

IN SITU SILICA REINFORCED RUBBER LATEX COMPOSITE: EFFECTS OF BLEND RATIO AND SILICA CONTENT

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Abstract

The effects of blend ratio and silica content were studied on mechanical, morphological, and thermal properties of rubber blends and composites. Natural rubber (NR) was blended with carboxylated styrene-butadiene rubber (XSBR) at different ratios of NR/XSBR, i.e., 1:1, 1:2, and 2:1. The optimum mechanical properties of NR/XSBR blends was obtained from NR/XSBR at the optimum ratio of 2:1. NR/XSBR with the optimum ratio was mixed with silica in silicate form. Commercial sodium silicate (CSS) was used to prepare the silica for use as reinforcing filler. NR/XSBR was firstly mixed with CSS to obtain the mixture of NR/XSBR/CSS. And then, acetic acid was dropped into the mixture to obtain the precipitated silica at various contents of silica (5, 10, and 20 phr). The addition of silica into NR/XSBR at the ratio of 2:1 can improve the thermal property of the NR/XSBR blends. By increasing silica contents, an insignificant difference in terms of tensile strength and elongation at break of the mechanical properties was observed. The best thermal properties were obtained from NR/XSBR/20Si composite.

Keywords: Natural rubber latex, Carboxylated styrene-butadiene rubber latex, Rubber blend, Silica, Rubber composite

Introduction

Natural rubber (NR) is one of the important agricultural products of Thailand that can be used to produce a wide of products due to high resilience, good tensile strength, and tear resistance, etc. (Chuayjuljit *et al.*, 2015; Vu *et al.*, 2015). The making of NR products covered many industries such as automotive (tires, belts, and seals), medical (gloves, tubes, and condoms), and others (shoes, furniture, and sponges), etc. (Rajan *et al.*, 2006).

However, NR is known that has low resistance for sunlight, ozone, and oxygen or heat aging because it contains the double bonds in the molecular structure (Jones and Tinker, 1997; Vu *et al.*, 2015). Therefore, the most productive of NR production are not preferred to use only NR but will be used with other rubbers or fillers to obtain the properties of the product required (Varkey *et al.*, 2000; Motaung *et al.*, 2011). The samples of manufacturing of tires

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were applied for NR with butadiene rubber (BR) or styrene-butadiene rubber (SBR), carbon black, and silica for improving wear, traction, and rolling resistance, etc. (Le *et al.*, 2010; Shan *et al.*, 2011).

The other rubbers and fillers, SBR and silica are interesting because they can improve some properties of NR such as mechanical and thermal properties. Varkey *et al.* (2000) studied the thermal degradation of NR/SBR latex blends by using the thermogravimetric method and they found that blending with SBR increased the thermal stability of NR. Poompradub *et al.* (2014) reported that the filling NR with in situ silica can not improve only the mechanical properties but also the thermal properties of the filled vulcanizates, and was superior compared with the ex-situ silica. SBR is the largest volume of synthetic rubber. It can polymerize by using the solution or emulsion technique. Moreover, it has the low reversion of resistance, high resistance of abrasion at higher speeds, and good resistance for flexible fatigue. However, the main drawbacks of SBR are poor oil and ozone resistances. The carboxylated SBR (XSBR) is one of the members of SBR polymerized with the emulsion polymerization of styrene, butadiene, and some strong acid monomer that like acrylic acid or methyl methacrylate acid. It has the good abrasion resistance, aging stability, hydrocarbon solvent resistance, and interaction with the functional filler that like silica (Alimardani and Abbassi-sourki, 2014). There are several reports that mentioned about the NR blended with XSBR to easily modify the mechanical properties of NR because of the polarity of XSBR (Stephen *et al.*, 2003). Also, the incorporation of XSBR into NR improves the thermal properties and gas permeability of NR (Stephen *et al.*, 2005). Silica is the important filler in the rubber industry that reduces heat buildup and improves the tensile strength, tear strength, and abrasion resistance of rubber composites (Ikeda and Kohjiya, 1997; Kohjiya and Ikeda, 2003). Moreover, it is known that in the tire industry, silica is extensively used to substitute with carbon black for reducing the rolling resistance of tire treads and enhance wet grip (Alimardani and Abbassi-sourki, 2014). Nevertheless, the above reports generally mentioned the mixing of rubber in a latex form which compounding of latex is the low energy of processing of consumption but normal interaction between filler and rubber that not good because there is not present the mastication step (Stephen *et al.*, 2006). Therefore, using of XSBR blended with NR composites may be solved this problem because it contained carboxyl groups which may be reduced the mastication step and compatible with silica that used as the filler in this study.

The aim of this research is focused on study of the effects of blend ratio between NR and XSBR at the ratio of 1:1, 1:2, and 2:1 on the mechanical, morphological, and thermal properties. The optimum NR/XSBR ratio was mixed with in situ silica at various contents (5, 10, and 20 phr). Mechanical, morphological, and thermal properties of NR/XSBR/Si composites were studied.

Materials and Methods

Materials

Natural rubber latex (NRL) with a solids content of 60wt% and high ammonia-treated latex was supplied by Chemical & Materials Co., Ltd. Carboxylated styrene-butadiene rubber latex (XSBR) was supplied by Jorakay Corporation Co., Ltd. Commercial sodium silicate (CSS) was supplied by Sigma-Aldrich Co., Ltd. Acetic acid was supplied by Merck & Co., Inc. Zinc oxide (ZnO), stearic acid, N-Cyclohexyl-2-Benzothiazole Sulfonamide (CBS), and sulfur were supported by Chemical Innovation Co., Ltd.

Preparation of NR/XSBR Sheets

NRL was blended with XSBR at different ratios of NR/XSBR, i.e., 1:1, 1:2, and 2:1 by using a magnetic stirrer for 30 mins. Rubber mixtures were poured onto the Teflon tray and dried at 60°C by using a hot air oven for 16 hr to obtain NR/XSBR sheets.

Preparation of NR/XSBR/Si Sheets

NR/XSBR at the ratio of 2:1 was mixed with CSS at various contents of silica (5, 10 and 20 phr) by using a magnetic stirrer for 30 mins to obtain NR/XSBR/CSS mixtures. Acetic acid was dropped into the NR/XSBR/CSS mixture until neutral to gain precipitated silica. The mixtures were poured onto the Teflon tray and dried at 60°C by using a hot air oven for 16 h to obtain NR/XSBR/Si sheets.

Preparation of NR/XSBR Blends and NR/XSBR/Si Composites

All samples were mixed with 5 phr ZnO, 2 phr stearic acid, 2.5 phr CBS, and 1 phr sulfur by using a two-roll mill machine to obtain compounds. Vulcanization of all compounds was done by using the compression molding machine at 150°C with optimum curing time (t_{c90}) that determined by Moving Die Rheometer (MDR) to obtain NR/XSBR blends and NR/XSBR/Si composites.

Mechanical Properties

The tensile properties of blends and composites were measured according to ASTM

D412 using a Universal Testing Machine (Instron 5565) with a crosshead speed of 500 mm/min and a load cell of 5 kN.

The hardness of blends and composites were measured according to ASTM D2240 using a Bareiss shore A (HPE II).

Morphological Properties

The morphology of blends and composites were investigated by Field Emission Scanning Electron Microscope (FE-SEM) using a Carl Zeiss (Auriga). All of the samples were coated with gold before testing.

Thermal Properties

The thermal stability of blends and composites were determined by thermogravimetric analysis (TGA) using a Mettler Toledo (TGA/DSC1). All samples were placed into an alumina pan and heated at the room temperature up to 800°C under nitrogen at a heating rate of 10°C /min.

Results and Discussion

Mechanical Properties of NR/XSBR Blends

The mechanical properties of NR, XSBR, and NR/XSBR at different ratios of blending are shown in Figure 1. All NR/XSBR blends showed higher modulus at 100% and 300% elongation than NR but lower than XSBR depending on the ratios of blending. This is because XSBR has a styrene content for making the XSBR harder and rubbery less than NR. NR/XSBR at the ratio of 2:1 showed the highest tensile strength and elongation at break due to its strain-induced crystallization (Stephen *et al.*, 2003). However, all NR/XSBR blends showed an insignificant difference of hardness.

Morphological Properties of NR/XSBR Blends

The morphological properties of NR, XSBR, and NR/XSBR at different ratios of blending are shown in Figure 2. The surface fracture by using the

tensile testing of XSBR showed the flattest surface when compared with NR and NR/XSBR at different ratios of blending. The surface roughness of NR/XSBR increased with NR content. The highest surface roughness was obtained from NR/XSBR at the ratio of 2:1. The rough fractured surface indicate that the samples was failed in a ductile manner which led to the good elongation at break (Boonmahitthisud *et al.*, 2017).

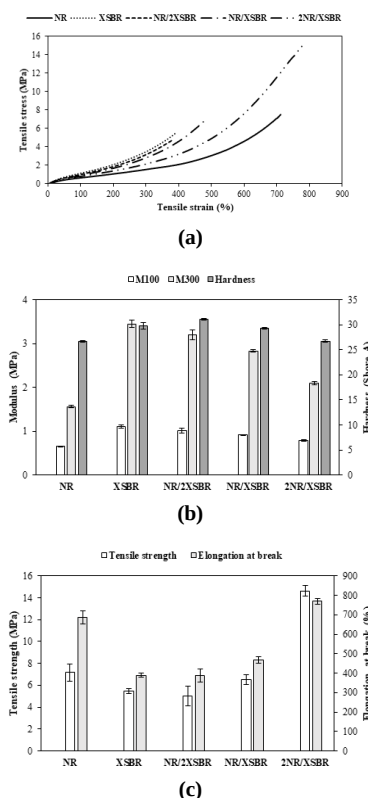


Figure 1. Mechanical properties of NR, XSBR, and NR/XSBR blends showing (a) stress-strain curve, (b) modulus at 100% elongation, modulus at 300% elongation, and hardness, and (c) tensile strength and elongation at break.

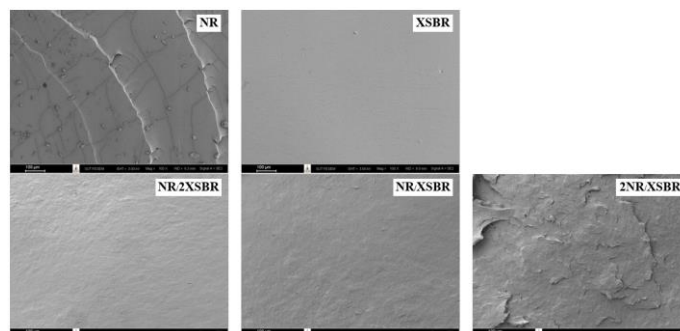


Figure 2. SEM images of NR, XSBR, and NR/XSBR blends.

Table 1. Degradation temperature at different weight loss levels of NR, XSBR, NR/XSBR blends, NR/XSBR/Si composites, and silica.

Sample	T _{30%} (°C)	T _{50%} (°C)	T _{70%} (°C)	T _{max} (°C)
NR/XSBR Blends				
NR	366	380	397	378
XSBR	401	421	442	415
2NR/XSBR	371	390	415	388
NR/XSBR/Si Composites				
2NR/XSBR/5Si	373	392	421	389
2NR/XSBR/10Si	376	400	433	390
2NR/XSBR/20Si	371	397	434	389
Silica	449	N/A	N/A	483

Thermal Properties of NR/XSBR Blends

The thermal properties in term of degradation of temperature at different levels of weight loss of NR, XSBR, and NR/XSBR at the ratios of 2:1 are listed in Table 1. NR showed the lowest degradation temperature compared with XSBR and NR/XSBR at the ratio of 2:1 because NR is a diene rubber that is highly susceptibility to degrade (Stephen *et al.*, 2006). NR/XSBR at the ratio of 2:1 showed higher degradation temperature than NR while XSBR showed the highest degradation temperature. XSBR can increase the degradation temperature of the NR/XSBR blend.

Mechanical Properties of NR/ XSBR/ Si Composites

NR/XSBR at the ratio of 2:1 was selected to be blended with silica at the different contents.

The mechanical properties of NR/XSBR and NR/XSBR blended with silica at different contents are shown in Figure 3. The modulus at 100% and 300% elongation of all NR/XSBR blended with silica were higher than those of NR/XSBR blends. With increasing silica contents, modulus at 100% and 300% elongation were higher due to the higher stiffness of fillers. That is the reason of the results of the hardness of NR/XSBR and NR/XSBR blended with silica at the different contents as well. However, NR/XSBR and NR/XSBR blended with silica at different contents showed a slight difference in tensile strength and elongation at break.

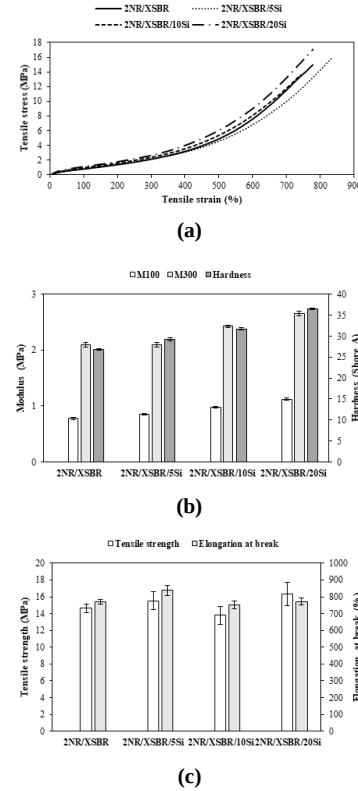


Figure 3. Mechanical properties of NR/XSBR blend and NR/XSBR/Si composites showing (a) stress-strain curve, (b) modulus at 100% elongation, modulus at 300% elongation, and hardness, and (c) tensile strength and elongation at break.

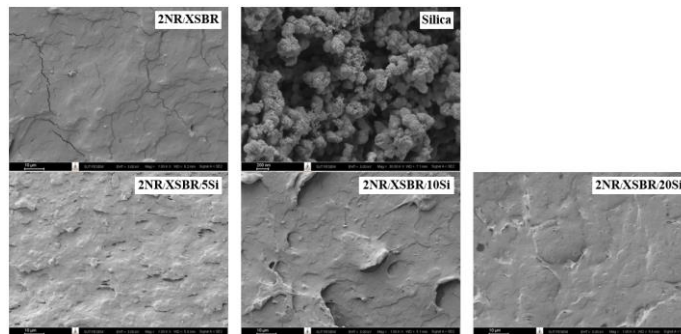


Figure 4. SEM images of NR/XSBR blend, silica, and NR/XSBR/Si composites.

Morphological Properties of NR/XSBR/Si Composites

The morphological properties of silica, NR/XSBR, and NR/XSBR blended with silica at different contents are shown in Figure 4. The surface fracture obtained from tensile testing of NR/XSBR showed a slightly rough surface when compared with NR/XSBR blended with silica at different contents. All NR/XSBR blended with silica showed similar rough surfaces. This led to the slight difference in elongation at break of NR/XSBR and NR/XSBR blended with silica at different contents since fracture surface can indicate failure manner which affected to the mechanical properties of samples. Silica particles were prepared by dropping acetic acid in CSS until neutral. This showed silica particles in a general form that is in spherical structure and partially agglomerated due to filler-filler interactions of silica (Choi, 2001; Stephen *et al.*, 2007).

Thermal Properties of NR/XSBR/Si Composites

The thermal properties in term of degradation temperature of NR/XSBR and NR/XSBR blended with silica at different contents are listed in Table 1. The degradation temperature of NR/XSBR and NR/XSBR blended with silica at the different contents showed an insignificant difference in degradation temperature in the early weight loss levels of degradation. However, considering 70% weight loss level it was found that the degradation temperature of NR/XSBR/Si composites increased with the addition of silica, due to the higher thermal stability of silica than NR and XSBR.

Conclusions

The blending of NR and XSBR can improve the thermal properties of NR. NR/XSBR at the ratio of 2:1 showed the highest tensile strength about 200% when compared with NR. The addition of silica into NR/XSBR at the ratio of 2:1 can improve the thermal properties of NR/XSBR blends with an insignificant difference in mechanical properties in terms of tensile strength and elongation at break. NR/XSBR at the ratio of 2:1 showed an increase in degradation temperature with increasing silica contents. Therefore, the best thermal properties were obtained from NR/XSBR/20Si composite.

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