

PRELIMINARY STUDY ON PEROXIDE VULCANIZATION WITH GAMMA IRRADIATION

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ABSTRACT

Peroxide pre-vulcanized natural rubber latex prepared by using gamma irradiation technique is an alternative over the conventionally prepared peroxide pre-vulcanized that used activator to promote the peroxide decomposition in natural rubber latex. Through this technique the problems aroused by some activators such as tends to darken the natural rubber latex film during the drying process can also be overcome. For this preliminary study, data obtained from crosslink density and mechanical measurements were used to evaluate the effectiveness of gamma irradiation in the vulcanization process. Increasing the quantity of tert-butyl hydroperoxide (t-BHPO) from 0.1 pphr to 0.3 pphr while the irradiation dose maintain at 12 kGy has successfully delivered peroxide vulcanized natural rubber latex films with average tensile strength, modulus @ 500% and modulus @ 700% around 15.33, 1.01 and 3.42 MPa, respectively. The effective pre-vulcanization irradiation dose with respect to maximum crosslinking density (85.8 %) was observed on film prepared at 0.1 pphr t-BHPO.

Keywords: Co-60, irradiation, latex, peroxide, vulcanization

INTRODUCTION

Peroxide vulcanization of natural rubber latex (NRL) has several advantages over the conventional vulcanization with sulphur such as less or absence of toxicity, free from nitrosamines and accelerator induced allergies, low in cytotoxicity and cleaner process (Cook et al., 1997; Makuuchi, 2003; Ma'zam et al., 1990; Pairu et al., 2016). These properties are important for many products, particularly catheters, surgical gloves and other medical and hospital supplies. For such uses, it is important that products are free of contaminants, toxic and carcinogenic components to avoid harmful effects in human beings (Roslim et al., 2015).

A conventional peroxide vulcanization of NRL is carried out by heating the latex containing mixture of organic peroxide and activator at 70°C. The reason activators were used in this method is to promote the peroxide decomposition in NR latex. With this compounding formulation and method, films with tensile strength approximately 18 MPa to 20 MPa can be produced (ASTM D3578, 2015; Ma'zam et al., 1990). Typically, tetra-ethylene pentamine, fructose and hydroxyacetone have been known to be a good promoter for the formation of rubber chains crosslinking. However, there are some cases where the use of activator tends to darken the NRL film during the drying process.

In this study, peroxides vulcanization of tert-butyl hydroperoxide (t-BHPO) at various quantities was carried out using gamma irradiation as another alternative for activator. Thus, this paper will

discuss on the effect of irradiation on the mechanical properties of the films. This study also extended to examine the effects of irradiation on crosslinking density of the peroxide-vulcanized NRL films.

MATERIALS AND METHODS

Materials

The latex utilised in this work was of a high ammonia type (HA latex) supplied by Revertex (M) Sdn. Bhd., Malaysia. The peroxides used were tert-butyl hydroperoxide (*t*-BHPO) supplied by Fluka. The stabilizer used was potassium laurate supplied by Tiarco Chemical (M) Sdn. Bhd., Malaysia and the antioxidant used was Aquanox Lp supplied by Aquaspersion (M) Sdn. Bhd., Malaysia. These materials were used as received.

Sample Preparation

A latex compounding formulation for control and peroxide vulcanization preparation using *t*-BHPO is given in Table 1 and Table 2, respectively. The peroxide, stabilizer, antioxidant 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 a couple of hours (Sofian et al., 2007). It was then transferred into 1 litres capacity screw capped plastic container and irradiated with gamma rays from a cobalt-60 source for a dose of 12 kGy. After irradiation, the latex was made into film by coagulant dipping method.

Table 1: Compounding formulation for control sample

Materials	Part Perhundred Rubber (pphr)
NRL (62% Total Solid content, TSC)	100
Stabilizer	0.06
Antioxidant	2.50
Water	Add to 52% TSC

Table 2: Compounding formulation for *t*-BHPO vulcanization

Materials	Part Perhundred Rubber (pphr)
NRL (62% TSC)	100
<i>t</i> -BHPO	0.1 / 0.3 / 0.5
Stabilizer	0.06
Antioxidant	2.50
Water	Add to 52% TSC

Irradiation

The latex formulations were irradiated using gamma rays from Co-60 isotope at MINTec-Sinagama Plant, Malaysian Nuclear Agency. The activities of Co-60 are 447,000 Curie with dose rate of 2.08 kGy/hr.

Measurement of Tensile Properties

Specimens for tensile testing were prepared using the coagulant dipping method. 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 minute. The latex film was finally dried at 100°C for 30 minute and subjected to tensile test using Universal Testing Machine Instron 5,564 in accordance to ASTM D412. The latex films samples were cut into dumbbell shape test pieces (Figure 1). Five samples were used for tensile test and a median value was taken as the final result.

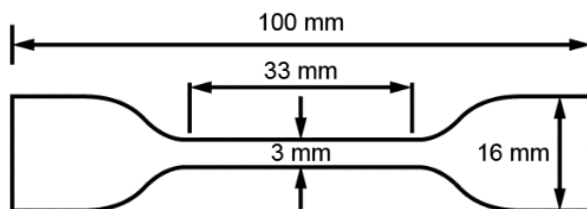


Figure1: Dimension of dumbbell cut

Fourier Transform Infrared spectroscopy (FTIR)

In this study, FTIR spectroscopy analysis was carried out using Bruker's Tensor II Platinum Attenuated total reflection (ATR) spectrophotometer. Range of wavenumber employed was 4000 – 500 cm^{-1} .

Determination of Gel Content

Gel content of the radiation crosslinked samples were determined by solvent extraction using toluene for 8 hours (ASTM D3616, 2014; Jayasuria et al., 2001). The extracted samples were dried in an oven at 70°C till constant weight was achieved. The gel fraction was calculated as Eq. 1:

$$\text{Gel content, \%} = \frac{w_1}{w_0} \times 100 \quad (1)$$

Where, W_0 and W_1 are the weights of the dried samples before and after extraction, respectively.

RESULTS AND DISCUSSION

Effect of Irradiation on Mechanical Properties of Peroxide Vulcanization

Tensile strength values are considered as the most commercial importance parameter, typically in gloves production. Based on ASTM D3578 (2015) and ASTM D3577 (2001), minimum tensile strength requirement to produce rubber examination gloves and rubber surgical gloves is 18 and 24 MPa, respectively. Based on the data obtained (Table 3), irradiation of NRL alone at 12 kGy manage to produced latex film with tensile strength of 5.42 MPa. However, the tensile strength from the three peroxide vulcanization films prepared at various quantities of *t*-BHPO recorded at 15.30 MPa, 15.35 MPa and 15.32 MPa. There are several factors why tensile strength from the three peroxide vulcanization films are lower compared to conventional peroxide vulcanization. One of the factors are there is possibility that the irradiation dose given during the peroxide vulcanization is insufficient. In the conventional peroxide vulcanization method, Loan (1967) has stated that the concentration of activator is necessarily in equimolar concentration to *t*-BHPO, so that the peroxide can diffuse steadily into rubber particles. Since in this study the role of the activator has been replaced with ionizing radiation, irradiation dose plays a major role to decomposing peroxide compounds completely. Therefore, the effects of irradiation dose should be taken into account in future studies.

Table 3: *t*-BHPO vulcanization effect on mechanical properties of films

Samples	NRL (control)	NRL + 0.1 <i>t</i>-BHPO	NRL + 0.3 <i>t</i>-BHPO	NRL + 0.5 <i>t</i>-BHPO
Modulus @ 500% (MPa)	0.51	0.91	1.14	0.98
Modulus @ 700% (MPa)	0.85	3.63	3.44	3.18
Tensile strength (MPa)	5.42	15.30	15.35	15.32

The other factors that maybe contribute to this matter are the occurrence of side reactions, which consume radicals (Keller, 1988; Loan, 1964). For examples, if oxygen molecules are present during the peroxide vulcanization process, it can couple to the radical in the polymer backbone to yield a hydroperoxide radical which will leads to polymer degradation instead of a crosslink. Because of this, peroxide cure must always be performed in the absence of oxygen (Alvarez, 2007).

Although the average tensile strength value obtained from the three peroxide vulcanization films is still 17% lower than ASTM D3578 requirement, this study has paved a way for further research in peroxide vulcanization using ionizing radiation. As anticipated, ionizing radiation has the potential to be used as an alternative for chemical compound activator in conventional peroxide vulcanization. So, it is proposed that high-energy ionizing radiation helps to decompose peroxide compound effectively and introduces a higher levels of free radicals thus promotes cross-linked reactions between the polymer chains.

To ensure all *t*-BHPO have been utilized, infra-red spectroscopy analysis has been used. Figure 2(a) showed the IR spectrum for *t*-BHPO compound. From the spectrum, it can be clearly observed the presence of functional groups of C-O at wavelength $1,365\text{ cm}^{-1}$. However, after the vulcanization process there is no trace of functioning group of C-O in peroxide vulcanized NRL samples (Figure

2(b)). So it can be conclude that all the peroxide has been consumed by radiation polymerization and hydrolysis during the radiation vulcanization process.

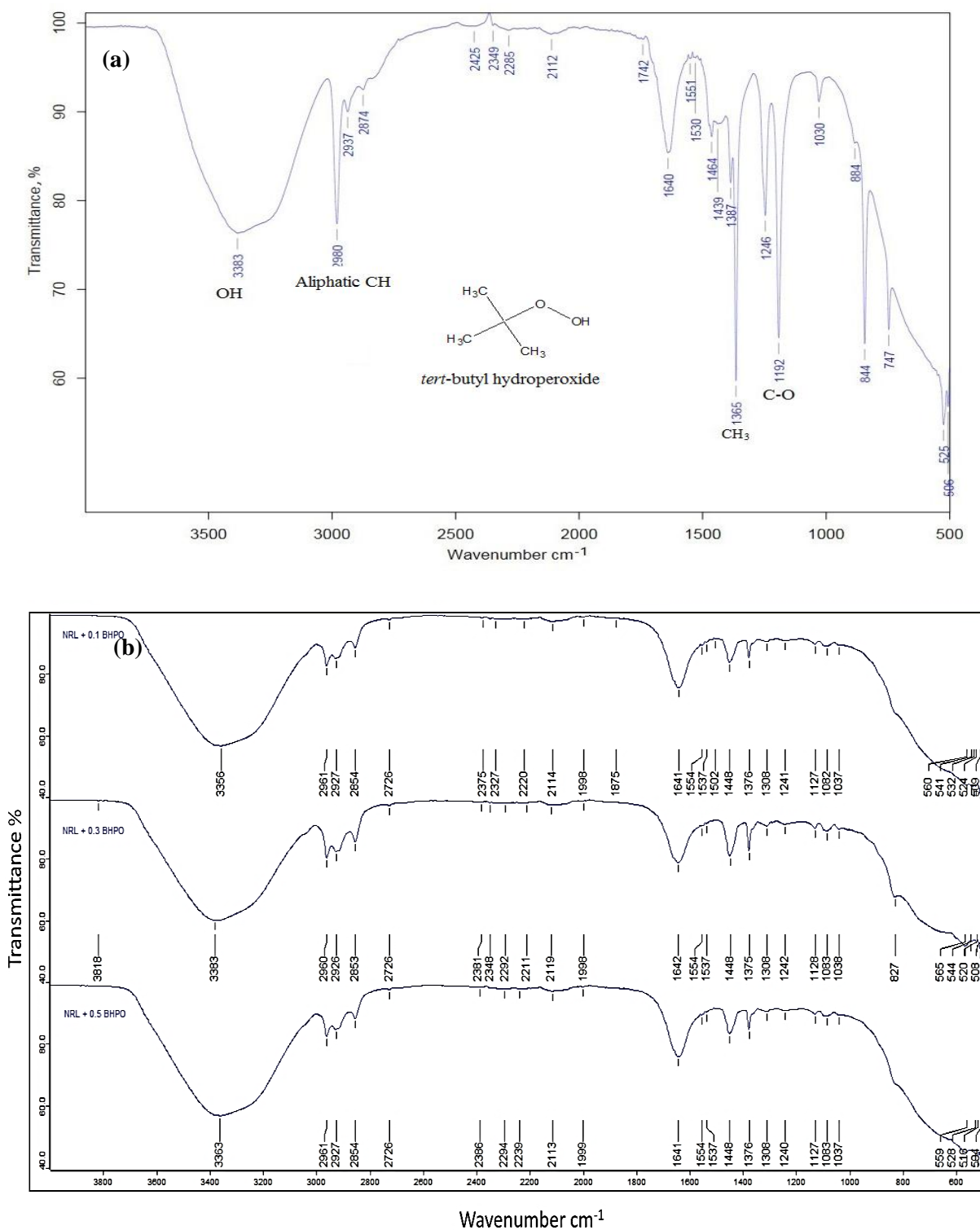


Figure 2: (a) Infra-red spectrum for *t*-BHPO and (b) infra-red spectrum for peroxide vulcanized NRL films at various amount of *t*-BHPO

Effect of Irradiation Doses on Gel Content of Peroxide Vulcanized NRL

Soxhlet extractor is used to perform the extraction with toluene on RVNRL for the purpose to determine the gel fraction/content, which is defined as that percent of a sample that does not dissolve in toluene. The crosslink or gelled polymers only swell up and not dissolve in any solvent. The gel content is determined indirectly from the amount of soluble fraction and directly by weighing the dried gel (ASTM D3616, 2014; Jayasuria et al., 2001).

Figure 3 shows the relationship between gel content with peroxide vulcanized NRL films prepared at various quantity of *t*-BHPO. It was observed that rubber film obtained from vulcanization with 0.1 pphr of *t*-BHPO produced 85.6% crosslink percentage compared to the control sample; 25.5%. However, it also showed that the percentage of gel content decreased as the amount of *t*-BHPO increased. Explanation for this observation is similar to tensile properties above.

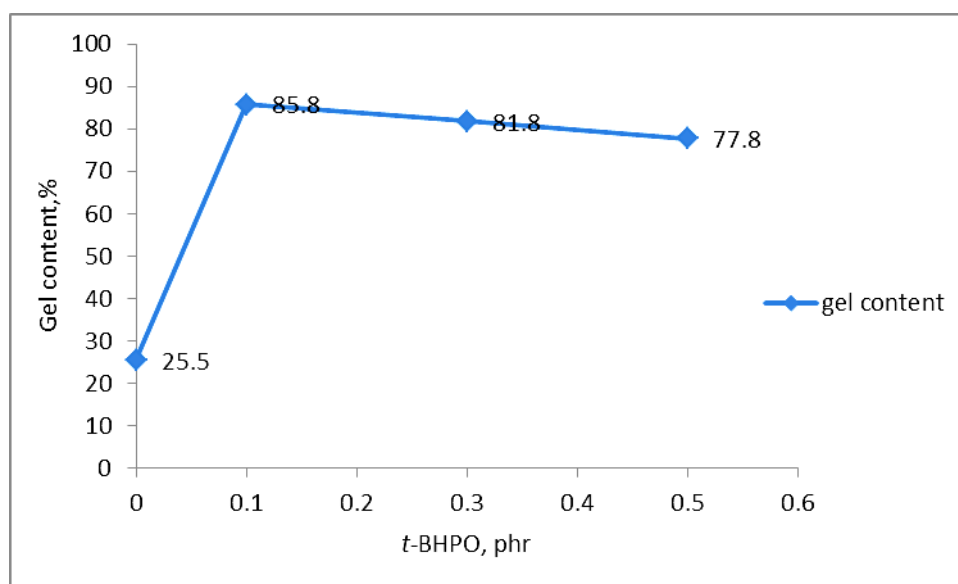


Figure 3: Gel fractions of peroxide vulcanized NRL films with different amount of *t*-BHPO

CONCLUSIONS

Ionizing radiation can be used to replace the role of the activators in peroxide vulcanization. The effectiveness of irradiation to promote decomposition of *t*-BHPO was assessed from the mechanical properties and crosslink density of peroxide vulcanized NRL films. For this preliminary study, the highest crosslinking density (85.8%) was obtained from the irradiation of compounding NRL of 0.1 pphr *t*-BHPO at irradiation dose of 12 kGy. Increasing in the *t*-BHPO quantity from 0.1 pphr to 0.3 pphr has successfully delivered peroxide vulcanized NRL films with average tensile strength, modulus @ 500% and modulus @ 700% around 15.33 MPa, 1.01 MPa and 3.42 MPa, respectively. For future study, effect of irradiation doses on peroxide vulcanization will be investigated.

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