

Effect of the Processing Conditions and the Addition of *trans*-Polyoctenylene Rubber on the Properties of Natural Rubber/Styrene–Butadiene Rubber Blends

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ABSTRACT: In this study, the influence of the processing conditions and the addition of *trans*-polyoctenylene rubber (TOR) on Mooney viscosity, tensile properties, hardness, tearing resistance, and resilience of natural rubber/styrene–butadiene rubber blends was investigated. The results obtained are explained in light of dynamic mechanical and morphological analyses. Increasing processing time produced a finer blend morphology, which resulted in an improvement in the mechanical properties. The addition of TOR involved an increase in hardness, a

decrease in tear resistance, and no effect on the resilience. It resulted in a large decrease in the Mooney viscosity and a slight decrease in the tensile properties if the components of the compounds were not properly mixed. The results indicate that TOR acted more as a plasticizer than a compatibilizer. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 445–451, 2008

Key words: blends; compatibilization; processing; rubber; structure–property relations

INTRODUCTION

To reduce costs, improve performance, and optimize the production in the tire industry, many blends of immiscible rubbers have been developed in recent years. These rubbers can be easily compatibilized with either chemical or mechanical methods, which result in compounds with a stable morphology and good properties for the final product.¹ Natural rubber (NR)/styrene–butadiene rubber (SBR) copolymer is an example of an immiscible rubber blend that is commonly used in tire parts.

For the last 10 years, *trans*-polyoctenylene rubber (TOR) has been added to NR/SBR rubber blends industrially. It is a high-performance polymer that presents a dual character: during processing, it has the function of a plasticizer, and after vulcanization, it behaves as a rubber. Because of this dual character, with the addition of TOR, (1) the processing of the NR/SBR blend is improved in terms of energy savings and the handling of intermediary compounds, and (2) the profile of vulcanization of the compound is changed: TOR acts as an unsaturated rubber and can make possible crosslinking with sulfur, sulfur donors, peroxides, or cure resins.² It is believed that the plasticizer effect of TOR could help

the compatibilization of the blend because of the reduction in the viscosity of the system, which could enhance the interaction between the blend components.³ However, these compatibilization characteristics of TOR are still not well understood. It was shown that the addition of TOR to SBR and NR rubber compounds improves their flexibility⁴ and affects the viscosity of NR compounds⁵ and the engineering properties of the resulting material. In particular, it was shown that the hardness, tensile modulus, and resilience increase, whereas tensile strength and elongation at break decrease when TOR is added to the NR/acrylonitrile–butadiene rubber (NBR) compound.² However, seldom have the changes in physical or engineering properties caused by the addition of TOR to the compound been correlated with the morphology of the compounds. In the case of NBR/NR, it was shown that TOR was located at the interface between NBR and NR.⁶ To our knowledge, no morphological study of SBR/NR blends to which TOR was added has been conducted so far. Therefore, more studies to describe how the TOR modifies the morphology and the properties of NR/SBR blends are necessary.

In this study, the effects of the processing conditions and the addition of TOR on the physical properties of NR/SBR blends were studied. A 2³ factorial experimental design (three independent variables in two levels) was applied to obtain information about the influence of each variable [concentration of TOR,

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TABLE I
Materials Used in This Study

Rubber	Characteristics	Source
NR, SMR 20 grade	$M_w = 500,000$ ML 1 + 4 (100°C) = 90	Seng Hin Kota, Tampin, Malaysia
SBR, SBR 1502 grade	$M_w = 200,000$ ML 1 + 4 (100°C) = 45	Petroflex, Triunfo, Brazil
TOR, 8012 grade	$M_w = 90,000$ ML 1 + 4 (100°C) < 10 Cis = 20%, trans = 80%	Degussa, Marl, Germany

M_w = weight-average molecular weight.

processing time of polymers (premix time), and processing time of compounds (repassé time)] on the Mooney viscosity and dynamometric properties. The results obtained are explained in light of dynamic mechanical and morphological analyses.

EXPERIMENTAL

Materials and sample preparation

Details about the rubbers used in this study are presented in Table I. The compound formulations and mixing times used are given in Table II. Figure 1 presents the physical structure of TOR.

The processing was divided in two steps: (1) premix and (2) repassé. In the first step (premix), NR and SBR with or without TOR were mixed in a Banbury internal mixer (Novo Hamburgo, RS) (Cope, model Lab Mix 1600) at an initial temperature of $40 \pm 5^\circ\text{C}$ at a speed of 77 rpm for a time called the *premix time* (see Table II). After this initial time, the antioxidants and carbon black were added to the Banbury mixer and mixed until the temperature reached 145°C . The mixture was then transferred to a two-roll mill (Cope, model MCLS) until all of the ingredients were completely incorporated. When the Banbury temperature was about 55°C , the mixture and the curing agents were added and mixed until the temperature reached 100°C . The rubber compounds were again mixed with a two-roll mill until the Banbury temperature decreased to 45°C . Then,

the compound was returned to the Banbury mixer for the last step for a time called the *repassé time* (see Table II). The final compound was then sheeted out in the two-roll mill and cured in an electrically heated press (Novo Hamburgo, RS) ($60\text{ cm} \times 60\text{ cm}$, Metalbor) for 10 min at 170°C and 50 kg/cm^2 pressure to mold test pieces for the physical tests. This time was optimized with a torque rheometer Monsanto MDR 2000E, (Mooney Viscometer and Duration 2001-Akron Ohio).

2³ factorial experimental design

Figure 2 shows a schematic representation of the 2³ factorial experimental design used in this study. This type of factorial design has been used by many authors to make studies of polymer blends easier and faster.^{7–10} As shown in Figure 2, the independent variables (premix, repassé, TOR, and concentration) adopted two levels, according to Table II. The experimental design resulted in eight different compounds (C1–C8, described in Table II). The other compounds listed in Table II (C9–C11) were three points chosen randomly to verify the regression equations obtained with the factorial experimental design.

Measurement of the physical properties

Ring-shaped specimens were cut from the cured compound sheets for the measurement of tensile

TABLE II
Compound Recipes Investigated

Ingredient (phr)	Compound name														
	NR1	NR2	SBR1	SBR2	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	C11
NR	100	100	0	0	60	60	60	60	45	45	45	45	45	45	45
SBR	0	0	100	100	40	40	40	40	40	40	40	40	40	40	40
TOR	15	15	15	15	0	0	0	0	15	15	15	15	2	18	5
Mixing time															
Premix time (min)	1	7	1	7	1	7	1	7	1	7	1	7	1	9.3	4
Repassé time (s)	0	45	0	45	0	0	45	45	0	0	45	45	15	50	35

All compounds contained 54 phr carbon black, 3.4 phr sulfur, 1.5 phr stearic acid, 5.0 phr ZnO, 2.0 phr antioxidant, and 1.3 phr accelerator.

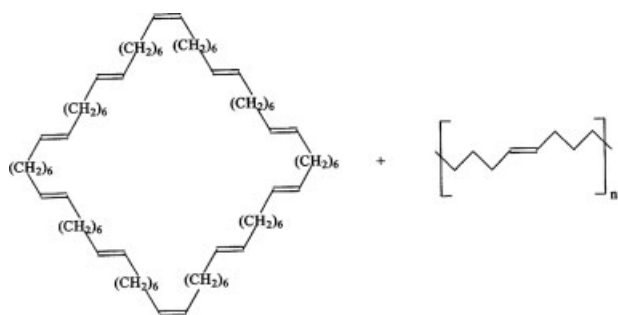


Figure 1 Chemical structure of TOR.

properties. The stress–strain curves were obtained with a tensile tester (Instron 4464) (Norwood, MA) at room temperature following ASTM D 412.

The Mooney viscosity (ML 1+4 at 100°C) of crude samples was obtained with a Mooney viscometer (Monsanto 1500) following ASTM D 1646.

The hardness, evaluated using an International Rubber Hardness Durometer (IRHD) of cured compounds was determined with an automatic durometer (Monsanto Duratron 2000I). Three measurements were made in each sample.

The resilience of cured compounds was determined with Maqtest equipment (France, SP) following DIN 53512. The results correspond to the average of six measurements.

The tear resistance was determined with a constant rate of specimen extension dynamometer (Instron, model 4464). The geometry chosen for the sample corresponded to type C of ASTM D 624. The results correspond to the average of eight measurements, which were conducted following ASTM D 624.

To determine the crosslink density, the equilibrium swelling method based on Flory–Rehner theory^{11,12} was used. The rubber compounds were swollen in specific reagents to evaluate (1) the total crosslink density (for this, *N*-heptane, petroleum ether, and toluene were used) and (2) the percentage of polysulfidric crosslinks (for this, *N*-heptane, propane-2-thiol, piperidine, petroleum ether, and toluene were used). After equilibrium, the crosslink density was calculated on the basis of the mass after swelling.

Measurement of the dynamic mechanical properties

The dynamic mechanical properties were measured from -130 to 100°C at $2^\circ\text{C}/\text{min}$ with a dynamic mechanical analyzer (New Castle, DE) (TA Instruments, model Q800) with rectangular samples with dimensions of $1.0\text{ mm} \times 5.0\text{ mm} \times 17.0\text{ mm}$ in the following conditions: frequency = 0.2 Hz , dynamic deformation = $5.0\text{ }\mu\text{m}$, and mode = multifrequency with a clamp single cantilever.

Morphology observations

For morphology observations, samples containing only the rubber components (NR, SBR, and TOR) and processed according to mixing times reported in Table II were used. In the rest of the article, the samples used for microscopy are named as blends and not compounds. The blends were sliced with a cryoultramicrotome (Wetzlar, Germany) (Leica EM FC6) at -130°C , which resulted in thin films with a thickness of around 40 nm . After that, the slices were deposited in copper grids and stained with OsO_4 vapors for 4 h and observed with a Carl Zeiss CEM 902 transmission electron microscope (Thornwood, NY) (acceleration voltage = 80 keV) with similar procedures to the ones reported by Zhao et al.¹³

RESULTS AND DISCUSSION

Physical properties

Table III presents the results of the physical properties of the different rubber compounds studied. The results of the Mooney viscosity, tensile strength, and elongation at break were analyzed with a 2^3 factorial experimental design and are discussed later in the article. None of the physical properties (hardness, resilience, tearing load, or energy) were affected by the change in processing conditions within the processing conditions examined in this study. However, the addition of TOR resulted in an improvement in hardness and a decrease in tearing resistance, which corroborated the results obtained by Nah and coworkers.^{2,6} The increase in hardness with the addition of TOR was probably due to the fact that the relative degree of crosslinking was much higher than for the

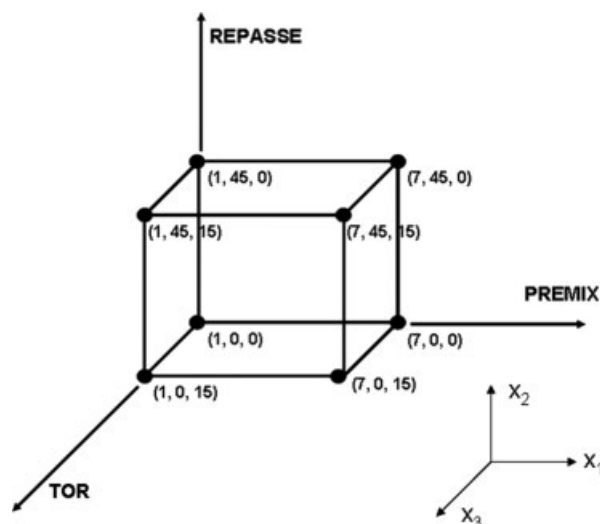


Figure 2 Schematic representation of the 2^3 factorial experimental design used.

TABLE III
Physical Properties of the Compounds

	Compound															
	NR1	NR2	SBR1	SBR2	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	C11	
Viscosity (Mooney) \pm 0.5	61.5	50.5	73.0	62.0	63.0	63.5	63.5	61.0	56.5	53.0	54.5	50.0	51.5	54.0	58.0	
Tensile strength at break (MPa) \pm 0.8	18.0	21.5	17.0	18.0	11.0	12.0	12.0	16.0	9.0	12.0	12.0	16.0	12.0	14.0	12.0	
Elongation at break (%) \pm 16	360	440	360	390	240	240	250	300	180	230	240	280	270	310	280	
Hardness (IRHD) \pm 0.5	78.0	77.5	79.0	78.0	77.0	78.0	78.5	79.0	84.0	84.0	85.5	85.5	89.0	86.0	86.5	
Resilience (%) \pm 0.5	30.5	25.0	28.0	25.0	30.0	30.0	30.0	29.0	31.0	30.5	30.0	32.0	27.0	29.0	28.0	
Tearing load (Kgf/cm) \pm 0.8	67.0	55.0	36.0	35.0	63.0	63.0	61.0	58.0	53.0	52.0	52.5	51.0	46.0	44.0	44.0	
Tearing energy (Kgf cm) \pm 0.8	82.0	54.5	20.0	20.0	56.0	56.0	56.0	47.0	29.0	32.0	28.0	32.5	32.0	39.0	32.0	
Total crosslink density \pm 0.1	4.0	3.8	2.5	2.1	4.1	4.0	4.0	3.9	4.5	4.4	4.3	4.4	4.6	4.0	4.5	
Polisulfidric crosslink (%) \pm 0.2	53.8	56.5	66.5	68.9	48.3	49.0	46.7	49.4	46.3	50.0	48.8	50.7	47.7	53.7	48.3	

other rubber components.⁶ However, no direct correlation between the degree of crosslinking of the compounds and the hardness could be found.

2³ factorial experimental design

Tables IV–VI present the effect of the different isolated variables (A: premix time, B: repasse time, and C: TOR content) and coupled variables (AB, AC, BC) on the Mooney viscosity, tensile strength, and elongation at break. These effects represent (in absolute numbers) which of the variables had more influence on the value of the property studied. The larger the value was, the larger the changes in the property related to this variable were. The coupled variables represent the synergistic effect of two variables on the property.

Multiple linear regression analyses were performed to obtain equations relating Mooney viscosity, tensile strength, and elongation at break to the processing parameters and concentration of TOR. In these equations, some of the variables were not considered because they did not present a significant influence on the physical properties. The equations obtained are shown as follows:

$$\text{Mooney viscosity} = 64.40 - (0.41 \times \text{Premix time}) - (0.63 \times \text{TOR content}) \quad (1)$$

$$\text{Tensile strength at break} = 9.10 + (0.48 \times \text{Premix time}) + (0.07 \times \text{Repassé time}) \quad (2)$$

$$\text{Elongation at break} = 212.33 + (5.42 \times \text{Premix time}) + (1.0 \times \text{Repassé time}) - (1.4 \times \text{TOR content}) \quad (3)$$

Response surface curves were obtained on the basis of these equations. The curves for Mooney viscosity, tensile strength, and elongation at break as a function of most influencing variables are presented in Figure 3(a–c), respectively. These curves were drawn for (1) a repasse time of 22.5 s, (2) a TOR concentration of 0, and (3) a TOR concentration of 7.5 phr.

Equations (1)–(3) were then tested to evaluate the physical properties of compounds 9–11. The comparison between the experimental values and the values obtained with eqs. (1)–(3) is shown Table VII.

The differences between the calculated and experimental values for the three variables studied were smaller than the experimental error for each experimental method, which indicated that the equations could be considered to predict the values of Mooney viscosity, tensile strength, and elongation at break.

The results presented Tables III–VI and Figure 3 indicate that the addition of TOR to the compounds resulted in a significant decrease in the Mooney viscosity, which was most likely due to a dilution effect of TOR, which had a much smaller viscosity than the other rubber compounds. This effect was larger

TABLE IV
Effects of the TOR Concentration and Processing Parameters on the Mooney Viscosity

Variable	Effect
Average	58.0 \pm 0.2
A: premix time	-2.5 \pm 0.4
B: repasse time	-1.9 \pm 0.4
C: TOR content	-9.4 \pm 0.4
AB	-0.8 \pm 0.4
AC	-1.5 \pm 0.4
BC	-0.6 \pm 0.4

TABLE V
Effects of TOR Concentration and Processing Parameters on the Tensile Strength at Break

Variable	Effect
Average	12.5 \pm 0.4
A: premix time	2.9 \pm 0.8
B: repasse time	2.9 \pm 0.8
C: TOR content	-0.6 \pm 0.8
AB	1.1 \pm 0.8
AC	0.3 \pm 0.8
BC	0.4 \pm 0.8

TABLE VI
Effects of the TOR Concentration and Processing Parameters on the Elongation at Break

Variable	Effect
Average	246.0 ± 6.3
A: premix time	32.5 ± 12.5
B: repasse time	45.0 ± 12.5
C: TOR content	-21.0 ± 12.5
AB	6.5 ± 12.5
AC	11.5 ± 12.5
BC	8.0 ± 12.5

when the TOR was properly mixed with the rubber compounds (see the difference between the viscosity of NR1 and NR2 and SBR1 and SBR2). The addition

TABLE VII
Comparison Between the Experimental and Estimated Values of the Mooney Viscosity, Tensile Strength, and Elongation at Break

		Compound		
		C9	C10	C11
Mooney viscosity	Calculated	53.0	55.0	59.5
	Experimental	51.5	54.0	58.0
	Variation (%)	2.8	1.8	2.5
Tensile strength at break	Calculated	13.5	15.5	13.0
	Experimental	12.0	14.0	12.0
	Variation (%)	11.1	9.7	7.7
Elongation at break	Calculated	248.5	281.0	262.0
	Experimental	270.0	310.0	280.0
	Variation (%)	8.7	10.3	6.9

of TOR also resulted in a decrease in the tensile properties when short mixing times were used. The results presented in Tables III–VI and Figure 3 also indicate that larger premix and repasse times improved the mechanical properties independently of the presence of TOR (see the tensile properties of C4 and C8).

To understand the changes in the properties brought on by the changes in the processing parameters and the addition of TOR, dynamic mechanical and morphological analyses were conducted. Figures 4 and 5 present the results of the dynamic mechanical analysis of the different compounds studied.

As shown in Figure 4, upon the addition of TOR to the blend, Storage extensional modulus (E') decreased in the glassy region ($< -60^\circ\text{C}$) and

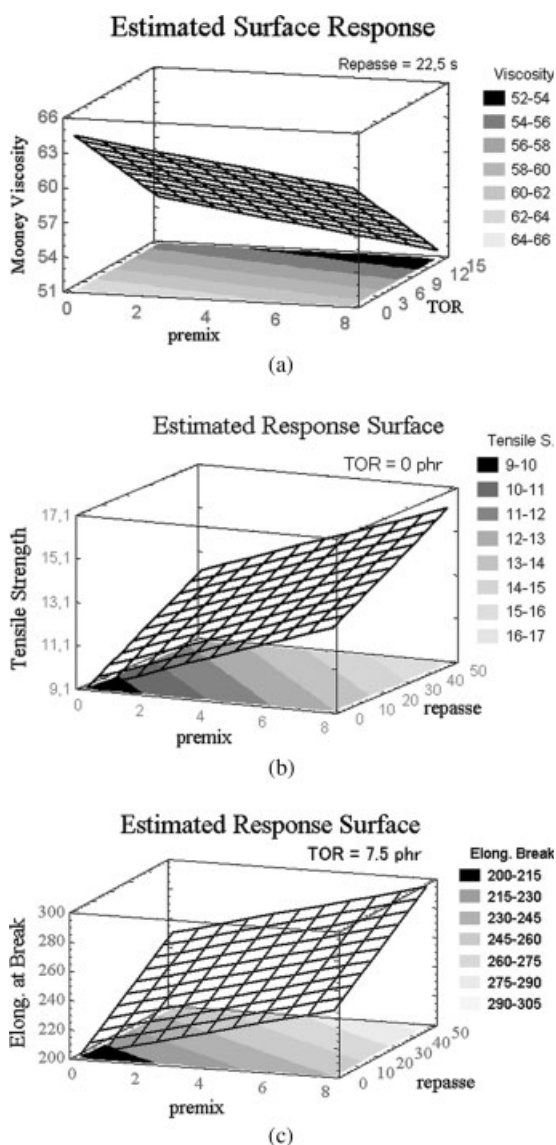


Figure 3 Surface responses for the different properties studied: (a) Mooney viscosity, (b) tensile strength at break, and (c) elongation at break.

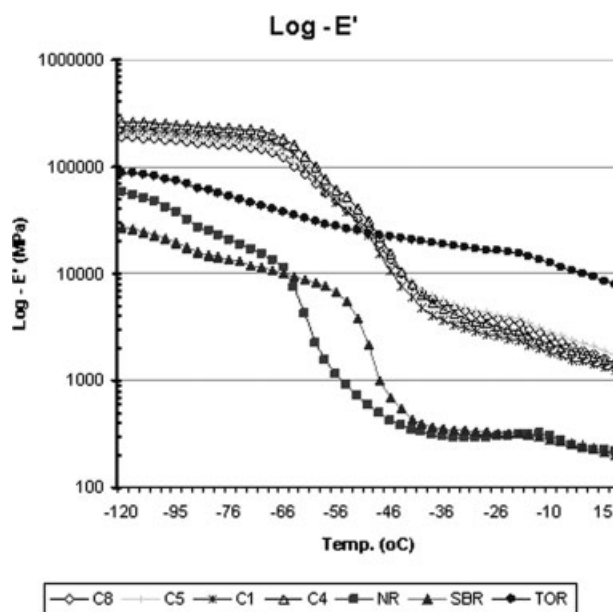


Figure 4 E' as a function of temperature for the different compounds studied.

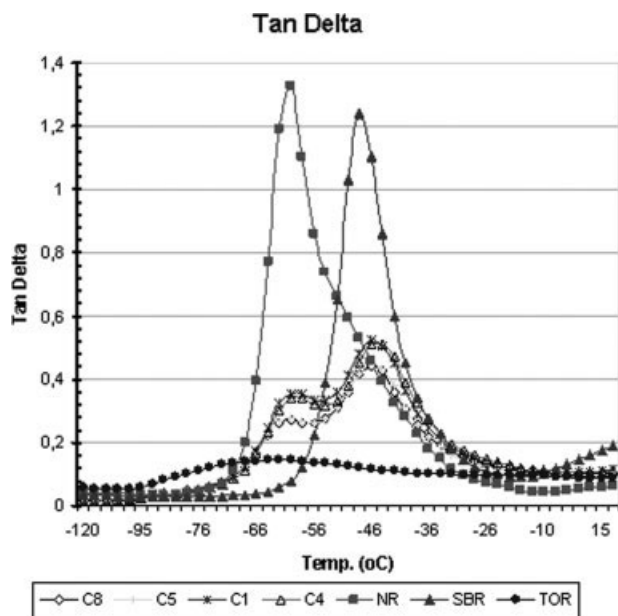


Figure 5 Tan δ as a function of temperature for the different compounds studied.

increased in the rubbery region ($> -40^\circ\text{C}$), which corroborated the results of Nah et al.⁶ As shown in Figure 5, tan δ showed a maximum at -59.0°C for NR, -46.0°C for SBR, and -61°C for the TOR pure phases. In a multicomponent system, dynamic mechanical analysis evaluates the changes in the individual glass-transition temperatures (T_g 's) of the components. These changes are indicative of the degree of interaction between the molecules of the immiscible polymers and, consequently, of the efficiency of compatibilization. The better the compatibilization, the closer the peaks related to the glass transition of the components.¹⁴⁻¹⁸ When the rubbers components were blended, even upon the addition of TOR or with an increase in the mixing time, the temperatures at which the maxima of tan δ occurred did not change, which indicated the strong immiscible character of the rubber forming the compounds. These results indicate that the compatibilization between the rubber compounds was not improved by the addition of TOR.

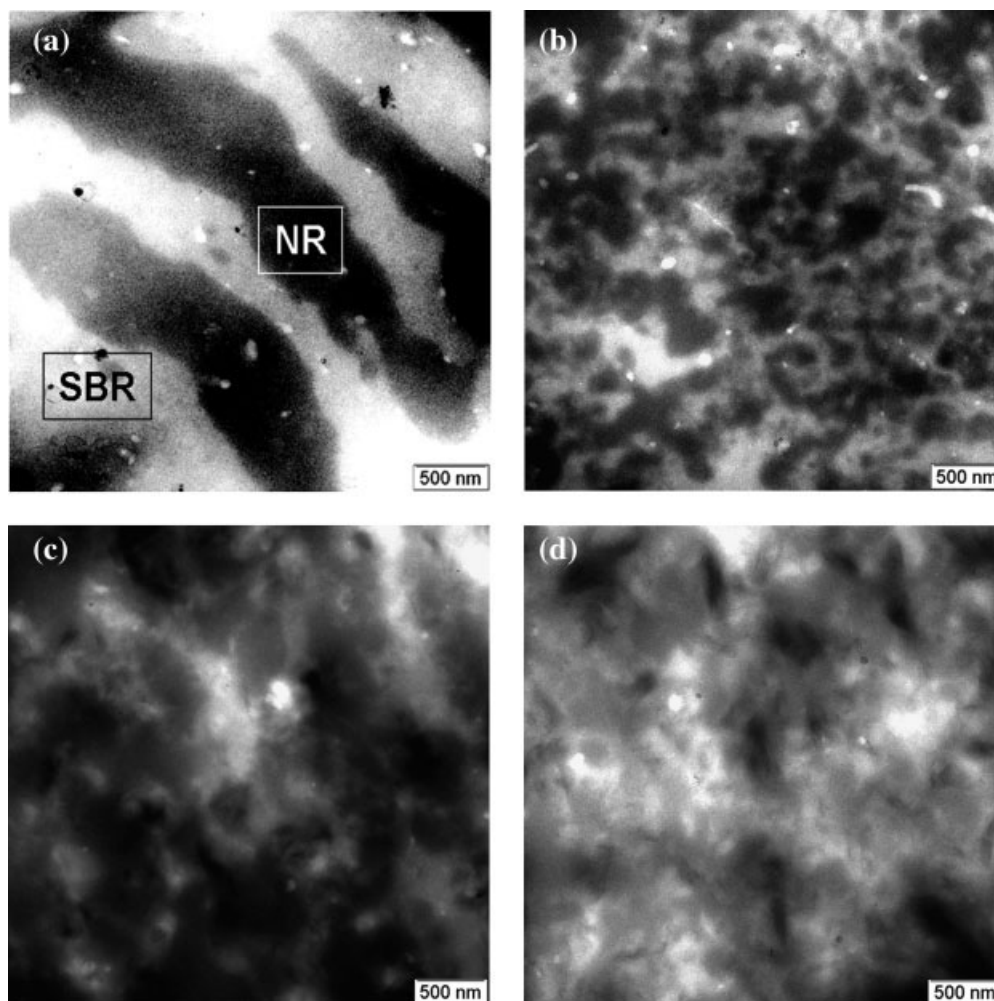


Figure 6 TEM micrographs of the blends: (a) NR/SBR = 60/40 (blend 1), premix time = 1 min, and repasse time = 0 s; (b) NR/SBR = 60/40 (blend 4), premix time = 7 min, and repasse time = 45 s; (c) NR/SBR/TOR = 45/40/15 (blend 5), premix time = 1 min, and repasse time = 0 s; and (d) NR/SBR/TOR = 45/40/15 (blend 8), premix time = 7 min, and repasse time = 45 s.

Figure 6 shows the morphology of blends examined in this study. Figures 6(a)–6(d) correspond to the morphologies of compounds 1, 4, 5, and 8, respectively. The dark regions correspond to the NR phase, and the gray regions indicate the SBR phase.

Blend 1, which did not suffer extensive mixing, presented a coarse morphology with large domains of NR and SBR. When the mixing times were increased, the rubber phases were mixed in a more intimate fashion, which explained the improvement in the mechanical properties observed (see Table III). When TOR was added to the blend, the NR domains were broken [see Fig. 6(c)] but were not as finely dispersed as when the mixing time was increased. This morphology behavior corroborated the results obtained by Chang et al.³ They correlated the improvement of compatibilization to the fact that TOR is located at the interface region, which reduces the interfacial tension between the rubbers and may facilitate the interaction of the rubbers.

CONCLUSIONS

The influence of the processing parameters and the addition of TOR on the physical properties of NR/SBR blends was examined in this study. A factorial experimental design was used to relate the Mooney viscosity, tensile strength at break, and elongation at break to the processing parameters and concentration of TOR used. The main conclusions can be summarized as follows:

1. The NR/SBR blends presented two T_g 's, which corresponded to the T_g 's of the individual phases and which indicated their strong incompatibility. This was not altered upon the addition of TOR and with an increase in processing time.
2. An increase in processing time (premix and repasse) considerably increased the tensile strength and elongation at break. This improvement in the mechanical properties was due to a finer morphology. With longer mixing times, the rubber phases were mixed in a more intimate fashion.
3. An increase in the TOR concentration decreased the Mooney viscosity of the compounds because of the polymer's plasticizer characteristic. It did not affect the mechanical properties (tensile strength and elongation at break) when a good mixing was provided to the compound. Also, an increase in the TOR concentration resulted in an increase in the hardness and a reduction in the tearing resistance.
4. TOR should be added to compounds to reduce the Mooney viscosity and, therefore, improve their processing, but proper mixing of the compounds should be carried out to obtain compounds with optimized properties.

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