Radiation vulcanization of natural rubber latex by Caesium-137 source

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Abstract. Radiation vulcanized natural rubber latex is a rubber latex vulcanized by using ionizing radiation such as gamma radiation or electron beam. Gamma radiation is preferred over electron beam due to its higher penetration power, and Cobalt-60 is commonly used as a gamma radiation source for the irradiation process. Caesium-137 is another source for gamma radiation but it is not commonly used for RVNRL preparation despite its longer half-life. Caesium-137 retains its source activity much longer than Cobalt-60 and a Caesium-137 based irradiation facility would require less replenishment compares with the one with Cobalt-60. One of the reasons preventing the application of Caesium-137 for RVNRL preparation is its lower gamma radiation energy. This study aimed to analyze RVNRL prepared by using Caesium-137 source from a gamma cell and to compare its tensile properties with RVNRL prepared by using Cobalt-60 source. Results showed evidence of radiation induced crosslinking in RVNRL prepared by Caesium-137 source. At radiation dose of 12 kGy, the tensile properties of RVNRL prepared by Caesium-137 source is comparable to those by Cobalt-60. At radiation dose below 12 kGy, the effectiveness of Caesium-137 in radiation vulcanization is found to be better than that of Cobalt-60.

1. Introduction
Radiation vulcanization of natural rubber latex (RVNRL) is a technology for vulcanizing natural rubber latex by using high energy ionizing radiation such as gamma radiation or electron beam [1-3]. The most significant advantage of this technology when comparing to conventional sulphur vulcanization of natural rubber is the absence of sulphur and its accelerators in RVNRL. Radiation vulcanization does not require sulphur to crosslink latex as oppose to sulphur vulcanization. Products made from RVNRL are free from sulphur and sulphur vulcanization accelerators residue, and as a result, these products are free from carcinogenic nitrosamine and SO\textsubscript{x} pollutants, having low ash residue upon incineration and very low cytotoxicity [4]. In short, they are more user and environmental friendly compared to products made from sulphur vulcanized latex. In radiation vulcanization, rubber chains in latex are crosslinked via free radicals mechanism. The free radicals involved are produced from the interaction between water and ionizing radiation, a process called radiolysis [5]. The use of monomer acrylate based sensitizer such as n-butyl acrylate in radiation vulcanization has reduced the amount of required radiation from 250 kGy to less than 15 kGy [6-8], which has remarkably reduces vulcanization cost and promises commerciality of RVNRL.

Malaysian Nuclear Agency possesses the only RVNRL facility in the country. It is a pilot plant designed for demonstrating the viability of RVNRL production for industry application and technology
transfer. It is based on Cobalt-60 source for gamma radiation and capable of producing 6000 ton of RVNRL annually when it is loaded with 1 MCi of Cobalt-60. Cobalt-60 has a half-life of 5.26 years [9]. Hence, the source needs replenishment in a regular manner in order to maintain its activity and production capacity, and the cost is considerably high. Caesium-137 is a potential replacement for Cobalt-60 as it is also a gamma radiation emitter [10]. It is better than Cobalt-60 in reducing frequency of source replenishment as it has longer half-life of 30.17 years. However, radiation energy of Caesium-137 is almost 50% lower than Cobalt-60’s. This leads to lower penetration power and ability to interact with medium it’s travelling in. It may also affect its effectiveness as a gamma radiation emitter for RVNRL. Therefore, it is crucial to investigate the suitability and effectiveness of Caesium-137 for RVNRL preparation. The objective of this paper is to report the tensile properties of RVNRL produced by Caesium-137 gamma irradiator and to compare the properties with RVNRL irradiated by Cobalt-60.

2. Experimental

2.1. Materials
Raw latex used in this work was high ammonia latex concentrate supplied by TT Latex, Jelebu, Negeri Sembilan. Sensitizer used was n-butyl acrylate (nBA) purchased from Sigma-Aldrich, Co., USA. Stabilizer used was Octosperse KL20, a 20% fatty acid soup produced by Tiarco Chemical (M) Sdn. Bhd., Ipoh, Perak. All the stated materials were used as received.

2.2. Sample preparation
RVNRL formulation were prepared in accordance to Table 1. Sensitizer, stabilizer and water were made into emulsion, added to raw latex and stirred slowly for at least 2 hours. Formulated latex was filled into capped PE bottles of 500 ml capacity. The latex samples were irradiated by using research loop at MINTech-Sinagama and gamma cell Biobeam GM8000 for 4, 8 and 12 kGy respectively. Both research loop at MINTech-Sinagama and gamma cell Biobeam Gm8000 are gamma irradiators available in Malaysian Nuclear Agency. The research loop uses Cobalt-60 while the gamma cell uses Caesium-137 as radiation source. The dose rate of the research loop and gamma cell were 2.11 kGy/hour and 0.73 kGy/hour respectively. Irradiated latex samples, now called RVNRL, were used to prepare latex dipped films for tensile tests. The films were conditioned in desiccator for at least 16 hours prior to testing.

| Table 1. RVNRL formulation. |
|-----------------------------|
| Ingredient      | Amount, part per hundred rubber (phr) |
| Latex concentrate | 100                      |
| nBA             | 5                         |
| Stabilizer      | 0.06                      |
| Water           | For dilution to 52% total solid content |

2.3. Tensile tests
Tensile tests were conducted in accordance with ASTM D412 standard using a Shimadzu universal testing machine model AG-XDplus, with a crosshead speed and controlled temperature of 500 mm/minute and 25±2 °C respectively. Tensile properties measured included modulus at 700 % elongation, tensile strength and elongation at break.
3. Results and discussion

Tensile properties of a latex vulcanizate such as tensile strength, modulus and elongation at break are the most basic properties referred by latex product manufacturers when judging the quality of a latex product. In the case of radiation vulcanization, changes in tensile properties under different vulcanization condition such as type of radiation, radiation dose and sensitizer are good indicators of the effects of such vulcanization condition. In this regards, the effects of gamma radiation from Caesium-137 source are investigated by studying tensile properties of RVNRL irradiated at various radiation dose.

Graphical representation of the result of modulus (at 700% elongation), tensile strength and elongation at break of RVNRL irradiated by Caesium-137 and Cobalt-60 sources at radiation dose ranged from 0 – 12 kGy are shown in Figure 1, 2 and 3 respectively. By referring to Figure 1, it is obvious that the modulus of RVNRL irradiated by Caesium-137 increases with radiation dose. Modulus of a latex article is reflected on its degree of stiffness, and it is directly proportional to crosslink density as a result of vulcanization [11]. Hence, the increase of modulus in RVNRL is an evidence of crosslinking in the latex upon exposure to gamma radiation from Caesium-137. This claim is supported by tensile strength and elongation at break of RVNRL irradiated by Caesium-137. In Figure 2, the trend of tensile strength against radiation dose of Caesium-137 is similar to modulus, which is due to the same reason, i.e. radiation induced crosslink. According to Figure 3, the change of elongation at break shows reverse trend compares to tensile strength and modulus. Elongation at break of RVNRL showed an instant increment upon irradiation but then reduced with the increase of radiation dose due to increase of embrittlement of RVNRL. This phenomenon is a consequence of increase in rigidity of rubber network as a results of radiation induced crosslink among rubber chains in irradiated latex [12]. The tensile test results of the RVNRL samples have elucidated the capability of gamma radiation from Caesium-137 in vulcanizing natural rubber latex.

Comparison of tensile properties between RVNRL prepared by using Caesium-137 and Cobalt-60 sources are also showed in Figure 1, 2 and 3. It is evident that tensile properties of RVNRL irradiated by Caesium-137 up to 8 kGy are better than RVNRL by Cobalt-60. There is no significant difference in tensile properties between both RVNRL samples at radiation dose of 12 kGy. The effectiveness of Caesium-137 gamma radiation is relatively higher than Cobalt-60 in RVNRL preparation when the latex is irradiated at radiation dose below 12 kGy. This finding is unexpected and rather on the contrary with the fact that the radiation energy and dose rate of Caesium-137 are about half and one-third of Cobalt-60's respectively. Theoretically, the rate of radiation polymerization is proportional to dose rate and monomer concentration [13]. Research also showed that vulcanization dose, i.e. the radiation dose that produces RVNRL with optimum tensile strength, of sensitized natural rubber latex irradiated with low energy electron beam decreases by increasing dose rate [14]. Obviously, besides dose rate, there is possibility of other factor or combination of factors such as radiation energy, irradiation condition and interaction between radiation and sensitizer that affect the outcome of irradiation process in a positive manner, that require further investigation.
Figure 1. Modulus at 700% elongation of RVNRL irradiated by Caesium-137 and Cobalt-60 source.

Figure 2. Tensile strength of RVNRL irradiated by Caesium-137 and Cobalt-60 source.

Figure 3. Elongation at break of RVNRL irradiated by Caesium-137 and Cobalt-60 source.
4. Conclusion
RVNRL can be prepared by using gamma radiation from Caesium-137 source. Caesium-137 gamma radiation is capable of inducing crosslink in rubber polymers. Despite its lower dose rate and radiation energy, the effectiveness of Caesium-137 is higher than Cobalt-60 when the source is used to vulcanize latex at radiation dose below 12 kGy. RVNRL irradiated at 12 kGy by both radiation source did not show significant difference in term of tensile properties.

5. References
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