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Preparation and Characterization of Epoxidized Natural Rubber and Epoxidized Natural Rubber/Carboxylated Styrene Butadiene Rubber Blends

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Abstract

In this study, epoxidized natural rubber (ENR) with 30 mol% epoxidation (ENR-30) was first prepared from natural rubber (NR) latex via *'in situ'* performic epoxidation using 0.5 M hydrogen peroxide and 0.75 M formic acid at 50°C for 4 hours. The prepared ENR-30 was blended with three different loadings of carboxylated styrene butadiene rubber (XSBR) (10, 20 and 30 wt%) in the latex stage. All ENR-30/XSBR blends had longer scorch time and cure time than neat ENR-30 as examined on a moving die rheometer. The tensile properties (tensile strength, modulus at 300% strain and elongation at break), thermal stability and oil resistance of the ENR-30/XSBR blends were investigated. The incorporation of XSBR into ENR-30 caused an increase in the modulus at 300% strain but deteriorated the tensile strength and elongation at break. However, the elongation at break of the blends was still high (540-630%) as compared to that of the neat ENR-30 (690%). The results from the thermal gravimetric analysis revealed an increased initial degradation temperature but a decreased thermal stability at high temperatures. The oil resistance of ENR-30 and ENR-30/XSBR blends in terms of the percentage volume change after immersion in the ASTM Oil No.1 and IRM 903 oil was better than that of the NR.

Keywords: Epoxidized natural rubber; Carboxylated styrene butadiene rubber; Rubber blend; Physical properties; Oil resistance.

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Introduction

Nowadays, Thailand is the largest producer and exporter of natural rubber (NR). Owing to its excellent properties including high mechanical strength, low heat build-up, excellent resilience and elasticity, high abrasion resistance and outstanding tacking, NR is wildly used in various areas such as tires, sealing materials and diary rubber items (1, 4) . Some drawbacks of NR such as poor ozone, weathering and thermal resistance are mainly due to its unsaturation hydrocarbon structure, while poor oil resistance and compatibility and adhesion with polar polymers are due to its non-polar nature. These result in the limitation in many applications of NR. Moreover, blending of NR with polar rubbers usually leads to immiscibility, phased separation and poor interfacial adhesion (5,6) .The introduction of polar group onto NR backbone is one of the approaches to overcome these problems. Epoxidation is a simple and effective method to increase the polarity of NR by incorporating polar epoxide groups into the molecular chains. NR can be chemically modified into epoxidized natural rubber (ENR) in latex stage with performic acid generated *in situ* from hydrogen peroxide and formic acid, where the double bonds (C=C) in NR are randomly converted into epoxide groups along the molecular chains (5, 6). Epoxidation results in an increase in the polarity, oil resistance and glass transition temperature (Tg) and a decrease in gas permeability of NR (7, 8). The extent of epoxidation is controlled by the peracid content, reaction temperature and reaction time (9). Thus, under controlled condition, specific level of epoxidation can be obtained. At present, two grades of ENR are available commercially, ENR-25 and ENR-50 indicating 25 and 50 mol% epoxidation, respectively. ENR is able to undergo strain crystallization and hence exhibits high strength as NR, however its ability to strain crystallize can retain up to about 50 mol% epoxidation (7) .In addition, the ENR of lower than 50 mol% epoxidation is a typical elastomer, while that of higher epoxidation becomes

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harder and lower resilience and elasticity (10) NR can be vulcanized in the usual manner applicable for unsaturated rubbers, but the use of sulphur as a vulcanizing agent is recommended, since its vulcanizate can possess some advantages of NR, including high tensile and tear strength. In this study, ENR with medium epoxide content (~ 30 mol%) was prepared to obtain ENR with a comparable resilience and elasticity but a higher oil resistance to NR. The prepared ENR was further blended with a synthetic-polar rubber, namely carboxylated styrene butadiene rubber (XSBR) in the latex stage, which is the easiest way of blending, resulting in a finer scale of dispersion.

XSBR is a copolymer of styrene, butadiene and a small amount of acrylic acid, and has been used as an adhesive in the carpet industry because of its good adhesion to polar substrate, good physical and chemical stability and low cost. (11-13). XSBR latex can be prepared by the emulsion polymerization of styrene and butadiene followed by carboxylation. The carboxyl group introduced by acrylic acid is a potential functional group for the formation of hydrogen bonding with polar polymer and filler. Moreover, XSBR has high colloid stability and high tolerance with the addition of large amount of mineral fillers, which facilitates its processability (14, 15). Because of the polarity of XSBR, it is expected to provide a miscible blend with ENR, and thus can modify the property for end product application. *Peng et al.* reported the miscible blend of nylon 6 and XSBR through the reaction of carboxyl group with the amine end group of nylon 6 during the melt blending, leading to an improvement in the notched impact strength of nylon 6 (11).

In this study, the in-house prepared ENR with about 30 mol% epoxidation was blended with various amounts of XSBR in the latex stage, and the curing characteristics, tensile properties, thermal stability and oil resistance of the blends were examined and compared.

Materials and Experimantal Procedures

Materials

High ammonia concentrated NR latex with 60% dry rubber content (DRC), sulfur, zinc oxide (ZnO), stearic acid, n-cyclohexylbenzothiazylsulphenamide (CBS), voltamol and bentonite were supplied by Rubber Research Institute of Thailand. XSBR latex (47% DRC) was obtained from Siam Synthetic Latex Co. Reagent-grade 98% formic acid (HCOOH), 30% hydrogen peroxide (H_2O_2), polyalcohol ethyleneoxide condensate (Terric 16A-16) and sodium carbonate (Na CO) were purchased from Sigma-Aldrich

Preparation and characterization of ENR

ENR was prepared via *in situ* epoxidation of NR using HCOOH and H_2O_2 as follows. NR latex was first diluted to 20% DRC with distilled water and stabilized with Terric 16A-16 under stirring for 1 h. The assigned amounts of formic acid (0.25-1 M of isoprene unit) and H_2O_2 (0.25-1 M of isoprene unit) were added into the stabilized NR latex according to the formulation in Table 1. The HCOOH was gently dropped into the stabilized NR latex at 40°C, followed by heating up to 50°C before adding the H_2O_2 with continuous stirring. The reaction was allowed to perform at 50°C for 4 hours. For further characterization, the obtained ENR latex was coagulated in methanol, washed with distilled water, soaked in sodium carbonate solution (5%), washed again until neutral, pressed into thin sheet (1.5-2 mm), and then dried at 60°C for 48 h.

The prepared ENRs were characterized for their mol% epoxidation using Fourier transform infrared spectroscopy (FT-IR) on a Nicolet 6700-FT-IR over a frequency range of 400-3,400 cm^{-1} The mol% epoxidation was calculated from Eq.(1) using data obtained from the characteristic FT-IR peaks at 870 and 835 cm^{-1} in according to Davey and Loadman (16).

$$\text{Mol \% epoxidation} = [A870/(A870+A835)]\times 100 \qquad (1)$$

Table 1. Chemical composition used for the preparation of ENR.

Ingredient	Formula						
	1	2	3	4	5	6	7
NR	100[a]	100	100	100	100	100	100
Terric16A-16	3[a]	3	3	3	3	3	3
H_2O_2	0.25[b]	0.50	0.75	1.00	0.75	0.75	0.75
Formic acid	0.75[b]	0.75	0.75	0.75	0.25	0.50	1.00

[a] dry content in g, [b] content in M of isoprene unit

Preparation of ENR/XSBR blends

The ENR/XSBR blends with different dry weight ratios (100/0, 90/10, 80/20 and 70/30) were prepared by blending of the two latices at an ambient temperature using a high speed mixer at 150 rpm for 30 minutes. The blend was then coagulated as described above.

Compounding, cure characterization and aulcanization

The dry rubber was compounded with ZnO (5 phr), stearic acid (2 phr), CBS (1 phr) and sulfur (2 phr) in an internal mixer (MX500-D75L90) at 70°C for 9 minutes, and the compound was then removed from the mixer and sheeted on a cold two roll mill for 1 minute. The cure characteristics were determined using a moving die rheometer (MDR A 0225-rheo Tech MD) at 130°C according to ASTM D2084. The respective scorch time (t_{s2}), cure time (t_{90}) minimum torque (M_L), maximum torque (M_H) and torque difference (Δ torque, M_H-M_L) were obtained from the rheograph. The compound was compressed in a compression molding machine (LP-S-20, LabTech Engineering) at 130°C according to the respective t_{90}.

Testing and characterization

The tensile test was performed on a dumbbell-shape specimen according to ASTM D412 using a universal testing machine (T-TS-01, Techpro) with a load cell capacity of 1 kN at a cross-head speed of 500 mm/min. At least five specimens were analyzed for the tensile strength, modulus at 300% strain (M300) and elongation at break.

The thermogravimetric analysis (TGA) was performed on a Mettler Toledo TGA/SDTA 851e analyzer over a temperature range of 30-1000°C at a heating rate of 20°C/minutes under a nitrogen atmosphere to evaluate the thermal stability of the sample.

The oil resistance was determined by measurement of change in volume of the sample after immersion in ASTM oil No.1 (IRM 901) and ASTM oil No.3 (IRM 903) at 100°C for 70 hours according to ASTM D471-79.

The morphology of the tensile fractured surface of the sample was observed by scanning electron microscopy (SEM; Jeol JSM-5410LV) under an accelerated voltage of 15 kV with a magnification of 500×. The samples were sputter coated with a thin layer of gold prior examination to improve the surface conductivity.

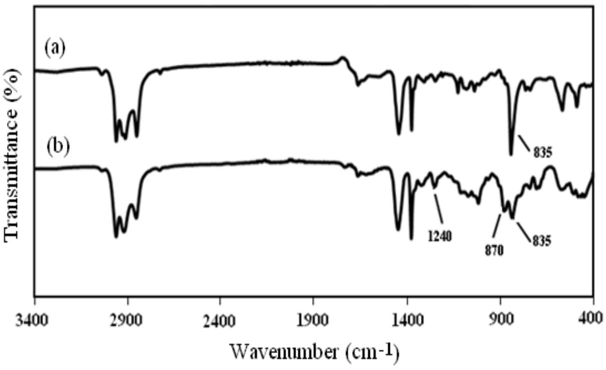

Figure 1. FT-IR spectra of the (a) NR and (b) ENR.

Results and Discussion

Figure 1 shows the FT-IR spectra of NR and a representative ENR. The characteristic peaks of NR (Figure 1(a)) appeared at 2860, 1650, 1450, 1375 and 835 cm^{-1} are assigned to the C-H stretching, C=C stretching, -CH$_2$- deformation, C-H deformation of CH$_2$ and =C-H deformation, respectively. As the C=C bonds in NR molecules were randomly converted into epoxide groups, new characteristic peaks at 1240 and 870 cm^{-1} attributed to the symmetric stretching and asymmetric stretching of epoxide ring, respectively (18, 17) appeared on the spectrum of ENR (Figure 1(b)), which have not been found on the spectrum of NR. Hence, as the mol% epoxidation increased, the peak at 870 cm^{-1} increased correspondingly, and the reduction in the number of C=C in ENR was reflected by the decrease in the peak at 1650 and 835 cm^{-1}. This confirmed the formation of epoxide rings from the reaction of performic acid (generated *in situ* from the reaction of HCOOH and H_2O_2) with the C=C bonds on the NR backbones. The calculated mol% epoxidation of the prepared ENRs using Eq. (1) and data from FT-IR spectra is listed in Table 2. The results showed an increased mol% epoxidation with increasing either formic acid or H_2O_2 content as a consequence of the increased performic acid content in latex that reacted with C=C bonds of NR, and the mol% epoxidation of ENRs was in the range of 17-46 mol%. It is known that ENR with low mol% epoxidation usually has higher strain crystallization, resilience and elasticity, but lower oil resistance than ENR with higher mol% epoxidation (7-10) .Therefore, with the balance of these properties, ENR with medium mol% epoxidation (~ 30 mol%), prepared from 0.5 M H_2O_2 and 0.75 M HCOOH (Formula 2) was used for blending with different loadings of XSBR (10, 20 and 30 wt%) in the latex stage. Accordingly, this ENR was denoted as ENR-30
.

Table 2. Mol % epoxidation of the prepared ENR.

Character	Formula						
	1	2	3	4	5	6	7
Mol % epoxidation	17	29.5	31.3	42	18.4	33.3	46

Table 3. Cure characteristics of the ENR-30 and ENR-30/XSBR blends.

ENR/XSBR (wt%/wt%)	t_{S2} (min)	t_{90} (min)	M_L (lbf-in)	M_H (lbf-in)	Δ Torque ($M_H - M_L$) (lbf-in)
100/0	11.2	18.2	0.57	4.94	4.38
90/10	16.8	23.0	0.59	4.62	4.03
80/20	18.2	29.1	0.75	4.43	3.68
70/30	22.3	31.2	0.85	4.15	3.30

Cure characteristic

The t_{s2}, t_{90}, M_L, M_H and Δ torque (M_H-M_L) of ENR-30 and its blends obtained from the MDR rheographs (not shown here) are summarized in Table 3. The t_{s2} is a measure of premature vulcanization while t_{90} is the optimum cure time of the vulcanizate. As ENR is vulcanized by sulphur, the t_{s2} and t_{90} are usually shorter than those of NR, because the isolated double bonds react more rapidly than the continuous double bonds (18) .Moreover, the epoxide group can activate the adjacent double bond, and thus accelerated the vulcanization process of ENR (18, 19, 21). From Table 3, the t_{s2} and t_{90} of ENR-30/XSBR blends increased with increasing XSBR content in the blend. This caused a less amount of ENR-30 and also the epoxide group in the blends. In addition, the reaction between the carboxyl group of XSBR and the epoxy group of ENR-30 may have been lowered the efficiency of epoxide group on activating the nearby double bonds. Table 3 also shows the results of M_L, M_H and M_H-M_L of ENR-30/XSBR blends. ML is commonly considered as the elastic modulus of the uncured blend, while the M_H generally correlates to the hardness and/or modulus of the vulcanizate (19, 20). Increased ML with increasing loading of XSBR might have resulted from the increased adhesion between ENR-30 and XSBR that enhanced the modulus of the uncured blend, while the decreased MH with increasing XSBR loading indicated increasing elasticity. The difference in MH and ML is a measure of the modulus of the compound, which in turn is a measure of crosslinking (20, 22) . It can also be seen that the MH-ML decreased continuously with increasing XSBR loading, indicating a decrease in the crosslink density of the rubber blend (21) .This is because the vulcanization process was hindered by the XSBR molecules.

Tensile testing

The tensile properties in terms of the tensile strength, elongation at break and modulus at 300% strain of ENR-30 and its blends are illustrated in Figure 2. As can be seen in Figure 2(a), the tensile strength of each of the three different ENR-30/XSBR blends was lower than that of the neat ENR-30 (~ 23.5 MPa) and also gradually decreased with increasing XSBR content (from 19.7 MPa at 10 wt% to 15.8 at 30 wt%). This was due to the lower amount of ENR-30 in the blends and the XSBR molecules that reduced the ability of the samples to undergo strain crystallization, leading to the decrease in the tensile strength. Figure 2(b) shows that as the modulus at 300% strain of all the blends was higher than that of the neat ENR-30 (~ 2 MPa) and increased with increasing XSBR content (from 2.5 MPa at 10 wt% to 4.1 MPa at 30 wt%), the elongation at break was lower than that of the neat ENR-30 (~ 691.3%) and decreased with increasing XSBR content (from 629.3% at 10 wt% to 540% at 30 wt%). The increase in the modulus at 300% strain was attributed to the chain entanglement and intermolecular attraction between ENR-30 and XSBR molecules that reduced the ability of the blends to deform under tension by restricting the mobility of the polymer chains, and the decrease in the elongation at break was also due to the same reason with the increase in the modulus at 300% strain. However, as can be noticed, the elongation at break of the blends was still largely retained.

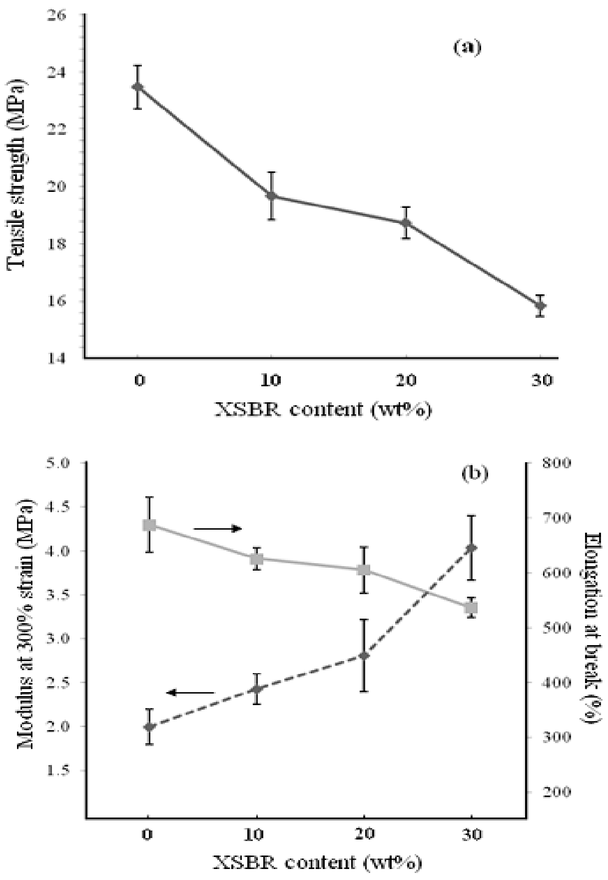

Figure 2. The (a) tensile strength and (b) modulus at 300% strain and elongation at break of the ENR-30 and ENR-30/XSBR blends.

TGA analysis

TGA was performed to evaluate the thermal stability of ENR-30 and its blends. The TGA curves of the samples are shown in Figure 3, while the values of *T*onset, *T*end set, *T*50% and *T*max are summarized in Table 4. TGA curves of ENR-30 and ENR-30/XSBR blends exhibited a similar egradation characteristic. This indicated that the addition of XSBR did not change the degradation mechanism of the ENR-30 but only influence the degree of degradation. It can be observed from Figure 3 and Table 4 that all the blends showed an increase in the *T*onset with increasing XSBR content by 2-7°C compared to that of the neat ENR-30, indicating that the XSBR delayed the initial degradation of ENR-30. This may be due to the chain entanglement and intermolecular attraction between ENR and XSBR molecules. However, the *T*50%, *T*max and *T*end set were all shifted to the lower temperatures with the addition of XSBR, suggesting the lower interaction between XSBR and ENR-30 at higher temperature and so reduced the thermal stability of the blends.

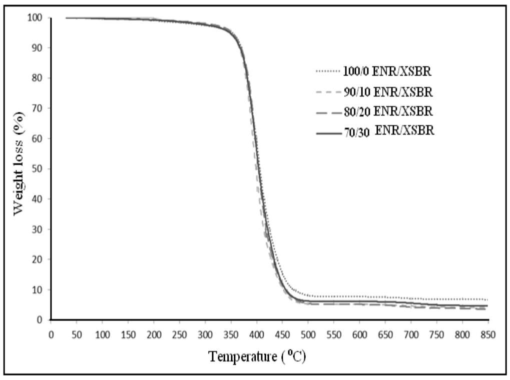

Figure 3. TGA thermograms of the ENR-30 and ENR-30/XSBR blends.

Table 4. TGA-derived data of the ENR-30 and ENR-30/XSBR blends.

ENR/XSBR (wt%/wt%)	*T*onset (°C)	*T*end set (°C)	*T*50% (°C)	*T*max (°C)
100/0	367	441	406	404
90/10	369	428	399	395
80/20	371	434	403	400
70/30	372	435	404	400

Oil resistance

Figure 4 shows the change in volume of ENR-30 and ENR-30/XSBR blends after being immersed in ASTM Oil No.1 and IRM 903 oil at 100°C for 70 hours. There was no result for NR as it dissolved in these standard oils. As the ASTM Oil No.1 is a lower polar hydrocarbon oil having higher aniline point (~ 124°C), the IRM 903 oil is a higher polar hydrocarbon oil with lower aniline point (~ 90°C). The results showed that the percentage volume change in ASTM Oil No.1 of all samples was lower than that in IRM 903 oil, indicating that ENR-30 and XSBR are polar rubbers. Thus, there was interaction between ENR-30 and XSBR in a dose-dependent manner via the epoxide and carboxyl groups in the blends. Consequently, the swelling level of all ENR-30/XSBR blends in the ASTM Oil No.1 was increased due to their lower polarity and crosslink density compared to those of the neat ENR-30, indicating inferior ASTM Oil No.1 resistance. Moreover, the volume change of ENR-30 in IRM 903 oil was higher than that of the blends, indicating that all the blends exhibited superior IRM 903 oil resistance. However, the blends filled with 20 and 30 wt% XSBR should have lower volume change because of their lower polarity, but this was opposed by their lower crosslink density

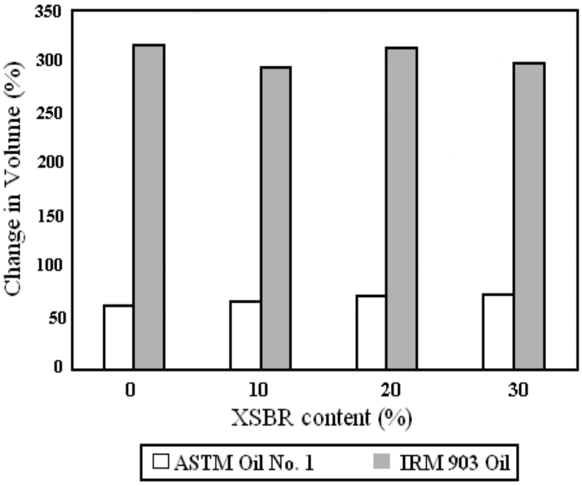

Figure 4. The change in volume of the ENR-30 and ENR/XSBR blends in ASTM Oil No.1 and IRM 903 oil.

SEM Analysis

Figure 5 shows representative SEM micrographs of the tensile fractured surfaces of the neat ENR-30 and ENR-30/XSBR blends. The fractured surface could imply an aspect of failure behavior. The images revealed a relatively rough and uneven topography occurred during the tensile test, indicating their ductile failure characteristic. This is in agreement with the results of the elongation at break. Moreover, a uniform morphology could be observed in all three ENR-30/XSBR rubber blends, suggesting that these two types of rubber were miscible during the latex stage blending and no evidence of phase separation was seen. This may be due to the good interfacial bonding between ENR-30 and XSBR as aforementioned

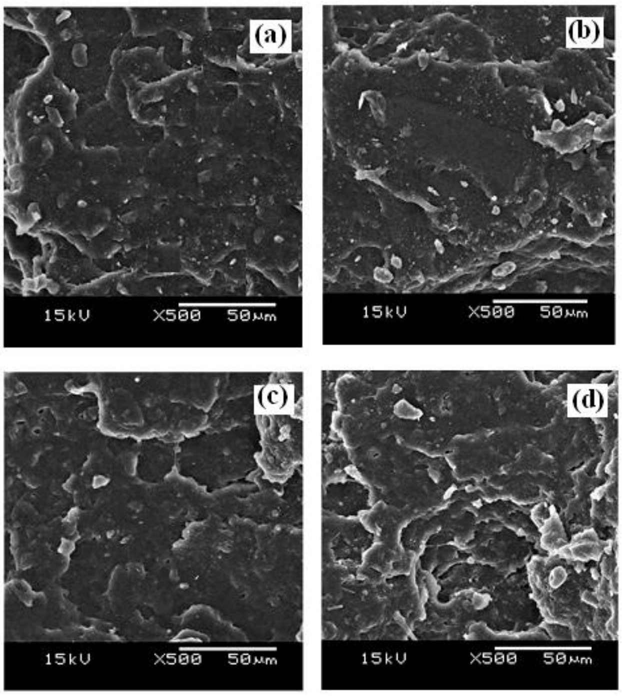

Figure 5. Representative SEM micrographs (500× magnification) of the (a) ENR-30 and the ENR-30/XSBR blends filled with (b) 10, (c) 20 and (d) 30 wt% of XSBR

Conclusions

Epoxidized natural rubber with about 30 mol% epoxidation was successfully prepared via *in situ* performic acid epoxidation from high ammonia concentrated natural rubber latex using 0.5 M hydrogen peroxide and 0.75 M formic acid in the presence of a surfactant at 50°C for 4 hours. The in-house prepared ENR-30 was blended with three different loadings of carboxylated styrene butadiene rubber (10, 20 and 30 wt%) in the latex stage. As the amount of XSBR in the blends increased, the scorch time, cure time, minimum torque, modulus at 300% strain, and T_{onset} were increased, while the maximum torque, Δ torque, tensile strength, elongation at break and thermal stability at high temperature ($T_{50\%}$, $T_{\text{end set}}$ and T_{max}) were decreased. However, oil resistance of the ENR-30 and its blends was better than that of the NR, since change could be measured after immersion in the ASTM Oil No.1 and IRM 903 oil, whereas that of the NR could not be detected.

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