Mechanical properties and thermogravimetric analysis of peroxide prevulcanized natural rubber latex induced by Co-60 γ radiation

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Abstract. The radiation and peroxide vulcanizations of natural rubber latex are sharing the same problem which is low mechanical properties on their latex. This makes it unsuitable to be use in the production of premium latex products such as surgical glove. Moreover, there are some cases where the use of sensitizers in radiation vulcanization and activators in peroxide vulcanization tends to produced latex film with unpleasant smell and darken color respectively during the drying process. For this study, radiation of latex formulations based on 0.1 pphr of tert-butyl hydroperoxide and 0.06 pphr of potassium laurate at various radiation doses showed increment of tensile strength with increasing of radiation doses; radiation at 25 kGy produced rubber film with tensile strength of 20.7 MPa which is almost 7 times higher than control.

1. Introduction

One of the major contributors to Malaysia’s national income is rubber and latex-based products. Based on Natural Rubber Statistics 2020 report [1], Malaysia’s manufactured rubber goods sales from year 2008 to 2020 showed a very encouraging increment, especially on rubber gloves product (Figure 1). From the data, it is shown that on 2019 the sale of rubber gloves alone contributed RM 16.35 billion to national income, an increment of 6.9 % from previous year. Therefore, a continuous research and development in latex technology is essential to guarantee the expansion of this positive sales performance.

In latex dipped products production such as surgical gloves, it is known that natural rubber latex needs to be vulcanized prior to use in rubber glove production. At present, there are three major types of vulcanization methods being used in natural rubber latex industries; namely sulphur, radiation and peroxide vulcanizations. However, sulphur vulcanization has a major drawback in the regards to its by products, i.e. nitrosamines and nitrosatables. These unwanted by products are carcinogenic materials which may cause cancer and chemical allergies [2,3].
The peroxide vulcanization of natural rubber latex (NRL) was introduced by the Malaysian Rubber Board (MRB) since the early 1990s. Alike the Radiation Pre-vulcanized Natural Rubber Latex (RVNRL) that was introduced by the Malaysian Nuclear Agency, peroxide vulcanization also faced the same problem which is produced low mechanical properties (tensile strength) latex. This makes it unsuitable to be use in the production of premium latex products such as surgical glove and etc. Moreover, there are some cases where the use of radiation sensitizer in radiation vulcanization and activators in peroxide vulcanization tends to produced NRL film with unpleasant smell and darken color during the drying process [4,5].

In conventional peroxide vulcanization, organic peroxide will be mixed with NRL and activators such as tetra-ethylene pentamine, fructose and hydroxyacetone before heating at 70 °C to produced prevulcanized NRL with tensile strength of approximately 18 to 22 MPa [6]. The function of these activators is to yield free radicals from peroxide to promote the formation of rubber chains crosslinking, whereas without the presence of the activator the crosslink reaction of the NRL will occur at very low rate [7].

Based on our previous study, the activator and co-agent in peroxide vulcanization are no longer needed when using gamma radiation because the high radiation energy from ionized radiation capable to promote the peroxide decomposition in NRL for the formation of rubber chains crosslinking [8]. For this study, the optimum radiation doses for vulcanization of NRL via peroxide vulcanization system are determined based on the mechanical properties (tensile strength) of the films. This study also extended to examine the effects of radiation on crosslinking density and thermal stability of the Peroxide Prevulcanized Natural Rubber Latex (PVNRL) films.

2. Materials and methods

2.1. Materials
The latex utilized in this work is a high ammonia type of latex (HA latex) supplied by Revertex (M) Pt. Ltd., Malaysia. The peroxide used were tert-butyl hydroperoxide (t-BHPO) supplied by Fluka, Switzerland and 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) Sdn. Bhd., Malaysia. These materials were used as received.

2.2. Preparation of PVNRL compounding formulations
Six kilogram (kg) latex compounding formulation for peroxide vulcanization preparation using \( t\)-BHPO is given in Table 1. The peroxide, stabilizer and water were first prepared into an emulsion before slowly added into the latex with gentle stirring. Once the addition of the emulsified materials was completed, the latex mixture was left stirring for three hours [8, 9]. It was then transferred into 6 separated one litre screw capped plastic container and irradiated with gamma rays from a cobalt-60 source at MINTec-Sinagama Plant, Malaysian Nuclear Agency (58778 Curie; dose rate 1.61 kGy/hr) at varying doses of 0, 5, 10, 15, 20 and 25 kGy respectively. After radiation, the latex was made into film by coagulant dipping method to measure its mechanical properties.

Table 1. Compounding formulation for \( t\)-BHPO vulcanization.

| Materials                  | Part per hundred rubber (pphr) |
|----------------------------|--------------------------------|
| NRL (62% Total solid content; TSC) | 100                            |
| \( t\)-BHPO                | 0.10                           |
| Stabilizer                 | 0.06                           |
| Antioxidant                | 2.50                           |
| Water                      | Add to 52% TSC                 |

2.3. Measurement of tensile properties
Specimens for tensile testing were prepared using the coagulant dipping method [3, 10]. 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 s. 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 minutes. The latex film was finally dried at 100°C for 30 minutes and subjected to tensile test using Universal Testing Machine Shimadzu M703911, 50N in accordance to ASTM D412 [11]. The latex films samples were cut into dumbbell shape test pieces (Figure 2). Five samples were used for tensile test and a median value was taken as the final result.

![Figure 2. Dimension of dumbbell cut](image)

2.4. Determination of gel content
The gel content of the crosslinked samples was determined by the extraction of samples in toluene for 8 hours using Soxhlet apparatus as required by [12, 13]. The extraction samples were dried in an oven at 70°C till constant weight was achieved. The gel fraction was calculated as Eq. (1):
Gel content, % = \( \frac{w_1}{w_0} \times 100 \)  \hspace{1cm} (1)

where \( w_0 \) and \( w_1 \) are the weights of the dried samples before and after extraction, respectively.

2.5 Thermogravimetric analysis (TGA) and Differential thermal analysis (DTA)
TGA and DTA analysis was performed using the Perkin Elmer model of Pyris 1 Thermal Analyzer where heating process was performed in a nitrogen environment at 30-650 °C temperature range with 10 °C / min heating rate.

3. Results and discussion

3.1 Effect of radiation doses on tensile strength of RVNRL
The suggested mechanisms for decomposition of peroxide by radiation were shown in Figure 3. In such a mechanism, RH, B and RR will represent natural rubber latex, peroxide and prevulcanized natural rubber latex.

\[ \text{Radiolysis of NR} \quad \text{RH} \quad \text{Radiolysis of water} \quad \text{H}_2\text{O} \quad \text{Hydrogen abstraction} \quad \text{RH} + \text{OH}^- \rightarrow \quad \text{R}^- + \text{H}_2\text{O} \]

\[ \text{Decomposition of peroxide} \quad \text{B} \quad \text{Hydrogen abstraction from polymer} \quad \text{B}^- + \text{RH} \rightarrow \quad \text{BH} + \text{R}^- \quad \text{Termination} \quad \text{R}^- + \text{R}^- \rightarrow \quad \text{R-R} \]

Figure 3. Mechanism for decomposition of peroxide by radiation

Parameters such as tensile strength and modulus values are very important in the production of latex dipped products. This is because some products have to meet certain standards. For example, the minimum tensile strength for surgical glove is 24 Mega Pascal (MPa) as required by the ASTM D3577-01a standard [14], while the minimum tensile strength for examination glove is 18 MPa as required by the ASTM D3578 – 05 [15]. However, from our previous study mixture of NRL and 0.1 pphr \( \text{t-BHPO} \) irradiated at 12 kGy only capable to produced PVNRL with 15 MPa tensile strength [8]. Thus, investigation on the precise amount of radiation dose is very important because it can give major impact on the mechanical properties of the latex [2].

Since the films are cast after radiation process, the particles coalesce together into transparency film during evaporation process of emulsion medium; the interaction between particles determines tensile strength and elongation at break of the film. Table 2 gives the mechanical properties of PVNRL samples that have been prepared by gamma radiation at various doses and tested as required by ASTM D412 standard.
Table 2. Mechanical properties of PVNRL irradiated at various dose (median value from tensile test).

| Sample       | Radiation dose (kGy) | Modulus @ 500% (MPa) | Modulus @ 700% (MPa) | Tensile strength (MPa) |
|--------------|----------------------|----------------------|----------------------|------------------------|
| PVNRL (Control) | 0                    | 0.31                 | 1.52                 | 3.1                    |
| PVNRL        | 5                    | 0.83                 | 2.85                 | 12.4                   |
| PVNRL        | 10                   | 0.97                 | 3.19                 | 17.5                   |
| PVNRL        | 15                   | 1.51                 | 4.54                 | 19.0                   |
| PVNRL        | 20                   | 1.35                 | 4.28                 | 20.0                   |
| PVNRL        | 25                   | 2.23                 | 5.06                 | 21.7                   |

It was observed that the tensile strength, modulus at 500 % and modulus @ 700 % of the films increase continuously with increasing radiation dose. The rubber film obtained from radiation at 25 kGy had a tensile strength, modulus at 500 % and modulus @ 700 % of 21.7, 2.23 and 5.06 MPa respectively; which is more than six times increment compared to control.

The increasing of the tensile strength of PVNRL is suggested due to the increasing of the intraparticle crosslink density (chemical crosslinking) caused from increasing radiation dose which leads to the formation of a three-dimensional network or rubber matrix [16]. Besides, the interparticle entanglement (physical crosslinking) also suggested to increase with the increasing dose because of the interparticle entanglements are depending on the free rubber chain ends at the surface of each latex particle, whereby these chains interpenetrate during film formation and contribute to the strength of the film by means of entanglements. [2].

3.2. Effect of radiation doses on gel content of PVNRL

The gel content or percentage of crosslinking is determined based on ASTM D3616-95 [12] requirement. The effect of radiation doses on gel content of PVNRL are shown in Table 3. From the table, it was observed that the extent of gel formation increases with the increasing of radiation dose, indicating increases in crosslink density of the polymer. At 25 kGy of radiation dose, PVNRL film produced 84.5 % crosslink percentage compared to the control sample at; 35.9 %.

Table 3. Effect of radiation doses on gel content of PVNRL.

| Sample       | Radiation dose (kGy) | Gel content (%) |
|--------------|----------------------|-----------------|
| PVNRL (Control) | 0                    | 35.9            |
| PVNRL        | 5                    | 69.1            |
| PVNRL        | 10                   | 75.3            |
| PVNRL        | 15                   | 82.6            |
| PVNRL        | 20                   | 83.9            |
| PVNRL        | 25                   | 84.5            |

3.3. TGA analysis

TGA analytical technique was used to determine a material’s thermal stability for PVNRL that was prepared at various radiation doses (Figure 4). When NRL are crosslinked by peroxides and radiation, C-C bonds are formed between individual rubber chains. The C-C bond is stronger and more thermal stable than the C-S bond formed by sulphur vulcanization.
Figure 4. TGA thermograms for PVNRL prepared at various radiation doses.

From the TGA analysis that was conducted on all PVNRL samples, it was observed that the weight loss of the PVNRL samples occurred in the temperature range of 300–540 °C corresponding to a degradation of the non-volatile residues (Table 4). Besides, $T_{\text{deg}}$ for the samples are around 378 °C. From the weight loss curves, a clearer picture of the effect of radiation doses on the thermal stability of the latex has been observed. The thermograms clearly show a less steep gradient for the entire PVNRL sample that was prepared from 5 to 25 kGy compared to the control (0 kGy). These results were attributed to an enhancement of the C-C crosslink density of PVNRL as consequence of the dose effect; whereas increasing of the C-C bond density also increase the thermal stability of the latex [17].

**Table 4. Decompositions temperature of PVNRL at various radiation doses**

| Radiation dose (kGy) | $T_0$ (°C) | $T_{\text{deg}}$ (°C) | $T_{\text{end}}$ (°C) |
|-----------------------|------------|------------------------|------------------------|
| 0                     | 350        | 378                    | 475                    |
| 5                     | 353        | 379                    | 505                    |
| 10                    | 353        | 378                    | 510                    |
| 15                    | 352        | 378                    | 520                    |
| 20                    | 353        | 378                    | 528                    |
| 25                    | 353        | 378                    | 535                    |

4. Conclusions
Peroxide prevulcanized natural rubber latex (PVNRL) with promising high tensile strength can be prepared by induced with Co-60 $\gamma$ radiation. Radiation of latex formulations based on 0.1 pphr of tert-butyl hydroperoxide ($t$-BHPO) and 0.06 pphr of potassium laurate as stabilizer at various radiation doses showed the increment of the tensile strength as the increasing of radiation doses. At radiation dose of 25 kGy, rubber film with tensile strength of 20.7 MPa and crosslink percentage of 84.5 % has been successfully produced.
5. References

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