Effect of low dose gamma irradiation on the tensile and thermal properties of natural rubber-based blend

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Abstract. Natural rubber (NR) is a renewable natural resource that has been utilized in many applications. Due to its low tensile strength, NR is commonly blended with another polymer to improve the properties of NR. However, most of the blended NR has miscibility issue, leading to poor mechanical properties. Gamma irradiation (GR) is a safe and green alternative than conventional chemical method for inducing crosslinking in blended NR. This study was aimed at investigating the mechanical and thermal properties of NR/liquid natural rubber/polystyrene-block-polysoprene block copolymer (NR/LNR/PS-b-PI) blend using GR method. The polymer blend is prepared according to the ratio of NR:LNR:PS-b-PI of 6:1:3 using an internal mixer. The NR/LNR/PS-b-PI blends are irradiated with gamma ray at doses of 0, 5, 6, 7, 8 and 9 kGy. Tensile and thermal tests are conducted to evaluate the properties of unirradiated and irradiated polymer blend. The tensile strength and modulus of the irradiated blend are increased with increasing irradiation dose before decrease at 9 kGy. Lower melting point of blend indicates that PS-b-PI are compatible in NR/LNR blend. The improvement in tensile properties of irradiated NR/LNR/PS-b-PI blend is related to the radiation-induced crosslinking.

1. Introduction

Demand for natural rubber (NR) in various sectors has increased owing to its properties such as high elasticity, low cost, good wear and weather resistance. However, NR has limited temperature stability and low tensile strength. Polymer blending technique is an alternative to improve NR performance in which two or more polymers are combined to produce new polymer blend with desired properties. The blending of natural rubber with other elastomers and polymer such as liquid natural rubber (NR/LNR) [1], polylactic acid (NR/PLA) [2], and styrene-butadiene rubber (NR/SBR) [3] have shown improvement in tensile properties compared to neat NR. It is known that the main problem associated with polymer blend is the immiscibility between polymer pairs that led to poor mechanical properties. Hence, many studies have been carried out to improve the miscibility of NR by adding NR with chemical compatibilizer such as maleic anhydride, methyl methacrylate and glycidyl methacrylate [4-6]. Although the properties of blended polymer may be improved, the high cost of compatibilizer materials increase production costs [7]. The addition of block copolymers (BCP) in the NR-based polymer blend has been widely studied [8-9]. Polystyrene-block-polysoprene (PS-b-PI) is a type of BCP consists of a glassy domain (PS) and rubbery part (PI). Chattopadhyay S. et. al (2001) blended natural rubber with polystyrene and reported that the addition of PS-b-PI has increased mechanical properties of the blend [8].
Gamma irradiation (GR) is a green and fast modification technology to induce crosslinking in polymer blend. GR has short curing time, low cytotoxicity, high productivity, and no residue in final products [10]. GR can modify the structure of materials by causing several reactions to occur in the system during irradiation such as chain crosslinking, scission and branching [11]. The property improvement of the polymer blend, however, depends on the irradiation dose of γ-irradiation treatment.

The main objective of this study is to evaluate the effect of the low gamma irradiation doses on the tensile and thermal properties of natural rubber/liquid natural rubber/polystyrene-\(b\)-polysisoprene (NR/LNR/PS-\(b\)-PI) polymer blend.

2. Description of the experiment and research methods

In this work, method of polymer blending and gamma irradiation have been chosen to fabricate irradiated NR/LNR/PS-\(b\)-PI blend. As experimental samples, the natural rubber (NR), liquid natural rubber (LNR) and polystyrene-\(b\)-polysisoprene (PS-\(b\)-PI) have been used. NR, in 62% solid content is purchased from Mardec Sdn Bhd and has been kept in ammonia to prevent degradation. The LNR, made through depolymerization of NR has been supplied by the Polymer Processing Laboratory, National University of Malaysia. The PS-\(b\)-PI block copolymer has been supplied by Takenaka Laboratory, Kyoto University, Japan. The preparation of the blended NR/LNR/PS-\(b\)-PI consist of blending NR: LNR: PS-\(b\)-PI at a ratio of 6:1:3 by weight percentage (wt.%) by using an internal mixer machine (Plasti-Corder, Brabender) at temperature of 190°C at a screw speed of 100 rpm for 15 minutes. The polymer blend has been kept overnight to achieve equilibrium expansion. Samples for the tensile test have been prepared using the hot press machine (LP 50, LabTech). The gamma irradiation has been carried out at a radiation facility in Malaysian Nuclear Agency, Selangor, Malaysia using Iridium-192 source. The samples have been irradiated at different doses of 5, 6, 7, 8 and 9 kGy in room temperature. Experimental studies are carried out to determine the optimum irradiation dose on the mechanical and thermal properties of irradiated NR/LNR/PS-\(b\)-PI blend. Tensile test has been carried out using the Universal Testing Machine (Model M350-10CT) in a three-point bending mode with a cell load of 5 kN. For thermal test, Differential Scanning Calorimetry (Mettler Toledo DSC 882e) has been used to determine the melting point of the samples. 5 mg of samples are heated from -50°C to 300°C with 10°C/min of heating rate. All data are then analyzed for discussion.

3. Results and discussion

Based on the results of the experimental studies, the effect of irradiation dose on the mechanical and thermal properties of NR/LNR/PS-\(b\)-PI polymer blend has been analyzed.

As shown in Figure 1 (a), it is observed that the tensile strength of NR/LNR blend is improved with the addition of block copolymer, PS-\(b\)-PI. The primary cause for the improvement in tensile strength could be due to the PS-\(b\)-PI has enhanced the compatibility of the polymer blend and help to increase the strength of the rubber. Similar effect of PS-\(b\)-PI as compatibilizer has been found in NR/PS blend [8]. The addition of PS-\(b\)-PI also increases the Young’s modulus of NR/LNR blend from 0.17 MPa to 0.91 MPa, as shown in Figure 1 (b). Upon gamma irradiation on the polymer blend and increasing the irradiation doses, a remarkable increase in tensile strength and modulus of irradiated samples can be observed. The maximum tensile strength and Young’s modulus is obtained in the sample irradiated with dose of 8 kGy, having values of 0.25 MPa and 3.4 MPa, respectively. Apparently, the Young’s modulus of 8 kGy-irradiated sample is 273% higher than unirradiated NR/LNR/PS-\(b\)-PI blend. This improvement is associated to the radiation-induced crosslinking [12].

It is discovered that the tensile strength and Young’s modulus decreased to 0.21 MPa and 2.98 MPa, respectively, when the polymer blend has been irradiated with a 9 kGy dose. The poor tensile properties suggest that the 9 kGy irradiation dose has promoted chain scission and eventually degrades the NR/LNR/PS-\(b\)-PI polymer blend.
The DSC melting thermograms of the neat PS-b-PI and NR/LNR/PS-b-PI polymer blend is shown in Figure 2. The melting temperature ($T_m$) has been determined at the base of the melting endothermic peak. The $T_m$ of the neat NR/LNR cannot be determined due to its $T_m$ is found lower than -60 °C [13]. The $T_m$ for PS-b-PI and NR/LNR/PS-b-PI polymer blend is at 152.67 °C and 68.33°C, respectively. The decrease of the $T_m$ of the polymer blend explains that the PS-b-PI is miscible in the NR/LNR blend during the blending process. For the $\gamma$-irradiated polymer blend, a slight increase in the $T_m$ is observed, except for 9 kGy-irradiated blend sample. The increase in $T_m$ of irradiated samples implied that the chain crosslinking has been generated by the irradiation procedure. However, an excessive irradiation dose of 9 kGy decreases the $T_m$ of NR/LNR/PS-b-PI to 57.33°C.

![Figure 1](image1.png)

**Figure 1.** (a) Tensile strength and, (b) Young’s modulus of NR/LNR blend and NR/LNR/PS-b-PI at various irradiation doses.

![Figure 2](image2.png)

**Figure 2.** DSC thermograms of the neat NR/LNR, PS-b-PI and NR/LNR/PS-b-PI polymer blend at various irradiation doses.
4. Conclusion
This research study has been done to investigate the effect of various irradiation doses on the mechanical and thermal properties of the natural rubber/liquid natural rubber/polystyrene-\textit{block}-polyisoprene polymer blend using the gamma irradiation method. It is shown that adding 3 wt% of block copolymer PS-\textit{b}-PI and low irradiation doses (5, 6, 7, and 8 kGy) have increased the tensile strength and Young’s modulus of polymer blends. The low doses of gamma irradiation have enhanced the chain crosslinking of the NR/LNR/PS-\textit{b}-PI polymer blend. It has been shown that 9 kGy irradiation dose decreases the tensile properties due to degradation process. From thermal test, a lower melting point found in NR/LNR/PS-\textit{b}-PI implied that PS-\textit{b}-PI is compatible in the NR/LNR blend. From this study, it is possible to determine the optimal irradiation dose which will allow maximum tensile and thermal properties improvement in NR/LNR/PS-\textit{b}-PI polymer blend.

5. References
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