

Article

Polyethylene Thin Film Coating Preventing the Degradation of Natural Rubber

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Abstract. In this research, natural rubber (NR) was directly mixed with polyethylene (PE) and was compressed at 150°C. The PE was then separated and migrated to form a thin film on the rubber surface during the vulcanization process. The tensile properties of composite film were rising with increasing the PE contents from 15 to 150 phr as well as the ozone aging properties. The surface topography of the composite film was examined by using scanning electron microscopy (SEM) and was found that the PE form lamellar crystallites on the rubber interface after ozone treatment. The effect of PE on NR cross-linking was also investigated using S K-edge XANES Spectroscopy.

Keywords: Natural rubber, degradation, coating, polyethylene.

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1. Introduction

Natural rubber (NR) has excellent mechanical properties but it likes any other polymers which are composed with highly unsaturated chain that is susceptible to oxidative degradation [1]. The double bond of NR molecule will be attacked by peroxy free radicals initiated scission reaction when the rubber is placed under strain in air at high temperature [2]. As well as ozone degradation which is the cause of surface cracking when the rubber is placed under strain in an ozone environment. These degradations are serious problem to shorten the serviceable life of rubber article. It is necessary to add antioxidants either natural or synthetic in rubber compound to prevent this oxidative reaction [3-5]. However, chemical antioxidants and antiozonants are very expensive and have many limitations when applied with rubber.

In this study, a study of phase morphology with blend ratio and its effects on ozone resistance properties will be investigated, and the resulting degradation of sulfur bonding will be studied accordingly.

2. Methodology

2.1. Compounding and Making Thin Film

Standard Thai Rubber (STR20) was milled and mixed with spindle oil using 2-rolls mill before adding the polyethylene (PE) powder with following ratios: 100:15, 100:30, 100:90, and 100:150 by weight of NR:PE at an ambient temperature. For compounding was also directly mixed with chemicals followed Table 1. The rubber compound was compressed and vulcanized at 150°C for 5 minutes to formed membrane with thickness not over than 0.4 mm, in approximately.

Table 1. Formulation of NR compound (phr = part per hundred of rubber).

Ingredient	phr
STR20	100.0
Spindle oil	200.0
Sulfur	15.0
MBT	10.5
ZnO	7.5
Stearic acid	3.0
Winstay L	3.0
PE Powder	vary

2.2. Characterization

The mechanical properties of membrane were carried out on a LLOYD instrument tensile tester. The samples were cut into dumbbell shape with dimension according to ASTM D412 (die C). Aging of the dumbbell specimens were carried out by placing under strain in an ozone environment at 75 pphm for 8, 16, and 24 hours. Tensile properties were operated at a cross-head speed of 500 mm/min.

The XANES measurement was carried out at the beamline 8 of the Synchrotron Light Research Institute (SLRI) in Thailand [6]. The measurements were performed in a fluorescence mode using a 5-grid ionization Lytle fluorescence detector. The photon energy scan was carried out using the Si(111) double crystal monochromator to cover the *K*-edge of sulfur. For the energy calibration, the maximum of the absorption peak (white line) of zinc sulfate ($ZnSO_4$) powder was used as the reference energy of 2481.4 ± 0.1 eV [7]. Surface morphology of membrane was studied using scanning electron microscope (SEM), JEOL JSM-5800 LV.

3. Results and Discussion

The membrane of PE, NR, and their blends has mechanical properties as shown in Fig. 1. The tensile strength of PE membrane is higher than NR membrane while the tensile strength of membrane from their blends is slightly increased when compared with NR membrane.

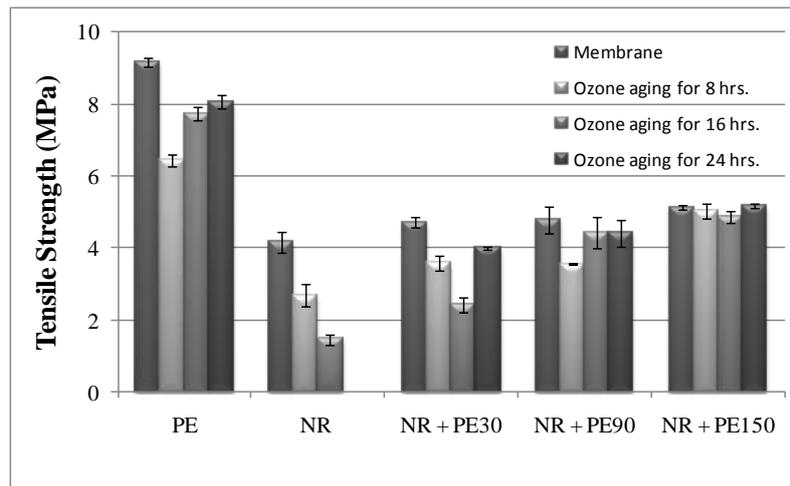


Fig. 1. Tensile strength of pure and blended membranes.

The tensile strength of PE membrane is dramatically decreased after ozone ageing for 8 hrs due to oxidative reaction while longer ozone ageing of PE membrane results in increasing of tensile strength. The PE scission chains might be oriented and formed crystalline structure to increases the tensile strength. On the other hand, the NR membrane is degraded with increasing ozone aging period until the rubber is broken down with ozone aging for 24 hr. The aging property of rubber blend membrane is improved with increasing the PE concentration because PE phase is separated and migrated to form thin film coating on the membrane surface during hot compression process.

The S K-edge absorption spectra of NR and their blends membrane as illustrated in Fig. 2. The sulfur cross-linking in rubber molecule was investigated cover photon energy range of 2460 to 2490 eV with the accuracy of photon energy up to within 0.2 eV. The S K-edge absorption peak would shift depending on sulfur environment. In this case the peak of S K-edge absorption was found at 2472.0 ± 0.2 eV for polysulfidic crosslink. The position of the peak in the absorption spectra shifts towards lower photon energy may be used as the indicator for the type of the σ^* resonance [8, 9]. The absorption peak area is increased and shifts towards lower photon energy with increasing the PE concentration corresponds with the mechanical properties of membrane.

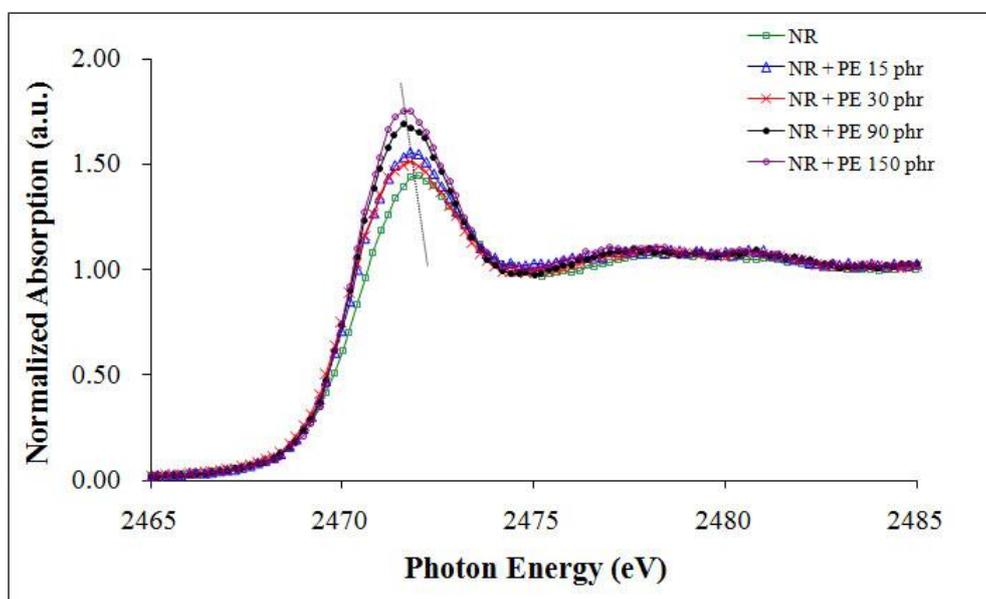


Fig. 2. XANES spectra of NR and their blends membrane.

The SEM images in Fig. 3 clearly showed that PE migrated to the surface and created a barrier film at bottom surface because PE was removed after immersing the membrane in xylene. The membrane is consisted of micro-pores at the bottom surface and cross-section after removing PE. This effect is similar to wax blooming which will carry chemical antiozonants to the surface of the rubber, improving their performance. In this study, the membrane prepared from NR blending with PE for 150 phr created highest thickness of the film and contribute to the ozone resistance.

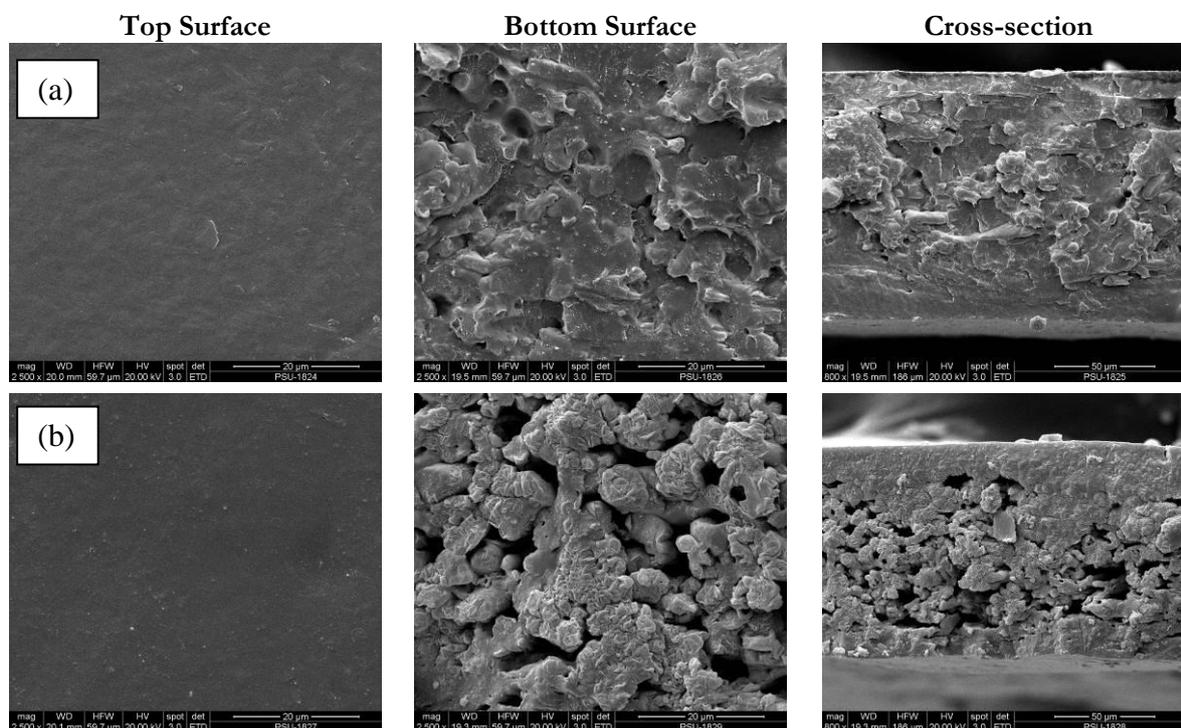


Fig. 3. SEM images of the membrane from NR blending with PE 150 phr before (a) and after (b) extraction with xylene.

The surface of NR membrane is cracked after ozone aging as shown in Fig. 4 while the PE coated membrane formed lamellae crystallites on the surface as shown in Fig. 5. Coated PE layer was oriented and the crystalline lamellae were grown in submicrometer size after ozone treatment. The crystalline size and number depend on ozone aging time. The increasing of crystalline lamellae corresponds with the tensile strength of PE coated membrane.

4. Conclusions

PE phase separated from NR phase to formed thin film coating on the membrane. The coating improved the ozone aging of the membrane without adding any antiozonants. The coating layer formed crystalline lamellae after treated the membrane with ozone resulted in preventing rubber oxidation reaction and improvement of membrane strength.

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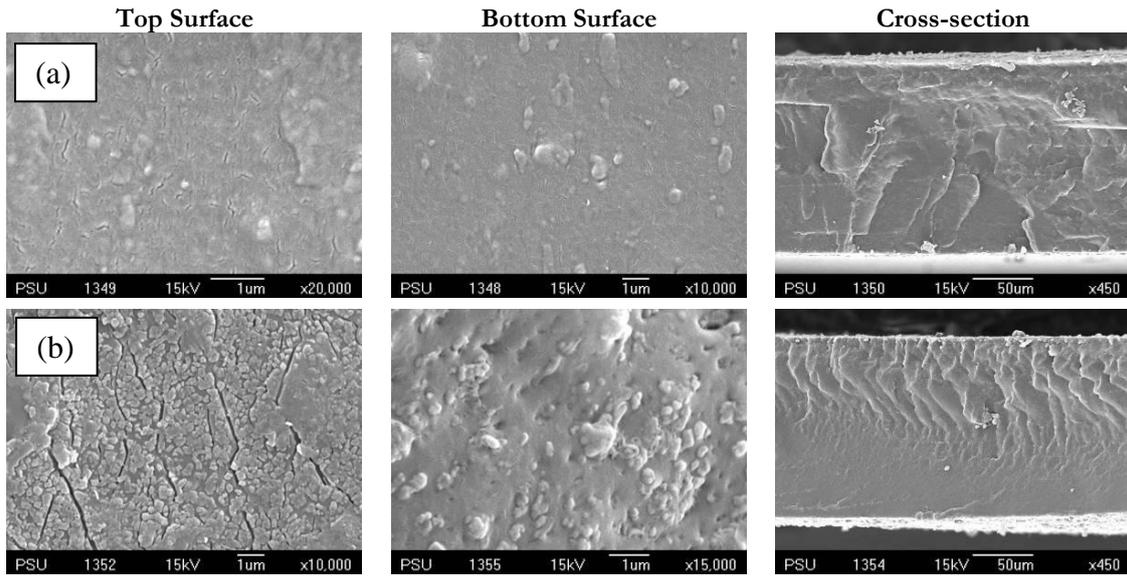


Fig. 4. SEM images of NR membrane before (a) and after (b) ozone aging at 75 pphm for 16 hrs.

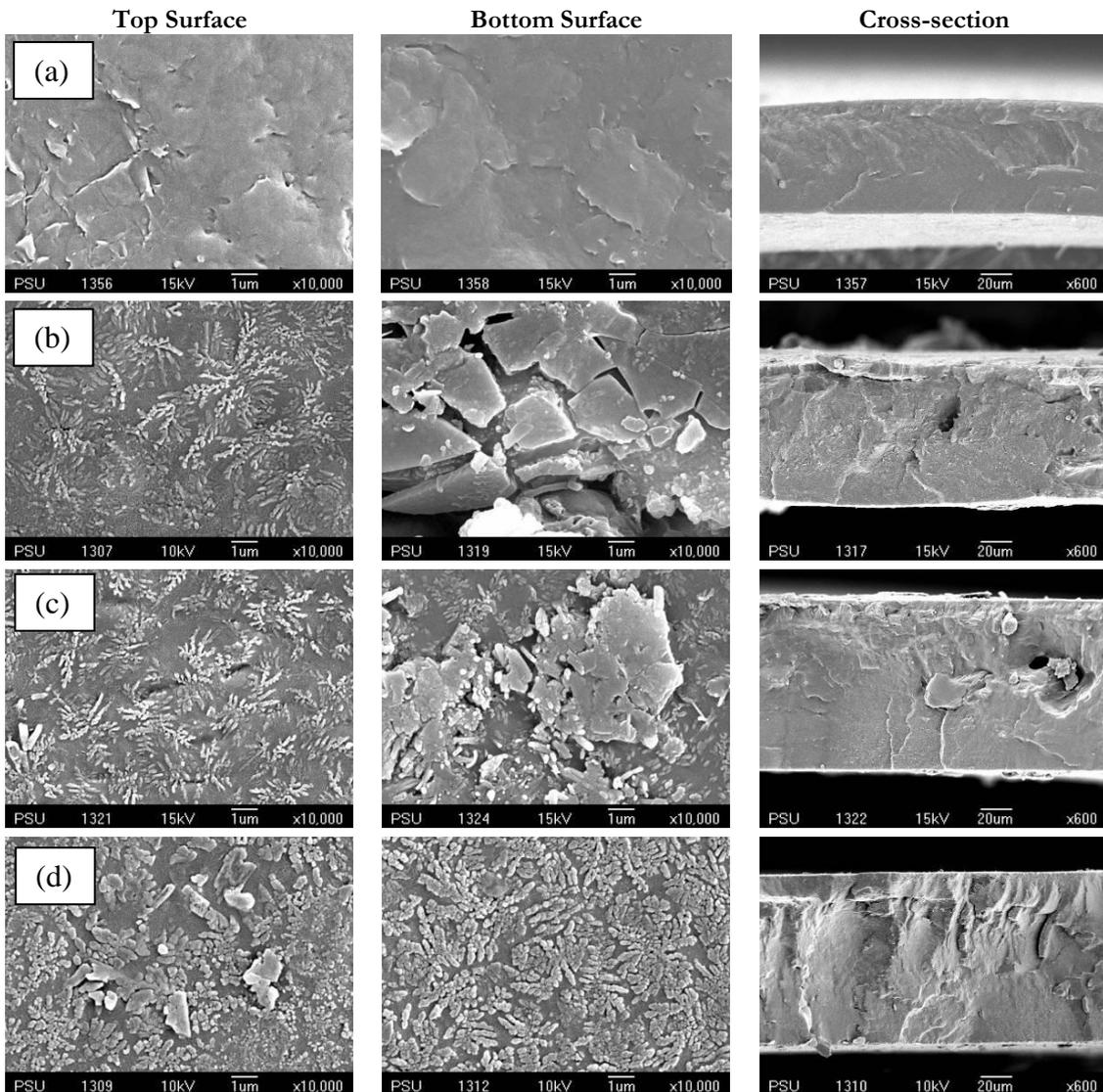


Fig. 5. SEM images of the membrane from NR blending with PE 150 phr before (a) and after ozone aging at 75 pphm for 8 hrs (b) 16 hrs (c) and 24 hrs (d).

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