Effects of post-gamma irradiation on swelling and mechanical properties of gamma vulcanized natural rubber latex (GVNRL) films

G Wicha1, K Intharaprasit1, E Wimolmalaz2, T Markpin2 and K Saenboonruang1,3,*

1 Department of Applied Radiation and Isotopes, Faculty of Science, Kasetsart University, Bangkok, Thailand 10900
2 Polymer Processing and Flow (P-PROF) Research Group, Division of Materials Technology, School of Energy, Environment and Materials, King Mongkut’s University of Technology Thonburi, Bangkok, Thailand 10140
3 Specialized center of Rubber and Polymer Materials for agriculture and industry (RPM), Faculty of Science, Kasetsart University, Bangkok, Thailand 10900

*Email: kiadtisak.s@ku.th, fscikssa@ku.ac.th

Abstract. Gamma vulcanized natural rubber latex (GVNRL) films have shown promising properties for various applications that require less hazardous chemicals used or released during manufacturing and/or utilization. Examples of potential applications include the uses as chemical-free latex gloves in medical or food-related facilities and as stretchable latex covers for food and agricultural products. However, due to possible degradation on swelling and mechanical properties of these films from post-gamma irradiation used for sterilization, thorough investigations are required in order to fully understand their possible changes and/or degradations in properties of interest. As a result, this work investigated on effects of post-gamma irradiation on swelling and mechanical properties of natural rubber latex (NRL) films, which were pre-vulcanized using 12-kGy and 24-kGy gamma irradiation. The properties of interest in this work included tensile modulus at 300% elongation, tensile strength, and elongation at break, as well as other related physical properties such as swelling ratios and crosslink densities. The results showed that, for samples before post-gamma irradiation, the GVNRL films with 24-kGy vulcanizing dose had higher tensile modulus, tensile strength, and crosslink density, but lower elongation at break and swelling ratio, than the films with 12-kGy vulcanizing dose. However, after post-gamma irradiation at the accumulated dose of 24 kGy, the films with 12-kGy vulcanizing dose showed significant improvements in the values of tensile modulus, tensile strength, and crosslink density, whereas the films with 24-kGy vulcanizing dose showed noticeably degradation in these properties. Hence, the overall results suggested that, while higher gamma vulcanizing doses could initially produce NRL films with higher mechanical strength, they were more negatively affected by post-gamma irradiation such that mechanical degradation could be observed.
1. Introduction
Due to possible use and/or release of hazardous chemicals and byproducts, including sulfur, -t-butyl-2-benzothiazolesulfenamide (TBBS), Wingstay-L, nitrosamines, and nitrosatable amines, from sulfur and peroxide systems used during the vulcanization of natural rubber latex (NRL), which may cause severe respiratory diseases, cancers, chemical allergies, and fatality to humans and aquatic life [1-3], gamma irradiation becomes an alternative vulcanization system that is considered safer during production, environmental-friendly, and free from accelerator-induced allergies. As a result, the interests in utilizing gamma vulcanized natural rubber latex (GVNRL) products in certain applications that require less chemicals used/released during production processes have been noticeably increasing. Examples of potential GVNRL products include NRL gloves in food and medical applications [4], of which contamination of hazardous chemicals in foods and patients is not acceptable.

In addition to using gamma irradiation to vulcanize natural rubber latex by crosslinking polymer chains, gamma rays are also used to sterilize a variety of different products such as single-use GVNRL surgical gloves, pharmaceutical packaging, and stretchable food covers [5]. The gamma sterilization process usually utilizes $^{60}$Co, which emits high-energy gamma rays (1.17 MeV and 1.33 MeV, with the average energy of 1.25 MeV) to kill microorganisms, preventing the potentials of growing or contaminating these harmful microorganisms into patients, medicines, or delicate foods. However, the possibilities of negative effects of post-gamma irradiation on mechanical properties of the irradiated products, especially in GVNRL, could not be ignored and, in fact, must be fully paid attention to as the degradation could reduce the performance and limit the full functionality of the products. As a result, this work investigated the effects of (24 kGy) post-gamma irradiation on GVNRL thin films, which was pre-vulcanized using 12 kGy and 24 kGy gamma rays and formed into testing specimens using dipping method. Properties of interest in this work include tensile properties (tensile modulus at 300% elongation, tensile strength, and elongation at break) and other related physical properties (swelling ratios and crosslink densities).

2. Experimental

2.1 Materials and chemicals
High-ammonia (HA) NRL supplied by the Rubber Authority of Thailand (RAOT) was used as the main matrix. Other chemicals that were also used in this work were 99.9% n-butyl acrylate (n-BA) and 10% potassium hydroxide (KOH) supplied by BASK (Thailand) and Gammaco (Thailand) Co., Ltd., respectively.

2.2 Preparation of GVNRL mixtures
NRL was continuously stirred using a top stirrer with a rotating speed of 300 rpm for 60 minutes. 0.25 phr of KOH was added to the NRL and stirred for another 10 minutes. Then, 5 phr of n-BA, which acted as a gamma vulcanization accelerator was added to the mixture and the stirring was continued for 40 minutes. The NRL mixture was later transferred to 5-L plastic containers and irradiated with gamma rays using a $^{60}$Co source at the accumulated doses of 12 and 24 kGy, respectively. It should be noted that the dose rate of $^{60}$Co used in this work was 2.1 kGy hour$^{-1}$ and the irradiation was carried out at the Thailand Institute of Nuclear Technology (Ongkharak, Nakhon Nayok Province). After the gamma irradiation, the pre-vulcanized NRL mixtures were kept in closed containers and stored in a freezer at the temperature of -4 oC for further uses.
2.3 Preparation of GVNRL thin films
Cylindrical glass molds with 5-cm diameter were thoroughly cleaned and dried at 60°C - 70°C for 60 minutes using a hot-air oven. The molds were then entirely dipped into a coagulant solution for 5 seconds and dried at 60°C - 70°C for 3 minutes. After the molds were completely dried, they were dipped into the GVNRL mixtures for 40 seconds and dried again at 100°C - 120°C for 30 minutes. Once the GVNRL thin films were formed around the molds and completely dried, the films were rolled out of the molds and left at room temperature for 2-3 hours before being post-gamma irradiated at the accumulated dose of 24 kGy using a 60Co source.

2.4 Testing on mechanical and physical properties
The tensile properties including tensile modulus at 300% elongation, tensile strength, and elongation at break of the GVNRL thin films (both with and without post-gamma irradiation) were investigated using a universal testing machine (Autograph AG-I 5kN, Japan) following ASTM D412-06 standard testing. For the measurements of swelling ratios and crosslink densities, each specimen was cut into a circular piece with a diameter of 2 cm and soaked in toluene at room temperature, following the ASTM D471-06 standard testing method. Initial weight before immersion (w1) and weights after 24-hour immersion (w2) were measured and the swelling ratios were calculated using equation 1 [6]:

\[
\text{Swelling ratio} = \frac{w_2 - w_1}{w_1} \times 100\% \quad (1)
\]

The crosslink density was determined at the equilibrium swelling state, in which the specimens were soaked in toluene for 72 hours. The crosslink density (n) was calculated according to Flory-Rehner equation as shown in equation 2:

\[
n = \frac{\frac{1}{2} \ln(1-V_t) + V_t + \chi V_r^2}{V_t(V_r^2 - V_t^2)} \quad (2)
\]

where \(V_t\) is the molar volume of toluene (106.1 cm³/mol), \(\chi\) is the interaction parameter (0.393 for NR-toluene system) [7], and \(V_r\) is the volume fraction of GVNRL, which was calculated according to equation 3:

\[
\frac{1}{V_r} = 1 + \left(\frac{w_2 - w_1}{w_1}\right) \quad (3)
\]

3. Results and Discussion
The results of tensile properties and swelling ratios/crosslink densities of GVNRL thin films with and without 24-kGy post-gamma irradiation are shown in Table 1 and Table 2, respectively, which suggested that, for specimens without post-gamma irradiation (0 kGy), the tensile modulus, tensile strength, and crosslink density increased with increasing gamma vulcanizing doses (from 12 kGy to 24 kGy), while elongation at break and swelling ratio decreased with increasing gamma vulcanizing doses. These behaviors were observed because gamma irradiation could initiate the crosslinking of NR chains by creating free radicals inside the NRL, of which the recombination of these radicals would result in the crosslinking of NR chains into 3D network. With higher gamma vulcanizing doses (24 kGy in this work), higher crosslinking of NR chains in the specimens was observed as illustrated in Table 2, which resulted in greater restriction of the mobility of NR chains due to the increase in NR chain crosslinking structure, increasing the overall strength and stiffness of the specimens [8].
Table 1. Mechanical properties of GVNRL thin films with and without 24-kGy post-gamma irradiation. (*Numbers after ± represent the standard deviation.*)

| Gamma vulcanizing dose (kGy) | Post-gamma irradiation dose (kGy) | Tensile modulus (MPa) | Tensile strength (MPa) | Elongation at break (%) |
|------------------------------|-----------------------------------|-----------------------|------------------------|-------------------------|
|                              | 0  | 24 | 0  | 24 | 0  | 24 | 0  | 24 | 0  | 24 | 0  | 24 |
| 12                           | 0.21 ± 0.03 | 0.23 ± 0.01 | 7.48 ± 1.78 | 8.88 ± 0.87 | 2387 ± 198 | 2393 ± 88 |
| 24                           | 0.23 ± 0.02 | 0.17 ± 0.01 | 8.10 ± 1.80 | 6.80 ± 0.84 | 2064 ± 129 | 2298 ± 154 |

Table 2. Swelling ratios and crosslink densities of GVNRL thin films with and without 24-kGy post-gamma irradiation. (*Numbers after ± represent the standard deviation.*)

| Gamma vulcanizing dose (kGy) | Post-gamma irradiation dose (kGy) | Swelling ratio (%) | Crosslink density (mol cm⁻³) |
|------------------------------|-----------------------------------|-------------------|-----------------------------|
|                              | 0  | 24 | 0  | 24 | 0  | 24 | 0  | 24 | 0  | 24 | 0  | 24 |
| 12                           | 977±47 | 875±34 | 1.25×10⁻⁵ | 1.53×10⁻⁵ |
| 24                           | 835±31 | 1111±19 | 1.66×10⁻⁵ | 9.9×10⁻⁶ |

However, as the specimens were post-gamma irradiated with the accumulated dose of 24 kGy, specimens, which were pre-vulcanized with 12 kGy and 24 kGy gamma rays, behaved in different ways. For instance, the specimens with 12-kGy gamma vulcanizing dose showed increasing tensile modulus, tensile strength, and crosslink density (lower elongation at break and swelling ratio) after post-gamma irradiation, while the specimens with 24-kGy gamma vulcanizing dose showed decreasing tensile modulus, tensile strength, and crosslink density (higher elongation at break and swelling ratio) after post-gamma irradiation. These behaviors could be explained by the fact that, since post-gamma irradiation could initiate both crosslinking and degradation, especially chain scission mechanism, to GVNRL thin films, the effects of crosslinking from post-gamma irradiation still dominated effects of chain scission as shown by the decrease in swelling ratio and the increase in crosslink density (Table 2), resulting in the overall increases of strength and stiffness of the specimens (Table 1). On the other hand, for specimens with already high gamma vulcanizing dose (24 kGy), the crosslink density created during the vulcanization process was already high. As a result, once the post-gamma irradiation was carried out on the specimens, the addition of crosslinking mechanism was lower and suppressed by the chain scission mechanisms, resulting in the overall reduction of strength and stiffness of the specimens [9]. From the overall results, it could be concluded that, although higher gamma vulcanizing doses could initially produce GVNRL thin films with higher crosslinking density, tensile strength, and stiffness than lower gamma vulcanizing doses, the post-gamma irradiation used during product’s sterilization could negatively affected the products by lowering overall crosslink density and strength of specimens, implying thorough optimization of gamma doses used for NRL vulcanization and sterilization must be investigated and carried out.

4. Conclusions
GVNRL thin films have great potentials to be utilized in various applications that require chemical-free and environmental-friendly products. However, the effects of post-gamma irradiation used during the
sterilization could have negative effects on mechanical properties of the GVNRL thin films. As a result, this work investigated mechanical properties of GVNRL thin films after being post-gamma irradiated with the accumulated dose of 24 kGy. The overall results revealed that higher gamma vulcanizing doses could initially produce GVNRL thin films with higher crosslink density, mechanical strength, and stiffness than the films with lower gamma vulcanizing doses. However, after being post-gamma irradiated at 24 kGy, films with initial higher gamma vulcanizing doses (24 kGy) showed more pronounced degradation than the ones with lower gamma vulcanizing doses (12 kGy), resulting in lower overall crosslink density and mechanical strength.

5. References

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