1.55</td>
<td>1.20</td>
</tr>
<tr>
<td>4. Emulsion of Vulcanox, 0.5 phr</td>
<td>1.91</td>
<td>1.71</td>
<td>1.31</td>
</tr>
<tr>
<td>5. Emulsion of Ionol, 0.5 phr</td>
<td>1.99</td>
<td>1.56</td>
<td>1.26</td>
</tr>
<tr>
<td>6. Emulsion of Nonox, 0.5 phr</td>
<td>1.99</td>
<td>1.62</td>
<td>1.22</td>
</tr>
<tr>
<td>7. Dispersion of Vulcanox, 1 phr</td>
<td>1.93</td>
<td>1.56</td>
<td>1.39</td>
</tr>
<tr>
<td>8. Dispersion of Ionol, 1 phr</td>
<td>1.85</td>
<td>1.55</td>
<td>1.42</td>
</tr>
<tr>
<td>9. Emulsion of Vulcanox, 1 phr</td>
<td>1.85</td>
<td>1.62</td>
<td>1.43</td>
</tr>
<tr>
<td>10. Emulsion of Ionol, 1 phr</td>
<td>1.71</td>
<td>1.51</td>
<td>1.43</td>
</tr>
<tr>
<td>11. Emulsion of Nonox, 1 phr</td>
<td>1.76</td>
<td>1.48</td>
<td>1.25</td>
</tr>
</tbody>
</table>
Table 5  Percentage of decreasing in tensile strength of rubber film, prepared from RVNRL, after aging at 70°C for 7 days and 14 days

<table>
<thead>
<tr>
<th>RVNRL treatment</th>
<th>RVNRL using CCl₄</th>
<th></th>
<th>RVNRL using n-BA</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>7 days</td>
<td>14 days</td>
<td>7 days</td>
<td>14 days</td>
</tr>
<tr>
<td>1. Without anti-oxidant</td>
<td>19.0</td>
<td>26.5</td>
<td>25.5</td>
<td>28.7</td>
</tr>
<tr>
<td>2. Dispersion of Vulcanox, 0.5 phr</td>
<td>13.9</td>
<td>20.1</td>
<td>24.2</td>
<td>25.7</td>
</tr>
<tr>
<td>3. Dispersion of Ionol, 0.5 phr</td>
<td>18.8</td>
<td>24.0</td>
<td>24.1</td>
<td>30.0</td>
</tr>
<tr>
<td>4. Emulsion of Vulcanox, 0.5 phr</td>
<td>12.1</td>
<td>17.9</td>
<td>20.9</td>
<td>22.8</td>
</tr>
<tr>
<td>5. Emulsion of Ionol, 0.5 phr</td>
<td>11.5</td>
<td>21.2</td>
<td>23.6</td>
<td>30.6</td>
</tr>
<tr>
<td>6. Emulsion of Nonox, 0.5 phr</td>
<td>12.3</td>
<td>25.3</td>
<td>21.7</td>
<td>28.1</td>
</tr>
<tr>
<td>7. Dispersion of Vulcanox, 1 phr</td>
<td>14.2</td>
<td>19.5</td>
<td>21.1</td>
<td>21.5</td>
</tr>
<tr>
<td>8. Dispersion of Ionol, 1 phr</td>
<td>15.0</td>
<td>21.9</td>
<td>19.9</td>
<td>25.2</td>
</tr>
<tr>
<td>9. Emulsion of Vulcanox, 1 phr</td>
<td>7.3</td>
<td>20.3</td>
<td>18.3</td>
<td>21.4</td>
</tr>
<tr>
<td>10. Emulsion of Ionol, 1 phr</td>
<td>13.5</td>
<td>20.5</td>
<td>18.4</td>
<td>24.8</td>
</tr>
<tr>
<td>11. Emulsion of Nonox, 1 phr</td>
<td>10.9</td>
<td>18.5</td>
<td>16.2</td>
<td>23.6</td>
</tr>
</tbody>
</table>
Table 6  Effect of aging time and antioxidant on crosslink density of film prepared from RVNRL. Aging at 70°C for 7 days and 14 days

<table>
<thead>
<tr>
<th>RVNRL treatment</th>
<th>Crosslink density, $10^{18}$ c.1/ml</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0 day</td>
</tr>
<tr>
<td>(A) RVNRL, using</td>
<td></td>
</tr>
<tr>
<td>4 phr of CCl$_4$; dose = 50 kGy</td>
<td></td>
</tr>
<tr>
<td>1. Without antioxidant</td>
<td>22.45</td>
</tr>
<tr>
<td>2. Emulsion of Ionol, 0.5 phr</td>
<td>20.72</td>
</tr>
<tr>
<td>3. Emulsion of Ionol, 1 phr</td>
<td>22.68</td>
</tr>
<tr>
<td>(B) RVNRL, using</td>
<td></td>
</tr>
<tr>
<td>5 phr of n-BA, dose = 10 kGy</td>
<td></td>
</tr>
<tr>
<td>1. Without antioxidant</td>
<td>20.22</td>
</tr>
<tr>
<td>2. Emulsion of Ionol, 0.5 phr</td>
<td>19.19</td>
</tr>
<tr>
<td>3. Emulsion of Ionol, 1 phr</td>
<td>17.57</td>
</tr>
</tbody>
</table>
5.14 Stabilization of Radiation Vulcanized Natural Rubber Latex Film

SHUKRI BIN HJ.AB WAHAB\textsuperscript{1)}, Siti S.B. Sulaiman\textsuperscript{1)}, K. Makuuchi\textsuperscript{2)}, R. Devendra\textsuperscript{3)} and Pansa C-P\textsuperscript{4)}

1) Rubber Research Institute of Malaysia, Selangor, Malaysia,
2) JAERI, TRCRE, Takasaki, Gunma, 370-12 Japan
3) Ceylon Institute of Scientific and Industrial Research, Colombo, Sri Lanka
4) Rubber Research Center, Hatyai, Thailand

Abstract

Radiation vulcanized natural rubber latex (RVNRL) film has poor aging characteristics especially after it has been subject to leaching. The effect of the addition of antioxidants on the aging properties of RVNRL obtained using carbon tetrachloride and n-butyl acrylate (n-BA) as sensitizers respectively were evaluated. Antioxidant 2'2'-methylene-bis-(4-methyl-6-tert-butyphenol) containing 0.8 phr was found to be the most effective for RVNRL produced by using CCl\textsubscript{4} as sensitizer and antioxidant 2,4-Bis[(octylthio)methyl]-o-cresol containing 1.0 phr for RVNRL produced by using n-BA as sensitizer. Antioxidant 2-mercaptobenzimidazole showed slightly less effective but gave less tendency for discoloration compared to 2,4-Bis[(octylthio)methyl]-o-cresol when used in the n-BA system.

1. Introduction

Films obtained from radiation vulcanised natural rubber latex (RVNRL) had poor aging characteristics especially after it had been subjected to leaching\textsuperscript{1,2}. Recently, much progress has been made to improve the physical and mechanical properties of RVNRL, especially the tensile strength, through proper selection of latex, use of new sensitizers and improved formulations, etc.,\textsuperscript{3,4}. Unfortunately, little work had been done to improve the poor aging characteristics of RVNRL obtained in those studies.

The need to protect latex films from degradation is crucial as most latex particles have a large surface area to volume ratio. The successful transfer of RVNRL technology to the industry therefore depends, to a greater extent, upon the impression of the products has in the mind of the consumers. Their appearance on display in stores, the condition in
which they are received and their durability during use make a lasting
impression of the product's quality to consumers.

This paper describes the results of the investigation on some anti-
oxidants with the objective to improve the aging characteristics of RVNRL
film obtained by using carbon tetrachloride (CCl₄) and using n-butyl
acrylate (n-BA) as sensitizers.

2. Experimental

The latex used in this work was a high ammonia centrifuged NR latex
concentrates produced by FELDA and DUNLOP of Malaysia. Carbon tetra-
chloride (CCl₄), n-butyl acrylate (n-BA), potassium hydroxide, potassium
laurate and ammonia were products made in Japan. The antioxidants used
were proprietary chemicals and are listed in Table 1. Solid antioxidants
were prepared as dispersion in water (25-50% total solids contents) con-
taining 1-2% dispersion agent (Dispersol LR from ICI) and ball-milled
for 20-24 hours. Liquid antioxidants were used as supplied.

The latex formulations using CCl₄ and n-BA as sensitizers in this
study are shown in Tables 2 and 3 respectively. The preparation procedure
for the latex mix containing CCl₄ as sensitizer was described in the
paper presented earlier⁵. The preparation procedure for n-BA system is
as follows: The latex, in a stainless steel drum, was diluted to ca. 50%
total solids contents (tsc) by adding 1.0% ammonia solution while stir-
ing. This was then followed by the addition of 10% KOH solution and
n-BA. The stirring continued for more than 2 hours and then left to
mature overnight at room temperature before irradiation. The irradiation
of latex was carried out at a fixed dose rate of 0.06 Mrad/hour for 19
hours (1.14 Mrad) at room temperature. After irradiation the latex was
kept at room temperature tightly covered to prevent any loss of volatile
materials such as ammonia.

The antioxidants were added into the latex at concentrations up to
2.0 phr and stirred for 2 hours to ensure that they mixed well. Test
samples were prepared by casting the latex on glass plates and drying
at room temperature until the films became clear. They were then sub-
jected to different leaching conditions and then dried at 70°C for
several hours until the films became clear again. Aging was carried
out at 70°C for 7 days and 100°C for 3 days as appropriate. After aging
the samples were kept in a dessiccator for 20-24 hours at 23°C before
testing. Tensile properties measurements were carried out in accordance to JIS K 6301-1975.

3. Results and Discussion

3.1 Characteristics of Latex After Irradiation

The physical properties of both latex mixes appeared unchanged after irradiation. The viscosity remained almost constant at 14-17 cPs. No change in colour and stability was observed. Excellent films with even and uniform texture were obtained upon casting and drying of latex on glass plates at room temperature. The time of drying varied between 15-20 hours depending upon the temperature and humidity of the room at the time of drying. The additions of antioxidants had no significant effect on the viscosity of both latex mixes.

3.2 RVNRL Prepared Using CCl₄

3.2.1 Effect of Leaching on Aged Film Properties

The results on the effect of leaching on the film properties of the latex mix (without the addition of antioxidant) aged at 70°C for 7 days are shown in Fig. 1 and 2 respectively. It is observed that latex films aged badly after leaching. The tensile strength of the films dropped very drastically depending on the time and temperature they were subjected to during leaching. The lowest tensile retention was recorded when the film was leached at 60°C for 1 hour. The reduction in the tensile strength of film was attributed to the loss in the naturally occurring antioxidants during leaching.

3.2.2 Effect of Antioxidants

The antioxidants used in this mix were Antage 2LX, Antage 3LX, Accel TP, Permanex WSO, Permanex WSP and Antage W-400 respectively. They were added at concentrations of 0-2.0 phr. The rubber films were leached at room temperature for 22 hours and aged at 70°C for 7 days after drying. The control was further dried at 100°C for one hour after leaching and drying at room temperature.

The results on the effect of Permanex WSO, Permanex WSP and Accel TP on tensile strength of films before and after aging are shown in Fig. 3, those of Antage 2LX and Antage 3LX in Fig. 4 and 5 and those of W-400 in Fig. 6. Generally, the tensile strength of the films obtained before aging was good (values varied between 32-36 MPa) and only decreased
slightly as the level of antioxidant increased probably due to a reduction in the inter-particles adhesion. However, upon aging the tensile strength of the films deteriorated badly except in the presence of Permanax WSP and Antage W-400. No protection was obtained using Antage 2LX and Antage 3LX probably because they were leached out (being soluble in water) during leaching. The best protection was obtained with Antage W-400 added at 0.8 phr. The highest tensile retention of 84% was obtained with this antioxidant.

3.3 RVNR Prepared Using n-BA

3.3.1 Effect of Leaching on Film Properties

The results on the effect of leaching in water and water containing 1% ammonia at room temperature for 24 hours on the film property with and without aging at 70°C for 7 days and 100°C for 3 days respectively are shown in Table 4. In the unaged state, it is observed that the leached films only gave marginally higher tensile strength compared to that of the unleached films. No significant difference in the tensile strength had been observed between the two leaching conditions. However, the elongation at break was higher when the latex films were leached in water containing 1% ammonia solution.

Unleached films appeared to be unaffected upon aging at 70°C/7 days or 100°C/3 days. Leached films were only slightly affected when aged at 70°C/7 days but badly affected at severe aging conditions of 100°C/3 days especially for those leached in water containing 1% ammonia. The elongation at break also dropped in line with the tensile strength. Leaching in ammoniated water was more effective compared to that in water alone as most materials (present in latex film including the naturally occurring antioxidants) are more soluble in alkaline medium. Hence, poor aged film properties were observed when leached in ammoniated water and aged at severe conditions of 100°C for 3 days. As expected the aged samples were darker compared to the unaged samples.

3.3.2 Effect of Antioxidants

The antioxidants used in this mix were Irganoxs 1520, 1076, 1035, 245, 1010, 565, Lowinox CPL, Vulkanox BKF, Permanex TQ, Permanex WSP, BHT and Vulcanox MB respectively. They were added at concentrations of 0 - 1.0 phr. Generally, the additions of antioxidants in unaged samples have no significant effect on the tensile properties (tensile strength and elongation at break) of the films except for Irganoxs 1076, 1010,
Lowinox CPL, Vulkanox BKF, Permanox TQ, BHT and Vulcanox MB where marginal increases in the tensile strength of the films were observed as shown in Table 5. While, a gradual and significant increase in tensile strength of latex films was observed with the addition of Vulcanox MB, a tensile strength of 22.6 MPa was achieved at 1.0 phr. The reason for this observation is obscured.

Table 6 showed the tensile strength of the same latex films after aging at 70°C/7 days. Better tensile strengths were obtained with the additions of Irganox 1520 and Vulcanox MB, even though the values were considered to be low. Tensile strength retentions of 96.8% and 71.2% were obtained with 1.0 phr of Irganox 1520 and Vulcanox MB respectively as shown in Table 7.

4. Conclusions

Radiation vulcanised natural rubber latex films obtained using n-BA as sensitizer has better ageing characteristics compared to that of RVNRL obtained using CCL4. Antioxidant 2'2-methylene-bis-(4-methyl-5-tert-butylyphenol) at 0.8 phr was found to be the most effective for RVNRL using CCL4 as sensitizer and antioxidant 2,4-Bis[(octylthio)methyl]o-cresol presence at 1.0 phr for RVNRL obtained using n-BA as sensitizer.

Acknowledgements

The authors wish to thank the Director of the Rubber Research Institute of Malaysia, Dr. Abd. Aziz Bin S.A. Kadir for permission to present this paper. Acknowledgements are also recorded to Dr. Sidek Bin Dulngali for useful discussion and En. Abd. Sukor Bin Mahat, for assistance in the research work.

References

5. Shukri, B.A.W., Effect of Heating and Leaching on Mechanical Properties of Radiation Vulcanised Natural Rubber Latex Film, in this proceedings.

<table>
<thead>
<tr>
<th>Product name</th>
<th>Supplier/manufacturer</th>
<th>Structure-based name</th>
<th>Physical form</th>
</tr>
</thead>
<tbody>
<tr>
<td>Permanex WSP</td>
<td>Vulnax/ICI</td>
<td>2,2'-methylene-bis-6- (alpha-methylcyclohexyl) p-cresol</td>
<td>crystalline powder, off-white</td>
</tr>
<tr>
<td>Vulkanox MB</td>
<td>Bayer</td>
<td>2-mercaptobenzimidazole</td>
<td>powder</td>
</tr>
<tr>
<td>Permanex WSO</td>
<td>Vulnax</td>
<td>High molecular weight phenolic compound</td>
<td>white crystalline powder</td>
</tr>
<tr>
<td>Antage W-400</td>
<td>Kawaguchi Chemical Ind. Co. Ltd.</td>
<td>2,2'-methylene-bis- (4-methyl-6-tert-butylphenol)</td>
<td>white powder</td>
</tr>
<tr>
<td>Accel TP</td>
<td>Kawaguchi Chemical Ind. Co. Ltd.</td>
<td>Sodium dibutylidithiocarbamate</td>
<td>Yellowish or reddish, semi-transparent, liquid content 40%</td>
</tr>
<tr>
<td>Irganox 1076</td>
<td>Ciba-Geigy</td>
<td>Octadecyl-3(3,5-di-tert-butyl-4-hydroxy-phenyl)-propionate</td>
<td>powder</td>
</tr>
<tr>
<td>Irganox 1010</td>
<td>Ciba-Geigy</td>
<td>Pentaerythritol-tetrakis[3-(3,5-di-tert-butyl-4-hydroxyphenyl)]-propionate</td>
<td>white powder</td>
</tr>
<tr>
<td>Irganox 1035</td>
<td>Ciba-Geigy</td>
<td>Thiodiethylene bis(3,5- di-tert-butyl-4-hydrocinnamate</td>
<td>white crystalline powder</td>
</tr>
<tr>
<td>Irganox 245</td>
<td>Ciba-Geigy</td>
<td>Triethyleneglycol-bis-3(3-tert-butyl-4-hydroxy-5-methylphenyl)-propionate</td>
<td>white crystalline powder</td>
</tr>
<tr>
<td>Irganox 1520</td>
<td>Ciba-Geigy</td>
<td>2,4-Bis[[(octylthiol)methyl]o-cresol</td>
<td>oily emulsion</td>
</tr>
</tbody>
</table>
Table 1 (Continued)

<table>
<thead>
<tr>
<th>Product name</th>
<th>Supplier/manufacturer</th>
<th>Structure-based name</th>
<th>Physical form</th>
</tr>
</thead>
<tbody>
<tr>
<td>Irganox 565</td>
<td>Ciba-Geigy</td>
<td>4-4,6-Bis(octylthio)-triazin-2-yl)amino-2,6-diterbutylphenol</td>
<td>white powder</td>
</tr>
<tr>
<td>Vulkanox BKF</td>
<td>Bayer Anchor Cynamid</td>
<td>2,2 Methylene-bis(4-methyl-6-tert-butyl phenol)</td>
<td>white powder</td>
</tr>
<tr>
<td>BHT</td>
<td>ICI</td>
<td>2,6-Di-tert-Butyl-p cresol</td>
<td>white crystal</td>
</tr>
<tr>
<td>Permanax TQ</td>
<td>ICI</td>
<td>Polymerised 2,2,4-tri methyl 1,2-dihydroquinoline</td>
<td>brown flakes</td>
</tr>
<tr>
<td>Antage 2LX</td>
<td>Kawaguchi Chemical Ind. Co. Ltd.</td>
<td>-</td>
<td>liquid</td>
</tr>
<tr>
<td>Antage 3LX</td>
<td>Kawaguchi Chemical Ind. Co. Ltd.</td>
<td>-</td>
<td>liquid</td>
</tr>
</tbody>
</table>
Table 2 Formulation for RVNRL prepared using CCl₄

<table>
<thead>
<tr>
<th></th>
<th>Part by weight</th>
<th>Batch weight (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FELDA HA, 60% drc</td>
<td>167.0</td>
<td>26,720</td>
</tr>
<tr>
<td>CCl₄</td>
<td>5.1</td>
<td>800</td>
</tr>
<tr>
<td>Potassium laurate</td>
<td>0.3</td>
<td>48</td>
</tr>
<tr>
<td>Water</td>
<td>add to 55% tsc</td>
<td>1,600</td>
</tr>
</tbody>
</table>

Table 3 Formulation for RVNRL prepared using n-BA

<table>
<thead>
<tr>
<th></th>
<th>Part by weight</th>
<th>Batch weight (kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DUNLOP HA, 60% drc</td>
<td>167.0</td>
<td>144.0</td>
</tr>
<tr>
<td>n-BA</td>
<td>5.1</td>
<td>4.4</td>
</tr>
<tr>
<td>KOH, 10%</td>
<td>2.1</td>
<td>1.8</td>
</tr>
<tr>
<td>Ammonia, 1%</td>
<td>30.2</td>
<td>26.0</td>
</tr>
</tbody>
</table>

Table 4 Effect of leaching on film properties of RVNRL prepared using n-BA as sensitizer

<table>
<thead>
<tr>
<th>Condition of leaching</th>
<th>Unaged T.S.(MPa) E.B.(%)</th>
<th>Aged 70°C/7d T.S.(MPa) E.B.(%)</th>
<th>Aged 100°C/3d T.S.(MPa) E.B.(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unleached</td>
<td>15.0 836</td>
<td>14.6 945</td>
<td>15.1 1121</td>
</tr>
<tr>
<td>Leached in H₂O for 24 hrs</td>
<td>18.7 984</td>
<td>12.3 973</td>
<td>6.7 972</td>
</tr>
<tr>
<td>Leached in H₂O containing 1% NH₃ 24 hrs</td>
<td>17.7 1003</td>
<td>11.6 1048</td>
<td>0.3 517</td>
</tr>
</tbody>
</table>

Table 5  Tensile strength (MPa) of unaged films

<table>
<thead>
<tr>
<th>Antioxidant</th>
<th>0</th>
<th>0.2</th>
<th>0.4</th>
<th>0.6</th>
<th>0.8</th>
<th>1.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>1520</td>
<td>17.1</td>
<td>16.5</td>
<td>17.5</td>
<td>17.4</td>
<td>17.9</td>
<td>17.4</td>
</tr>
<tr>
<td>1076</td>
<td>17.7</td>
<td>20.1</td>
<td>19.5</td>
<td>20.1</td>
<td>21.0</td>
<td>21.7</td>
</tr>
<tr>
<td>1035</td>
<td>17.1</td>
<td>16.3</td>
<td>17.6</td>
<td>17.4</td>
<td>17.3</td>
<td>18.8</td>
</tr>
<tr>
<td>245</td>
<td>17.1</td>
<td>16.0</td>
<td>16.5</td>
<td>18.0</td>
<td>16.7</td>
<td>16.7</td>
</tr>
<tr>
<td>1010</td>
<td>17.7</td>
<td>19.3</td>
<td>19.6</td>
<td>19.6</td>
<td>19.0</td>
<td>20.2</td>
</tr>
<tr>
<td>565</td>
<td>17.1</td>
<td>16.9</td>
<td>17.0</td>
<td>16.8</td>
<td>17.5</td>
<td>16.0</td>
</tr>
<tr>
<td>CPL</td>
<td>17.1</td>
<td>19.1</td>
<td>20.3</td>
<td>21.2</td>
<td>18.9</td>
<td>19.7</td>
</tr>
<tr>
<td>BKF</td>
<td>17.7</td>
<td>18.9</td>
<td>21.0</td>
<td>19.4</td>
<td>19.4</td>
<td>20.1</td>
</tr>
<tr>
<td>TQ</td>
<td>17.7</td>
<td>18.6</td>
<td>19.7</td>
<td>19.5</td>
<td>20.0</td>
<td>20.4</td>
</tr>
<tr>
<td>WSP</td>
<td>17.7</td>
<td>17.5</td>
<td>18.7</td>
<td>18.7</td>
<td>18.1</td>
<td>17.7</td>
</tr>
<tr>
<td>BHT</td>
<td>17.7</td>
<td>18.9</td>
<td>18.3</td>
<td>18.6</td>
<td>18.9</td>
<td>20.4</td>
</tr>
<tr>
<td>Vulk.MB</td>
<td>17.7</td>
<td>20.0</td>
<td>21.4</td>
<td>21.0</td>
<td>22.5</td>
<td>22.6</td>
</tr>
</tbody>
</table>

Films leached in water containing 1% NH₃ for 24 hours at room temperature.
Table 6  Tensile strength (MPa) of film aged at 70°C/7ddays

<table>
<thead>
<tr>
<th>Antioxidant</th>
<th>Concentration of antioxidant (phr)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
</tr>
<tr>
<td>1520</td>
<td>12.3</td>
</tr>
<tr>
<td>1076</td>
<td>12.3</td>
</tr>
<tr>
<td>1035</td>
<td>-</td>
</tr>
<tr>
<td>245</td>
<td>-</td>
</tr>
<tr>
<td>1010</td>
<td>12.3</td>
</tr>
<tr>
<td>565</td>
<td>12.3</td>
</tr>
<tr>
<td>CPL</td>
<td>11.0</td>
</tr>
<tr>
<td>BKF</td>
<td>11.0</td>
</tr>
<tr>
<td>TQ</td>
<td>11.0</td>
</tr>
<tr>
<td>WSP</td>
<td>11.0</td>
</tr>
<tr>
<td>BHT</td>
<td>11.0</td>
</tr>
<tr>
<td>Vulk.MB</td>
<td>11.0</td>
</tr>
</tbody>
</table>

Films leached in water containing 1% NH$_3$ for 24 hours at room temperature.
Table 7  Retained tensile strength (%) after aging at 70°C/7 days

<table>
<thead>
<tr>
<th>Antioxidant</th>
<th>Concentration of Antioxidant (phr)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
</tr>
<tr>
<td>1520</td>
<td>69.7</td>
</tr>
<tr>
<td>1076</td>
<td>69.7</td>
</tr>
<tr>
<td>1035</td>
<td>-</td>
</tr>
<tr>
<td>245</td>
<td>69.7</td>
</tr>
<tr>
<td>1010</td>
<td>69.7</td>
</tr>
<tr>
<td>565</td>
<td>69.7</td>
</tr>
<tr>
<td>CPL</td>
<td>62.3</td>
</tr>
<tr>
<td>BKF</td>
<td>62.3</td>
</tr>
<tr>
<td>TQ</td>
<td>62.3</td>
</tr>
<tr>
<td>WSP</td>
<td>62.3</td>
</tr>
<tr>
<td>BHT</td>
<td>62.3</td>
</tr>
<tr>
<td>Vulk.MB</td>
<td>62.3</td>
</tr>
</tbody>
</table>

Films leached in water containing 1% NH₃ for 24 hours at room temperature.
Fig. 1 Tensile strength of cast films after leaching and aging. Leached in hot water, 70°C, and aged at 70°C for 7 days.

Fig. 2 Tensile strength of cast films after leaching and aging. Leached for 1 hr. and aged at 70°C for 7 days.
Fig. 3 Effect of WSO, WSP and TP on tensile strength of films leached and unleached followed by aging at 70°C for 7 days.
Fig. 4 Effect of Antaga 2LX on tensile strength of films before and after aging

Fig. 5 Effect of Antaga 3LX on tensile strength of films before and after aging
Fig. 6 Effect of Permanax W-400 on Tensile Strength of Films Before and After Aging
5.15 Development of Surgical Gloves from Radiation Vulcanized Natural Rubber Latex

NGUYEN QUOC HIEN, Doan Binh, Vo Tan Thien, Le Hai,
Nguyen Tan Man and Vo Thi Thanh

Dalat Nuclear Research Institute, Dalat, Vietnam

Abstract

Natural rubber latex (55% DRC) containing 3 phr of CCl₄ was irradiation γ-rays from Co-60 source at a dose rate of 7.5 kGy/h. Specifications of irradiated latex and mechanical properties of the radiation vulcanized latex were studied. The maximum tensile strength which was obtained at 25 kGy was 240 kg/cm². The viscosity of the irradiated latex kept constant value under 30 kGy. The G value for crosslinking calculated from swelling is 17.0. Chlorine contents measured with activation analysis increased with increasing irradiation dose. 400 kg of latex was vulcanized at 25 kGy and used for production of rubber gloves in an existing factory with coagulant dipping process. The physical properties of the rubber gloves were as follows: tensile strength; 220-250 kg/cm², elongation at break; 950%, permanent set; 5-10%, aging residual tensile strength after at 70°C for 72 hours; 70-80%. The gloves were accepted for domestic use as surgical and examination gloves.

1. Introduction

The annual production of natural rubber in Vietnam is about 40,000-50,000 ton. More than 2,000 ton of centrifuged latex per year is used for producing surgical and houseware gloves, condoms, rubber foam and others. However there are still lacking appropriate technology for consumption of a large amount of latex. Therefore R & D of efficient process for vulcanization and modification of rubber latex is very necessary in Vietnam.

Studies to apply ionizing radiation for modification of polymer materials and for making new materials have been carried out mainly at the Dalat Nuclear Research Institute in Vietnam. A R & D program on radiation vulcanization of natural rubber latex (RVNRL) began in 1987. The objective of this R & D program is to replace chemicals for vulcanization with γ radiation because the radiation vulcanization process is
much simpler and more efficient than other processes. In this paper accomplishment of R & D on RVNRL in Vietnam is reported.

2. Experimental

2.1 Radiation Source

A Co-60 γ irradiator "Issledavachen" characterized as follows is used for irradiation.

- volume of irradiation vessel: 4 litters
- dose rate: 7.5 kGy/h
- irradiation temperature: 25°C.

2.2 Materials

The natural rubber latex was supplied by the Thuanan Rubber Factory located nearby Ho Chi Minh City. The characteristics of the latex are as follows.

- DRC: 60%
- TSC: 61.8%
- NH₃: 2.5%
- VFA No.: 0.05
- KOH No.: 0.85
- MST: 268s
- Viscosity: 37cP

Toluene, CCl₄, and benzene were of analytical grade and other chemicals such as sodium lauryl sulphate (SLS), CaCl₂ etc. were of technical grade. All chemicals were used as received without purification.

2.3 Formulation and Irradiation

The total solid content of latex was adjusted to 55% by 2% ammonia water. Sensitizer emulsion was prepared by stirring the following formulation for one hour.

- CCl₄: 18 g
- SLS: 18 g
- 2% ammonia water: 25 ml

The sensitizer emulsion was then added into 1 kg of latex. Stirring was kept for one hour and the formulated latex was then allowed to stand overnight. Irradiation was done by batch of 500 ml latex in polyethylene bottle at required dose.
2.4 Methods and measurements
2.4.1 Measurement of viscosity

The viscosity of latex was measured with a Haak-Falling-Ball Viscometer at ambient temperature.

2.4.2 Physical properties

Films were cast from irradiated latex onto the leveled glass and kept standing at room temperature until dry. The thickness of film was estimated about 0.3 mm. The dried films were heated at 70°C for 30 minutes and stored in desiccator. The physical properties were measured with a Tensile Tester DY-22, ADEMELE LHOME CY according to national standard (TCVN-84).

2.4.3 Swelling and gel content measurement

About 1g of vulcanized rubber film was put into benzene for 48 hrs to measure swelling. Gel content of vulcanized rubber film was measured after shaking in toluene at room temperature.

2.4.4 Calculation of G value

Based on data of equilibrium swelling, statistic average molecular weight between crosslinks (Mc) was calculated using Flory-Rehner equation¹.

The G value for crosslinks, Gc (numbers of crosslinks/100 eV) was calculated using following formula².

\[
G_c = 4.8 \times 10^6 / D(kGy) \times M_c
\]

Where \( D(kGy) \) is absorbed dose. The ratio of G value for degradation Gd and Gc (Gd/Gc) was calculated using the Charlesby-Pinner method.

2.4.5 Chlorine content

All samples of film were leached in distilled water and then dried to constant weight. The chlorine content was measured by neutron activation analysis method at Dalat nuclear research reactor.

2.4.6 Test production of rubber gloves

About 400 kg of latex was vulcanized at 25 kGy. Phenolic antioxidant was then added into irradiated latex. Test production of gloves was carried out in a existing rubber factory in Ho Chi Minh City by coagulant dipping process using 10% CaCl₂ solution as coagulant.
3. Results and Discussions

3.1 Radiation vulcanization Behavior

It is shown in Fig. 1 that the tensile strength (Tb) increased with increasing dose. At 25 kGy Tb is 250 kg/cm². Figure 2 shows the relationship between viscosity of the irradiated latex and dose. At the dose lower than 30 kGy, viscosity of irradiated latex is 30 cP and stable at least two months after irradiation. At the dose higher than 30 kGy, viscosity is increased and then decreased slowly during storage. Figure 3 shows the effect of dose Mc of rubber films from irradiated latex. It is generally accepted that Mc of the suitably cured latex is between 4,000 - 7,000 when measured using benzene as solvent. It can be seen that the latex was well cured at the dose higher than 25 kGy.

dose higher than 25 kGy.

Figure 4 shows changes in gel content with dose. The gel content was sharply increased at the dose less than 10 kGy. About 95% gel was obtained at 25 kGy. Table 1 shows the calculated Gc-value and Gd/Gc ratio of natural rubber irradiated at different forms. The Gc-value is 17 in case of latex + 3 phr CCl₄, while the dry rubber and latex without sensitizer is 1.5 and 2.5-3.0, respectively. From these values it can be said that the Gc increases from 1.5 to 2.5-3.0 by the presence of water. The effect of CCl₄ sensitizer is to increase Gc from 2.5-3.0 to 17. Also it is clear that CCl₄ sensitizer at 3 phr caused an slight effect on enhancement of Gd.

Figure 5 shows the effect of irradiation dose on the chlorine content in radiation vulcanized latex films. It can be seen that the chlorine content is slightly increased with increasing irradiation dose. This suggests that following reactions will take place during irradiation.

\[
R + CCl₄ \rightarrow RCl + CCl₃ \\
\text{-C-}C-C- + Cl \rightarrow \text{-C-}C-C-C- \quad \text{Cl}
\]

3.2 Properties of Rubber Gloves

More than 4,000 pairs of rubber gloves were prepared. Contents of heavy metal and toxic elements was under allowed level. The physical properties of the rubber gloves were as follows.

tensile strength : 220-250 kg/cm²
elongation at break: 950%
permanent set : 5-10%

Tensile strength after at 70°C for 72 hours is 70-80% of the original one. The quality of gloves is better compared with commercially available medical gloves because the Tb and elongation at break were higher than those of commercially available medical gloves (Tb=200 kg/cm², Eb 700-750%). According to national standard, the gloves made from RVNRL are acceptable as surgical and examination gloves.

4. Conclusions

The R & D on RVNRL using CCl₄ as sensitizer and test production of rubber gloves from RVNRL have been done. Natural rubber latex (60% DRC) contained 3 phr CCl₄ and irradiation dose at 25 kGy were found out as the optimum for the radiation vulcanization process. The rubber gloves made from RVNRL are found to be acceptable as surgical and examination gloves.

Acknowledgments

We are greatly indebted to Prof. Pham Dzuy Hien, Director, Dalat Nuclear Research Institute for encouragement and continued interest. The contributions of many co-workers are also gratefully acknowledged.

References

Table 1  Gc and Gd/Gc for NR irradiated in different forms

<table>
<thead>
<tr>
<th>NR Form</th>
<th>Gc</th>
<th>Gd/Gc</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry rubber</td>
<td>1.5</td>
<td>0.65*</td>
</tr>
<tr>
<td>Latex (60% DRC)</td>
<td>2.5-3.0</td>
<td>0.25*</td>
</tr>
<tr>
<td>Latex + 3 phr CCl₄</td>
<td>17.0</td>
<td>0.06</td>
</tr>
</tbody>
</table>

* our previous work

Fig. 1  Relationship between tensile strength of irradiated latex film and dose
Fig. 2 Effect of irradiation and storage on the viscosity of latex

Fig. 3 The dependence of the statistic average molecular weight of the irradiated latex films on the dose
Fig. 4 Gel content as a function of the dose

Fig. 5 Chlorine content in the irradiated latex films
5.16 Sensitization in Radiation Grafting, Curing and Vulcanization Processes

J.L. CARNETT\textsuperscript{1)}, P.A. Dworjanyn\textsuperscript{1)}, S.J. Bett\textsuperscript{2)} and H.P. Dang\textsuperscript{2)}

1) School of Chemistry, University of New South Wales, Kensington, New South Wales 2033, Australia,  
2) Polycure Pty. Ltd., Sydney, Australia.

Abstract

Common parameters between radiation grafting, curing and vulcanisation processes are discussed. Additives for accelerating all three processes are reported. Acrylate monomers, particularly multifunctional acrylates, are sensitisers for the three reactions. These monomers (i) increase yields in grafting under certain radiation conditions (ii) speed up rates of polymerisation and cross-linking in the cure process, and (iii) lower the radiation dose required to achieve vulcanisation of natural rubber latex. Basic studies of electron interactions with these acrylate monomers using Fourier Transform ion cyclotron resonance mass spectrometry indicate that ionic reactions may contribute to the currently accepted free radical polymerisation mechanism involved in all three radiation processes. Based on curing work, the toxicological properties of acrylate, particularly multifunctional acrylates, are shown to be important when these monomers are used in vulcanisation processes. For this purpose, the guide lines (Draize values) developed for curing processes are of relevance to vulcanisation.

1. Introduction

The current interest\textsuperscript{1} in radiation induced vulcanization of natural rubber latex (KVNRL) has prompted mechanistic comparisons to be made between vulcanization work and other related radiation processes\textsuperscript{2}. The possibility that common parameters may exist between radiation grafting, curing and vulcanisation is being actively investigated. Thus, technological advances in any one of the fields could be immediately applied to the other two.

Grafting is the copolymerisation of a monomer (M) to a backbone polymer (equation 1). Curing is the rapid polymerisation of an oligomer monomer mixture to form a coating which is essentially bonded by physical
forces to the substrate. As equation 2 shows (O=smallomer), where relevant, the cured film does not follow the contours of the substrate, e.g. cellulose surfaces, but gives a smooth finish by filling in the valleys in the surface. Vulcanisation is essentially crosslinking of a substituted oelphin (equation 3).

\[
\begin{align*}
\text{\begin{equation}1\end{equation}}
\end{align*}
\]

\[
\begin{align*}
\text{\begin{equation}2\end{equation}}
\end{align*}
\]

\[
\begin{align*}
\text{\begin{equation}3\end{equation}}
\end{align*}
\]

Radiation grafting has been performed for over thirty years\(^3\)\(^-\)\(^8\). whilst curing processes were developed twenty years ago. Systematic work in RVRNL has only been in progress for ten years, although, intermittent, isolated studies were carried out earlier. An important feature common to all three of these radiation induced processes is the use of sensitisers to either speed up the polymerisation reaction or to enhance the degree of crosslinking. This leads to an overall lowering of the radiation dose required to achieve processing of a finished product. Common sensitisers used in all three processes are acrylate monomers.

It is the purpose of this paper to review work using acrylate sensitisation in grafting and curing and to relate the results from those two fields to RVRNL. The properties of the sensitisers, especially the acrylates, required to accelerate these three radiation induced reactions will be discussed. In particular, the toxicological properties of the acrylates are important since much work has been performed with these
materials in curing and the conclusions for this work will be of value in RVNRL. Finally, common mechanistic aspects of the three processes have been investigated. In particular, the possibility that ionic intermediates, in addition to conventionally accepted free radical processes, may participate in all three systems especially RVNRL is considered. This proposal originates from basic work on the effects of electron impact studies with the sensitizers using Fourier Transform Ion Cyclotron Resonance mass spectrometry (FTICR). Details of the mass spectrometric experiments will be outlined.

2. Experimental

The cellulose used was Whatman 41 filter paper, whilst the low density polyethylene was supplied by Union Carbide as film (0.12 mm) and the polypropylene was isotactic, double oriented film (0.06 mm ex-She1). Of the monomers, styrene was provided by Monsanto Chemicals Australia Pty Ltd and the remainder were obtained from Poycurc Pty Ltd in Sydney. These included trimethylolpropane triacrylate (TMPTA), trimethylolpropane trimethacrylate (TMPTMA), propoxylatedglyceryl triacrylate (PGTA), tripropyleneglycol diacrylate (TPGDA), neopentylglycol dimethacrylate (NPGDMA) and divinyl benzene (DVB). All monomers were purified by column chromatography on alumina prior to use.

2.1 Grafting Methods

The procedures used for grafting were modifications of those previously discussed. For the ionising radiation experiments grafting reactions were performed in stoppered pyrex tubes (1.5 × 2.5 cm) containing monomer solutions (20 ml) at room temperature, all reactions being carried out in duplicate. For the actual irradiations, polymer films or cellulose strips of the appropriate size were immersed in the polymer solutions and the tubes irradiated in a 1200 Ci cobalt-60 source. After irradiation the films were removed from solution and solvent washed in a soxhlet for 72 hours. If acid was used, especially for the cellulose runs, the films and paper strips were washed with methanol:dioxane (1:1) prior to soxhlet extraction. After removal of homopolymer, grafted samples were dried to constant weight, the percentage graft being calculated as the percentage increase in weight of the grafted strip. For cellulose, all strips were humidified to 65% R.H. at 20°C prior to
weighing, before and after treatment.

For the UV grafting studies a process similar to that described previously for the gamma work was used. Thus, monomer solutions (20 ml) were prepared in stoppered pyrex tubes, quartz being considered unnecessary since reasonable rates of reaction can still be achieved using the simpler pyrex system. The tubes to be irradiated were positioned on a motor driven, ventilated, circulating drum, at distances of 12 to 30 cm from the UV source, which was a 90 W medium pressure mercury lamp. Polymer films were so positioned during irradiation that the films were perpendicular to the incident irradiation. At the completion of the irradiation, films and paper strips were treated as per the gamma system.

2.2 Curing Techniques

For the radiation rapid cure experiments appropriate resin mixtures containing oligomers, monomers, flow additives and sensitisers (UV) were applied to the substrate as a thin coating, the material placed on a conveyor belt and then exposed to UV and EB sources. The time taken to observe cure for each of the samples was then measured on a relative basis. The UV systems used were a Primarc Minicure unit with lamps of 200 W per inch and a Fusion unit with lamps of 300 W per inch. Two EB facilities were utilised, namely, a 500 KV Nissin machine and a 175 kV ESI unit.

2.3 Radiation Induced Vulcanisation of Natural Rubber Latex (RVNRL)

The latex used was commercially available from Malaysia and was kindly donated by Ansell International Pty. Ltd. Prior to use, the latex was diluted to 40% rubber content by addition of 1% aqueous ammonia. The polyfunctional monomer, NPGDMA (5% v/v on rubber solids of latex) was added to the latex and the mixture stirred slowly for several hours. The mixture (50 ml) was irradiated in a stoppered 2.5 cm test tube at approximately $8.7 \times 10^5$ rad/h to a range of total doses from $2 - 10 \times 10^6$ rad in the spent fuel element facility of the Australian Nuclear Science and Technology Organisation. After irradiation, the latexes were dried on glass plates at room temperature for several days, then at 80°C for one hour. Appropriate physical tests were performed in the Ansell laboratories.
3. Results and Discussion

3.1 Grafting - sensitisation with multifunctional acrylates and acids

A range of novel sensitisers have been found to enhance radiation grafting yields under a variety of experimental conditions. Acrylate monomers, particularly multifunctional acrylates (MFAs), are very effective for this purpose as the data below demonstrate. Mineral acids are another class of materials which are useful for increasing yields in these reasons. Mechanistically both groups of sensitisers appear to operate in a different manner, thus synergistic effects in grafting enhancement are observed when both classes of compounds are included in the same grafting solution.

3.1.1 Multifunctional Acrylates

The data in Table 1 show that the inclusion of a typical multifunctional acrylate (MFA) such as trimethylolpropane triacrylate (TMPTA) in additive amounts in a styrene monomer solution enhances the radiation grafting of the monomer to polyethylene film at almost all monomer concentrations studied. The increase in yield is particularly evident at the monomer concentration (50%) corresponding to the Trommsdorff peak. A plausible explanation for the role of MFAs such as TMPTA in the grafting reactions involves enhanced branching. Thus branching of the grafted polystyrene can occur when one end of the TMPTA, immobilised during grafting, is bonded to the growing chain; the other two ends are unsaturated and free to initiate new chain growth by scavenging reactions (Fig. 1). The new branched polystyrene chain may eventually terminate, cross-linked by reacting with an adjacent polystyrene chain, or immobilised TMPTA radical. Grafting is thus enhanced mainly by branching with the grafted polystyrene chain.

3.1.2 Mineral Acids

In addition to the MFAs other additives have been discovered to increase radiation grafting yields in these current systems. Thus the presence of mineral acids, like sulphuric, can increase the grafting yields when styrene is radiation grafted to backbone polymers such as the polyolefins and cellulose (Table 2). In very early studies of this acid enhancement in radiation grafting, wool was used as backbone polymer. Large grafting yields were observed with styrene and ethyl acrylate under these conditions particularly with sulphuric acid, but no systematic mechanistic study of the reaction was performed at that
time. Much later other research workers confirmed this acid effect with wool using the radiation grafting of methyl methacrylate\textsuperscript{12}. Again no satisfactory mechanistic conclusion for the acid enhancement was proposed. In the present work polyethylene and polypropylene are used as representative synthetic polymers, whereas cellulose typifies a naturally occurring macromolecule. With all three backbone polymers in Table 2, the presence of acid leads to increased graft at all monomer concentrations studied particularly at the Trommsdorff peak. When compared to enhancement due to the MFAs, the profiles of the increase in yield are different, indicating a different mechanism for each class of additive.

In previous studies with cellulose\textsuperscript{13} it was obvious that the mechanistic role of acid in these grafting reactions involved a number of competing processes. It was suggested that acids, at the concentrations used, did not markedly affect the precipitation of the grafted chains or the swelling of the backbone polymer. Instead it was proposed that the acid enhancement was due to a radiation chemistry phenomenon involving increased G(H) yields and thermalised electrons (equations 4 to 6).

\begin{align*}
\text{CH}_3\text{OH} + \text{H}^+ & \rightarrow \text{CH}_3\text{OH}_2^+ \\
\text{CH}_3\text{OH}_2^+ + e & \rightarrow \text{CH}_3\text{OH} + \text{H}^+ \\
\text{CellOH} + \text{H}^+ & \rightarrow \text{CellOH}_2^+ \\
\end{align*}

(4) \hspace{1cm} (5) \hspace{1cm} (6)

These processes can lead to increased numbers of grafting sites by abstraction reactions with the trunk polymer (equation 7, where CellOH represents cellulose).

\begin{align*}
\text{CellOH} + \text{H}^+ & \rightarrow \text{CellO}^+ + \text{H}_2 \\
\end{align*}

(7)

More recent work on the acid effect indicates that acid leads to an increase in styrene solvent intermediates (MS\textsuperscript{-}) in the grafting solution, such species resulting in more grafting sites as in equation 8.

\begin{align*}
\text{MS}^- + \text{CellOH} & \rightarrow \text{MSH} + \text{CellO}^+ \\
\end{align*}

(8)

It has also been proposed\textsuperscript{14} that in the presence of acid in the chain length of oligomer in the grafting solution is shortened and the numbers
of shortened chains is increased. The shorter oligomer chains can diffuse more readily into the swollen backbone polymer to achieve more efficient termination at a grafting site. The increase in concentration of oligomer chains in the bulk of the solution would also result in an increase in viscosity of both the grafting solution and the solution that is absorbed within the backbone swollen polymer, thus leading to the enhanced Trommsdorff peak as observed experimentally in the presence of acid. More recent work\(^5\)\(^,\)\(^15\) indicates that the radiation chemistry mechanism for grafting enhancement is an over simplification of the process. This earlier mechanism fails to explain a number of subsequent observations which include (i) the occurrence of grafting enhancement only at certain acid and monomer concentrations (ii) the efficacy of sulphuric, nitric and perchloric over other acids and (iii) the presence of grafting enhancement in the pre-irradiation and post-irradiation techniques where radiolytically produced hydrogen atoms are not available.

Mechanistically one of the most important observations concerning the acid effect is the recent detailed systematic study of the swelling of polyethylene in the presence of methanolic solutions of styrene\(^15\). In this system the styrene monomer uptake by the polyethylene was measured by employing tritium labeled styrene. Data obtained by the application of this technique in Table 3 indicate that partitioning of nonpolar monomer into nonpolar media may be significantly improved by the presence of dissolved electrolyte. This partitioning behaviour may be interpreted as an example of the salting out technique employed in solvent extraction. In the present grafting system the driving force for the increased partitioning of monomer into substrate is the reduced solubility of styrene in the bulk solution due to the presence of dissolved electrolyte. The net result of this driving force is higher rates of monomer diffusion into, and equilibrium monomer concentration within, the substrate. The high concentration of monomer at the grafting site favours propagation of the growing chains. The enhanced grafting yield (Table 4) is usually associated with a corresponding increase in molecular weight (Table 5) and there is no evidence for an increase in the number of chains initiated. Thus overall, according to this theory, it is proposed that increased partitioning of monomer occurs in the graft region of the backbone polymer when acids are dissolved in the bulk graft solution. This permits higher concentrations of monomer to be available for grafting at a particular backbone site in the presence of these additives. The
extent of this improvement in monomer partitioning depends on polarities of monomer, substrate, solvent and also on the concentration of acid. It is thus the effect of these ionic species on partitioning which is essentially responsible for the observed increase in radiation grafting yields in the presence of acids. Radiolytically generated free radicals can also be expected to make some contribution to the effect in a system where initiation occurs by ionising radiation, however this radiation chemistry explanation does not appear to be the dominant pathway for enhancement.

3.1.3 Synergistic Effects of MFAs with Acids

In support of the above proposal that the mechanism of enhancement with MFAs and acid is different, synergistic effects are observed for the grafting of styrene to polyethylene film (Table 6) when both additives are incorporated into the same monomer solution. The trends in reactivity can be more clearly observed if the data in Table 6 are graphed (Fig. 2). These synergistic results are of importance in a preparative context since yields are improved for the same radiation dose.

3.2 Curing – Sensitisation with MFAs and organic additives

The role of additives in industrial radiation processing is also important particularly in radiation rapid cure formulations initiated by either UV or EB[^2]. In such systems additives are utilised to control properties like flow, slip, gloss etc. and these are typified by materials such as the silanes (Z6020) produced by Dow and the fluorinated alkyl esters (FC-430) marketed by 3M. Curing formulations consist essentially of low molecular weight oligomers (predominantly acrylates such as urethane acrylates, epoxy acrylates, polyester acrylates) containing acrylate monomers usually MFAs. Curing processes are essentially rapid polymerisation of these oligomer/monomer mixtures onto substrates, the adhesion between the polymer film and the substrate being essentially due to physical bonding forces. An important aspect of curing reactions is the possibility that concurrent grafting with curing occurs leading to improved properties of the finished product, particularly in adhesion and flexibility. It is thus valuable to determine the effect of these additives used in curing formulations on the analogous grafting process since they may influence the degree to which concurrent grafting may occur during the curing process. If they retard grafting then their use in curing formulations could be limited, whereas the converse is
valid if they enhance grafting. The principles involved with the use of curing additives to improve slip and flow are the same whether the process is initiated by ionising radiation as with electron beam or UV. For example, with UV, the data in Table 7 show the results for the effect of three curing additives on a model photografting system namely, styrene to polypropylene. The three additives used are urea (viscosity adjuster), a fluorinated alkyl ester (flow enhancer) and a silane (slip improvement). The data show that urea and the alkyl ester lead to mild grafting enhancement whilst the silane is a retarder at all monomer concentrations studied due presumably to the repulsion effect of the silicon.

The most dramatic effect is demonstrated when TMPTA is added to a monomer solution containing these three curing additives. Under these TMPTA conditions, an increase in grafting yield of almost two orders of magnitude is observed (Table 8). Thus the TMPTA effect is unique since large increases in graft are observed even in the presence of retarders such as the silane. The structure of the acrylate monomer also influences this enhancement affect since TMPTA > PETA > DPGDA > HEMA (Table 9).

Finally, the above enhancement affect appears to be a general phenomenon in grafting initiated by ionising radiation and UV as the data in Fig. 3 show. Here TMPTA accelerates the grafting of styrene in methanol to polypropylene film using ionising radiation as initiator. Inclusion of urea leads to synergistic effects with TMPTA resulting in corresponding increases in graft similar to those observed for the photochemical system.

Overall the results show that commercial additives used in curing formulations in low concentrations can markedly affect grafting. However when MFAs like TMPTA are used the properties of each monomer can override the detrimental affects of retarders such as the silanes to give a better product with increased yields. Thus the mechanistic role of the MFA in curing processes is not only to speed up cure and crosslinking it can also markedly affect the occurrence of concurrent grafting during cure.

3.3 Vulcanisation - Sensitisation with acrylates and methacrylates

Acrylate monomers have been used over recent years to reduce the radiation dose required to vulcanize rubber, originally 30 Mrads. For this purpose extensive work particularly with MFAs and multifunctional methacrylates (MFMs) has recently been performed. Currently MFMs such as trimethylolpropane trimethacrylate (TMPTMA) are being used to sensitize this reaction which is essentially the crosslinking of liquid isoprene.
Where EB is utilised for this process, a dose of 6 megareads is required. With gamma radiation however, this dose for vulcanization can be lowered even further in the presence of either MFAs or MFMA\textsuperscript{1}, neopentylglycol dimethacrylate (NPDMMA) currently being the most efficient of these sensitisers for this purpose. A number of groups have confirmed these data including the present authors\textsuperscript{18}. Later work has indicated that acrylate monomers of lower functionality such as 2-ethylhexyl acrylate and n-butyl acrylate are an improvement for RVNRL with gamma ray processing\textsuperscript{19}. As well as being able to accelerate the polymerisation reaction, these acrylate additives require specific additional properties related to the end use of the finished product made from RVNRL. One of the products fabricated from RVNRL are gloves which are particularly important since they involve contact with human tissue and thus toxicological properties of materials like the acrylate sensitisers used in both actual processing and finished formulation need to be considered.

3.4 Toxicological properties of radiation sensitisers

With the commercial development of rapid polymerisation curing processes requiring the use of acrylate monomers, particularly MFAs, extensive work has been performed on the toxicological properties of these monomers since problems with skin irritancy have been encountered in both the curing reaction and the end use of the finished product. From this curing (and to a much lesser extent grafting) work, methods have been developed for testing dermatological and allergic reactions of these acrylate monomers on human skin\textsuperscript{20,21}. Recommended standards for the use of these materials have been developed. RVNRL processes now use analogous monomer systems to sensitise the crosslinking process and to lower the radiation dose required for vulcanisation. The following conclusions derived from curing and grafting will thus be of value in these radiation vulcanisation processes, particularly in the final choice of the acrylate monomer for sensitising the RVNRL process.

The accepted method now adopted worldwide for determining the skin irritancy potential of these monomers is the Draize test\textsuperscript{22} or variations of this method. The test is performed on the shaved, intact and abraded skin of New Zealand albino rabbits under extreme conditions that are rarely encountered in commercial practice. The results are expressed numerically on a scale from 0 to 8, the value obtained for each acrylate being its primary irritation index (PII). On the basis of the PII, the
monomer is accorded a classification as shown in Table 10.

Unfortunately the numerical values of the PII vary considerably from group to group because of the nature of the test, however, the accuracy of the figures is still sufficient to act as a guide to the irritancy potential for the acrylates. It is generally accepted that for industrial use of the type discussed here acrylates should have a PII no higher than 3.

When extrapolating from curing to vulcanising processes it is important to examine the reasons for the choice of type of sensitiser involved in each process. Thus with curing, speed of reaction generally predominates whereas with vulcanising it is essentially crosslinking. For curing, acrylates, particularly MFAs are preferred. This conclusion leads to difficulties in that two of the best MFAs for cure, namely, hexanediol diacrylate (HDDA) and TMPTA possess unusually high Draize ratings, HDDA being a particular problem with a Draize value of 6.0. A compromise in physical and toxicological properties is thus required and a monomer which is a compromise in properties has now been generally accepted as one of the best for application in the curing field. The monomer is tripropyleneglycol diacrylate (TPGDA). In contrast to curing, vulcanisation processes are essentially crosslinking and the methacrylates such as TMPTMA and NPGDMA are preferred over the acrylate analogues for this purpose. Fortunately the Draize values of the methacrylates are much lower than the acrylates (e.g. hydroxyethyl acrylate, 6.7; hydroxyethyl methacrylate, 1.0). For curing processes the methacrylates are usually too slow (factor of 2 or 3), so the acrylates need to be used in this application, whereas for vulcanisation this limitation is not relevant. However recent work indicates that monofunctional acrylates such as 2-ethylhexylacrylate and n-butyl acrylate are to be preferred over NPGDMA for RVNRL in the gamma radiation technique. Under these conditions the Draize ratings of these two monomers needs to be examined carefully to see if they are acceptable for these industrial processes. With EB, TMPTMA is still the preferred monomer for RVNRL, thus skin irritancy is less of a problem with this system since the Draize of the methacrylates is significantly lower than the corresponding acrylates.

3.5 Mechanism of RVNRL—role of ions

Currently free radical processes are considered to predominate in
radiation polymerisation work of the type discussed in this paper. Recent basic studies of the mechanism of EB curing have demonstrated the interesting possibility that ions may play a mechanistic role in this rapid polymerisation process, especially when high electron doses are involved\(^2\). Currently EB machines are available with the capacity to deliver 1500 Mrad m/min i.e. 1 Mrad at 1500 m/min or more conveniently 3 Mrads at 500 m/min. Under these processing conditions high yields of negatively and positively charged ionic species are formed. The problem to be considered is whether such species can initiate further polymerisation and, if so, whether such an ionic rapid polymerisation mechanism is relevant to RVNRL.

In this respect mass spectrometry is a valuable tool for basic studies of this aspect of the reaction since the technique involves ion formation by electron impact and related phenomena. Recent developments\(^2\) in Fourier Transform Ion Cyclotron Resonance mass spectrometry (FTICRMS) are particularly relevant since, by this technique, ion molecule reactions can be progressively observed over a period of time. With monomers, there is the possibility of observing oligomerisation reactions. Using data for TPGDA (one of the most commonly used monomers in EB curing) the FTICRMS spectra are shown in Fig. 4. Using chemical ionisation conditions it is seen that the ion of m/z 113 is large in all spectra. As the residence time for TPGDA molecules in the mass spectrometer is increased, other ions at higher m/z increase progressively in intensity such that after 60 seconds, m/z 113 is no longer the largest ion but is replaced by ions at 502, 413 and 359, presumably formed from ion molecule reactions involving fragments of the sample molecules. There thus appears to be an increase in higher molecular weight species, i.e. oligomerisation, with time.

These FTICRMS results in Fig. 4 offer an interesting mechanistic interpretation of EB curing reactions. The fact that ions with m/z higher than the molecular ion are formed from fragments and molecules in the FTICR as the time of rotation increases indicates that ion molecule reactions involving cationic species, as depicted in equation 9, are favoured processes in this system,

\[
R^+ + M \rightarrow RM^+ \quad (R, \text{ fragment} ; M, \text{ TPGDA}) \quad \text{(9)}
\]

where R is the fragment and M represents TPGDA. A plausible explanation
for the ion at m/z 413 is an ion molecule process (equation 9) where R is the fragment -CH₂(CH₃)CHOCOCH=CH₂ from M, which is TPGDA (molecular ion m/z 300). Importantly these species constitute the predominant ions in the FTICR spectrum over the time scale used. For longer times, higher molecular weight species above the molecular ion are observed presumably from ion molecule reactions, and continue to increase in intensity and molecular weight the longer the monomer remains in the source, i.e., polymerisation of the positive primary ion occurs. Analogous polymerisation processes in this monomer system are also found in the negative ion mode. These are gas phase observations but they raise the interesting possibility that similar ionic processes may occur in condensed phases such as curing and vulcanisation reactions, especially utilising electrons from EB machines delivering very high dose rates. Under these conditions, compared with the gas phase, frequency of collisions in the condensed phase would be very much lower, however, the efficiency of such collisions in the condensed phase would be higher due to cage affects and mobility considerations. If conditions can be found where ionic processes predominate in these fast polymerisation processes for the same radiation dose, then products possessing new properties may be capable of being made. Previously ionic processes in radiation polymerisation systems were only considered to occur under extremely anhydrous conditions, however this conclusion may need to be modified due to these recent mass spectrometric studies. More importantly, relevant to the current vulcanisation work where reactions are performed in aqueous ammoniacal media, negative ions from the monomer would be readily scavenged under these conditions, however polymerisation by the positive ion mode still remains a viable alternative to the currently accepted free radical process.

Acknowledgements

The authors thank the Australian Institute of Nuclear Science and Engineering, the Australian Research Grants Committee and Polycure Pty Ltd for the support of this research.
References

17. Bez, W., in this proceedings.
19. Makuuchi, K., in this proceedings.


Table 1  Effect of trimethylolpropane triacrylate as additive in radiation grafting styrene to polyethylene

<table>
<thead>
<tr>
<th>Styrene in methanol (% v/v)</th>
<th>Graft %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>N.A.</td>
</tr>
<tr>
<td>20</td>
<td>14</td>
</tr>
<tr>
<td>30</td>
<td>37</td>
</tr>
<tr>
<td>40</td>
<td>76</td>
</tr>
<tr>
<td>50</td>
<td>109</td>
</tr>
<tr>
<td>60</td>
<td>90</td>
</tr>
<tr>
<td>70</td>
<td>89</td>
</tr>
</tbody>
</table>

\(^a\) Irradiated to 2.4\times10^5\ rad at 4.1\times10^4\ rad/h; N.A.=no additive; TNPTA=trimethylolpropane triacrylate (1\% v/v).

Table 2  Effects of acid additive on radiation grafting of styrene in methanol to polyolefins and cellulose

<table>
<thead>
<tr>
<th>Styrene in methanol (% v/v)</th>
<th>Polyethylene</th>
<th></th>
<th>Polypropylene</th>
<th></th>
<th>Cellulose</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>N.A.</td>
<td>H⁺</td>
<td>N.A.</td>
<td>H⁺</td>
<td>N.A.</td>
<td>H⁺</td>
</tr>
<tr>
<td>20</td>
<td>14</td>
<td>19</td>
<td>29</td>
<td>218</td>
<td>8</td>
<td>24</td>
</tr>
<tr>
<td>30</td>
<td>37</td>
<td>51</td>
<td>94</td>
<td>150</td>
<td>17</td>
<td>33</td>
</tr>
<tr>
<td>40</td>
<td>76</td>
<td>81</td>
<td>50</td>
<td>85</td>
<td>22</td>
<td>31</td>
</tr>
<tr>
<td>50</td>
<td>109</td>
<td>134</td>
<td>37</td>
<td>55</td>
<td>21</td>
<td>27</td>
</tr>
</tbody>
</table>

\(^a\) Irradiated to total dose of 2.0\times10^4\ rad at dose rates of 3.0\times10^6\ rad/h (polypropylene) and 4.0\times10^6\ rad/h (cellulose); total dose 2.4\times10^5\ rad at 4.1\times10^4\ rad/h (polyethylene); sulfuric acid (0.2M).
Table 3 Variation in styrene absorption from methanol solution by polyethylene with time\(^a\)

<table>
<thead>
<tr>
<th>Time of Swelling (h)</th>
<th>Styrene Absorption (mg styrene/g polyethylene)</th>
<th>No Additive</th>
<th>H(_2)SO(_4) (0.1M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0.5</td>
<td>38.8</td>
<td>42.8</td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>40.5</td>
<td>44.3</td>
<td></td>
</tr>
<tr>
<td>2.0</td>
<td>42.5</td>
<td>45.8</td>
<td></td>
</tr>
<tr>
<td>12.0</td>
<td>45.6</td>
<td>53.3</td>
<td></td>
</tr>
<tr>
<td>20.0</td>
<td>45.4</td>
<td>54.0</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Technique used involved tritiated styrene with 30\% styrene in methanol solutions (% v/v) and polyethylene film (0.12 mm) at 25°C. The styrene was tritiated by palladium catalysed exchange with T\(_2\)O. Scintillation counting was used to determine tritium.

---

Table 4 Effect of acid in radiation grafting\(^a\) of styrene in methanol to cellulose\(^b\) under conditions close to Trommsdorff peak

<table>
<thead>
<tr>
<th>Styrene (%)</th>
<th>Graft %</th>
<th>No Additive</th>
<th>H(_2)SO(_4) (0.1M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>32</td>
<td>34</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>66</td>
<td>120</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>106</td>
<td>153</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>112</td>
<td>95</td>
<td></td>
</tr>
<tr>
<td>35</td>
<td>110</td>
<td>60</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Irradiation in air at 24°C, dose rate 3.3\(\times\)10\(^4\) rad/h, total dose 5.0\(\times\)10\(^5\) rad.

\(^b\) Whatman 41 filter paper.
Table 5  Effect of acid on number-average molecular weights ($\bar{M}_n$) of copolymer from radiation grafting of styrene in methanol to cellulose under conditions in table 4

<table>
<thead>
<tr>
<th>Styrene (%)</th>
<th>No Additive</th>
<th>$\bar{M}_n \times 10^5$</th>
<th>H$_2$SO$_4$ (0.1M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>3.5</td>
<td>4.8</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>5.0</td>
<td>9.8</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>7.7</td>
<td>10.0</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>12.0</td>
<td>8.6</td>
<td></td>
</tr>
<tr>
<td>35</td>
<td>9.2</td>
<td>7.6</td>
<td></td>
</tr>
</tbody>
</table>

Table 6  Synergistic effect of acid and TMPTA additives for enhancing radiation grafting of styrene in methanol to polyethylene film$^a$

<table>
<thead>
<tr>
<th>Styrene (2% v/v)</th>
<th>Neutral</th>
<th>Graft (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>H$^+$</td>
</tr>
<tr>
<td>20</td>
<td>14</td>
<td>19</td>
</tr>
<tr>
<td>30</td>
<td>37</td>
<td>51</td>
</tr>
<tr>
<td>40</td>
<td>76</td>
<td>81</td>
</tr>
<tr>
<td>50</td>
<td>109</td>
<td>134</td>
</tr>
<tr>
<td>70</td>
<td>89</td>
<td>73</td>
</tr>
</tbody>
</table>

$^a$ Dose rate of $4.1 \times 10^4$ rad/h to $2.4 \times 10^5$ rad with H$_2$SO$_4$ (0.2 M); TMPTA at 1% v/v.
Table 7 Effect of organic additives (urea, silanes, fluorinated alkylesters) on UV grafting styrene to polypropylene$^a$

<table>
<thead>
<tr>
<th>Styrene in methanol (% v/v)</th>
<th>N.S.</th>
<th>BEE</th>
<th>BEE+U</th>
<th>BEE+U+Si</th>
<th>BEE+U+FE</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>&lt;5</td>
<td>&lt;5</td>
<td>&lt;5</td>
<td>&lt;5</td>
<td>&lt;5</td>
</tr>
<tr>
<td>30</td>
<td>&lt;5</td>
<td>35</td>
<td>30</td>
<td>18</td>
<td>23</td>
</tr>
<tr>
<td>40</td>
<td>&lt;5</td>
<td>39</td>
<td>46</td>
<td>31</td>
<td>53</td>
</tr>
<tr>
<td>50</td>
<td>&lt;5</td>
<td>17</td>
<td>19</td>
<td>13</td>
<td>16</td>
</tr>
<tr>
<td>70</td>
<td>&lt;5</td>
<td>14</td>
<td>11</td>
<td>7</td>
<td>10</td>
</tr>
</tbody>
</table>

$^a$ Irradiated 8h at 24cm from 90W lamp at 20°C; N.S.=no sensitisier; BEE=benzoin ethyl ether (1% w/v)-sensitisier; U=urea (1% w/v); Si=silane (1% v/v); Z-6020 supplied by Dow; FE=fluorinated alkyl ester (1% v/v); FC-430 supplied by 3M.

Table 8 Effect of TMPTA in presence of organic additives in photografting styrene to polypropylene$^a$

<table>
<thead>
<tr>
<th>Styrene in methanol (% v/v)</th>
<th>N.S.</th>
<th>BEE</th>
<th>BEE+U</th>
<th>BEE+additives +TMPTA</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>&lt;5</td>
<td>&lt;5</td>
<td>&lt;5</td>
<td>260</td>
</tr>
<tr>
<td>30</td>
<td>&lt;5</td>
<td>35</td>
<td>30</td>
<td>588</td>
</tr>
<tr>
<td>40</td>
<td>&lt;5</td>
<td>39</td>
<td>46</td>
<td>711</td>
</tr>
<tr>
<td>50</td>
<td>&lt;5</td>
<td>17</td>
<td>19</td>
<td>368</td>
</tr>
<tr>
<td>70</td>
<td>&lt;5</td>
<td>14</td>
<td>11</td>
<td>131</td>
</tr>
</tbody>
</table>

$^a$ Conditions as in Table 7; additives used were urea, silane and fluorinated alkyl ester; TMPTA (1% v/v).
Table 9 Effect of structure of multifunctional acrylate as additive in photografting styrene to polypropylene$^a$

<table>
<thead>
<tr>
<th>Styrene in methanol (% v/v)</th>
<th>N.A.</th>
<th>TMPTA</th>
<th>PETA</th>
<th>DPGDA</th>
<th>HEMA</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>&lt;5</td>
<td>38</td>
<td>24</td>
<td>29</td>
<td>&lt;5</td>
</tr>
<tr>
<td>30</td>
<td>35</td>
<td>190</td>
<td>188</td>
<td>186</td>
<td>61</td>
</tr>
<tr>
<td>40</td>
<td>39</td>
<td>603</td>
<td>426</td>
<td>356</td>
<td>44</td>
</tr>
<tr>
<td>50</td>
<td>17</td>
<td>366</td>
<td>133</td>
<td>178</td>
<td>36</td>
</tr>
<tr>
<td>70</td>
<td>14</td>
<td>179</td>
<td>78</td>
<td>89</td>
<td>26</td>
</tr>
</tbody>
</table>

$^a$ Conditions as in Table 7; BEE (1% w/v) as sensitiser in all runs; N.A. = no additive; acrylate monomers (1% v/v); TMPTA = trimethylolpropane triacrylate; PETA = pentaerythritol tetracrylate; DPGDA = dipropylene glycol diacrylate; HEMA = hydroxyethyl methacrylate.

Table 10 Toxicological classification of Draize values for skin irritancy

<table>
<thead>
<tr>
<th>Draize Value (PII Number)</th>
<th>Classification</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 - 0.5</td>
<td>non-irritant</td>
</tr>
<tr>
<td>0.5 - 2.0</td>
<td>mild or slight irritant</td>
</tr>
<tr>
<td>2.0 - 5.0</td>
<td>moderate irritant</td>
</tr>
<tr>
<td>5.0 - 8.0</td>
<td>strong irritant</td>
</tr>
</tbody>
</table>

Fig. 1 Reaction of multifunctional acrylate with polymer radical by gamma irradiation
Fig. 2  Synergistic effects of TMPTA and acid in gamma radiation grafting of styrene in methanol to polyethylene film at 4.1×10^5 rad/h to 2.4×10^5 rad: (○) styrene, methanol; (△) styrene, methanol, sulphuric acid (0.2 M); (□) styrene, methanol, TMPTA (1% v/v); (●) styrene, methanol, TMPTA (1% v/v), sulphuric acid (0.2 M)

Fig. 3  Effects of urea and TMPTA on gamma radiation grafting of styrene in methanol to polypropylene film at 6.5×10^5 rad/h to 2.5×10^5 rad: (●) no additive; (○) TMPTA 1% v/v; (■) urea (1% w/v); (□) TMPTA (1% v/v) and urea (1% w/v)
Fig. 4 FTICRMS of TPGDA
(a) EI (b) Cl2 seconds (c) Cl20 seconds (d) Cl60 seconds
DEVELOPMENT OF SENSITIZER AND VULCANIZATION MECHANISM

5.17 Combination Effect of Carbon Tetrachloride with 2-Ethylhexyl Acrylate as a Sensitizer for Radiation Vulcanization of Natural Rubber Latex

RANSI DEVENDRA\(^1\) and K. Makuuchi\(^2\)

1) Ceylon Institute of Scientific and Industrial Research, Colombo, Sri Lanka,
2) JAERI, TCRE, Takasaki, Gunma, 370-12 Japan

Abstract

Investigation showed that a combination of 2-ethylhexyl acrylate (2-EHA) and carbon tetrachloride as a sensitizer system for radiation vulcanization of natural rubber latex is effective to reduce the vulcanization dose. This combination is effective over a wide range so that it can be selected depending on the radiation cost and chemical cost. Swelling data indicate that the addition of carbon tetrachloride to 2-EHA increases the efficiency of the crosslinking reaction. A combination of 1 phr carbon tetrachloride and 1 phr 2-EHA will lead to a more economical system than the system using 5 phr carbon tetrachloride as sensitizer.

1. Introduction

It has been reported that when natural rubber latex is irradiated with high energy radiation such as gamma radiation, it undergoes crosslinking. But the vulcanization dose for an acceptable latex film properties was high; hence, it had no practical interest. Later, by the use of a sensitizer such as CCl\(_4\) (carbon tetrachloride) it was observed that it is possible to reduce the vulcanization dose to a large extent\(^1,\(^2\). If CCl\(_4\) is used as a sensitizer at 5 phr, the vulcanization dose can be reduced to about 40 kGy. But due to the high cost of radiation for the process to be economically viable, it was necessary to reduce the vulcanization dose, for example, to 10 kGy. Therefore, the need for further reduction in vulcanization dose in radiation vulcanization of natural rubber latex led to the investigation of other sensitizers\(^3,\(^5\). From the sensitizers investigated, polyfunctional and monofunctional monomers
showed a promising effect for reduction in the vulcanization dose. However the dose reduction to an amount close to 10 kGy using monomer alone showed the process to be uneconomical due to the high cost of monomer.

In this paper the effect of \( \text{CC}_4 \), monomer and their combinations on vulcanization dose reduction is reported. Here, the work was carried out using \( \text{EHA} \) (2-ethylhexyl acrylate) as the monomer. Some of the physical properties of vulcanized latex films and their aging properties using different sensitizer systems were also investigated and are reported.

2. Experimental

2.1 Material

Felda HA, high ammonia preserved natural rubber latex concentrate was obtained from Malaysia. Carbon tetrachloride, 2-ethylhexyl acrylate, sodium hydroxide, hydrochloric acid and toluene were obtained from Wako Chemical Company Ltd Japan. Potassium laurate was obtained from Nippon Oils and Fats Company Japan. All chemicals were used without further purification.

2.2 Sample Preparation and Irradiation

Samples for irradiation were prepared according to a standard formulation as follows.

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>phr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural rubber latex</td>
<td>100</td>
</tr>
<tr>
<td>Potassium Laurate</td>
<td>0.1</td>
</tr>
<tr>
<td>Water</td>
<td></td>
</tr>
<tr>
<td>to reduce the DRC to 50%</td>
<td></td>
</tr>
<tr>
<td>Monomer</td>
<td></td>
</tr>
<tr>
<td>CCl(_4)</td>
<td></td>
</tr>
<tr>
<td>as specified</td>
<td></td>
</tr>
<tr>
<td>as specified</td>
<td></td>
</tr>
</tbody>
</table>

First the potassium laurate was dissolved in water and it was added to the latex to dilute the latter to 50% DRC. Then, requisite amounts of monomer were added to the diluted latex while stirring. Stirring was continued for one hour. The mix was left for about 16 hours and irradiated to different radiation doses in 75 ml glass bottles with screw caps. Radiation from Co-60 source was used for sample irradiation at a dose rate of 10 kGy/h.
2.3 Film Preparation
Films were cast with thickness 0.8 - 1.0 mm from irradiated latex using levelled glass molds. Then the films were dried at room temperature until they became transparent.

2.4 Leaching
Films were first immersed in appropriate solution for 48 hours. Then they were washed with distilled water and finally they were dried at room temperature.

2.5 Aging
Accelerated aging of latex films was carried out for 72 hours in an air circulating oven at 100°C.

2.6 Tensile Strength Measurement
After proper drying at room temperature, films were heated at 70°C for one hour and conditioned for 24 hours at room temperature. Then the tensile strength of prepared latex films was measured using a Instron Universal testing machine according to JIS k 6308 - 1975.

2.7 Swelling Measurements
Films of 1 mm thickness were cut into 1 cm x 1 cm size and immersed in solvent for one week. During the immersion period the solvent was replaced with fresh solvent. The weight of the swollen sample was determined by blotting the excess solvent. The sample weight was taken as the weight of the de-solventized sample. Swollen samples were de-solventized by drying in a vacuum oven at 40°C to a constant weight. In this study toluene was used as the swelling solvent. All swelling tests were carried out at room temperature. Volume fraction of the swollen vulcanizate was calculated as in equation (1).

\[ \frac{V}{(V_m + V)} \]  

(1)

Where \( V \) is the volume of the polymer and \( V_m \) is the volume of the solvent in the swollen network.

2.8 Determination of Gel Content
First a known weight of the irradiated monomer was swollen in toluene
for one week. Then the undissolved part was separated by filtering through a Gooch type crucible of pore size 2. Finally the weight of the undissolved fraction was determined after removing the solvent completely by drying in an vacuum oven at 40°C to a constant weight. The gel content is calculated as a percentage of weight of the undissolved part to original weight of the material.

2.9 Measurement of Viscosity

The viscosity of irradiated latex was measured at 34°C using the Visconic EMD type viscometer (a cone and plate viscometer). A shear rate of 384 sec\(^{-1}\) was used during the measurement.

3. Results and Discussion

3.1 Effect of CCl\(_4\) as Sensitizer

It was reported\(^6\) that the crosslink density of a polymer network can be determined by carrying out swelling measurement in a suitable solvent. Figure 1 shows the variation of volume fraction of swollen vulcanizate in toluene with radiation dose when different concentrations of CCl\(_4\) were used as sensitizer. It can be seen that with the increase in CCl\(_4\) concentration, the volume fraction of the swollen network increases. Therefore it can be said that with the increase in sensitizer concentration the crosslinking reaction increases. Figure 2 shows the tensile strength of cast films from irradiated latex having different concentrations of CCl\(_4\) as the sensitizer for different radiation doses. It can be seen that by increasing the CCl\(_4\) concentration the vulcanization dose has been reduced, but the reduction is not significant above 15 phr CCl\(_4\) concentration. Therefore by increasing the CCl\(_4\) concentration only, it is not economically possible to reduce the vulcanization dose close to 10 kGy.

3.2 Effect of 2-Ethylhexyl Acrylate as Sensitizer

Figure 3 shows the variation of volume fraction of swollen vulcanizate in toluene with radiation dose for different 2-EHA concentrations as the sensitizer. This has a similar effect as in the case of CCl\(_4\) when used as the sensitizer. Figure 4 shows the corresponding tensile strength and radiation dose relationship for 2-EHA. It can be seen that when 2-EHA monomer is used as the sensitizer, with an increase in con-
centration of monomer, there is a significant reduction in vulcanization dose. However there is also a reduction in optimum tensile strength. This may be due to some of the polymerized monomer which act as plasticizer. From Figs 3 and 4 it can also be said that at optimum tensile strength vulcanizates have similar crosslinking densities. Although the content of 5 phr of 2-EHA gave acceptable tensile strength values at 20 kGy, this value of radiation dose of 20 kGy was still too high and work was done to see whether CCl₄ will have a synergistic effect in reducing the vulcanization dose in the presence of 2-EHA.

3.3 Effect of 2-Ethylhexyl Acrylate and CCl₄ Combination as Sensitizer

The use of CCl₄ as a sensitizer in radiation vulcanization of natural rubber latex will lead to a network with carbon-carbon crosslink, whereas 2-EHA will lead to a system which has some physical crosslink⁵ or some chemical crosslinking occurring through grafting. It is reported⁷ that CCl₄ acts as a chain transfer agent in free radical polymerization of monomer. Due to this effect, free radical polymerization of 2-EHA will lead to oligomerization in the presence of CCl₄. It is observed that acrylic monomers undergo gel formation when irradiated with high energy radiation. Table 1 shows the final gel content in toluene of 2-EHA with and without CCl₄ after irradiating with gamma radiation to a dose of 30 kGy. It is seen that the addition of CCl₄ to 2-EHA reduces the gel formation significantly. This may be due to the chain transfer effect of CCl₄. Therefore the use of this sensitizer combination in radiation Vulcanization would be expected to retard the crosslinking reaction. However we have found that this situation is different in the presence of natural rubber latex.

Figure 5 shows the variation of tensile strength with radiation dose for a sensitizer system which has CCl₄ and 2-EHA. It is seen that at 2 phr concentration of sensitizer, the sensitizer combination shows a drastic reduction in the vulcanization dose. Figure 6 shows the swelling characteristics of the different sensitizer combinations at 2 phr concentration. This shows that combinations of CCl₄ and 2-EHA increase the crosslinking reaction of natural rubber latex in the presence of radiation. Therefore the results reveal that combinations of CCl₄ and 2-EHA is an effective combination of sensitizer for radiation vulcanization of natural rubber latex.

Figures 7 and 8 shows the effect of different concentration of CCl₄.
for two fixed concentrations of monomer 2-EHA on their swelling characteristics at different radiation doses. It is seen that even with the increase in the concentration of CCl₄, the crosslinkability of the final sensitizer combination increases. Figure 9 shows the effect of 1 phr of CCl₄ on vulcanization dose and tensile strength over a range of concentrations of 2-EHA as sensitizer. It can be seen that with the addition of CCl₄ for each monomer concentration the vulcanization dose has reduced. Also there is an increase in the optimum tensile strength. The increase is more significant at high concentrations of monomer. This may be due to more efficient utilization of monomer in the network formation when CCl₄ is used in combination with monomer.

3.4 Effect of Different Film Treatments

It is reported that in sulphur vulcanizates, the structure of the vulcanizate has a great influence on the properties of the final vulcanizate. In radiation vulcanization, although the structure of the vulcanizate is not fully understood it is clear, that the structure of the vulcanizate can vary depending on the sensitizer used. Therefore vulcanized latex films made out of selected sensitizer systems were subjected to different treatment. The results are shown in Table 2 and discussed below.

3.4.1 Physical properties of films

The physical properties such as 300% modulus, tensile strength and elongation at break have increased in all vulcanizates tested after water leaching. This may be due to the removal of water soluble material in the cast film by leaching resulting in better particle coalescence and hence, formation of stronger films during subsequent drying. It is also seen that there is no significant difference in these properties between different vulcanizates. This shows that it is possible to select the sensitizer system without affecting the properties of the final vulcanizate significantly.

3.4.2 Aging properties

Water soluble natural antioxidants are known to be present in natural rubber latex. Therefore vulcanized latex films were aged without leaching with water so that they contained some natural antioxidants. The temperature of 100°C was selected to subject the latex films for better accelerated aging conditions. From the results it can be said that the aging properties of sensitizer combination does not differ significantly
from the vulcanizates prepared using either monomer or CCl₄ as the sensitizer.

3.4.3 Effect of acids and alkali leaching

The increase in tensile strength after leaching with 10% NaOH is not as high as when it was leached with water. This may be due to the hydrolysis of network bound proteins which would have brought down the overall crosslinking density. From the results it can be said that the effect of sodium hydroxide on vulcanize prepared with different sensitizer systems has no significant difference. The reduction in tensile strength due to hydrochloric acid is not clear. The large reductions observed in certain cases may be due to improper selection of the vulcanization dose of the vulcanizates.

3.5 The Effect on Viscosity

It is reported that some monomers when used as sensitizers in radiation vulcanization of natura rubber latex have a large effect on the final viscosity of the irradiated latex. Some monomers lead to complete destabilization of the latex. Table 3 shows the final viscosity of two irradiated latex prepared using two sensitizer systems. The results show that although sensitizer combination have a high percentage of monomer, the final irradiated latex have a viscosity comparable to the presently used irradiated latex sensitized by 5 phr of CCl₄.

3.6 The Economic of Radiation Vulcanization of Natural Rubber Latex

It is reported that the cost of radiation will depend on the country where the irradiation is carried out. Countries like Japan have high irradiation costs while countries like Indonesia have a fairly low cost of irradiation. But the cost of chemicals will be the opposite to this situation due to their availability. Both these situations will govern the overall cost of production of radiation vulcanized natural rubber latex. Table 4 shows the vulcanization dose and the corresponding chemical cost for different sensitizer combinations. From the table it can be seen that in the case of countries where there is high radiation cost, they can use a sensitizer combination which has a high monomer content. Combination such as 1 phr CCl₄ and 1 phr 2-EHA will lead to a sensitizer system which is more efficient and economical than the existing 5 phr CCl₄.

However the vulcanization dose for any given system will depend on
the history and the type of the latex used. It was also noted that when latex is treated with an oxidizing agent such as hydroperoxides, it is possible to reduce the vulcanization dose further.

4. Conclusions

The results obtained show that combination of CCl$_4$ and 2-EHA lead to a sensitizer system which is more efficient than CCl$_4$ or 2-EHA when used as the sensitizer. Vulcanizates prepared using sensitizer combinations have physical properties comparable to vulcanizates prepared with CCl$_4$ or 2-EHA as the sensitizer. The effectiveness of the combination over a range of concentrations makes it more promising as sensitizer so that it can be selected according to the country of manufacture of radiation vulcanized natural rubber latex to minimize the processing cost.

Acknowledgements

The authors thank The International Atomic Energy Agency (IAEA) and The United Nations Development Programme (UNDP) for providing funds to carry out this project. They also thank The Japan Atomic Energy Research Institute, Takasaki Radiation Chemistry Research Establishment Japan for providing facilities to carry out the experiments.

References

Table 1 Gel content of 2-EHA and CCl$_4$ mix at 30 kGy radiation dose

<table>
<thead>
<tr>
<th>Sample</th>
<th>Gel content in toluene, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-EHA</td>
<td>75.8</td>
</tr>
<tr>
<td>2-EHA + CCl$_4$ (5:1)</td>
<td>0.7</td>
</tr>
</tbody>
</table>

Table 2 Different treatments on vulcanized latex films

<table>
<thead>
<tr>
<th>Sensitizer system</th>
<th>2-EHA, phr</th>
<th>CCl$_4$, phr</th>
<th>Vulcanization dose, kGy.</th>
<th>Before leaching</th>
<th>After Leaching with water(a)</th>
<th>Aged 72 h. at 100°C(b)</th>
<th>Treatment(c)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Tensile Strength, MPa.</td>
<td>300% Modulus, MPa.</td>
<td>Elongation at Break, %</td>
<td>Tensile Strength, MPa.</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>5</td>
<td>5</td>
<td>23.8</td>
<td>0.82</td>
<td>1045</td>
<td>18.3</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>-</td>
<td>0.5</td>
<td>21.9</td>
<td>0.80</td>
<td>1040</td>
<td>19.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>22.6</td>
<td>0.80</td>
<td>1035</td>
<td>21.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>21.5</td>
<td>0.80</td>
<td>1040</td>
<td>20.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>23.4</td>
<td>0.80</td>
<td>1045</td>
<td>21.6</td>
</tr>
</tbody>
</table>

(a)(c) leached for 48 hours
(b) without leaching
Table 3 The effect of different sensitizer systems on the final viscosity of irradiated latex

<table>
<thead>
<tr>
<th>System</th>
<th>Viscosity (cp) at 34°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCl₄ (5 phr)</td>
<td>14.0</td>
</tr>
<tr>
<td>2-EHA (5 phr) +</td>
<td>16.9</td>
</tr>
<tr>
<td>CCl₄ (1 phr)</td>
<td></td>
</tr>
</tbody>
</table>

Table 4 Chemical cost and vulcanization dose for different sensitzers

<table>
<thead>
<tr>
<th>Sensitizer System</th>
<th>Cost of Chemicals</th>
<th>Vulcanization dose, kGy.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCl₄ (5 phr)</td>
<td>900</td>
<td>50</td>
</tr>
<tr>
<td>2-EHA (5 phr)</td>
<td>1750</td>
<td>30</td>
</tr>
<tr>
<td>2-EHA (5 phr) +</td>
<td>1950</td>
<td>10</td>
</tr>
<tr>
<td>CCl₄ (1 phr)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-EHA (1 phr)</td>
<td>550</td>
<td>40</td>
</tr>
<tr>
<td>CCl₄ (1 phr)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Fig. 1 The effect of CCl₄ concentration on the volume fraction of vulcanized latex films swollen in toluene. (○) 0 phr, (□) 1 phr, (▲) 2 phr and (○) 5 phr.

Fig. 2 Tensile strength (Tb) of irradiated latex films in the presence of different concentration of CCl₄ as sensitzers. (○) 5 phr, (□) 10 phr, (▲) 15 phr and (○) 20 phr.
Fig. 3 The effect of 2-EHA concentration on the volume fraction of vulcanized latex films swollen in toluene. (○) 3 phr, (△) 4 phr, (○) 5 phr, (□) 6 phr, (●) 8 phr and (■) 10 phr.

Fig. 4 Variation in tensile strength (Tb) with radiation dose when different amounts of 2-EHA is used as sensitizer. (○) 3 phr, (□) 4 phr, (○) 5 phr, (△) 6 phr, (●) 8 phr and (■) 10 phr.
Fig. 5 Variation in tensile strength ($T_b$) with radiation dose for different sensitizer systems. (○) 2 phr CCl$_4$, (□) 2 phr 2-EHA, (○) 1 phr CCl$_4$ + 1 phr 2-EHA and (△) 5 phr CCl$_4$.

Fig. 6 The effect of sensitizer concentration on the volume fraction of vulcanized latex films swollen in toluene. (○) 2 phr CCl$_4$, (●) 2 phr 2-EHA, (□) 1 phr CCl$_4$ + 1 phr 2-EHA and (○) 5 phr CCl$_4$. 

- 302 -
Fig. 7 Variation in tensile strength (Tb) with radiation dose when 3 phr 2-EHA is use in combination with different amounts of CCl₄. (●) 0 phr, (○) 0.5 phr, (○) 1 phr, ( □ ) 1.5 phr and (△) 2 phr.

Fig. 8 Variation in tensile strength (Tb) with radiation dose when 6 phr 2-EHA is use in combination with different amounts of CCl₄. (●) 0 phr, (○) 0.5 phr, (○) 1 phr, ( □ ) 1.5 phr and (△) 2 phr.
Fig. 9 Effect of monomer concentration and CCl₄ on maximum tensile strength (Tb) and vulcanization dose. (○) 0 phr CCl₄, (○) 1 phr CCl₄.
5.18 Selection of Hydroperoxides as Co-Sensitizer for n-Butyl Acrylate

PARINYA AROONVISOOT\(^1\) and K. Makuuchi\(^2\)

\(^1\) Prince of Songkla University, Hat-Yai, Thailand  
\(^2\) JAERI, TRCRE, Takasaki, Gunma, 370-12 Japan

Abstract

A hydroperoxide was selected as a co-sensitizer for n-butyl acrylate (n-BA) in the presence of potassium hydroxide (KOH) in natural rubber latex to reduce the irradiation dose for vulcanization. n-BA used together with a hydroperoxide was more effective as sensitizer for latex vulcanization. The latex prepared by adding hydroperoxide before adding n-BA was more stable than the latex with n-BA alone. From four hydroperoxides studied, t-butyl hydroperoxide exhibited high vulcanization efficiency at low concentration and at a low dose of 8 kGy.

1. Introduction

Natural rubber (NR) latex can be vulcanized by radiation in the presence of carbon tetrachloride (CCl\(_4\)) as sensitizer at around 40 kGy\(^1\). A monofunctional acrylate, 2-ethylhexyl acrylate (2-EHA), when used as a sensitizer could reduce the vulcanization dose to 30 kGy\(^2\), and this reduced to 15 kGy when 2-EHA was used as a co-sensitizer\(^3\) with CCl\(_4\). As the smell of rubber films prepared by using 2-EHA was strong due to the residual 2-EHA, a new sensitizer system consisting of n-butyl acrylate (n-BA) in the presence of KOH as stabilizer was studied\(^4\). n-BA could replace the 2-EHA/CCl\(_4\) system and required a lower optimum dose of 10-15 kGy. Devendra and Makuuchi\(^3\) reported that adding cumene hydroperoxide to latex containing 2-EHA and CCl\(_4\) could reduce the vulcanization dose to 10 kGy. This paper reports the effect of hydroperoxide used as a co-sensitizer with n-BA in the presence of KOH on the radiation vulcanization of NR latex.

2. Experimental

2.1 Materials

The NR latex used was a commercially available centrifuged latex
concentrate (Dunlop HA) imported from Malaysia. The latex was diluted with 1% NH₄OH (aq) to a dry rubber content of 50% weight. 2 phr of 10% KOH (aq) was used as stabilizer. The hydroperoxides and n-BA used are listed in Table 1. All chemicals were reagent grade and used as obtained.

2.2 Irradiation and Measurements

n-BA and KOH were added to NR latex and mixed with a magnetic stirrer for one hour. The mixture was kept for 14 h at room temperature (25°C); then the hydroperoxide was added and mixed with a magnetic stirrer for one hour. The mixture was kept for one hour before irradiation. This procedure was called Method 1. Method 2 was the same procedure but the hydroperoxide was added before adding n-BA. About 80 ml of the mixture was irradiated in a 100 ml plastic bottle with screw cap. Irradiation was carried out with 10 kCi of Co-60 at a dose rate of 8 kGy/h.

The viscosity of the latex sample was measured at 25°C with a cone-plate type viscometer, Model EMD from Tokyo Keiki Co. Ltd. Dried films were prepared from the irradiated latex by casting on glass plates. After drying at room temperature, films were leached with distilled water for 20 h and then dried at room temperature. The films were heated at 70°C for one hour and left at room temperature. Aging test was carried out in an air oven at 70°C for 48 h in accordance with ASTM D573. For acid-base resistance test, the films were immersed in 10% HCl (aq) or NaOH (aq) for 48 h in accordance with JIS Z-4810.

The tensile properties such as tensile strength, elongation at break and tear resistance of the films were determined in accordance with ASTM D412 and D624 using a Toyoseki Strograph tensile machine with a crosshead speed of 500 mm/min. The permanent set property of film was determined in accordance with ASTM D12.

For the determination of volume swelling ratio, a sample was weighed and immersed in toluene for one week. The swollen sample was taken out and quickly blotted with filter paper and weighed. The volume swelling ratio was calculated by using the following equation:

\[ Q = \frac{V_2}{V_1} = 1 + \left(\frac{d_r}{d_s}\right)\left(\frac{W_2}{W_1}\right) - \frac{d_r}{d_r} \]

where \( V_1, \ W_2, \ W_1 \) and \( W_2 \) are the volume and weight of sample before and after immersion, and \( d_r \) and \( d_s \) are the densities of rubber (0.93 g/cm³) and toluene (0.87 g/cm³) respectively.
3. Results and Discussion

3.1 Method of Preparation

It was found that the latex viscosity increased as the stability of latex decreased. The latex viscosity increased rapidly during the first 4 to 6 days storage and after that it decreased. The viscosity of latex prepared by Method 1 (see Fig. 1a) did not show any significant difference among the hydroperoxides and n-BA. The viscosity of all the latex with hydroperoxides added using Method 2 (see Fig. 1b) was lower than that with n-BA alone. Also, latex containing hydroperoxide and n-BA prepared by Method 2 was more stable than those prepared by method 1 and was also more stable than latex containing n-BA alone.

The physical properties of latex prepared by Method 1 (see Table 2) did not show any significant difference among the hydroperoxides and n-BA. The tensile strength of films from all latex containing hydroperoxides added using Method 2 (see Table 3) was generally higher than that containing n-BA alone, and the swelling ratio was generally lower. This means that the crosslinking density increased by adding hydroperoxide before adding n-BA.

From the above results, latex prepared by Method 2 was selected for the subsequent experiments.

3.2 Effect of Hydroperoxide Concentration

The tensile strengths of films prepared from the irradiated latex with various concentrations of hydroperoxides i.e. 0.1, 0.5, 1.0 phr are shown in Fig. 2a, 2b, 2c and 2d. The tensile strength increased with dose up to a maximum value and then decreased. All the hydroperoxides enhanced the tensile strength values at around 8 kGy, except HPO4 which did not show any effect. It was concluded that at 0.1 phr HPO1 exhibited the best efficiency, but the other hydroperoxides required more than 0.1 phr.

The swelling ratio is used as a measure of degree of vulcanization. From Fig. 3a, 3b, 3c and 3d, the swelling ratio decreased with increasing dose, and all the hydroperoxides except HPO4 lowered the swelling ratio value obtained with n-BA alone. It is clear that hydroperoxide accelerates the vulcanization of NR latex by n-BA.

Table 4 shows the tensile strength of films with 5 phr of n-BA and HPO1 at low concentrations i.e. 0.05, 0.1, 0.15 phr, and HPO2 and HPO3
at 0.25, 0.50, 0.75 phr. The optimum concentration of HPO1 is 0.1 phr, HPO2 is 0.75 phr, and HPO3 is 0.5 phr at 8 kGy.

3.3 Other Physical Properties of NR Latex with n-BA and Hydroperoxides.

The viscosities of NR latex irradiated from 0 to 40 kGy with 5 phr of n-BA and 0.1 phr of HPO1 and after storage of 24 h at room temperature are shown in Table 5. At dose lower than 12 kGy, the viscosity of NR latex increased due to the residual n-BA, and at the same dose, the viscosity of NR latex with both n-BA and hydroperoxide was higher than that with n-BA alone. It means that HPO1 itself effected the vulcanization and the residual n-BA increased.

Effect of n-BA concentration

The effect of n-BA concentration and dose on Tb of films prepared from RVNRL with 0.1 phr of HPO1 and various concentration of n-BA is shown in Fig. 4. Figure 5 shows a complete summary of the data obtained from Fig. 4. The vulcanization dose decreased with increasing n-BA concentration. The decreasing in Max Tb with increasing n-BA concentration may be due to the increasing of ungrafted poly n-BA which acts as a plasticizer. From these results the optimum concentration of n-BA with 0.1 phr of HPO1 is 5 phr.

Aging properties

When the leached and without antioxidant films prepared from RVNRL with 5 phr of n-BA were aged at 70°C for 48 h, their surface became sticky indicating degradation, while the films prepared from RVNRL with 5 phr of n-BA and 0.1 phr of HPO1 showed no coloration and no surface degradation. They also had a better heat resistance and acid-base resistance (Table 6). It was concluded that HPO used together with n-BA enhanced crosslinking and physical properties of the films.

4. Conclusion

Irradiated NR latex prepared by adding a hydroperoxide before n-BA was more stable than latex irradiated with n-BA alone. Hydroperoxides enhanced the physical properties of radiation vulcanized latex with n-BA as sensitizer. At 8 kGy and with 5 phr n-BA, HPO1 exhibited optimum tensile strength at 0.1 phr, while the other hydroperoxides required more than 0.1 phr.
References

### Table 1 Hydroperoxides and n-BA used

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Formula</th>
<th>Purity, %</th>
<th>Active oxygen, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>t-Butyl hydroperoxide&lt;sup&gt;a&lt;/sup&gt; (HPO1)</td>
<td>C&lt;sub&gt;4&lt;/sub&gt;H&lt;sub&gt;10&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;</td>
<td>69.0</td>
<td>12.25</td>
</tr>
<tr>
<td>Cumene hydroperoxide (HPO2)</td>
<td>C&lt;sub&gt;9&lt;/sub&gt;H&lt;sub&gt;12&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;</td>
<td>83.0</td>
<td>8.72</td>
</tr>
<tr>
<td>Para menthane hydroperoxide (HPO3)</td>
<td>C&lt;sub&gt;10&lt;/sub&gt;H&lt;sub&gt;20&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;</td>
<td>54.5</td>
<td>5.06</td>
</tr>
<tr>
<td>Diisopropylbenzene hydroperoxide (HPO4)</td>
<td>C&lt;sub&gt;12&lt;/sub&gt;H&lt;sub&gt;18&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;</td>
<td>54.0</td>
<td>4.44</td>
</tr>
<tr>
<td>n-Butyl acrylate&lt;sup&gt;b&lt;/sup&gt; (n-BA)</td>
<td>C&lt;sub&gt;7&lt;/sub&gt;H&lt;sub&gt;12&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;</td>
<td>99.3</td>
<td>-</td>
</tr>
</tbody>
</table>

<sup>a</sup> All HPOs used were supplied by Nihon Yoshi Co. Ltd.

<sup>b</sup> Supplied by Toagosei Chem. Ind. Co. Ltd.

### Table 2 The physical properties of NRL films prepared from latex with 5 phr of n-BA and 0.5 phr of different HPOs, prepared by method 1 irradiated at 12 kGy

<table>
<thead>
<tr>
<th>Hydroperoxide</th>
<th>Tb, MPa</th>
<th>Eb, %</th>
<th>300% Modulus</th>
<th>Swelling ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>25.6</td>
<td>1182</td>
<td>0.55</td>
<td>7.11</td>
</tr>
<tr>
<td>HPO1</td>
<td>26.8</td>
<td>1327</td>
<td>0.46</td>
<td>7.14</td>
</tr>
<tr>
<td>HPO2</td>
<td>25.3</td>
<td>1215</td>
<td>0.76</td>
<td>7.04</td>
</tr>
<tr>
<td>HPO3</td>
<td>25.6</td>
<td>1218</td>
<td>0.74</td>
<td>7.10</td>
</tr>
<tr>
<td>HPO4</td>
<td>25.3</td>
<td>1047</td>
<td>1.09</td>
<td>6.70</td>
</tr>
</tbody>
</table>
Table 3  The physical properties of NRL films prepared from latex with 5 phr of n-BA and 0.5 phr of different HPOs, prepared by method 2 irradiated at 12 kGy

<table>
<thead>
<tr>
<th>Hydroperoxide</th>
<th>Tb, MPa</th>
<th>Eb, %</th>
<th>300% Modulus</th>
<th>Swelling ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>25.6</td>
<td>1182</td>
<td>0.55</td>
<td>7.11</td>
</tr>
<tr>
<td>HPO1</td>
<td>28.6</td>
<td>1147</td>
<td>0.45</td>
<td>6.81</td>
</tr>
<tr>
<td>HPO2</td>
<td>25.8</td>
<td>1091</td>
<td>0.56</td>
<td>6.36</td>
</tr>
<tr>
<td>HPO3</td>
<td>30.5</td>
<td>1290</td>
<td>0.49</td>
<td>7.30</td>
</tr>
<tr>
<td>HPO4</td>
<td>25.6</td>
<td>1204</td>
<td>0.95</td>
<td>6.79</td>
</tr>
</tbody>
</table>

Table 4  Tensile strength of films with 5 phr of n-BA and different concentration of HPOs, irradiated at 4, 8, and 12 kGy

<table>
<thead>
<tr>
<th>hydroperoxide,conc.</th>
<th>4 kGy</th>
<th>8 kGy</th>
<th>12 kGy</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>14.1</td>
<td>19.7</td>
<td>26.1</td>
</tr>
<tr>
<td>HPO1, 0.05 phr</td>
<td>14.9</td>
<td>23.4</td>
<td>26.3</td>
</tr>
<tr>
<td>0.10 phr</td>
<td>16.4</td>
<td>26.4</td>
<td>26.8</td>
</tr>
<tr>
<td>0.15 phr</td>
<td>24.2</td>
<td>24.0</td>
<td>25.0</td>
</tr>
<tr>
<td>HPO2, 0.25 phr</td>
<td>23.0</td>
<td>23.0</td>
<td>23.7</td>
</tr>
<tr>
<td>0.50 phr</td>
<td>23.3</td>
<td>24.7</td>
<td>21.6</td>
</tr>
<tr>
<td>0.75 phr</td>
<td>21.1</td>
<td>26.5</td>
<td>24.2</td>
</tr>
<tr>
<td>HPO3, 0.25 phr</td>
<td>18.2</td>
<td>25.7</td>
<td>24.3</td>
</tr>
<tr>
<td>0.50 phr</td>
<td>16.6</td>
<td>26.4</td>
<td>25.2</td>
</tr>
<tr>
<td>0.75 phr</td>
<td>18.9</td>
<td>25.8</td>
<td>25.3</td>
</tr>
</tbody>
</table>
Table 5 Viscosity of irradiated NRL with 5 phr of n-BA and 0.2 phr of HPO1 after storage 24 h

<table>
<thead>
<tr>
<th>NRL with</th>
<th>Viscosity, cP</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>non-irradiated</td>
<td>4 kGy</td>
<td>8 kGy</td>
<td>12 kGy</td>
<td>24 kGy</td>
</tr>
<tr>
<td>n-BA</td>
<td>40.8</td>
<td>34.6</td>
<td>32.0</td>
<td>24.8</td>
<td>25.7</td>
</tr>
<tr>
<td>n-BA/HPO1</td>
<td>47.8</td>
<td>45.1</td>
<td>34.0</td>
<td>25.8</td>
<td>25.8</td>
</tr>
</tbody>
</table>

Table 6 Physical properties of irradiated NRL films with 5 phr of n-BA and 0.1 phr of HPO1 at 8 and 12 kGy

<table>
<thead>
<tr>
<th>Properties</th>
<th>n-BA</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>8 kGy</td>
<td>12 kGy</td>
<td>8 kGy</td>
<td>12 kGy</td>
<td></td>
</tr>
<tr>
<td>Tb, MPa</td>
<td>21.8</td>
<td>25.4</td>
<td>28.8</td>
<td>28.0</td>
<td></td>
</tr>
<tr>
<td>Eb, %</td>
<td>1000</td>
<td>975</td>
<td>950</td>
<td>925</td>
<td></td>
</tr>
<tr>
<td>Tear resistance, kg/cm</td>
<td>14.7</td>
<td>17.6</td>
<td>21.5</td>
<td>17.4</td>
<td></td>
</tr>
<tr>
<td>Permanent set, %</td>
<td>10.0</td>
<td>6.0</td>
<td>7.5</td>
<td>5.0</td>
<td></td>
</tr>
<tr>
<td>Tb after aging&lt;sup&gt;a&lt;/sup&gt;, MPa</td>
<td>-</td>
<td>-</td>
<td>14.5</td>
<td>10.6</td>
<td></td>
</tr>
<tr>
<td>Eb after aging&lt;sup&gt;a&lt;/sup&gt;, %</td>
<td>-</td>
<td>-</td>
<td>950</td>
<td>975</td>
<td></td>
</tr>
<tr>
<td>NaOH resistance&lt;sup&gt;b&lt;/sup&gt;</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tb, MPa</td>
<td>16.0</td>
<td>20.7</td>
<td>25.1</td>
<td>25.3</td>
<td></td>
</tr>
<tr>
<td>Eb, %</td>
<td>975</td>
<td>1000</td>
<td>950</td>
<td>975</td>
<td></td>
</tr>
<tr>
<td>HCl resistance&lt;sup&gt;b&lt;/sup&gt;</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tb, MPa</td>
<td>18.2</td>
<td>20.9</td>
<td>21.4</td>
<td>21.6</td>
<td></td>
</tr>
<tr>
<td>Eb, %</td>
<td>1000</td>
<td>1000</td>
<td>950</td>
<td>975</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup> Aged at 70°C for 48 h.

<sup>b</sup> Immersed in 10% aq solution for 48 h.

- 312 -
Fig. 1 Relationship between storage and viscosity of RVNRL with 5 phr of n-BA and 0.5 phr of different HPOs irradiated at 12 kGy.

■ = control, □ = HPO 1, △ = HPO 2, ○ = HPO 3, ○ = HPO 4
Fig. 2: Changes in tensile strength of the films prepared from RMR with 5 phr of n-RHA and different concentration of HP0 at various dose.

(a) HP0 1
(b) HP0 2
Fig. 3 Changes in swelling ratio of the films prepared from RVNRL with 5 phr of n-BA and different concentration of HPOs at various dose.

(□) = control, (○) = 0.1 phr, (△) = 0.5 phr, (○) = 1.0 phr
Fig. 4 The effect of n-BA concentration and dose on tensile strength of the films prepared from RVNRL with 0.1 phr of HPO 1 and various concentration of n-BA.

- (○) = 3 phr,
- (●) = 4 phr,
- (△) = 5 phr,
- (□) = 7 phr,
- (○) = 9 phr

Fig. 5 The effect of n-BA concentration on the vulcanization dose and the maximum tensile strength of the films prepared from RVNRL with 0.1 phr of HPO 1 and various concentration of n-BA.
5.19 Effect of Hydrogen Peroxide on the Radiation Vulcanization of Natural Rubber Latex Sensitized with Carbon Tetrachloride and n-Butyl Acrylate

YANTI S. SABARINAH and F. Sundardi

Centre for the Application of Isotopes and Radiation, Jln. Cinere, Pasar Jumat, Jakarta Selatan, Indonesia

Abstract

An investigation to reduce the optimum irradiation dose for the radiation vulcanization of natural rubber latex (RVNRL) by the addition of hydrogen peroxide before irradiation had been carried out. The optimum irradiation dose decreased slightly while the maximum tensile strength of the RVNRL film increased slightly with the addition of a small amount (2.5 phr of 30% solution) of hydrogen peroxide. The crosslink density of the RVNRL film also decreased slightly with increased addition of hydrogen peroxide. However excessive amount of hydrogen peroxide added caused reduction in the film tensile strength and crosslink density.

1. Introduction

Studies to reduce the optimum irradiation dose for the radiation vulcanization of natural rubber latex (RVNRL) had been done by the addition of acrylic monomers before irradiation by many investigators\(^1\)-\(^4\). Combinations of acrylic monomers and carbon tetrachloride (CCl\(_4\)) as sensitizers had also been studied. A combination of 1 phr n-butyl acrylate (n-BA) and CCl\(_4\) had been found promising as it required as optimum irradiation dose of 20 to 30 kGy and good ageing properties were obtained\(^5\).

This paper presents the results obtained from a study on the effect of adding small amounts of hydrogen peroxide (H\(_2\)O\(_2\)) to natural rubber (NR) latex before irradiation. The latex was irradiated using a sensitizer system containing 1 phr n-BA and 1 phr CCl\(_4\). The effects of H\(_2\)O\(_2\) on the tensile strength and crosslink density of the RVNRL film were studied. The H\(_2\)O\(_2\) added to the latex was expected to diffuse into the NR particles and formed crosslinks.

- 319 -
2. Experimental

NR latex concentrate was obtained from PTP XI Pasir Waringin, West Java. The total solid content and dry rubber content of the latex were about 60% and 59% respectively. Technical grade n-BA was used after removal of the inhibitor present. Other chemicals such as CCl₄, H₂O₂, benzene, etc. were also of technical grade and were used without further purification. The concentration of H₂O₂ used were 1%, 10% and 30% in water. The latex was added with H₂O₂ solution, agitated and stored overnight before irradiation. The amounts of H₂O₂ solution added were varied from 2.5 phr to 40 phr. The sensitizer used was a combination of 1 phr n-BA and 1 phr CCl₄. The samples were then irradiated in a Co-60 irradiator at a dose rate of 3 kGy/h and at room temperature. The irradiation doses were varied from 10 kGy to 40 kGy. The viscosity of irradiated latex was determined by Viscometer MD Sn. Cast films were prepared from the irradiated latex, leached overnight in 1% aqueous solution of calcium chloride, dried at room temperature and then heated at 70°C for one hour. The mechanical properties of the film was determined by an Instron Universal Testing machine (Model 1122). The crosslink density of the film was determined by swelling ratio method based on Flory and Rehner equation⁶ as follows:

\[ V_0 = K \times Q^{-5/3} \]

where

\[ V_0 = \text{crosslink density, c.1/ml,} \]
\[ K = 4.71 \times 10^{20}, \text{for benzene/NR system,} \]
\[ Q = \text{volume swelling ratio.} \]

3. Results and Discussion

As addition of H₂O₂ solution diluted the latex, the latex viscosity decreased. Figure 1 shows the effect of adding H₂O₂ solution on the latex viscosity after irradiation. Without the addition of H₂O₂, the viscosity of the irradiated latex was 69 mPa.s. Adding 30 phr of 30% H₂O₂ solution decreased the latex viscosity to 12 mPa.s. The decrease in viscosity was just due to latex dilution.

Figure 2 shows the effect of adding H₂O₂ solution at various concentrations on the RVNR film tensile strength. The addition of 10%
and 30% H₂O₂ solutions gave maximum tensile strength at 5 phr and 2.5 phr respectively (corresponding to 0.5 phr and 0.75 phr pure H₂O₂ respectively). With more H₂O₂ added the tensile strength decreased. The addition of 1% H₂O₂ solution caused a gradual increase in the tensile strength, and the maximum tensile strength was not yet reached even after adding about 40 phr of solution (or about 0.4 phr pure H₂O₂).

The effect of H₂O₂ on the crosslink density of the film followed similar trend (Fig. 3) as the effect on tensile strength. It appeared that by adding small amounts of H₂O₂ before irradiation crosslinking through peroxidation occurred. However, if too much of H₂O₂ was added, the excess free H₂O₂ would have the capability to inhibit the crosslinking process through monomeric bridges.

The maximum crosslink density (16 × 10⁻¹⁸ c.1/ml) of the film was achieved by adding about 2.5 phr of 30% H₂O₂ solution (corresponding to 0.75 phr of pure H₂O₂) and irradiating the latex at 10 kGy. This maximum crosslink density could also be achieved by adding about 5.0 phr of 10% H₂O₂ solution (corresponding to 0.5 phr of pure H₂O₂) also at 10 kGy irradiation dose. With 1% H₂O₂ solution, it was estimated that 50 phr of the solution was required for maximum crosslink density.

The effect of irradiation dose on the film tensile strength is shown in Fig. 4. The results showed that the addition of 2.5 phr 30% H₂O₂ solution enhanced the tensile strength and decreased the optimum irradiation dose from about 22 kGy to about 17 kGy.

At similar irradiation dose, a higher crosslink density was also observed for film prepared from latex irradiated in the presence of 2.5 phr 30% H₂O₂ solution (Fig. 5). In order to obtain a film with crosslink density of 17.7 × 10⁻¹⁸ c.1/ml, an irradiation dose of about 22 kGy was required for latex with no H₂O₂ whereas about 17 kGy was required for latex added with 2.5 phr 30% H₂O₂ solution. It appeared that this was in agreement with the irradiation dose for maximum tensile strength. It should be noted that a crosslink density of about 17.7 × 10⁻¹⁸ c.1/ml is the least amount of crosslinks needed to obtain a totally three-dimensional network throughout the NR matrix. Too much crosslinks in a molecule will hinder crystallization of the molecule under stretching and consequently reduces the tensile strength of the film.

Figure 6 shows the effect of irradiation dose on the modulus of the film. The modulus increased as the irradiation was increased and was higher in the presence of H₂O₂. These results were also in agreement
with the increase of crosslink density with increasing irradiation dose.

4. Conclusion

The addition of small amounts (0.5 to 0.75 phr) of H$_2$O$_2$ to NR latex before irradiation caused a slight reduction in the optimum irradiation dose from about 22 kGy to about 17 kGy with a sensitizer system consisting of 1 phr CCl$_4$ and 1 phr n-BA.

References

Fig. 1 Effect of adding hydrogen peroxide on the viscosity of the RVNRL.

Fig. 2 Effect of adding hydrogen peroxide to NR latex before irradiation on the tensile strength of the RVNRL film. Dose of irradiation = 10 kGy.
Fig. 3  Effect of adding hydrogen peroxide to NR latex before irradiation on the crosslink density of the RVNRL film. Dose of irradiation = 10 kGy.

Fig. 4  Effect of irradiation dose on the tensile strength of the RVNRL film with or without hydrogen peroxide addition before irradiation.
Fig. 5 Effect of irradiation dose on the crosslink density of the RVNRL film with or without hydrogen peroxide addition before irradiation.

Fig. 6 Effect of irradiation dose on the modulus of the RVNRL film with or without hydrogen peroxide addition before irradiation.
5.20 n-Butyl Acrylate as a Sensitizer for Radiation Vulcanization of Natural Rubber Latex

CHEN ZHONGHAI\(^1\) and K. Makuuchi\(^2\)

1) The Research Institute of Latex Industry, Ministry of Chemical Industry, Zhuzhou, Hunan, People's Republic of China
2) Takasaki Radiation Chemistry Research Establishment, JAERI, Takasaki, Gunma, Japan

Abstract

As a sensitizer for radiation vulcanization of NR latex n-butyl acrylate (n-BA) has several advantages such as high sensitizing efficiency and easiness of removal of residue by drying. However n-BA tends to destabilize NR latex. A study to stabilize NR latex against n-BA has been carried out. The most effective stabilizer is potassium hydroxide. By the addition of 0.2 phr KOH the stability of NR latex is sufficiently improved to withstand the addition of 5 phr n-BA. The sensitizing efficiency of n-BA is so high that the vulcanization dose is 15 kGy with 5 phr n-BA without the addition of carbon tetrachloride as a co-sensitizer. The radiation vulcanized NR latex has enough stability for a 90 days storage.

1. Introduction

Recently the radiation vulcanized natural rubber (NR) latex was used for a test production of rubber gloves\(^1\). Physical properties of the gloves met the specification of Japanese Industry Standard JIS K 4301 for protective rubber gloves for radioactive contamination. However the smell of the gloves was bad due to the presence of trace amount of 2-ethylhexyl acrylate (2EHA) which was used as the sensitizer for radiation vulcanization of NR latex (RNWRL) together with carbon tetrachloride (CCl\(_4\)) (weight ratio:2EHA/CCl\(_4\)=4/1) which was developed by Devendra and Makuuchi\(^2\). It was also anticipated that the remaining 2EHA will cause skin irritation to the users of the gloves. It is hard to remove the remaining 2EHA in the gloves due to low vapor pressure of the monomer. It is also hard to polymerize completely the remaining 2EHA in the latex. Further irradiation than vulcanization dose results in a lowering of the
physical properties of latex rubber. Other monomers which have high
vapor pressure than 2EHA were tested to replace 2EHA. Among monofunc-
tional acrylates n-butyl acrylate (n-BA) was selected as a substitute
of 2EHA because n-BA has higher vapor pressure and sensitizing efficiency
on RVNRL than 2EHA. However n-BA is not suitable as a sensitizer be-
cause it tends to destabilize NR latex. For instance NR latex containing
5 phr n-BA coagulates within several hours.

In this paper, stability of NR latex containing n-BA is discussed.
A simple method has been developed to improve the stability sufficient
to withstand the addition of 5 phr n-BA. In addition, the physical prop-
erties of the radiation vulcanized NR latex with n-BA are reported.

2. Experimental

2.1 Materials

Commercially available high ammonia NR latexes were used. Industrial
grade acrylic monomers, 2EHA and n-BA containing 15 phr MEHQ were sup-
plied from Toa Gousei Chemical Industries Co. Ltd., Japan. Other chemi-
cals such as potassium hydroxide (KOH), CCl₄, toluene and ligroin were
purchased from Wako Pure Chemical Industries Co. Ltd., Japan. Surfactants
used were sodium lauryl sulfate (SLS), potassium laurate (LK-2, Nippon
Oil & Fats Co. Ltd.), polyethylene glycol alkylphenylether (EA160, Dai-
ichi Kogyo Seiyaku Co. Ltd., HLB:16), polyoxyethylene (20) sorbitan
monolaurate (Twee 80, HLB:10.5) and polyoxyethylene (20) sorbitan
monooleate (Twee 60, HLB:15.6). All chemicals were used without further
purification.

2.2 Sample preparation and irradiation

NR latex was diluted with ammonia solution (1.7%) to reduce the
total solid contents to 50%. A sensitizer was added to the diluted NR latex while stirring. Stirring was continued for more than one hour
and the mixture was left overnight. The mixed NR latex was poured into
50 ml screw capped glass bottles then irradiated with gamma-rays from
Co-60 sources. Dose rate was 10 kGy/h, unless otherwise noted.

2.3 Measurement of viscosity

The apparent viscosity (viscosity) of NR latex was measured at 25°C
by a coneplate type rotary viscometer model EMD made by Tokyo Keiki Co.
Ltd., Japan. Since NR latex is a typical non-Newtonian fluid, the viscosity depends on the shear rate. The revolving speed of the cone rotor was kept at 100 rpm (shear rate: 384.0/sec). The range of measurable viscosity is between 13-128 cP at this shear rate.

2.4 Film preparation and tensile testing
Films were prepared by casting about 30 g of the irradiated NR latex onto glass plates, 17 cm x 11 cm. Films dried at room temperature were immersed in distilled water for one night to leach out water soluble components from the films. The films then dried at room temperature and heated at 70°C for one hour. The tensile testing was carried out at room temperature with a tensile testing machine, Strograph model R1 made by Toyo Seiki Seisakusyo Ltd. The crosshead speed was 500 mm/min.

2.5 Measurement of swelling ratio
Small piece of the films were immersed in toluene at room temperature for one week. Swelling ratio was calculated from the weight change of sample.

3. Results and Discussion

3.1 Stabilization of NR latex against n-BA
Viscosity of NR latex containing n-BA is used as a measure of stability of NR latex against n-BA. Table 1 presents viscosity changes of NR latexes containing various amount of n-BA/CCl₄ (weight ratio: 4/1). The viscosity increases with increasing the concentration of n-BA. The viscosity also increases with storage time except latexes containing 1 and 2 phr n-BA/CCl₄. The latex containing n-BA/CCl₄ more than 3 phr is coagulated after storage for one night. While the NR latex containing 1 phr n-BA/CCl₄ is quite stable even after storage for 11 days as shown in Fig. 1. However 1 phr n-BA/CCl₄ is not sufficient to enhance the radiation vulcanization of NR latex.

Several surfactants were added to NR latex before the addition of n-BA/CCl₄ to improve the stability of NR latex sufficient to withstand the addition of 5 phr n-BA/CCl₄. The effect of surfactants on the viscosity of NR latex containing 5 phr n-BA/CCl₄ is summarized in Table 2. An alkyl sulfate, SLS has higher stabilizing effect than a fatty acid soap, LK-2. Stabilizing effect of nonionic surfactants were less than
that of anionic SLS. Among nonionic surfactants EA160 having HLB value of 16 shows the highest stabilizing effect. However these surfactants are not sufficient to withstand the addition of 5 phr n-BA/CCl₄. It was found that KOH has excellent stabilizing effect. The NR latex containing 0.5 phr KOH and 5 phr n-BA/CCl₄ still remains low viscosity even after 20 days as shown in Table 2.

The stability of NR latex also decreases when hydrophilic polyfunctional monomers such as neopentylglycol diacrylate (A-NPG) was added to the latex⁴. This destabilization is due to the formation of hydrogen bonds between NR particles through A-NPG molecules which are localized on the surface of NR particles. The stability can be improved by increase in the solubility of A-NPG into the NR particles by the addition of solvents such as ligroin and benzene. However ligroin does not stabilize NR latex against n-BA. This means that the destabilization of latex by n-BA is not caused by the hydrogen bonding between NR particles. The fact that KOH acts as an excellent stabilizer suggests that specific interaction between adsorbed n-BA and materials containing carboxyl groups on the rubber surface caused the destabilization of latex against n-BA. The role of KOH is to modify the surface materials by ionization of carboxyl groups. This interaction is thought to be so strong that the solubility on n-BA in rubber particles dose not increase by the addition of ligroin.

Minimum concentration of KOH to stabilize NR latex against the addition of 5 phr n-BA is 0.2 phr. Another important factor in terms of latex stabilization is a colloidal stability against irradiation. The effect of irradiation on the viscosity of NR latex containing 5 phr n-BA and 0.2 phr KOH is shown in Fig. 2. The viscosity is decreased by the irradiation. This means that n-BA concentration on rubber particles is reduced by radiation-induced polymerization.

3.2 Physical properties of radiation vulcanized latex films

Figure 3 shows the effect of dose on the tensile strength (Tb) of latex films prepared from the NR latex irradiated in the presence of 5 phr CCl₄, n-BA and n-Ba/CCl₄. Figure 4 and 5 show elongation at break (Eb) and swelling ratio of the same rubber films. A maximum tensile strength (max Tb) was not achieved with radiation dose of 60 kGy when the latex irradiated without sensitizer. While a max Tb was obtained at 40 kGy in the presence of CCl₄. The dose to achieve a max Tb (vul-
canization dose) was reduced to 15 kGy by the addition of n-BA. Contrary to expectations, the addition of CCl₄ to n-BA dose not reduce the vulcanization dose. However data of Eb and swelling ratio indicate that CCl₄ enhances slightly the sensitizing effect of n-BA.

The effect of the concentration of n-BA on max Tb and vulcanization dose is summarized in Fig. 6. The vulcanization dose decreases with increasing n-BA concentration. At high concentration of n-BA Tb decreases slightly. The maximum Tb is obtained at 4 phr n-BA.

The effect of dose rate of γ-rays on the radiation vulcanization of NR latex sensitized with 5 phr n-BA is shown in Fig. 7. The dose rate is controlled from 0.5 kGy/h to 10 kGy/h by varying the distance from the Co-60 sources. The Tb decreases slightly with increasing dose rate. Vulcanization dose, however, does not affected by dose rate.

The storage stability of the radiation vulcanized NR latex is shown in Table 3. Physical properties such as Tb and Eb are not influenced by storage time. It can be concluded that the radiation vulcanized NR latex has a high storage stability.

4. Conclusion

Following conclusion are derived from the above results.
- The stability of NR latex against n-BA is improved by the addition of KOH.
- The sensitizing efficiency of n-BA is sufficient for RVNRL without co-addition of CCl₄.
- A maximum tensile strength is obtained by irradiation to 15 kGy with 5 phr n-BA.
- The storage stability of the radiation vulcanized NR latex is enough for a 90 days storage.

References

Table 1  Effect of concentration of n-BA/CCl₄ mixture (weight ratio:n-BA/CCl₄ = 4/1) and storage time on viscosity of NR latex

<table>
<thead>
<tr>
<th>Storage (days)</th>
<th>VISCOSITY (cP)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
</tr>
<tr>
<td>1 phr n-BA/CCl₄</td>
<td>15</td>
</tr>
<tr>
<td>2 phr n-BA/CCl₄</td>
<td>15</td>
</tr>
</tbody>
</table>

X : viscosity higher than 128 cP

Table 2  Effect of surfactants on the viscosity of NR latex containing 5 phr n-BA/CCl₄

<table>
<thead>
<tr>
<th>Storage (days)</th>
<th>VISCOSITY (cP)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
</tr>
<tr>
<td>KOH</td>
<td>14</td>
</tr>
<tr>
<td>LK-2</td>
<td>15</td>
</tr>
<tr>
<td>SLS</td>
<td>14</td>
</tr>
<tr>
<td>EA160</td>
<td>15</td>
</tr>
<tr>
<td>Tween 60</td>
<td>15</td>
</tr>
<tr>
<td>Tween 80</td>
<td>15</td>
</tr>
</tbody>
</table>

X : viscosity higher than 128 cP
XX : coagulated

Table 3  Storage stability of radiation vulcanized NR latex with 5 phr n-BA in the presence of 0.2 phr KOH. Latex films were prepared every 15 days

<table>
<thead>
<tr>
<th>Days</th>
<th>Tensile strength (MPa)</th>
<th>Elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>29</td>
<td>980</td>
</tr>
<tr>
<td>15</td>
<td>29</td>
<td>980</td>
</tr>
<tr>
<td>30</td>
<td>31</td>
<td>900</td>
</tr>
<tr>
<td>45</td>
<td>29</td>
<td>940</td>
</tr>
<tr>
<td>60</td>
<td>29</td>
<td>940</td>
</tr>
<tr>
<td>75</td>
<td>30</td>
<td>1000</td>
</tr>
<tr>
<td>90</td>
<td>30</td>
<td>970</td>
</tr>
</tbody>
</table>
Fig. 1 Effect of concentration of n-BA/CCL₄ mixture (weight ratio: n-BA/CCL₄=4/1) and storage time on viscosity of NR latex.

Fig. 2 Effect of irradiation on viscosity of NR latex in the presence of 0.2 phr KOH and 5 phr n-BA. The latex was stored for one night at room temperature before irradiation.
Fig. 3 Effect of sensitizer on the tensile strength. Samples were prepared from the NR latex irradiated in the presence of 5 phr CCl₄, n-BA and n-BA/CCl₄.

Fig. 4 Elongation at break of the same sample in Fig. 3.
Fig. 5  Swelling ratio of the same sample in Fig. 3.  Fig. 6  Effect of the concentration of n-BA on the maximum tensile strength and vulcanization dose.
Fig. 7 Effect of dose rate of γ-rays on the radiation vulcanization of NR latex sensitized with 5 phr n-BA.
5.21 Radiation Vulcanization Mechanism of Liquid Isoprene with 2-Ethylhexyl Acrylate

CHYAGRIT SIRI-UPATHUM\textsuperscript{1)}, K. Makuuchi\textsuperscript{2)} and I. Ishigaki\textsuperscript{2)}

1) Faculty of Engineering, Chulalongkorn University, Bangkok, Thailand
2) Takasaki Radiation Chemistry Research Establishment, Takasaki, Japan.

Abstract

The mechanism of radiation vulcanization of liquid isoprene rubber (LIR) with 2-ethylhexyl acrylate (2-EHA) monomer has been investigated as part of a development of new sensitizer for radiation vulcanization of natural rubber latex (RVNRL). To elucidate the mechanism, intermediate products formed during the vulcanization were isolated and determined for their chemical functionalities by \textsuperscript{13}C-NMR and FT-IR techniques. The intermediate products isolated were confirmed to contain chemical functionalities both from LIR and 2-EHA with vinyl double bond still existed. This suggested that the crosslinking to form three-dimensional network was through the grafted products of 2-EHA onto the backbone of LIR while the unreacted pendant double bonds in 2-EHA molecules served as the reactive sites for such crosslinking.

1. Introduction

Some acrylic monomers such as 2-ethylhexyl acrylate (2-EHA) and n-butyl acrylate (n-BA) have been found to enhance the radiation vulcanization of natural rubber latex (RVNRL)\textsuperscript{1). Prior to this discovery, CCl\textsubscript{4} and some polyfunctional monomers (PFM) were used and were proposed to be used as sensitizers for RVNRL respectively\textsuperscript{2-5). The advantages of 2-EHA over CCl\textsubscript{4} as sensitizer for RVNRL are low toxicity of the former and excellent heat resistance of rubber products prepared from the latex. 2-EHA is also readily soluble in NR latex and needs no co-addition of a solvent like PFM. Relatively lower price of 2-EHA than PFMs is another main factor to consider 2-EHA as a suitable sensitizer for RVNRL.

It is normally believed that the polyfunctionality of a monomer is essential to enhance the radiation crosslinking. A general accepted mechanism is a 2-step reaction: a graft polymerization of PFM onto the
backbone of the polymers occurs first and subsequently pendant chains containing double bonds are formed\(^6\)-\(^7\). In the case of 2-EHA and n-BA, they are monofunctional monomers (i.e. contain one C = C bond) and cross-linking (entanglement) model has been proposed based on GPC measurement of molecular weight distribution of irradiated LIR and 2-EHA\(^1\). In the present investigation, the elucidation of radiation vulcanization mechanism has been studied to obtain the possible crosslinked product structure of LIR with 2-EHA.

2. Experimental

2.1 Material

The LIR used was of high trans 1,4-addition of molecular weight 28,000 supplied from Kuraray Co. Japan. This liquid polyisoprene was used as a model polymer for NR to avoid the complexity of NR latex. 2-EHA, tetrahydrofuran (THF), chloroform, methanol were all chemically pure and used as obtained.

2.2 Irradiation

Mixtures of 2-EHA and LIR of weight ratio: 50/50, 20/80, 10/90 and 5/95 were conditioned and degassed 2-3 times at 0.005 torr in glass ampules at liquid nitrogen temperature. Irradiations were carried out with a 10 kGy/h \(^{60}\)Co source at room temperature at doses ranging from 5 to 60 kGy.

2.3 Method

The structure of LIR radiation-vulcanized with 2-EHA was studied by analysing the irradiated mixtures. If vulcanization has taken place through covalent bonding between LIR and 2-EHA, the intermediate products will be grafted products of 2-EHA molecules on to the backbone of the LIR, and their molecular weight will increase. The molecular weight will not increase if the entanglement is the predominant mechanism. Further confirmation were done by the analyzing the chemical functionality of the intermediate products after isolation from the irradiated mixtures by using \(^{13}\)C-NMR and FT-IR. The intermediate products were isolated by means of preparative GPC.
2.4 Measurements

The irradiated mixture of LIR and the monomer was dissolved in THF and the molecular weight distribution was measured with a high performance liquid chromatograph (HLC-802 R, Toyo Soda Manufacturing Co Ltd) operated at 40°C with four GPC columns. Gel content and degree of conversion of 2-EHA were done by measuring the weight loss after dissolution in THF and CH₃OH at 80°C and at room temperature for 24 hours respectively.

To confirm the identification of the intermediate products, $^{13}$C-NMR spectra and FT-IR absorption bands of such products were measured. (A GSX FT NMR spectrometer, JEOL and a JIR-100D, JEOL were used). Irradiated mixture solution in CHCl₃ was isolated for intermediate products using HLC-837 (Toyo Soda Manufacturing Co Ltd) with 1 inch diameter, 2 GPC columns.

3. Results and Discussion

3.1 Surveys of the Intermediate Products Formed

Figure 1(a), 1(b) and 1(c) indicate radiation induced polymerization of LIR with 2-EHA at various doses for 2-EHA concentration of 5, 10 and 20% respectively. As seen in the figures, the higher the doses and the higher the 2-EHA content, the higher the gel fraction obtained with only slight changes in the degrees of conversion which were generally greater than 80% from a dose of 10 kGy. Homo (poly 2-EHA) and the presumed grafted products of 2-EHA and LIR so formed during the earlier stages of vulcanization were thus formed at relatively low doses and low 2-EHA contents in LIR. The non existence of these intermediate products at high 2-EHA concentration and at high irradiation doses suggested that the reaction had proceeded to the final crosslinked product. Figure 2(a), 2(b), 2(c) and 2(d) show the GPC chromatograms of irradiated product in THF and filtered through 0.45 µm filter disc. At low doses or low concentration of 2-EHA in LIR, there existed two fractions which showed higher molecular weight distribution than LIR. Figure 3 shows the fraction of intermediate products formed in irradiated LIR with 2-EHA at various doses. [Higher content of the two intermediate products combined with respect to unreacted LIR in the irradiated mixture could be obtained from 50 kGy irradiation of 5% 2-EHA in LIR. This dose and this 2-EHA concentration were selected to prepare intermediate products for further chemical functionality analyses].
Irradiation of the LIR alone did not show any branched or crosslinked product up to a dose of 60 kGy as observed by GPC chromatogram and % gel content respectively. Only some degraded products were found from doses of 50 kGy and higher. Their Mn and Mw values at various doses are shown in Fig. 4.

Irradiation of 2-EHA alone gave crosslinked product and homo poly (2-EHA). Their gel content and degree of conversion at various doses are shown in Fig. 5. It is evident that 2-EHA is very reactive to cross-linking by irradiation despite of its monofunctionality. In Fig. 6 it is shown the molecular weight distribution of homo poly (2-EHA) formed by the irradiation of 2-EHA at various doses. Figure 7 shows the molecular weight of irradiated 2-EHA at different doses. The lowering of the molecular weight of homo poly (2-EHA) with higher radiation doses made the identification of homo poly (2-EHA) in irradiated products of LIR with 2-EHA difficult by GPC.

3.2 Isolation of the Intermediate Products

Figure 8 shows the GPC chromatogram of product mixture of 5% 2-EHA in LIR after irradiation at 50 kGy. Two components with Mn of 880,000 and 1,300,000 and Mw 120,000 and 165,000 were isolated by preparative GPC. Two other components shown in the chromatogram in Fig. 8 are unreacted LIR and 2-EHA respectively.

3.3 Analyses of the Intermediate Products

Chemical functionality of the two intermediate products were examined by using $^{13}$C-NMR and FT-IR techniques. Figure 9 shows the $^{13}$C-NMR spectra of 2-EHA, LIR and isolated Fraction 1. $^{13}$C-NMR of Fraction 2 was exactly the same as that of Fraction 1 and is not shown in this figure. It can be seen from these spectra that signals from both 2-EHA and LIR are present in Fraction 1 spectrum. Three different signals from Fraction 1 spectrum at 132.31, 130.89 and 128.82 ppm correspond to C = , -CH= and H-C-structures respectively, signifying that the intermediate products contain these functionalities.

FT-IR spectra of these isolated two fractions show the presence of all absorption bands expected from both LIR and 2-EHA. The extent of grafting is determined by the absorbance ratio at 836 cm$^{-1}$ (C = C of 1,4-polyisoprene) and at 1375 cm$^{-1}$ (-CH group in the isolated fractions) as shown in Table 1. These values are significantly decreased by some 20%
for Fraction 1 and 17% for Fraction 2, thus confirming the presence of grafted products. The reduction in the relative intensity of poly-isoprene double bond to CH$_3$ group in Fraction 2 compared to that of Fraction 1 also confirmed the lower molecular weight (lower number of 2-EHA molecules grafted) of Fraction 2 than Fraction 1 as indicated by the GPC chromatogram in Fig. 8.

3.4 Postulation of Grafted Product Structures

The presence of C = and HC = structures in the $^{13}$C-NMR spectra of the intermediate products suggests that the formation of \( \cdot \text{CH} = \text{CH} - \text{COOR} \) radical during the irradiation process. The formation of this radical was proposed by Rao and Rao$^5$ and the chain transfer is through the \( = \text{C} - \cdot \text{O} \) radical. After the abstraction of a H atom from position 1 of the acrylate, the proposed radical and alcohol with alkene unsaturation are formed.

Infrared spectra on the irradiated 2-EHA in this investigation have also indicated the presence of - OH group and \( = \text{C} \equiv \text{C} - \text{structure.} \) The formation of the proposed radical is thus possible and it is to be adapted here to illustrate the crosslinking of LIR with 2-EHA by radiation.

A tentative mechanism for the formation of the intermediate products with double bonds formed at side chains is as follows:

\[
\text{CH}_2 = \text{CH} - \text{COOR} \xrightarrow{\gamma} \cdot \text{CH} = \text{CH} - \text{COOR} \\
(\text{I}) \hspace{2cm} (\text{II})
\]

As this acrylate free radical is more mobile than the LIR chain, it attacks a double bond in an adjacent chain.

\[
\text{CH} = \text{CH} - \text{COOR} \\
\text{II} + \cdot \text{CH}_2 - = \text{CH} = \text{CH}_2 \rightarrow \cdot \text{CH}_2 - = \text{CH} = \text{CH}_2 \\
\text{CH}_3 \hspace{1cm} \text{CH}_3 \\
(\text{III}) \hspace{2cm} (\text{IV})
\]

This LIR free radicals may abstract a H atom from one of the methylene group in an adjacent polymer chain and the newly formed rubber free radicals may recombine with the proposed radical. This results in the formation of intermediate products.
III + IV $\longrightarrow$ $\searrow\text{CH} - \text{C} = \text{CH} - \text{CH}_2\searrow + \text{V}$
(adjacent chains)

$\searrow\text{CH}_2 - \text{C} = \text{CH} - \text{CH}_2\searrow$

$\text{CH}_3$

(V)

$\text{CH} = \text{CH} - \text{COOR}$

(VI)

$\text{CH} = \text{CH} - \text{COOR}.$

II + V $\longrightarrow$ $\searrow\text{CH} - \text{C} = \text{CH} - \text{CH}_2\searrow$

$\text{CH}_3$

(VII)

2-EHA radical may attack the above intermediate. Although this seemed likely, the presence of $\text{C} = \text{C}$ structure in the $^{13}\text{C}$-NMR spectrum suggests this to be so.

VII + $\searrow\text{CH}_2 - \text{CH}$

O

$\text{CH} = \text{CH} - \text{COOR}$

OR

$\searrow\text{CH} - \text{C} = \text{CH} - \text{CH}_2\searrow$

$\text{CH}_3$

(VIII) + $\searrow\text{CH}_2 - \text{CH}$

O

R

CH = CH - COOR

VIII + II $\longrightarrow$ $\searrow\text{CH} - \text{C} = \text{CH} - \text{CH}_2\searrow$

$\text{CH}_3$

(IX)

4. Conclusions

The radiation vulcanization of LIR with 2-EHA follows a chemical crosslinking mechanism. The formation of a three-dimensional network is through the grafting of 2-EHA onto the backbone of the LIR with the pendant double bonds in 2-EHA molecules serving as the active site for the network formation.

Acknowledgements

The authors would like to thank Mr. N. Hayakawa and M. F. Hosoi, Department of Development, Takasaki Radiation Chemistry Research Estab-
lishment (TRCRE) for valuable $^{13}$C-NMR spectra and FT-IR spectra. One of us (C.S.) would like also to appreciate the support of the scientist exchange program for a period of 6 months at TRCRE from Science and Technology Agency (STA) Japan to conduct this research work.

References

<table>
<thead>
<tr>
<th></th>
<th>R.I.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Original LIR</td>
<td>0.5917</td>
</tr>
<tr>
<td>Irradiated LIR</td>
<td>0.5969</td>
</tr>
<tr>
<td>(50 kGy)</td>
<td></td>
</tr>
<tr>
<td>Isolated fraction 1</td>
<td>0.4723</td>
</tr>
<tr>
<td>Isolated fraction 2</td>
<td>0.4937</td>
</tr>
</tbody>
</table>

![Graphs showing gel content and conversion degree of irradiated LIR with 2EHA](image)

Fig. 1 Gel content and conversion degree of irradiated LIR with 2EHA
(Δ% conversion, ◦% gel)
Fig. 2 Molecular weight distribution of irradiated LIR with 2EHA
Fig. 3  Fraction of intermediate products formed in irradiated LIR with 2EHA (with respect to unreacted LIR)

Fig. 4  Molecular weight distribution of irradiated LIR
Fig. 5 Gel content and conversion degree of irradiated ZEHA
Fig. 6 Molecular weight distribution of irradiated 2EHA
Fig. 7 Molecular weight distribution of irradiated 2EHA

Fig. 8 GPC chromatogram from a preparative GPC of irradiated products in 5% 2EHA with LIR irradiated to 50 kGy; intermediate products: fraction 1 and 2 were isolated and collected
Fig. 9 $^{13}$C-NMR spectra of 2EHA, LIR and isolated fraction 1
RVNRL WITH ELECTRON BEAMS AND NEW IRRADIATOR FOR RVNRL

5.22 Radiation Vulcanization of Natural Rubber Latex Using 300 keV Electron Beam Machine

W. Sofiarti, MARGA UTAMA and F. Sundardi

Centre for the Application of Isotopes and Radiation, J. Cinere Pasar Jumat, Jakarta Selatan, Indonesia

Abstract

A study has been done on radiation vulcanization of natural rubber (NR) latex using an Electron Beam (EB) Machine of 300 keV. The penetration range of the beam in NR latex is between 0.3 mm and 0.4 mm. The effect of sensitizer was also studied. The optimum dose of irradiation is about 250 kGy for NR latex without sensitizer, while using 4 phr of CCl₄ as a sensitizer the optimum dose decreases to about 140 kGy, and to about 120 kGy by using a mixture of CCl₄/n-BA as sensitizer. A NR latex having a green strength of the film about 2 MPa was used in this experiment, which yielding a maximum tensile strength about 18 MPa for the film prepared from the irradiated NR latex. A tensile strength of about nine time of its green strength has been achieved. A comparison study with the film prepared from Co-60 irradiation of NR latex has been made. It was found that without sensitizer, the optimum dose of irradiation was almost the same, which was about 250 kGy. Sensitizing effect of CCl₄ or a combination of CCl₄/n-BA were not as good as in gamma irradiation. It was concluded that EB irradiation of NR latex showing almost the same effect as gamma irradiation, except the small effect of sensitizer for EB irradiation of NR latex.

1. Introduction

Radiation vulcanization of natural rubber (NR) latex using gamma rays of Co-60 had been studied for years and now coming to its commercialization. One of the handicap of using radiation technology is the high cost of irradiation using gamma rays of Co-60. With the increasing in price of Co-60 in the last five years, from US$1.00 to US$1.75 per Ci, the irradiation cost of NR latex will be much affected.
It is therefore necessary to study the application of electron beam (EB) for irradiation of NR latex, where the irradiation cost expected to be much lower than that for gamma irradiation. Another advantage in using EB machine is that it can be shut down if unused. One of the handicap in using EB irradiation is the low penetration of the beam on matter such as NR latex. For a 300 keV EB machine, the beam penetration is about 0.3 mm in NR latex, and becoming about 3 mm for 3 MeV EB machine. In this case a special irradiation chamber is needed to meet the requirement. It appears that EB machine will become the future irradiation source for many radiation processing application\(^{1-6}\).

This paper presents the results of the preliminary study on EB irradiation of a thin layer of NR latex. The effect of CCl\(_4\) and n-butyl acrylate (n-BA), the optimum dose of irradiation, and the physical properties of the film are presented. The physical properties of the film compared to that one prepared from gamma irradiation of NR latex.

2. Experimental

Concentrated NR latex was from Pasir Waringin, West Java, and was used without dilution. The rubber content of the concentrated latex was about 60\%. The sensitizer used were CCl\(_4\) and n-BA, and were used without purification. These sensitizers were blended with NR latex in the form of an emulsion in water. Both, the latex samples either with or without sensitizer, were poured in a glass plate up to a thickness between 0.2 and 0.3 mm. This is suitable thickness for EB irradiation of 300 keV. This sample was then irradiated with various dose of irradiation from 20 kGy up to 200 kGy, using a beam current of 20 mA. An inert gas (N\(_2\)) was flown into the irradiation chamber, and the dose of irradiation was determined by adjusting the conveyor speed. Figure 1 shows the relation between conveyor speed and irradiation dose.

Irradiated samples were then dried at room temperature and removed from the glass plates. The removed samples were tested without leaching. The physical properties of the film such as tensile strength, modulus, elongation at break etc. were determined by using Instron Testing Machine, Model 1122. Gel fraction of the films were determined by extraction of the samples with benzene for about 48 hours. The weight of the samples was measured before and after extraction.

A comparison study was also made with the film prepared from gamma
irradiated NR latex from the same NR latex. Irradiation was carried out in glass tubes, in a Co-60 irradiation chamber, at room temperature. The thickness of those samples was about 0.1 mm. The dry samples were removed from the plates and the physical properties were determined.

3. Results and Discussion

Figure 2 shows that the optimum dose of EB irradiation of NR latex is about 250 kGy. The maximum tensile strength of films prepared from EB irradiated NR latex is about 20 MPa, using a NR latex with the green strength of about 2 MPa, that is about ten times of its green strength. Using CCl4 sensitizet (4 phr), the optimum dose of irradiation is found about 150 kGy, which is lower than that without CCl4. In this case the maximum tensile strength of the film is about 18 MPa, which is about nine times of its green strength. Using a combination of CCl4 and n-BA as a sensitizet, the optimum dose of irradiation will be more lower, which is about 120 kGy, with a maximum tensile strength of 18 MPa. It appears that both CCl4 or n-BA in an EB irradiation of NR latex still showing a sensitizing effect, although not as good as in a gamma irradiation. This is probably due to the very high irradiation dose rate for EB irradiation compared to gamma irradiation. For an information, typical EB irradiation dose rate is usually up to several of ten thousands kGy/hour, which is about several thousand times of that gamma irradiation dose rate.

Modulus of the film prepared from EB irradiated NR latex showing a higher value in case of using CCl4 or CCl4/n-BA sensitizers compared to that without sensitizet. It indicates a higher crosslink density of the film prepared from EB irradiation using CCl4 or combination of CCl4/n-BA. Figure 3 shows that modulus increases with increasing in dose of irradiation. The increase of modulus is proportional with the irradiation dose. A combination of CCl4 and n-BA showing a better sensitizing effect than that CCl4 alone. In order to achieve the same modulus for the three kinds of films, for instance 2.5 MPa for modulus 600%, the NR latex without sensitizet needs an EB irradiation dose about 220 kGy, with CCl4 needs about 150 kGy, while with CCl4/n-BA needs only about 130 kGy.

Figure 4 shows the effect of EB irradiation on gel fraction of the film in benzene. A higher gel fraction of film is shown by the film
prepared from EB irradiation of NR latex using CCl₄ or combination of CCl₄/n-BA compared to that without the sensitizer. A higher gel fraction is also indicating a higher crosslink density. It is found that the gel fraction reaches a maximum value at irradiation dose less than 100 kGy, much lower than the optimum dose of EB irradiation of NR latex, with or without sensitizer. The soluble fraction in benzene consists of non rubber material such as ester, low molecular weight hydrocarbon, and uncrosslink natural rubber. Low molecular weight NR causes a difficulty in reaching a three dimensional network, and this fraction easily soluble in benzene. So a high soluble fraction of irradiated NR latex in benzene indicates a high fraction of low molecular weight of NR in the film.

Figure 5 shows the effect of irradiation dose on the physical properties of the film prepared from gamma irradiated NR latex. It appears that the effect of CCl₄ or a combination of CCl₄/n-BA on the optimum dose of gamma irradiation of NR latex is more significant than that of EB irradiation. The optimum dose of gamma irradiation of NR latex is about 30 kGy using a combination of CCl₄/n-BA, and about 40 kGy using CCl₄ alone (4 phr). The optimum irradiation dose for NR latex without sensitizer is about 250 kGy, almost the same as using EB irradiation. The maximum tensile strength of the film is also almost the same as using EB irradiation.

4. Conclusion

EB irradiation of NR latex has almost the same effect as gamma irradiation. The effect of sensitizer in EB irradiation of NR latex is smaller than by gamma irradiation.

References

2. MILLER, S.M., SPINDLER, M.W., and VALE, R.L., Proceeding of Symposium on Industrial Uses of Large Radiation Sources, Salzburg (1963)
4. SUNDAARDI, F., Majalah BATAN, IX (4) (1976)
5. SUNDAARDI, F., Plastic and Rubber Processing and Application, 5, (1985)
6. YANTI SABARINAH S., and F. SUNDARDI, Pertemuan ilmiah proses radiasi dalam industri, sterilisasi dan aplikasi teknik nuklir dalam hidrologi, Jakarta, Desember (1988)
Fig. 1 Relation between conveyor speed and EB irradiation dose for various beam current

Fig. 2 Influence of EB irradiation on NR latex, with or without sensitizer
Fig. 3 Influence of EB irradiation on NR latex, with or without sensitizer

Fig. 4 Effect of EB irradiation on gel fraction in benzene of NR film prepared from irradiated latex, with or without sensitizer
Fig. 5 Effect of gamma rays irradiation on tensile strength of NR film prepared from irradiated NR latex, with or without sensitizer
5.23 Radiation Vulcanization of Natural Rubber Latex with 3 MeV Electron Beams (Part 1)

CHEN ZHONGHAI\(^1\) and K. Makuuchi\(^2\)

1) The Research Institute of Latex Industry, Ministry of Chemical Industry, Zhuozhou, Hunan, People's Republic of China
2) Takasaki Radiation Chemistry Research Establishment, JAERI, Takasaki, Gunma, Japan

Abstract

The sensitized radiation vulcanization of natural rubber latex has been carried out with a 3 MeV, 25 mA Dynamitron electron accelerator. Latex was irradiated over a range of dose rate from 0.3 to 60 kGy/sec in the presence of sensitizers such as \( \text{n-butyl acrylate}, 2\)-ethylhexyl acrylate, and 1,6-hexanediol diacrylate. The sensitized vulcanization of NR latex with electron beams is greatly affected by dose rate. The vulcanization dose increases with increasing dose rate. The maximum tensile strength of rubber films from the irradiated latex decreases slightly with increasing dose rate. There is negligible effect of dose rate on the viscosity of the irradiated latex.

1. Introduction

Radiation vulcanization of natural rubber latex (RVNRL) has several advantages over the conventional vulcanization with sulfur such as low cytotoxicity and absence of nitorosamine. Reduction in the cost of irradiation has been desired for industrial application of RVNRL. It is widely accepted that the irradiation cost of electron beam (EB) is lower than that of \( \gamma \)-rays\(^1\). Few investigations, however, have been made on the RVNRL with EB. Laizier et al.\(^2\) used a 6 MeV, 10 kW linear electron accelerator to study the feasibility of RVNRL. A pilot plant was installed in the Center for the Application of Ionizing Radiations, Corbeville, French\(^3\). The pilot plant had an irradiation cell with latex circulating pump for continuous vulcanization. The irradiation capacity was more than 1 ton of NR latex per hour. It was reported that the EB irradiated latex and the resulting rubber films exhibit quite good properties which make them suitable for any conventional
use of rubber latex. For instance, the tensile strength (Tb) of films of NR latex was 300 kg/cm² when the latex was irradiated to 10 kGy with EB in the presence of small amount of carbon tetrachloride (CCl₄). It was reported also that there is no dose rate effect in R VNRL.

Liu Wenyi et al. carried out a study on R VNRL with EB with a 2 MeV, 0.15 mA van de Graaff electron accelerator. The NR latex diluted to 50% of total solid contents was irradiated to 300 kGy with a dose rate of 43.2 kGy/h without sensitizer. The latex was stirred during irradiation in a vessel to irradiate homogeneously. Rubber devices such as catheters, tubes for blood transfusion were produced from the irradiated latex for clinical demonstration. These rubber devices exhibited good aging properties and high transparency.

These previous investigations had completed by early 70'. Recently new sensitizer systems consisting of acrylic monomers have been developed. It is worthwhile to study again the R VNRL with EB from technoeconomical point of view. In this paper, we report on the dose rate effect and the sensitizing efficiency of acrylic monomers as the first part of a series of research on R VNRL with 3 MeV EB.

2. Experimental

2.1 Materials

Commercially available high ammonia NR latexes were used. Sensitizer used were n-butyl acrylate (n-BA, containing 15 phr MEHQ, Toa Gousei Chemical Industry Co. Ltd.), 1,6-hexanediol diacrylate (A-HD, containing 100 phr MEHQ, Shin-Nakamura Chemical Co. Ltd.), and a mixture of 2-ethylhexyl acrylate (2EHA, containing 15 phr MEHQ, Toa Gousei Chemical Industry Co. Ltd.) and CCl₄ (weight ratio, 4:1) mixture. Other chemicals such as potassium hydroxide, and toluene were purchased from Wako Pure Chemical Industries Co. Ltd., Japan. All chemicals were used without further purification.

2.2 Irradiation and measurement

NR latex was stabilized with 0.2 phr KOH with 10% KOH aqueous solution, and then diluted with ammonia solution (1.7%) to reduce the total solid contents to 50%. The sensitizer was added to the diluted NR latex while stirring. Stirring was continued for more than one hour.
and the mixture was left overnight. About 100 g of the mixture was poured into polyethylene bags (size; 15 cm x 10 cm, thickness; 0.02 mm). The thickness of the mixture was 0.7 cm. A 3 MeV, 25 mA Dynamitron electron accelerator was used for irradiation. The extrapolated and the effective ranges of 3 MeV EB are 1.51 and 1.06 g/cm in CTA⁸, respectively. The samples were irradiated on a conveyor 20 cm under the beam window. The dose rate was controlled by varying the beam current and the speed of the conveyor. Dose rate was measured with a CTA (cellulose triacetate) dosimetry. The dose per one pass under the beam window is 10 kGy under following conditions: accelerating voltage; 3 MeV, beam current; 1 mA, conveyor speed; 2.17 m/min.

Viscosity, Tb, and swelling ratio were measured according to the previous paper⁶.

3. Results and Discussion

3.1 Effect of sensitizer

The effect of the sensitizers on RVNRL with EB was investigated. Figure 1 presents the Tb of rubber films prepared from the latex irradiated with 3 MeV, 1 mA EB in the presence of 5 phr n-BA. The effect of 5 phr 2EHA/CCL₄ (4/1) mixture and 5 phr A-HD are presented in Fig. 2. It is clear that these sensitizer systems are also effective to enhance RVNRL with EB. The sensitizing efficiency of each sensitizer, however, decreases remarkably compared with RVNRL with γ-rays. For instance, the vulcanization dose of NR latex in the presence of 5 phr n-BA is 15 kGy when irradiated with γ-rays⁶, but it increases to 150 kGy with EB at a dose rate of 60 kGy/sec. Among sensitizer systems tested here, the most effective one for RVNRL with EB is A-HD, showing the highest Tb and the lowest vulcanization dose, similar to RVNRL with γ-rays⁷. The vulcanization dose, however, is 6 times higher compared with RVNRL with γ-rays.

Swelling ratios of these samples presented in Fig. 3 indicates the high crosslink density of the sample irradiated in the presence of A-HD. This is due to the presence of two C=C bonds in one molecule of A-HD. Utilization of A-HD, however, is limited due to its toxicity⁹. It is not easy to remove trace amount of A-HD which remains in the irradiated latex.

The viscosity of the irradiated latex with EB is shown in Table 1. Electron beam irradiation had no remarkable effect on the viscosity.
3.2 Effect of dose rate

In a previous paper we have reported the dose rate effect on RVNRL with γ-rays. When the dose rate was varied from 0.5 kGy/h to 10 kGy/h, the maximum Tb (max Tb) decreases slightly with increasing dose rate, but no significant difference in the vulcanization dose. The effect of the dose rate of EB on Tb is presented in Fig. 4. Irradiation was made at dose rate ranging from 10 kGy/h (γ-ray) to 60 kGy/sec (EB) in the presence of 5 phr n-BA. Evidently the vulcanization dose increases with increasing dose rate. This means that the efficiency of crosslinking decreases with increasing dose rate. The vulcanization dose at a dose rate of 60 kGy/sec increases to 150 kGy from 15 kGy at a dose rate of 10 kGy/h with γ-rays. The vulcanization dose and the max Tb are plotted against dose rate in Fig. 5. The max Tb decrease slightly with increasing dose rate.

While in the absence of sensitizer there is no dose rate effect on Tb as presented in Fig. 6. Swelling ratio and gel fraction also are not affected by dose rate as shown in Fig. 7. These facts show that the dose rate effect is caused by the presence of sensitizer.

The viscosity of the irradiated latex at high dose rate (60 kGy/sec) is shown in Table 2. The latex sensitized with n-BA is quite stable. While the remarkable increase in viscosity was observed in the latex containing A-HD.

The fact that vulcanization dose increases with increasing dose rate will causes a serious problem for application of RVNRL with EB in industry. Usually an electron accelerator is operated at as high dose rate as possible to reduce irradiation cost per unit volume of an object. In case of RVNRL with sensitizer, it is necessary to irradiate more dose at high dose rate than at low dose rate. Although the irradiation cost of EB per unit dose is lower than that of γ-rays, RVNRL with EB will not be economical due to the high irradiation dose. Reduction of the vulcanization dose at high dose rate will be discussed in part 2 of this series.

4. Conclusion

The use of high dose rate EB for RVNRL is demonstrated. Max. Tb decreases slightly with increasing dose rate. The effect of dose rate on the viscosity of the irradiated latex is also not significant.
Remarkable dose rate effect on RVNR, not previously recognized, was observed in the sensitized RVNR. The vulcanization dose increases with increasing dose rate.

References

2. J. Laizier, M.T. Hoel and M. Pordes, Large Radiation Sources for Industrial Processes, p. 165, IAEA, 1969
5. Private letter from Hu Yumuh
6. Chen Zhonghai and K. Makuuchi, in this Proceedings
Table 1  Viscosity of the same sample in Fig. 2 and Fig. 3

<table>
<thead>
<tr>
<th>Dose (kGy)</th>
<th>20</th>
<th>40</th>
<th>60</th>
<th>80</th>
<th>100</th>
<th>120</th>
</tr>
</thead>
<tbody>
<tr>
<td>2EHA/CCl₄</td>
<td>10</td>
<td>10</td>
<td>15</td>
<td>45</td>
<td>85</td>
<td>X</td>
</tr>
<tr>
<td>n-BA</td>
<td>20</td>
<td>22</td>
<td>25</td>
<td>35</td>
<td>45</td>
<td>50</td>
</tr>
<tr>
<td>A-HD</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
</tr>
</tbody>
</table>

X: Viscosity higher than 128 cP

Table 2  Viscosity of the latex irradiated at a dose rate of 60 kGy/sec in the presence of sensitizer

<table>
<thead>
<tr>
<th>Dose (kGy)</th>
<th>30</th>
<th>60</th>
<th>120</th>
<th>150</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-BA</td>
<td>10</td>
<td>12</td>
<td>25</td>
<td>85</td>
</tr>
<tr>
<td>2EHA/CCl₄</td>
<td>15</td>
<td>15</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>A-HD</td>
<td>25</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
</tbody>
</table>

X: Viscosity higher than 128 cP
Fig. 1 Effect of 5 phr n-BA on Tb.
Irradiation condition:
3 MeV; 1 mA; conveyor speed, 2.1

Fig. 2 Effect of 5 phr 2EHA/CCL₄ (weight ratio: =5/1)
and 5 phr A-HD on Tb.
Irradiation condition: 3 MeV; 1 mA;
conveyor speed, 2.17 m/min.
Fig. 3  Swelling ratios of the same sample in Fig. 2

Fig. 4  Effect of dose rate of EB on Tb Sensitizer: 5 phr n-BA
Fig. 5 Effect of dose rate of EB on vulcanization

dose and maximum Tb

Sensitizer: 5 phr n-BA

Fig. 6 Effect of γ-ray and EB irradiations on

NR latex in the absence of sensitizer
Fig. 7: Swelling ratio and gel fraction of the samples in Fig. 6.
5.24 Radiation Vulcanization of Natural Rubber Latex with 3 MeV Electron Beams
(Part 2)

SAMANTHA S. SOORIYARACHCHI¹, K. Makuuchi²)
F. Yoshii²) and I. Ishigaki²)

1) Atomic Energy Authority, Colombo, Sri Lanka
2) Takasaki Radiation Chemistry Research Establishment,
JAERI, Takasaki, Gunma, Japan

Abstract

A kinetic study has been made on the sensitized radiation vulcanization of natural rubber latex with high dose rate electron beams. The rate of vulcanization (R_{vul}) depends on the sensitizer concentration (M) and the dose rate (I). Following equation was obtained.

R_{vul} = k \cdot M^{0.5} \cdot I^{0.75}

An advantage of the high dose rate vulcanization is found in aging properties. The rubber film prepared from the electron beams vulcanized NR latex was superior to those prepared from gamma-rays vulcanized NR latex.

1. Introduction

A previous paper¹ has discussed the sensitized radiation vulcanization of natural rubber latex (RVNRL) with electron beams (EB) from a 3 MeV, 25 mA Dynamitron electron accelerator. This study showed that the sensitized RVNRL with EB is greatly affected by the dose rate. The vulcanization dose increases with increasing the dose rate. For instance, the vulcanization dose of NR latex in the presence of 5 phr n-BA is around 12 kGy when irradiated with γ-rays, but it increases to 150 kGy with EB at a dose rate of 60 kGy/sec. This will be a serious problem for application of RVNRL with EB in industry. Even if the irradiation cost of EB per unit dose is lower than that of γ-rays, RVNRL with EB may not be economical due to high dose. To overcome this problem, a study has been carried out to reduce the vulcanization dose of the sensitized RVNRL with EB. Since the sensitized RVNRL proceeds by a mechanism of graft polymerization of n-BA onto rubber molecules², the
rate of vulcanization is supposed to increase with increasing concentration of n-BA. In this paper the effect of n-BA concentration on the rate of RVNRL is discussed. The dose rate effect on the rate of vulcanization is also presented.

The previous paper also showed that there is no significant difference between EB and γ-rays in the physical properties such as tensile strength (Tb) and elongation at break (Eb) if the latexes were irradiated at the vulcanization dose. In this paper, aging properties of rubber film prepared from vulcanized NR latex with EB (EB film) were compared with those prepared from vulcanized NR latex with γ-rays (γ-rays film) to characterize the RVNRL with EB.

2. Experimental

2.1 Materials

Commercially available high ammonia NR latexes were used. Sensitizer used was n-butyl acrylate (n-BA) containing 15 phr MEHQ, supplied from Toa Gousei Chemical Industry Co. Ltd. Other chemicals such as potassium hydroxide (KOH), and toluene were purchased from Wako Pure Chemical Industries Co. Ltd., Japan. All chemicals were used without further purification.

2.2 Irradiation and measurement

Procedure of irradiation and measurement of physical properties of vulcanizates are described in a previous paper.

Crosslink density of vulcanized NR was determined from the swelling ration using Flory Rehner equation.

For aging test, rubber films were aged in an air oven at 70°C.

3. Results and Discussion

3.1 Effect of n-BA concentration

Since the stability of NR latex containing n-BA decreases with increasing the concentration of n-BA, irradiation was carried out immediately after the addition of n-BA to prevent coagulation of the latex. The effect of the concentration of n-BA on Tb of the film prepared from the irradiated NR latex is shown in Fig. 1. The concentrations of n-BA were 5, 10, and 20 phr. The irradiation conditions were
as follows: 3 MeV, 1 mA, conveyor speed; 2.17 m/min, 10 kGy/pass, 
dose rate; 14 kGy/min. It is clear that the vulcanization dose de-
creases with increasing the concentration of n-BA. The effect of 
the concentration of n-BA on Eb and 300% modulus are shown in Fig. 2 and 3. 
The modulus increases and Eb decreases with increasing dose and the 
n-BA concentration. The values of modulus and Eb, however, do not 
depend on the n-BA concentration at the vulcanization dose as summarized 
in Table 1.

Figure 4 shows the effect of n-BA concentration on the crosslink 
density. The crosslink density increases with increasing n-BA con-
centration and dose. From the initial slope of these lines, the rate of 
vulcanization (number of network moles of chain/cm³/min) was estimated 
and plotted against n-BA concentration as shown in Fig. 5. There is a 
linear relationship between logarithm of the n-BA concentration (M) and logarithm of the rate of vulcanization (R_vul). From the slope of 
the straight line, following equation is give.

\[ R_{vul} = k_1 M^{0.5} \]  

Where \( k_1 \) is a constant.

The distinct effect of higher concentration of n-BA on the reduc-
tion of the vulcanization dose has been clarified. However the con-
centration of n-BA to be added to NR latex is limited due to the 
destabilization of the latex. A new stabilizer should be developed to 
add sufficient amount of n-BA to reduce the vulcanization dose equivalent 
to the γ-ray vulcanization.

3.2 Effect of dose rate

The dose rate effect on the kinetics of RVNRL was evaluated using 
the similar method described above. Figure 6 shows effect of dose rate 
on the crosslink density. Irradiation were carried out over a wide 
range of dose rate from 0.2 (γ-ray) to 680 kGy/min. From the initial 
slope of this figure, the rate of vulcanization \( R_{vul} \) was calculated and 
plotted against the dose rate \( I \) as shown in Fig. 7. It gives a linear 
relationship with slope equal to 0.75. The dependence of the rate of 
vulcanization on the dose rate is given by

\[ R_{vul} = k_2 I^{0.75} \]  

Where \( k_2 \) is constant. Thus, from equations (1) and (2), the empirical 
relationship takes the following equation.
\[ R_{\text{vol}} = k M^{0.5} I^{0.75} \]  

(4)

Where \( k \) is constant.

The mechanisms of RVNRL in the presence of vinyl monomer was investigated using liquid polyisoprene as a model rubber. The proposed mechanisms consists of homopolymerization of monomers, graft polymerization of monomers onto rubber molecules, and crosslink formation between homopolymers and branch polymers. The rate of RVNRL in the presence of n-BA is supported to be related with the rate of polymerization of n-BA.

The rate of radiato-induced polymerization of viny monomer in ideal conditions is described as follows.

\[ \text{Rate of polymerization} = k M I^{0.5} \]  

(4)

The rate of RVNRL, however, depends on the monomer concentration largely and less on the dose rate compared with the radiation-induced polymerization. The site of radical formation and polymerization of n-BA and the distribution of n-BA in rubber particles make more complex the mechanisms of the RVNRL.

3.3 Aging properties

Aging properties of EB films were compared with those of \( \gamma \)-ray films. The EB films were prepared from the NR latex irradiated to 90 kGy at a dose rate of 14 kGy/min, and the \( \gamma \)-ray films from the NR latex irradiated to 15 kGy at a dose of 10 kGy/min. Both latexes were irradiated in the presence of 5 phr n-BA. Both films have nearly equal crosslink densities \( (6 \times 10^{-5} / \text{cm}^2) \) and do not contain any artificial antioxidants. Changes in \( T_b \) of both films with aging time at 70°C are shown in Fig. 8. In this figure the effect of leaching of the films with water for 24 hours is also shown. Tensile strength of the unleached film increases with aging time. While the leached film exhibits higher \( T_b \) at early stage of aging, then loses aging resistance. The degree of loss of resistance is higher in \( \gamma \)-ray film than EB film. This suggests the difference in crosslink structures between EB film and \( \gamma \)-ray film, particularly the molecular weight of bridges between NR molecules, consisting of poly (n-BA). It is supposed that the molecular weight of bridge is lower and the numbers of bridges is larger in EB film than in \( \gamma \)-ray film. The details of the structure of the bridges should be investigated further.
4. Conclusion

The dependence of the rate of vulcanization on the sensitizer concentration \( M \) and the dose rate \( D \) of EB was estimated. The rate of vulcanization decreases with increasing dose rate and sensitizer concentration.

\[
R_{\text{vul}} = k M^{0.5} D^{0.75}
\]

The aging resistance of rubber films prepared from vulcanized NR latex with electron beams was superior to those prepared from vulcanized NR later \( \gamma \)-rays. This suggests that the molecular weight of bridge is lower and the numbers of bridges is larger in EB film than in \( \gamma \)-ray film.

References

3. Adolphe Chapiro, Radiatio Chemistry of Polymeric Systems, p. 129, Interscience Publisher 1962
Table 1 Effect of n-BA concentration on vulcanization dose and physical properties of vulcanizates

<table>
<thead>
<tr>
<th>n-BA concentration (phr)</th>
<th>5</th>
<th>10</th>
<th>20</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vulcanization dose (kGy)</td>
<td>80</td>
<td>50</td>
<td>30</td>
</tr>
<tr>
<td>Tensile strength (MPa)</td>
<td>29</td>
<td>28</td>
<td>27</td>
</tr>
<tr>
<td>Elongation at break (%)</td>
<td>1,030</td>
<td>1,000</td>
<td>980</td>
</tr>
<tr>
<td>300% Modulus</td>
<td>0.9</td>
<td>0.9</td>
<td>0.8</td>
</tr>
<tr>
<td>Crosslink density (10^-5 mole/cm^3)</td>
<td>5.8</td>
<td>5.2</td>
<td>5.3</td>
</tr>
</tbody>
</table>
Fig. 1 Effect of n-BA concentration on tensile strength. Irradiation condition: 3 MeV; 1 mA; conveyor speed, 2.17 m/min

Fig. 2 Effect of n-BA concentration on 300% modulus. Irradiation condition: same with Fig. 1
Fig. 3 Effect of n-BA concentration on elongation at break.  
Irradiation condition: same with Fig. 1

Fig. 4 Effect of n-BA concentration on crosslink density.  
Irradiation condition: same with Fig. 1
Fig. 5  Effect of n-BA concentration on rate of vulcanization.  
Irradiation condition: same with Fig. 1

Fig. 6  Effect of dose rate on crosslink density
Fig. 7 Effect of dose rate on rate of vulcanization

Fig. 8 Effect of aging on Tₐ
5.25 Application of RVNRL in Europe

WILLFRIED BEZ

Kautschuk-Gesellschaft, Frankfurt, West Germany

Abstract

Due to strict regulation of nitrosamines in environment and rubber products, development of a nitrosamine free vulcanization process is desired. A study has been carried out on RVNRL with electron beams. A Dynamitron electron accelerator was used for RVNRL at 1.5 MW and 20 and 25 mA. The vulcanization dose is 60 kGy with 5 phr trimethylolpropane trimethacrylate. Several kinds of rubber products such as surgical gloves, urinal condoms, and cork soles were produced from the radiation vulcanized latex and evaluated by latex customers. Good running properties were reported. However it was requested to increase tensile strength and to reduce stickiness and permanent set.

1. Introduction

The aim of this paper is to describe the present situation in crosslinking systems of natural rubber latex by the consuming industry in Europe and possible reasons to use radiation vulcanized natural rubber latex for the production of special articles. As already been known, natural rubber latex conventionally is cured by the reaction with sulfur, zinc oxide and accelerators. As accelerators mainly dithiocarbamates are used.

\[
\begin{array}{c}
R \\
N \quad C \quad S \\
\parallel \quad S \\
R
\end{array}
\]

\[\text{Zn} \quad 2\]

From the chemical structure it is obvious that these products are causing the formations of amines and carbon disulfide. By reaction of the amines with nitrogenoxide originating from the drying process or environment, nitrosamines could be detected. Today these nitrosamines are regarded as highly cancerogenic\(^1\).

This is considered the most unwelcome aspect of this curing system.
The German rubber industry is hit because there are by the law limitations of nitrosamines in the production of rubber teats for baby bottles as well as for children toys. This law called Nitrosamine-Gegenstandeverordnung is in force since 01 January 1982. Since September 1988 these limitations are integrated in the XXI BGA Recommendation for the special category.

Further nitrosamine problems will arise in home industry. The "Gefahrstoffverordnung", another German law adopted in 1986 is not allowing any volatile nitrosamines in the environment of production facilities.

There are other European countries which have a similar legislation, however the German BGA is the forerunner in many aspects. Another disadvantage of the dithiocarbamate accelerators is their allergic potential. This is a problem especially obvious in connection with examination, surgical and household gloves as well as urinal condoms.

The main sensitizers were found to be the rubber accelerator of the carbamate and the thiuram group. Furthermore from Australian publications, a cellular toxicity of latex catheters is known and referred to the dithiocarbamate accelerators.

All these difficulties and problems could be avoided by changing from sulfur crosslinking to radiation vulcanization of natural rubber latex. In 1986 Kautschuk-Gesellschaft, one of the leading dealers of natural rubber latex in Europe came to the decision to study the prospects of irradiation intensively.

The publication of M. Ridwan in Indonesia informed about the pilot plant for crosslinking natural rubber latex by gamma rays. After discussion at BATAN in May 1986, this prevulcanized latex was checked in laboratory for a possible introduction of this product in the European market. Laboratory results and first plant trials by customers were somewhat successful with tensile strength and ageing properties to be improved. However carbon-tetrachloride which was used as a sensitizer could not be accepted under health aspects. The low capacity of the plant as well as the long transport distance to Europe caused to look for a radiation equipment available in Germany.
2. Electron Beam Radiation

An installation based on Electron Beam Radiation has been chosen for the further elaboration. It is a Dynamitron equipment with a maximum voltage of 1.5 MV and a maximum power of 37.5 kW. For trials the equipment were run at between 20 and 25 mA and 1.5 MV at maximum power. Radiation input was about 12-15 Mrad per hour. Irradiation using this equipment began in October 1987. For the first experiment, the full ammonia centrifuged latex was placed on metal plates (with thickness of about 4 mm) having elevated edges. The plates were mounted on a table which could be moved automatically under the scanner of the electron beam equipment during the radiation treatment.

At the beginning, carbon tetrachloride with 5 phr was used as a catalyst/sensitizer. Irradiation was carried out step by step with 4, 6 and 8 Mrad. It was necessary using carbon tetrachloride to have a standard for comparing other sensitizer. The amount of latex for each experiment was about 4-5 kg. The sensitizer in all the following radiation trials were emulsified before adding to the latex. In the same manner was also tested Neopentylglycol dimethacrylate and trimethylol propa trimethacrylate as sensitzers.

In case of using carbon tetrachloride (dose 4 Mrad), the latex viscosity increased to more than 800 mPa.s, while the samples treated with 6 and 8 Mrad coagulated during the viscosity measurement. Additionally it was found low tensile strength of latex films compared with the results using polyfunctional monomers (Table 1).

After this experimental stage, namely in July 1988, an equipment was constructed to irradiate a latex in the same manner but continuously (300 kg for each trial). Based on Table 1, TMPT was used as sensitizer with 5 phr and a dosage of 6 Mrad. Film with tensile strength up to 26.4 MPa was obtained.

3. Test Production

Having produced adequate quantity of latex, the latex was sampled to different customers for their testing, mainly to the latex dipping industry in Europe. Trials have been made at several producers manufacturing surgical, examination, electricians and household gloves. Normally these gloves are coagulant dipped. Only for the electricians gloves, a heat sensitive formulation is used.
The positive statements of the customers were: good running properties during production, good handling of ready articles, however the colour of gloves a little bit darker but-acceptable. In case of electricians gloves the electric resistance compared to conventional sulfur cured product was much higher.

Other properties which have to be improved are: heat ageing of ready articles (two weeks at 70°C), and if possible a higher tensile strength. Furthermore it was reported that the films casted from the radiation vulcanized natural rubber latex was high in water absorption.

Other products which are reviewing are urinal and normal condoms. Plant trials have been carried out and good running properties were stated. Nevertheless a higher tensile strength is desirable. In one case the condoms were blown up for testing on pin holes and a high permanent set has been claimed. Another statement at this factory was a higher stickiness of the condoms during drying compared to normal production.

A special requirement in producing urinal condoms is to avoid skin irritation. The expected anti allergic effects of RNVRNL are tested at a University clinic presently.

Another application is a special kind of cork soles. Up to now these are produced by mixing cork granulates with sulfur post cured latex. This mixture is filled in moulds and vulcanized. Because of environmental reason, the customer is interested to change to radiation vulcanized latex in order to avoid nitrosamine build up in the production premises. First trials were very successful.

4. Conclusion

To summarized the experience gathered in introducing the radiation vulcanized natural rubber latex in the market, we have to fulfil the demands of the interested customers by improving the ageing properties, increasing the tensile strength and reducing the permanent set of the ready articles.

For this purpose further irradiation trials are planned, and the author is quite confident that the information gathered at this Symposium will contribute to achieve the properties meeting the needs of the buyers.

Concerning the price situation the author believes that although the expenses for Electron Beam treatment are higher than traditional prevulcanization, but they are acceptable due to the superior properties
of RVNRL. The author very much hope that the idea of natural rubber latex radiation will become an important alternative of crosslinking worldwide. For this purpose a continuous flow of technical exchange should be the aim of the participants present.

References
1. "Das Nitrosaminproblem" OFC, Rudolf Preussmann, Verlag Chemie 1983
2. Bundesgesetzblatt, Jahrgang 1981, Teil I Seite 1406
3. Bundesgesundheitsblatt 31, nr 9, September 1988, Seite 365
4. Gefahrstoffverordnung-Gef Stoff V 1986-Deutscher Bundes-Verlag
5. P.J. Frosch, C. Mercedes Bavn und Rita Schutz, Der Hautarzt (1987) 38: 210-217

Table 1 Properties of irradiated latex and film prepared by using different catalysts and dose of EB radiation

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Dose kGy</th>
<th>Tensile Strength MPa</th>
<th>Elongation at Break %</th>
<th>Viscosity RTV 3/100 mPa.s</th>
<th>Coagulum Content %</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCl₄</td>
<td>40</td>
<td>8.9</td>
<td>1004</td>
<td>815</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>9.6</td>
<td>978</td>
<td>coagulate</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>8.6</td>
<td>922</td>
<td>coagulate</td>
<td>-</td>
</tr>
<tr>
<td>NPG</td>
<td>40</td>
<td>10.8</td>
<td>1034</td>
<td>115</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>14.3</td>
<td>1007</td>
<td>130</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>15.4</td>
<td>938</td>
<td>235</td>
<td>-</td>
</tr>
<tr>
<td>TMPT</td>
<td>40</td>
<td>16.9</td>
<td>1010</td>
<td>90</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>19.1</td>
<td>1007</td>
<td>126</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>19.0</td>
<td>968</td>
<td>125</td>
<td>0.01</td>
</tr>
</tbody>
</table>
5.26 An Alternative Option Study of Malaysian Latex Irradiator

MUHD NOOR BIN MUHD YUNUS

Nuclear Energy Unit, Kompleks PUSPATI Bangi, 43000 Kajang Selangor, Malaysia

Abstract

A Technical study and evaluation was made to select the best alternative to Malaysia with regard to Latex Irradiator at experimental scale. Some cost comparison which lead to economic evaluation was also done.

The two option in so far considered were between utilising multipurpose Irradiator against purchasing a category I dry storage Irradiator, both for the above intention.

Finally a recommendation to utilise the existing multipurpose Irradiator was made due to technical and economical merits.

1. Introduction

Malaysia participated in the regional programme of RVNRL via RCA-UNDP project way back in early 1980's. RVNRL research project was intensified in Malaysia only in 1988, when the government first introduced special R&D budget through Intensified Research in Priority Area (IRPA) programme. The Project is under collaboration with Rubber Research Institute of Malaysia (RRIM) and nuclear Energy Unit (UTN) to spearhead the technology development in Malaysia. Under those circumstances there is a need for a latex irradiator. Initially an experimental latex irradiator is required.

UTN is equipped with two gamma irradiators, one of category I, in accordance to American National Standard Institute (ANSI) classification, having four (4 Nos) liters irradiation chamber, and the latest is category IV panoramic multipurpose irradiator. A category I, 10 kCi Irradiator was donated by International Atomic Energy Agency (IAEA) in 1986, and of late found to be of limited use with regard to RVNRL project. A category IV, panoramic 200 kCi irradiator, called SINAGAMA, was constructed in 1988 and currently providing a multipurpose irradiation, having medical disposable as the biggest consumer of irradiator time. Some small scale latex experiment being carried out by RVNRL
group in this irradiator.

Since the demand for disposable medical product irradiation in Malaysia was very high, it was anticipated that SINACAMA could not spare her time sufficient for RVNRL project. Thus a procurement of category II, 10 kCi portable irradiator was considered. This consideration was done upon consulting RCA-UNDP expert, report on RVNRL irradiator design, followed by invitation of the expert to Malaysia for detail discussion. Category II Irradiator was considered instead of a bigger plant was due to economic reasoning and the current demand of research scale irradiator.

2. Projection of Irradiator Requirement

Result of RVNRL group research showed that the achievement until now is very promising, though further investigations are required to reduce the dose of vulcanization to 10 kGy. It is expected by the end of 1989, the finding on 17 kGy dose of vulcanization is finalised. This means that from now until the end of 1989, tested data have to be collected from member countries to confirm the finding using Malaysian irradiated latex. A 100-200 liter of latex per batch is required to be processed at 17 kGy to meet the needs. Figure 1 presents time schedule of RVNRL program in Malaysia.

In 1990 research activities will be devoted on vulcanization at 10 kGy, besides doing market studies. The amount of latex required is still in the region of 100-200 liter per batch and this could be handled with ease by a research scale irradiator. A pilot scale irradiator is not required for that purpose until 1991. UTN felt that such irradiator should be financed by Malaysian private sector. The reason being that, this pilot scale irradiator could be scaled up to commercial scale when needed with ease, and, such commercial scale plant is best operated privately. Cost analysis should be conducted following the finding of 17 kGy dose of vulcanization. This analysis should be paralleled to research work in order to keep the industry well informed on the status of development. The ultimate goal of cost analysis is to convince the industry that the project is economically viable. Cost analysis followed by a pilot plant operation will further strengthen the proof of project viability. It is anticipated that a lead time of three years is required before a commercial plant could be materialised.
3. Alternative Irradiator for Research

The two alternatives for Malaysia in selecting research irradiator for RVNRL comprise of:
(a) Utilising the existing SINAGAMA without disturbing the medical product irradiation service, and
(b) Purchasing a new portable irradiator meeting the research capacity requirement.

3.1 SINAGAMA Facility

UTN has built Sinagama multipurpose batch irradiator in 1988. Initially the plant was for research work and medical product service sterilization. The plant is best suited for carrier type, floating irradiation, though static irradiation also anticipated. The shielding design capacity is 2 MCi with current Co-60 source loading approximately 170 kCi.

The plant is housed in a 42m × 26m floor area of warehouse building. The cell, irradiation chamber of 5m × 7m × 3.8m and approximately 1.9 m thick concrete shielding is located at the centre of the warehouse. The source is normally stored in a 7 m deep deionised water contained in a stainless steel lined pool. Roof hatch, which could be opened via a 6 ton crane located on top of the cell, is provided for loading and unloading of source cask.

A total of 74 Co-60 pencils are loaded in one of the two source rack, distributed and arranged in slab form, in order to achieve a uniform dose distribution. The two source racks are independently driven, having two mode of operation, one for the static irradiation and the other for floating irradiation.

The irradiator was equiped with 18 Nos of aluminium carrier, having a displacement volume of about 1 cubic meter each. Only 9 carriers are used for each batch irradiator, and the other for the next batch. The carriers formed part of the source pass mechanism. Only two passes selected since it is designed for multipurpose.

However provision for upgrading is allowed within the plant. Since only two passes of product allowed, especially with low density medical product irradiation, much of the irradiation energy is wasted. A typical medical product with density 0.2 g/ml only absorbed 10% of the radiation energy.

Irradiation rigs and benches are going to be provided to facilitate
research works. As the carriers could be removed from the irradiation chamber, and the plant is designed to operate in dual modes, it is always possible to have time sharing static irradiation, even with bulk material.

RWNRL research group has started irradiating natural rubber latex in SINAGAMA at various doses using simple static irradiation rack. The latex are filled into 80 numbers' drink bottles placed on a steel rack to form a plane having overall dimension of 120 cm(H) 200 cm(W). The samples are placed parallel to and at about 0.6 m from the center of the source slab. Total sample volume is about 20 liters. Samples are rotated manually at a predetermined intervals. Doses of 10 kGy to 100 kGy are experimented. This static irradiation is done on time sharing basis when there is no medical product to be irradiated. A 10 kGy dose is achieved within approximately 7 hours. Samples at the center received higher dose than the one on the sides.

In order to meet the demand of a bigger volume of irradiated latex, a much bigger irradiation rig was constructed. This rig consisting of eight rotating drums, placed in vertical plane parallel to the source slab as shown in Fig. 2. Centre to centre distance between rotary drum to the centre line is approximately 120 cm, upon considering simultaneous irradiation with medical product.

The drums are rotated by rubber rollers, driven by a motor, through sprocket and chain drive. Speed regulation is made possible by gear reduction and speed controller. Two rigs were constructed with the possibility of coupling them to form 16 Nos drums irradiated at one time. Each drum can take about 30 litres of latex which corresponds to about 240 litres of latex per rig or batch.

Table 1 shows some calculation results for simultaneous irradiation at 17 kGy dose for latex and medical product having density of 0.2 g/ml within the carrier. The calculation based on the following relationship:

\[ P = \frac{D \times X}{360 \times E} \]  

(1)

where 
- \( P \) = radiation power, kW
- \( D \) = dose delivered, kGy
- \( X \) = processing rate, kg/h
- \( E \) = radiation utilisation efficiency, %
It shows that the processing rate is about 50 ton/year, which is about half of the portable category II irradiator capacity considered in the option study. Some dosimetry experiment is currently being done to confirm that calculation.

3.2 Portable Irradiator

UTN has considered on purchasing a category II portable irradiator from India. The design basically based on IAEA expert report on R/NRL irradiator design. This study was done to find other alternatives for latex irradiator of laboratory scale, apart from utilizing the existing multipurpose facility.

Basic layout and essential features of the irradiator are shown in Figs. 4 and 5. UTN proposed to design the cask as such to accomodate universal source geometry and design as well as to facilitate changing of source within UTN using SINAGAMA pool.

This irradiator is design for simplicity and safety. It is easily dismantled, transported and installed at site within a short period. The design capacity of the irradiator is 100-200 ton/y, which suitable for research work as well as for market evaluation on products from R/NRL.

The shield for irradiation chamber is constructed of lead encased with steel. The size of irradiation chamber is 85×80×70 cm with the overall size of 140×140×120 cm. The irradiator should be placed in a 30 cm thick concrete shielded room of 420×470×300 cm high in order to reduce the leakage radiation to a permissable level.

The source is normally stored in a source cask which serve also as a transport cask. A 95×80 cm diameter pit, in the shielded room is required to place this cask. The maximum capacity of the source cask is 25 kC of Co-60.

Source lifting system for irradiation is achieved by using a cable winch driven by motor at one end, outside the shielded area. Source cage is lifted within a guide tube to ensure safe and smooth movement of the top shield source unit. Various controls to ensure safety is incooperated with the unit.

The irradiation platform is an integral part of the irradiation chamber door. This assembly is openable as a unit and thus facilitate loading and unloading of the product. This irradiation platform together with turntable, capable of rotating around their own axes.
Uniformity in target material thus achieved by that rotation of turn table. Four drums, each of 40×30 cm diameter, are possible to be irradiated within the chamber at any batch, thus giving a total irradiation volume of 100 l/batch. Total cost of this type of irradiator is estimated to be US$135,000.00.

4. Discussion of Alternative Option

From technical point of view, a latex irradiation rig installed in SINAGAMA does not pose any problem. Having latex irradiation based on time sharing also does not impose any technical problem. However, the plant utilization efficiency for medical product sterilization service is reduced. This reduction, economically not tolerable since UTN is bounded by a service contract with medical product producers to provide irradiation service. Thus conflicts might arises between giving service on one side and conducting research for latex irradiation on other. For this very point, the procurement of a portable irradiator was opted.

This situation might be resolved by having simultaneous irradiation of medical product and latex within Sinagama. Table 1 depicts some calculation results on simultaneous irradiation. The dose rate, of 0.26 kGy/h for 100 kCi source, available as waste radiation out from medical product carrier having density of 0.2 g/ml is still sufficiently high. It is possible to process 3.2 kg/h of latex with dose of 17 kGy. This, corresponds to 44 ton/year on assuming 8000 hours working time with existing 170 kCi Co-60 source. The time taken for one batch irradiation is about 44 hours.

It is felt that this irradiation time is a little too long. It is thus suggested that the Co-60 source is to be increased to say 300 kCi. Irradiation time expected is 25 hours per batch at 17 kGy with processing rate of about 77 ton/year. These values seem reasonable with processing rate almost equivalent to that portable irradiator opted to be purchased earlier.

The upgrading of the Co-60 source is well justified due to the following:

1. Demand for medical product irradiation is far exceeding the Sinagama capacity. Thus the net increase in Co-60 cost could be covered through irradiation service charge.

2. The gain in utilizing waste radiation could be realized through savings in not having to purchase dry storage portable irradiator
which was estimated to cost US$ 135,000.00. Thus the net increase in investment cost is only US$ 45,000.

Purchasing portable irradiator is seen to have some positive points, among which are:

(1) The plant is dedicated to latex irradiation, and thus the plant operation is straight forward and simple. Problem of cross-contamination does not arise at all.

(2) The plant is simple and could be used for other research activities.

However there are a few disadvantages against the purchase of the portable irradiator, among which are:

(1) Budget for such purchase could only be made available in 1991 through Sixth Malaysian Plan.

(2) If it is under Sixth Malaysian Plan, the plant would be ready in 1992, and this is too late for research work.

(3) Additional cost of US$ 135,000.00 to be incurred is much costlier than having a simple irradiation rig installed in Sinagama which cost only about US$ 9,000.00.

5. Conclusion

As far as research requirement is concerned, existing latex irradiation rig operated simultaneously with medical product is adequate. The capacity is 44 ton/year with irradiation time of 44 hour.

References


Table 1  Estimate of processing rate of a 100 kCi
Co-60 source for 17 kGy

<table>
<thead>
<tr>
<th>Density of Medical Product g/ml</th>
<th>Dose Rate kGy/h</th>
<th>Processing Rate kg/h</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.400</td>
<td>4.9</td>
</tr>
<tr>
<td>0.1</td>
<td>0.340</td>
<td>4.1</td>
</tr>
<tr>
<td>0.15</td>
<td>0.296</td>
<td>3.6</td>
</tr>
<tr>
<td>0.20</td>
<td>0.260</td>
<td>3.2</td>
</tr>
<tr>
<td>0.25</td>
<td>0.227</td>
<td>2.8</td>
</tr>
<tr>
<td>0.30</td>
<td>0.198</td>
<td>2.4</td>
</tr>
</tbody>
</table>

Note: Efficiency E = 5%
Fig. 1 Projection of procurement timing of latex irradiators in Malaysia
Fig. 2 Cross-section of Sinagama Irradiator
Fig. 3 Portable batch irradiator for NRL
Fig. 4 Portable NRL batch irradiator

1 Radiation source
2 Top shield
3 Guide tube
4 Guide roller
5 Lead flask
6 Source lifting device
7 Biological shield
8 Shielded door
9 Product box
10 Drive motor for product box
11 Irradiation platform
5.27 Improved Dry Type Irradiator

WORKSHOP FOR USES OF RADIATION, JAPAN ATOMIC INDUSTRIAL FORUM*

1-1-13 Shinbashì, Minatoku, Tokyo, 105 Japan

Abstract

The dry type irradiator designed by Aggarwal has been redesigned and reevaluated. Major improvements were made in the three points, namely the shielding structure of building, the handling of radiation source, and the handling of reactor vessel. The labyrinth system is replaced by the fit-in type shielding door. The bottom loading system of radiation source is changed to the top loading system. The reaction vessel is carried into the irradiation cell while the fit-in type shielding door is left open. As a result, the processing cost is reduced from $0.8 to $0.23/kg.

* TOMOHITO KIDA Mitsui Engineering & Shipbuilding Co., Ltd.
  Y. Tabata Tokyo University
  K. Ishigure Tokyo University
  K. Makuuchi JAERI, TCRE
  I. Ono Industrial Research Institute of Kanagawa Pref.
  H. Matsuzawa Yoshizawa L.A. Ltd.
  H. Aoki Taisei Corp.
  S. Tsujimura The Shimizu Construction Co., Ltd.
  K. Kimura Fujita Corp.
  Y. Yamamoto Takenaka Komuten Co., Ltd.
  S. Wada Mitsubishi Kakoki Kaisha, Ltd.
  T. Hattori Kimura Chemical Plants Co., Ltd.
  S. Koreki Toshiba Engineering & Construction Co., Ltd.
  K. Tsuji Hitachi Zosen, Corp.
  I. Umeda NKK Corp.
  Y. Hoshi Nissin-High Voltage Co., Ltd.
  K. Nagakura Sumitomo Heavy Industries, Ltd.
  Y. Sato Radia Industries Co., Ltd.
1. Introduction

Three types of irradiators were designed\(^1\) for radiation vulcanization of natural rubber latex: portable, dry and wet type. The research groups in the countries which participate in the RCA project already made cost evaluation on the basis of the design specification: construction cost and operation cost as well as the vulcanization cost of the natural rubber latex. Since the prices in Japan are high and the government's examination is severe, the cost evaluated in Japan was the highest among the other countries\(^2\).

It might be possible to reduce the processing cost by reviewing the design specifications of the irradiator. The dry type irradiator was selected to be redesigned and reevaluated, because this type has the highest possibility of realization among the other types.

This paper describes the specifications of the improved design of the irradiator and the cost evaluation.

2. Original Design

The original specifications of the dry type irradiator were as follows (Fig. 1):

- Building size: 20 m x 20 m
- Irradiator overall size: 14.3 m x 10.1 m
- Irradiator cell size: 4 m x 4 m
- Maximum Co-60 capacity: 100 kCi
- Processing method: Batch or continuous as desired
- Total annual production: 500 tons

The biological shielding was of labyrinth type. In the case of the batch processing, it was necessary to put in/out the reactor vessel through the narrow labyrinth entry every time the natural rubber latex was changed. The radiation source was housed in the source storage flask placed in the underground portion and pulled up into the irradiation cell when irradiation was made. The reactor vessel had cylindrical space in the center in which the source-plug assembly was put when the irradiation was carried out.

3. New Design

The criteria for improving the design were:
(1) To secure safety and performance equivalent to or higher than those of the original design specifications.
(2) To reduce the construction and operation cost to a lower level than that of the original design.
(3) To increase the annual processing capacity.

The major improvements were shielding structure, radiation source handling system, and the reactor handling system. The labyrinth type shielding was changed to the fit-in type shielding door. Bottom loading system of radiation source was changed to top loading system. The reactor vessel handling was improved in such a way that it could be easily transported by a monorail hoist and a truck. Figure 2 shows the basic layout of the plant.

Building. The fit-in type shielding door reduced the volume of the shielding concrete, and contributed to the curtailment of the construction cost.

The reactor vessel transporting in/out route was shortened and the transporting in/out time was reduced, making it possible to shorten the down time. It also had the effect of decreasing the overall dimensions of the irradiation cell and the storage area. The building area was reduced to 1/2 of the original design.

For the radiation source handling, the top loading was adopted, and so the underground portion was not required. This made it possible to cut down the excavation cost. The building was of one story structure in its entirely and only the upper part of the irradiation cell has the upper floor portion.

The fit-in type shielding door was made of concrete and closed/opened by electric motor.

Source storage flask. Since the top loading was adopted for the radiation source, the source storage flask was arranged on the irradiation cell. The flask shielding was made of lead, and in its center the source-plug assembly was housed. The plug shielding was also made of lead. The flask, in combination with the plug, had a sufficient shielding capacity.

The source storage flask was designed to serve both as a storage container and as a transportation flask (Fig. 3).
Radiation source unit. The cylindrical source cage design was adopted like the radiation source of the original design. The source-plug assembly was linked to the drive unit temporarily set on the source storage flask and lifted by an electric motor. This drive unit was installed only when the flask was fixed to the building and was removed when transported.

Reactor vessel. The reactor vessel was brought into the irradiation cell after the vessel was charged with natural rubber latex. The irradiation cell was provided with a truck which moved on the same rail as for the shielding door. The reactor vessel was placed on this truck by means of the chain block, transported into the irradiation cell, and then the shielding door was closed. The reactor vessel was taken out in the reverse procedure after irradiation. The reason why this type of handling was adopted was to reduce the transporting in/out time.

The natural rubber latex was stirred by the stirrer to secure homogeneity during irradiation. At least two reactor vessels were prepared. While one vessel was being irradiated, the other was charged with the latex, thus reducing the down time (Fig. 4).

Specifications. The specifications of the improved dry type irradiator were as follows:

1. Maximum Co-60 capacity : 120 kCi
2. Radiation dose : 10 kGy
3. Utilization efficiency : 50 %
4. Processing rate : 1,500 tons/year
5. Annual operation time : 6,000 hours
6. Processing method : batch
7. Building size : 14 m × 14 m × 4.1 m (6.4 m)
8. Irradiation cell size : 3 m × 3 m
9. Irradiation cell shielding : concrete
10. Source flask size : diameter 1.2 m × height 2.4 m
11. Source flask shielding : Lead
12. Reactor vessel size : diameter 2 m × height 1.3 m
13. Ventilation : 20 airchanges/hour
14. Safety : Mechanical and electrical interlocks.
4. Cost Estimation

On the basis of the improved design specifications, the cost of construction was calculated. The construction cost consisted of the following elements:

- Building cost
- Irradiator cost
- Radiation source cost
- Miscellaneous expenditures (initial planning, design etc.)

The operation cost, which consisted of the following elements, was calculated in view of the respective elements:

- Salaries to the personnel
- Source replenishment
- Facility maintenance
- Utilities
- Overheads
- Contingency etc.

In order to determine the unit processing cost, the average investment method was adopted. The annual cost was calculated by this method and the result was devided by the total annual production to find the unit processing cost. The specific calculation method was the same as the cost evaluation method used on the original irradiator.

The unit processing cost was estimated to be ¥ 35/kg which is US$ 0.23/kg at the present exchange rate.

5. Conclusion

The design improvement of the dry storage type irradiator reduced the construction and operation costs and also increased the annual production in comparison with the original design. As a result, it was known that the radiation vulcanization of natural rubber latex would be sufficiently economical if the irradiator would be constructed in Japan.
References

2. "Minutes of the Meeting of Natural Research Group Leader on Technology Development Program for Radiation Vulcanization of Natural Rubber Latex (RVNRL)," Kunming, 7-9 September (1988)
Fig. 1 Dry Storage NRL Irradiator (Original Design)
Fig. 2 Dry Storage NRL Irradiator (New Design)
Fig. 3 Source Storage Flask

Fig. 4 Reactor Vessel
6. SUMMING-UP ADDRESS
6.1 Summing-up Address

VITOR MARKOVIC, IAEA

1. Technology Development

Significant progress has been made in the last five years in development of technology for RNVRL. Most of the work done has been reported at this Symposium. The coordinated research efforts within the scope of the RCA (Regional Cooperative Agreement) for South-East Asia and Pacific Region, as part of UNDP project, have been the driving force and source of new initiatives in this field. It was encouraging to see the revival of interest for RNVRRL in Europe (F.R. Germany, UK). The latex reprocessing industry, conspicuously, although relatively well represented at the Symposium, had proportionally little to report. With few exceptions the focal point of R&D work still resides with Academia, Research Institutions or Rubber Research Institutes. The latest may, hopefully, provide the necessary link with industry and promote transfer of technology.

The following are the main highlights of new developments, as seen this Symposium.

(1) New sensitizers were developed and studied. They effectively replace the CCl4, as initiator of RNVRRL and reduce the dose requirements to the range of 15-20 kGy.

(2) Experimental evidence was shown that new additives are not cytotoxic and do not produce nitrosamines.

(3) The first commercial product - rubber protective gloves - based on RNVRRL, has been recently released in Japan.

(4) Specifications of RNVRRL are acceptable for several products; the technical feasibility has been tested and demonstrated at the pilot scale.

(5) Basic designs of several simple, low cost irradiators are available.

2. Problems and Concern

Fundamental basis of RNVRRL is still very weak. Compared with other systems (synthetic polymers, for example) the RNVRRL is poorly understood and relatively little studied. There is very little understanding of
radiation chemistry of NRL, crosslinking mechanism and factors influencing it. The symposium provided no evidence in support of progress in this direction. There is a reason to expect that the lack of fundamental knowledge may slow down or inhibit the technology development.

This situation is understandable taking into account the complexity of NRL system. The study of simplified systems and model system may be the path that can lead to some advances.

Intercomparison of data from different laboratories is very difficult because of different experimental procedures, quality of latex, test methods, etc. The standardization is urgently needed.

In particular, the following studies are required before the technology may attract the broader industrial interest:
- improvement and control of stability (on aging);
- shortening of leaching times;
- complete toxicological investigations (as required for new materials).

3. Potential for Commercialization of RVNRL Technology

RVNRL as any other radiation technology must be competitive: technically and economically.

Several factors may determine the interest of industry to apply this technology. Although no comprehensive analysis was presented at the Symposium, the elements of the overall picture emerged from different contributions. They are briefly discussed here.

(1) Quality of (RVNRL) products

In general, at its best, the RVNRL products are only comparable to specifications and quality of sulphur vulcanized products. It is hard to expect strong incentive of industry to use RVNRL from that point of view.

The (limited) exceptions are possible, as demonstrated at the Symposium (protective gloves, laser baloons), if some of the properties of the RVNRL are essential and make other comparative factors irrelevant.

(2) Process control and quality assurance

Process control in RVNRL is not yet understood as well as that for the competitive technology and, for sure, the experience is much more limited. Even if significantly improved, this aspect may not result in
special advantages for RVNRL as compared to conventional technology.

(3) Safety

Three aspects of safety may be of concern.

a) Occupational safety

The usage of RVNRL would be of advantage to occupational safety because RVNRL which is free from nitrosamines, gives a good workshop environment.

b) Environmental safety

Radiation technology could have marginal advantage (no sulphur, no zink, low ash content, etc.). In some special products it may be of primary importance (example: protective gloves for the work with radioactive materials).

c) End-user safety

This is where the most important and potentially decisive advantage of RVNRL may exist. The demonstrated lack of nitrosamines (or far below the acceptable limits) and absence of cytotoxicity equal with the new and important quality of RVNRL products.

It has to be understood, however, that this quality will play an important role only if regulations would require better end-user safety of latex products. The present trend is definitely going in this direction and, once reinforced, the RVNRL could easily satisfy the strict safety requirements.

d) Economics

The problem of economics was not addressed in the comprehensive way at the Symposium, since, understandably, the emphasis was on technique and technology development. A detailed comparative analysis, for some specific product (or products) still remains to be done. Most of economic data, published and presented so far, are preliminary, of limited value and scope and applicable, at best, for rough orientation. In general, the RVNRL is not economically superior to conventional technology and, at the best, could be comparable. Again, no special incentive from industry on the basis of pure economics is to be expected.

One of the aspects of radiation technology, the service irradiation, has not yet been addressed at all in the case of RVNRL, although this technology can make the best use of economy of scale of radiation services. The RVNRL is easily applicable as service irradiation providing irradiated latex to a number of small industries, at the low cost
equivalent to high capacity throughput. This approach is worth a detailed feasibility study.

e) Other factors

The social, political, cultural and other factors should not be overemphasized since they play the minor role in comparative evaluation of RVNRL and conventional technology. The experience from other successful (and unsuccessful) industrial applications of radiation technology should be taken into account. It would be wrong and self-deluding to assume, in general, that industry is ignorant and reluctant to use radiation. The past experience shows that whenever it found profit and incentive to use it, there was no real obstacle.

The promotion of technology and dissemination of information, as at this Seminar, certainly play an important role to avoid misunderstandings and misconceptions.

4. Conclusions

(1) RVNRL is a technically viable technology for a number of products.
(2) RVNRL technology is immediately applicable to some special products.
(3) Further technology development (refinement) is needed and expected. The stronger participation and involvement of industry is desirable.
(4) Promotion of technology to industry is necessary.
(5) Service RVNRL deserves a detailed technoeconomical feasibility study and might be especially relevant to developing countries.
(6) Broader use of RVNRL technology may depend on regulations concerned with end-user safety.
### Author Index

<table>
<thead>
<tr>
<th>Author</th>
<th>Pages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bett, S. J.</td>
<td>5.16</td>
</tr>
<tr>
<td>Bez, W.</td>
<td>5.25</td>
</tr>
<tr>
<td>Binh, D.</td>
<td>5.15</td>
</tr>
<tr>
<td>Chen, Z. H.</td>
<td>5.20, 5.22</td>
</tr>
<tr>
<td>Chyagrit, S.</td>
<td>5.5, 5.21</td>
</tr>
<tr>
<td>Dang, H. P.</td>
<td>5.16</td>
</tr>
<tr>
<td>Dedik, E. S.</td>
<td>5.13</td>
</tr>
<tr>
<td>Devendra, R.</td>
<td>5.11, 5.14, 5.17</td>
</tr>
<tr>
<td>Dworjanyan, P. A.</td>
<td>5.16</td>
</tr>
<tr>
<td>Fujita, H.</td>
<td>1.2</td>
</tr>
<tr>
<td>Garnett, J. L.</td>
<td>5.16</td>
</tr>
<tr>
<td>Gazeley, K. F.</td>
<td>5.8</td>
</tr>
<tr>
<td>Haf, L.</td>
<td>5.15</td>
</tr>
<tr>
<td>Herwinarni</td>
<td>5.2, 5.6</td>
</tr>
<tr>
<td>Hien, N. Q.</td>
<td>5.15</td>
</tr>
<tr>
<td>Iramani, D.</td>
<td>5.6</td>
</tr>
<tr>
<td>Iskandar, S.</td>
<td>5.2, 5.6</td>
</tr>
<tr>
<td>Ishigaki, I.</td>
<td>5.1, 5.4, 5.9, 5.10, 5.21, 5.24</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>JAIF, Workshop</td>
<td>5.27</td>
</tr>
<tr>
<td>Jindarom, C.</td>
<td>5.5</td>
</tr>
<tr>
<td>Kaniwa, M.</td>
<td>4.1</td>
</tr>
<tr>
<td>Karunaratne, S. W.</td>
<td>4.6, 5.12</td>
</tr>
<tr>
<td>Kobayashi, M.</td>
<td>1.1</td>
</tr>
<tr>
<td>Koike, G.</td>
<td>5.3</td>
</tr>
<tr>
<td>Krisda, S.</td>
<td>5.5</td>
</tr>
<tr>
<td>Machi, S.</td>
<td>3.1</td>
</tr>
<tr>
<td>Makuuuchi, K.</td>
<td>4.3, 5.1, 5.4, 5.6, 5.9, 5.10, 5.11, 5.14, 5.17, 5.18, 5.20, 5.21, 5.23, 5.24</td>
</tr>
<tr>
<td>Man, N. T.</td>
<td>5.15</td>
</tr>
<tr>
<td>Manoon, A.</td>
<td>1.3</td>
</tr>
<tr>
<td>Markovic, V.</td>
<td>6.1</td>
</tr>
<tr>
<td>Marga, U.</td>
<td>5.2, 5.6, 5.13, 5.22</td>
</tr>
<tr>
<td>Name</td>
<td>Page Numbers</td>
</tr>
<tr>
<td>------------------</td>
<td>--------------</td>
</tr>
<tr>
<td>Muhd, N. B. M. U.</td>
<td>383</td>
</tr>
<tr>
<td>Nakamura, A.</td>
<td>79</td>
</tr>
<tr>
<td>Niepel, H.</td>
<td>111</td>
</tr>
<tr>
<td>Norjanah, M.</td>
<td>157</td>
</tr>
<tr>
<td>Ono, S.</td>
<td>198</td>
</tr>
<tr>
<td>Pansa, C.</td>
<td>216, 245</td>
</tr>
<tr>
<td>Parinya, A.</td>
<td>305</td>
</tr>
<tr>
<td>Pendle, T. D.</td>
<td>27, 189</td>
</tr>
<tr>
<td>Saito, T.</td>
<td>146, 207</td>
</tr>
<tr>
<td>Samantha, S.</td>
<td>368</td>
</tr>
<tr>
<td>Sato, Y.</td>
<td>146</td>
</tr>
<tr>
<td>Shimamura, Y.</td>
<td>88</td>
</tr>
<tr>
<td>Shukri, B. A. W.</td>
<td>216, 245</td>
</tr>
<tr>
<td>Sidek, B. D.</td>
<td>100</td>
</tr>
<tr>
<td>Siti, S. B. S.</td>
<td>245</td>
</tr>
<tr>
<td>Sofiarti, W.</td>
<td>350</td>
</tr>
<tr>
<td>Sumarti, M.</td>
<td>169</td>
</tr>
<tr>
<td>Sundardi, F.</td>
<td>132, 169, 234, 319, 350</td>
</tr>
<tr>
<td>Takehisa, M.</td>
<td>146</td>
</tr>
<tr>
<td>Thanh, V. T.</td>
<td>260</td>
</tr>
<tr>
<td>Thien, V. T.</td>
<td>260</td>
</tr>
<tr>
<td>Thomas, E. V.</td>
<td>178</td>
</tr>
<tr>
<td>Tsuchiya, T.</td>
<td>79</td>
</tr>
<tr>
<td>Tsushima, K.</td>
<td>127</td>
</tr>
<tr>
<td>Yamashita, S.</td>
<td>42</td>
</tr>
<tr>
<td>Yanti, S.</td>
<td>319</td>
</tr>
<tr>
<td>Yoshii, F.</td>
<td>127, 157, 169, 198, 207, 368</td>
</tr>
<tr>
<td>Yoshikawa, M.</td>
<td>15</td>
</tr>
</tbody>
</table>