Investigation of Radiation Vulcanization of Natural Rubber Latex for the Production of Rubber Gloves by using Gamma Radiation

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Abstract: ***Radiations vulcanization of natural rubber latex (RVNRL) has been developed extensively through various research and development programme. This holds important benefits for rubber industries in Southeast Asia and the Pacific region. Myanmar also has developed an increasing number of rubber plantations and many rubber raw materials are processed to manufacture medical products, household items and industrial mechanical parts. In this paper, the radiation effect on the vulcanization of natural rubber latex and the synergistic effect of urea addition along with n-butyl acrylate (n-BA) sensitizer on the crosslinking density and mechanical properties of RVNRL film for the production of rubber gloves have been investigated. The various concentration of urea (0.1, 0.2, 0.3, 0.4 and 0.5) (phr) was used in the experiment. Tensile strength, elongation at break, modulus at 500%, swelling ratio, gel content and crosslinking density were determined. Tensile strength and modulus at 500%, gel content and crosslinking density were found increasing with absorbed dose, as well as the proportion of n-BA concentration in the rubber phase in presence of urea. The radiation dose for better cross-linking of natural rubber latex with six parts per hundred rubber (phr) n-BA was 15 kGy absorbed dose according to the research. The results also show that addition of 0.3 parts per hundred rubber (phr) urea to the latex before irradiation caused the crosslinking density and tensile strength increase respectively. RVNRL is suitable for production of gloves, balloons, baby teats, rubber products for medical and hygienic used and many other dipped products due to the absence of carcinogenic and toxic products. The rubber gloves were produced using the optimum condition of six parts per hundred rubber (phr) of n-BA, 0.3 (phr) of urea and 15 kGy absorbed dose of gamma radiation. In the RVNRL process, radiation energy replaces the use of a sulfur-based process and produces a material that has all properties of the conventional product.***

Keywords: Gamma radiation, Natural rubber latex, N-butyl acrylate, Radiation Vulcanization

1. Introduction

Rubber has been cultivated in Myanmar since the early 1900s, primarily in Mon State. Total rubber acreage in Myanmar has now reached 1.43 million acres and Myanmar ranks ninth in the world, according to the Myanmar Rubber Planters and Producers Association (MRPPA), in terms of rubber production. In addition, the government also has a 30-year plan to obtain 1.5 million acres of planted area of rubber in the country, and the capacity to produce nearly 300,000 metric tons (MT) per annum. The government promotes and protects rubber production and support smallholder farmers through technology and knowledge transfer [1].

Radiation vulcanization of natural rubber latex (RVNRL) is suitable for production of gloves, condoms, balloons, baby teats and many other dipped products readily exploited by the users. Rubber products for medical and hygienic uses are obviously the most promising applications of RVNRL technology because of the absence of carcinogenic and toxic products. In this paper, advanced and effective radiation vulcanization technique is utilized to introduce the technology in rubber industries in Myanmar. It uses gamma radiation to initiate vulcanization, a process that chemically bonds molecules to promote rubber elasticity and strength. Significant progress has been made in the last 30 years in developing new rubber material using radiation technology that holds important benefits for industries in Southeast Asia and the Pacific. Recently, the conventional methods namely "dipping" and sulfur vulcanization techniques are widely used to concentrate latex form. RVNRL offers several advantages over conventional vulcanization with sulfur such as better latex stability, lower modulus, less or absence of toxicity problem, better clarity of products, less environmental pollution, lower ash content and absence or lower acid combustion gases [2].

However for this technology to become commercially viable, it is essential that (i) the dose required to bring about vulcanization be brought down to the about 10-15 kGy and (ii) the concentration of the sensitizer required for adequate crosslinking should be minimized [3]. This has prompted mechanistic comparisons to be made between vulcanization and related processes. The use of n-butyl acrylate (nBA) as sensitizer has already resulted in reducing the radiation dose required to vulcanize rubber from 300 kGy to 15 kGy. However, there is still a need to further reduce the dose requirement without increasing n-BA concentration. The way to fulfil the requirement is the using of urea [4]. The purpose of the present work is to study the effect of addition of urea on the crosslinking density and mechanical properties of the radiation vulcanized natural rubber latex films to see whether similar improvement can also be obtained for the radiation vulcanization process.

Natural rubber latex (NRL) is a dispersion of natural rubber particles in water. It comes from Hevea Brasiliensis plantation [5].The properties of natural rubber can be improved by vulcanization. Vulcanization is an important chemical reaction of rubber. NRL can be vulcanized by irradiation without and with radiation vulcanization accelerator. Latex being a natural product, the physicmechanical characteristics of radiation products is dependent upon the origin and the micronutrients present in the latex [6],[7].

Product from RVNRL have high transparency, due to the absence of curing ingredients, and this is desirable for products such as gloves, teats and soothers and some catheters. The process parameters are sensitizer concentration, radiation dose, concentration of rubber particles in the latex, effect of various concentrations of urea and ambient conditions of irradiation. The product depends upon these parameters [8].

Indonesia researchers reported the production of household and examination gloves in pilot plant scale in 2004. In this report, RVNRL compared with sulfur vulcanization and the properties of gloves were reported. It indicates that RVNRL have low protein, lipids and carbohydrate content to ensure that the finished articles have the minimal amount of residual protein containing the allergens and safe for use. From these advantages characteristic of RVNRL, it can be recommended that the potential application of RVNRL is good for production of medical products, condom, teats, balloons, and gloves for food contact [9].

2. Experimental

The natural rubber latex (NRL) was prepared and irradiated in gamma chamber. The irradiated rubber latex was prepared to produce the household glove. The properties of rubber film and glove were measured by using an H-5000E tensile machine. The crosslink density of rubber film was estimated by Flory-Rehner equation.

2.1. Materials

The rubber latex used in this work was high ammonia centrifuged 55 % (Dry Rubber Content) DRC natural rubber latex obtained from RTTCRP (Research, Technology & Training Centre For Rubber Products), Yangon, Myanmar. N-butyl acrylate (n-BA), high ammonia solution (NH4OH), potassium hydroxide (KOH) and urea were obtained from Able chemical store, Mandalay. All of reagents are Analar grade.

2.2. Irradiation of NRL

The concentrated NRL (13.5 litres) used in the production of gloves was diluted to 50% DRC by adding 1.5% dilute ammonia solution. The 10% KOH solution (0.5 phr) was added into the preparation solution while stirring. And then optimum concentration of n-Butyl acrylate (6.0 phr) was added into the latex solution while stirring. Samples were prepared by addition of urea with concentrations of (0.3phr).The stirring was continued for two hours and the solution was left overnight at room temperature to mature before irradiating. The radiation dose (15.0 kGy) was applied in a gamma chamber as shown in Figure (1).

2.3. Preparation of Rubber Gloves

Rubber gloves were prepared using the medium size of hand mold. The Radiation Vulcanized Rubber Latex (RVRL) was prepared in a container. The mold was heated up at 80°C for 2-3 min and was dipped into coagulation (This solution was prepared with 10% calcium chloride). The mold was removed and was heated again. After that, the mold was dipped into the rubber latex for 30 sec and was removed. A thin layer of the rubber latex covering the hand mold was vertically placed in the oven and was heated up at 100°C in hot-air oven. And then, the rubber glove was powdered to strip from the mold as shown in Figure (2).

Figure 1: Irradiation of natural rubber latex in the gamma chamber

Figure 2: Flow Diagram of the Production of Household Glove

2.4. Tensile Strength Measurement

The tensile test (tensile strength, modulus at 500% elongation and elongation at break) of RVNRL films was conducted using dumbbell-shaped test specimens and measured by using an H-5000E tensile testing machine according to BS 903 Pt A2.

2.5. Swelling and Gel Content Measurement

About one gram of radiation vulcanized rubber film was soaked in benzene for 36 hours to measure swelling. Based on the equilibrium swelling data measurement, the crosslink density was estimated by Flory-Rehner equation as follow [10]:

$$V_O = K \times Q^{-5/3} \qquad (1)$$

Where, V_O = crosslink density c.l/ml,
K = 4.71 x 10^{20} for benzene/NR system,
Q = swelling ratio.

The swelling ratio (Q) of the rubber films was calculated by measuring the mass of the sample before and after immersing in benzene [11]:

$$Q = \frac{W_s - W_d}{W_d} \qquad (2)$$

Where Wd and Ws are the weight of dry and swollen sample in benzene, respectively.

The swollen samples were then dried in an oven at 50°C for 12 hours to remove the residual solvent. The gel content of specimens was calculated the following equation [12]:

$$\text{Gel content}\ (\%) = \frac{W_{ds}}{W_d} \times 100 \qquad (3)$$

Where Wd and Wds are the weight of dry RVNRL films before and after being swollen in benzene, respectively.

3. Results and Discussion

3.1. Tensile Test of Films and Gloves

The tensile strength of irradiated rubber films obtained by mixing various concentration of urea and n-butyl acrylate sensitiser with NRL at various absorbed doses was shown in Figure (3). The value of the tensile strength of rubber films increased with increase amount of n-butyl acrylate concentration and urea concentrations in the mixed at 15 kGy dose. These results show that the tensile strength was optimum at the 0.3 phr urea concentration of 6 phr normal butyl-acrylate and 15 kGy dose. The increase in tensile strength may be due to increased cross-linked between rubber and the sensitiser as well as urea concentration in the mixed. This can occur that increase the homogeneous cross-link density. It was known that with increase crosslink density, tensile strength increased.

The tensile strength of films of modulus at 500% elongation increased with increase in concentration of urea as shown in Figure (4).The maximum tensile strength of irradiated rubber film with 6 phr n-butyl acrylate was obtained 14.5 Mpa at the absorbed dose of 15 kGy. Figure (5) shows the elongation at break of films with various composition of n-BA at various absorbed doses. It was found that the elongation at break decreased with increase in urea concentration.

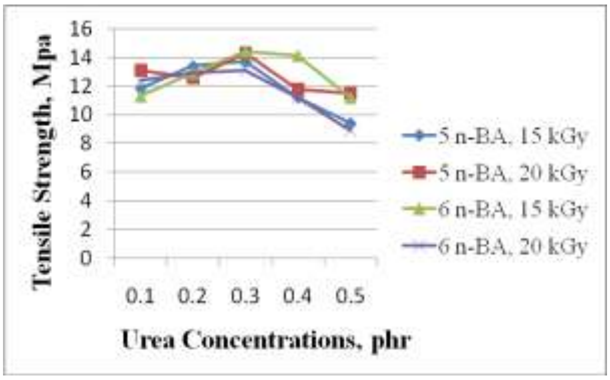

Figure 3: Tensile Strength of Rubber Film at Various Urea Cocentrations of 5 n-BA and 6 n-BA at 15 kGy and 20 kGy Dose

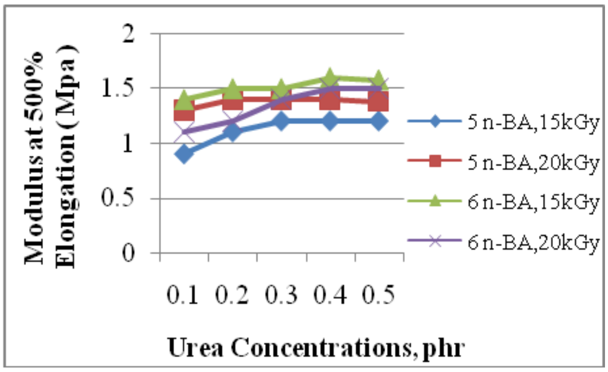

Figure 4: Modulus at 500% Elongation of the Rubber Film

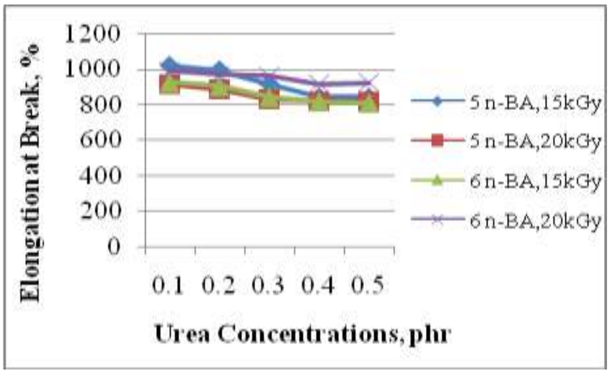

Figure 5: Elongation at Break (%) of the Rubber Film

The tensile test of the resulted rubber gloves were carried out with other three types of commercial gloves as shown in Figure (6). The properties of rubber glove were measured by using an H-5000E tensile machine. The tensile strength of glove (experiment) obtained by mixing optimum concentration of urea and n-butyl acrylate with NRL at 15 kGy absorbed doses was shown in Table 1. From this table, it was observed that the maximum tensile strength was found in black rubber glove and the minimum was pink glove. The properties of the gloves are directly proportional to the prize of gloves. The tensile strength of white rubber glove (experiment) was 14.3 Mpa and there was no other ingredient in rubber phase. The white glove was soft and transparent than other gloves and good for biological and water-based material. The gloves are perfect for everyday cleaning and protect the skin irritation. Although the tensile strength was not very high, the resulted gloves were suitable for market.

Figure 6: Comparison of Glove (Experiment) with Other Gloves (in Market)

Table 1: Comparison of Tensile Test of the Rubber Gloves

Gloves	Tensile Strength, Mpa	Elongation at Break, %
Black (Thailand)	18.3	722
Orange (Thailand)	15.4	825
White (Experiment)	14.3	838
Pink (China)	9.1	914

3.2 Swelling and Gel Content Measurements

Figure (7) shows the gel contents of the rubber latex films with various composition of n-BA at various absorbed doses. It was observed that the optimum value of gel content was found at 0.3 phr of urea concentration. And then, there was no change remarkably. The increase of gel content indicated the formation of three dimensional networks during radiation vulcanization.

The swelling ratios of the rubber latex films prepared under different irradiation doses in the presence of various sensitizers and urea concentrations after leaching with benzene solvents were investigated and the results were mentioned in Figure (8). From this figure, it was observed that the swelling ratios of rubber latex films decreased until the 0.3 phr of urea concentration. Beyond this concentration, the swelling ratio of 5 n-BA, 20 kGy slightly increased and the swelling ratio of 6 n-BA, 15 kGy continuously decreased until the 0.4 phr. The swelling ratio decreased that of with increasing urea concentrations. In the radiation vulcanization process, it is essential to know the response of network structure depending on the process parameters such as radiation dose, sensitizer concentration and ambient conditions.

The natural rubber latex is subjected to radiation vulcanization to gain induced crosslinking. The crosslink density of rubber film was estimated by Flory-Rehner equation. The cross-linking density of the rubber film on the various concentration of urea was shown in Table 2. From this table, it was observed that the cross-linking density increased with increasing the concentration of urea. The optimum cross-linking density was found at the 0.3 phr urea concentration of 6 phr n-BA, 15 kGy. Beyond that concentration, the cross-linking density of 5 n-BA, 20 kGy of latex film slightly decreased which indicates depolymerization or chain scissors of the polymers.

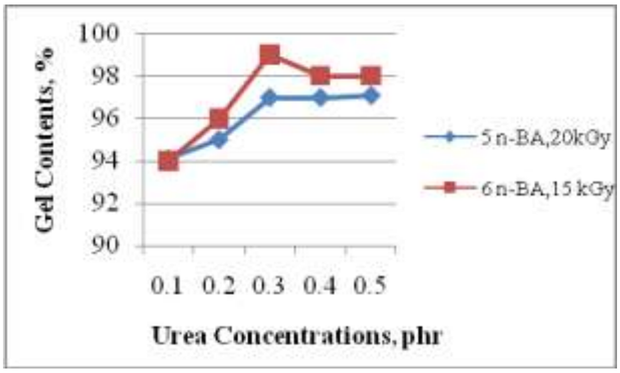

Figure 7: Gel Content (%) of the Rubber Film on the Various Concentration of Urea

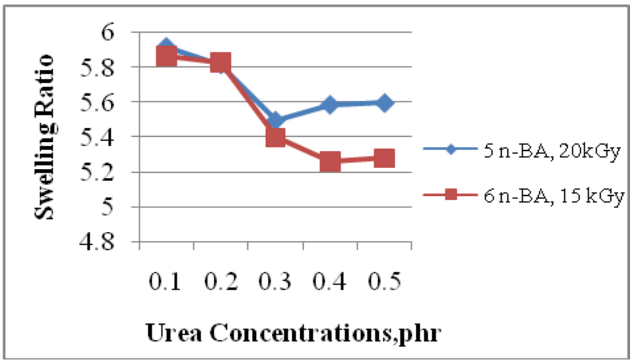

Figure 8: Swelling Ratio of the Rubber Film on the Various Concentrations of Urea

Table 2: Crosslinking Density of the Rubber Film on the Various Concentration of Urea

	Cross-link density (c.l/ml)				
	0.1 phr of urea	0.2 phr of urea	0.3 phr of urea	0.4 phr of urea	0.5 phr of urea
5n-BA, 20 kGy	2.43×10^{19}	2.5×10^{19}	2.75×10^{19}	2.68×10^{19}	2.67×10^{19}
6n-BA, 15 kGy	2.46×10^{19}	2.49×10^{19}	2.83×10^{19}	2.85×10^{19}	2.74×10^{19}

4. Conclusions

The swelling ratios, cross-linking density, gel content, tensile strength and elongation at break of the NRL films were investigated for variable radiation doses and various concentrations of n-butyl acrylate sensitiser and urea. Tensile strength of irradiated rubber film with 6 phr n-butyl acrylate attained maximum at the absorbed dose in the range of 15 kGy. Elongation at break and the swelling ratio decreased with the increase amount of urea added for rubber latex. Gel content and degree of cross-link density of the rubber films increased with increase urea concentration as well as with increase absorbed doses. The results indicated the increase of cross-linking during vulcanization. The presence of urea may increase the solubility, and hence concentration of the n-BA in the rubber phase which results in the increased crosslinking density as well as improved tensile strength of the film. These results are found in similar trend as reported by Indonesia researcher in 2004. The report has shown that the addition of 0.3 phr of urea to latex does not have any adverse effect on the properties of latex.

So from this study, it has been proved that the cross-linking of the NR latex film with n-BA sensitiser and urea addition can be done by gamma radiation. The household rubber gloves were produced by using the optimum condition of the research. Although the tensile strength of gloves was not very high, the gloves provide a comfortable, flexible fit and are perfect for most everyday cleaning and protect the skin irritation causing by protein allergies. Gloves can be produced from a variety of materials including latex, vinyl, nitrile & high density polyethylene (poly). Each type of material has different properties to meet a wide range of needs. These RVNRL gloves have suitable properties for biological and water-based material. This technology will be introduced to rubber industries in Myanmar. By using these techniques local rubber production will be developed to export finished or semi-finished products, rather than raw materials only.

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