Radiation dose required for the vulcanization of natural rubber latex via hybrid gamma radiation and peroxide vulcanizations

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Abstract. To enhance the crosslinking of prevulcanized natural rubber latex, combination of irradiation and peroxide vulcanizations were used. Through this method, hexanediol diacrylate (HDDA) from irradiation vulcanization acted as the main sensitizer, while cumene hydroperoxide (CHPO) from peroxide vulcanization would act as the co-sensitizer. The effects of irradiation doses on the mechanical properties of latex film were investigated. 16 kGy irradiation dose, 2.5 parts per hundred rubber (pphr) of HDDA, 0.1 pphr of CHPO and 2.5 phr of Aquanox LP antioxidant were found to be the optimum conditions for compounding formulation. The rubber film obtained had tensile strength, modulus at 500% and modulus at 700% of 27.7, 3.5 and 12.4 MPa respectively, which is more than 21% increment compared to control film. Besides, the crosslink percentage of the rubber film showed 7% increment from 90.7% to 97.7%.

1. Introduction

Radiation vulcanization of natural rubber latex (RVNRL) and peroxides vulcanization of natural rubber latex (PVNRL) have several advantages over the conventional vulcanization with sulphur such as less or absence of toxicity, free from nitrosamines and accelerator induced allergies, low in cytotoxicity and cleaner process [1-3]. These properties are important for many products, particularly catheters, surgical gloves and other medical and hospital supplies. For such uses, it is important that the products are free of contaminants, toxic and carcinogenic components to avoid harmful effects in human beings. However, the tensile strength of end products from both processes still failed to achieve a minimum of 24 Mega Pascal (MPa) as required by ASTM D3577-01a; which is the Standard Specification for Rubber Surgical Gloves [4].

Based on our previous studies, hybrid vulcanization method which consisted of radiation and peroxide vulcanizations could help to improve the mechanical properties of the vulcanized natural rubber latex films [5][6]. In this paper, the required radiation doses for vulcanization of natural rubber latex via hybrid irradiation and peroxide vulcanizations systems are determined. The other factor such
as effect of molecular structure of peroxide on the mechanical properties of irradiated latex film is also investigated.

2. Materials and Methods

2.1. Materials

The latex utilized in this work was a high ammonia type of latex (HA latex) supplied by Revertex (M) Pt. Ltd., Malaysia. The sensitizer and co-sensitizer used were hexanediol diacrylate (HDDA) supplied by Allnex, China and cumene hydroperoxide (CHPO) supplied by Merck, Germany respectively. The stabilizer used was potassium laurate supplied by Tiarco Chemical (M) Pt. Ltd., Malaysia and the antioxidant used was Aquanox Lp supplied by Aquaspersion (M) Pt. Ltd., Malaysia. These materials were used as received.

2.2. Preparation of RVNRL compounding formulations

A typical latex compounding formulation for RVNRL (control) preparation is given in Table 1. The sensitizer, stabilizer, antioxidant and water were homogenized into an emulsion prior to addition into the latex with gentle stirring [5][6]. Once the addition of the emulsified materials was completed, the latex mixture was left stirred for three hours. It was then transferred into a one litre screw capped plastic container and irradiated with gamma rays from a Cobalt-60 source at a dose of 12 kGy [6][7]. After almost 6 hours of irradiation, the RVNRL was formed into film by coagulant dipping method.

Table 1. Compounding formulation of standard RVNRL (control).

| Materials                             | Part per hundred (phr) |
|---------------------------------------|------------------------|
| NR Latex (62% Total Solid Content)    | 100                    |
| Stabilizer                            | 0.06                   |
| HDDA                                  | 2.50                   |
| Antioxidant                           | 2.50                   |
| Water                                 | Add to 52% Total Solid Content |

The experiment was repeated by adding 0.1 phr of CHPO as the co-sensitizer into 9 kg of latex as formulated in Table 2 [6]. It was then transferred into 9 separated one litre screw capped plastic container and irradiated with gamma rays from a cobalt-60 source at varying doses of 2, 4, 6, 8, 10, 12, 14, 16 and 18 kGy respectively.

Table 2. Compounding formulation of RVNRL with co-sensitizer.

| Materials                             | Part per hundred (phr) |
|---------------------------------------|------------------------|
| NR Latex (62% Total Solid Content)    | 100                    |
| Stabilizer                            | 0.06                   |
| HDDA                                  | 2.50                   |
| CHPO                                  | 0.10                   |
| Antioxidant                           | 2.50                   |
| Water                                 | Add to 52% Total Solid Content |
2.3. Irradiation
The latex formulations were irradiated using gamma rays from Co-60 isotope at MINTec-Sinagama Plant, Malaysian Nuclear Agency. Currently the activities of Co-60 are 447000 Curie with dose rate of 2.08 kGy/hr.

2.4. Measurement of tensile properties
Specimens for tensile testing were prepared using the coagulant dipping method to simulate the production of gloves in the gloves production line, where a glass plate was immersed in the coagulant and then placed in an oven at 100°C to partially dry the coagulant. It was then immersed in the latex compound for 20 seconds. The wet gel was allowed to consolidate at 100°C for 1 minute, and followed by leaching in distilled water at 60°C for 5 minute to remove hydrophilic materials and excess chemicals from latex dipped produce by washing them in hot water. The latex film was finally dried at 100°C for 30 minute and subjected to tensile test using Universal Testing Machine Instron 5564 in accordance to ASTM D412 [8]. The latex films samples were cut into dumbbell shape test pieces (Figure 1). Five samples were used for tensile test and a median value was taken as the final result.

![Figure 1. Dimension of dumbbell cut](image)

2.5. ATR spectroscopy
In this study, FTIR spectroscopy analysis was carried out using Bruker's Tensor II Platinum Attenuated total reflection (ATR) spectrophotometer.

2.6. Determination of gel content
The gel content of the crosslinked samples were determined by the extraction of samples in toluene for 8 hours using Soxhlet apparatus [9][14]. The extraction samples were dried in an oven at 70°C until constant weight was achieved. The gel fraction was calculated as Eq. i:

\[
\text{Gel content, } \% = \frac{w_f}{w_o} \times 100
\]

where \(w_o\) and \(w_f\) are the weights of the dried samples before and after extraction, respectively.

3. Results and discussion

3.1. Effect of irradiation doses on tensile strength of RVNRL
In gloves production, tensile strength and modulus values are considered as the commercial importance parameter. Tensile strength value are referred to the extent of the film undergo stress, whilst modulus values are always referred as the degree of crosslinking in the films [10]. Thus, the precise amount of irradiation dose is very important in preparation of RVNRL because the irradiation dose gives a major impact on the mechanical properties of RVNRL [2].

In previous studies, aliphatic type peroxide; \(t\)-butyl hydroperoxide successfully have helped to produce rubber film with tensile strength, modulus at 500% and modulus at 700% of 27.0, 3.0 and
11.0 MPa respectively at irradiation dose of 6 kGy [11]. However, in this study CHPO with aromatic molecular structure was found to give totally different results as compared to peroxide with aliphatic molecular structure. Table 3 gives the mechanical properties of control and hybrid RVNRL-peroxide samples that have been prepared by gamma irradiation at various doses and tested as required by ASTM D412 standard.

| Sample                        | Irradiation dose (kGy) | Modulus @ 500% (MPa) | Modulus @ 700% (MPa) | Tensile strength (MPa) |
|-------------------------------|------------------------|----------------------|----------------------|-----------------------|
| RVNRL (Control)               | 12                     | 2.8                  | 10.5                 | 22.5                  |
| Hybrid RVNRL-peroxide (D2)    | 2                      | 0.9                  | 2.5                  | 9.3                   |
| Hybrid RVNRL-peroxide (D4)    | 4                      | 1.5                  | 4.9                  | 15.6                  |
| Hybrid RVNRL-peroxide (D6)    | 6                      | 2.2                  | 7.5                  | 18.9                  |
| Hybrid RVNRL-peroxide (D8)    | 8                      | 2.4                  | 8.8                  | 22.7                  |
| Hybrid RVNRL-peroxide (D10)   | 10                     | 2.5                  | 9.1                  | 23.8                  |
| Hybrid RVNRL-peroxide (D12)   | 12                     | 2.9                  | 11.3                 | 24.3                  |
| Hybrid RVNRL-peroxide (D14)   | 14                     | 3.0                  | 12.3                 | 26.4                  |
| Hybrid RVNRL-peroxide (D16)   | 16                     | 3.6                  | 12.4                 | 27.3                  |
| Hybrid RVNRL-peroxide (D18)   | 18                     | 3.5                  | 13.5                 | 27.3                  |

It was observed that rubber film obtained from irradiation at 16-18 kGy had tensile strength, modulus at 500% and modulus at 700% of 27.3, 3.5 and 12.4 MPa respectively, which was more than 21% increment as compared to control. In contrast to the use of aliphatic type peroxide, decomposition of peroxide with aromatic molecular structure required high irradiation dose to engender the radical reaction. This is due to the high energy required to break aromatic rings that are very stable, where the electron density is delocalized in the ring so each bond is more similar to 1.5 bonds than either single or double bonds [12]. Besides that, higher irradiation dose also help to increase the mechanical properties of hybrid RVNRL-peroxide films due to the enhancement of the intraparticle crosslink density (chemical crosslinking) caused from monogeneity of the hybrid radiation and peroxide vulcanizations [2][6][13].

Infra-red spectroscopy has been used to investigate the substances have been used in the reaction. Figure 2(a) to 2(d) show that there is no sign of residue HDDA and/or peroxide found in RVNRL samples because they are believe to be consumed by radiation polymerization and hydrolysis during the radiation vulcanization process. According to Figure 2(b) and 2(c), it can be clearly observed the presence of functional groups of C-O at wavelength ranges 1181-1225, while functional groups of C=O from HDDA and C=C (aromatic) from CHPO clearly observed at wavelength 1719 cm$^{-1}$ and 1701 cm$^{-1}$ respectively. However, there is no sign of functioning group of C=C (aromatic), C-O and C=O in the hybrid RVNRL-peroxide spectrums in Figure 2d. So it can be concluded that both HDDA and CHPO has been consumed during the vulcanization process.
Figure 2 (a). Infra-red spectrum for polyisoprene.

Figure 2(b). Infra-red spectrum for hexanedioldiacrylate.
Figure 2(c). Infra-red spectrum for cumene hydroperoxide.

Figure 2 (d). Infra-red spectrums for hybrid RVNRL-peroxide at various irradiation doses.
3.2. Effect of irradiation doses on gel content of hybrid RVNRL-peroxide

Soxhlet extractor is used to perform the extraction with toluene for the purpose of determining the gel fraction/content of RVNRL, which is defined as the percentage of a sample that does not dissolve in toluene. The crosslinked or gelled polymers only swell up and not dissolve in any solvent. The gel content is determined indirectly from the amount of soluble fraction and directly by weighing the dried gel [9, 14]. Figure 3 shows the relationship between gel content with irradiation doses. As shown, the extent of gel formation increases with the increasing of irradiation dose, indicating increases in crosslink density of the polymer. From the graph, it was observed that at 16 kGy of irradiation dose, hybrid RVNRL-peroxide film produced 97.7 % crosslink percentage and 7 % increment compared to the control sample at 90.7 %. However, it is also showed that the percentage of gel content decreased as the irradiation dose increased. This happens when the interparticle entanglement (physical crosslinking) starting to decreased when the irradiation dose increased. The interparticle entanglements are depended on the free rubber chain ends at the surface of each latex particle. These chains interpenetrate during film formation and contribute to the strength of the film by means of entanglements. The length of free rubber chain ends decreases with the increasing of irradiation dose because it is equivalent to molecular weight between crosslink [2]. Thus, the degree of crosslink in hybrid RVNRL-peroxide latex films increases up to maximum level and then will decrease with the increasing dose.

![Figure 3. Effect of Irradiation Doses on Gel Fraction of Hybrid RVNRL-peroxide.](image)

4. Conclusion

RVNRL with good tensile strength can be prepared by hybrid radiation and peroxide vulcanizations. Irradiation of latex compounding formulation based on 2.5 phr of hexanediol diacrylate (HDDA) as sensitizer, 0.1 phr of cumene hydroperoxide (CHPO) as co-sensitizer and 2.5 phr of Aquanox LP as an antioxidant at irradiation dose of 16 kGy can produced rubber film with tensile strength of 27.3 MPa with crosslink percentage of 97.7%. With that, it is concluded that the molecular structure of the peroxide has a great effect on the irradiation dose required for the vulcanization process, where the peroxides with aromatic structure will require higher irradiation dose compared to the aliphatic peroxides.
5. References

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