Effects of *trans*-Polyoctylene Rubber (TOR) on the Properties of NR/EPDM Blends

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ABSTRACT: *trans*-Polyoctylene rubber (TOR) was melt blended with an incompatible NR/EPDM (70/30) blend. Mixing torque and temperature were reduced as TOR was added to NR/EPDM blend. The curing characteristics of the blend were affected as TOR participated in vulcanization and became a part of network. A scanning electron micrograph demonstrated that addition of TOR improved the compatibility of the blend and thereby led to a finer phase morphology. The ozone resistance of the blends was determined in terms of a critical stress–strain parameter. The critical stored energy density for ozone cracking was significantly enhanced for the TOR containing rubber blend. It was believed that the improvement in ozone resistance arised from finely dispersed ozone-resistant EPDM particles in the blend. TOR caused an improvement in dynamic properties and an increase in tensile modulus, but a decrease in tensile stress and elongation at break of the rubber blend. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 749–756, 1999

Key words: *trans*-polyoctylene rubber (TOR); NR/EPDM blends; ozone resistance; phase morphology; compatibility

INTRODUCTION

Natural rubber (NR) is prone to be deteriorated by ozone attack due to highly unsaturated polymeric backbone. In general, improvement in the poor ozone resistance of NR can be achieved by blending it with low unsaturated rubbers such as ethylene-propylene-diene rubber (EPDM).^{1,2} However, when NR is blended with high concentration of EPDM, such as 35 to 45 phr, required for adequate ozone protection, it cannot avoid the diminution of mechanical properties, because of the difference in cure rate and the lack of thermodynamic compatibility of the two polymers.³ Many efforts have been made to overcome the incompatibility of cure rate by grafting accelerator onto EPDM,⁴ bromination of EPDM,⁵ slight precuring of EPDM before blending,⁶ or the carboxylation of EPDM.^{7–9} However, studies on improving the morphology of blend have rarely been reported, even though the fine morphology is an important factor to determine the ozone resistance as well as mechanical properties of the blends.^{10,11}

It has been reported that the compatibility of immiscible binary rubber blends could be improved by the addition of small amount of a third polymeric component.^{12–16} For example, the homogeneity of highly incompatible acrylonitrile– butadiene rubber/ethylene–propylene–diene rubber (NBR/EPDM) blend was greatly improved by the addition of chlorinated polyethylene¹² and *trans*-polyoctenylene rubber (TOR),¹³ probably

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Materials	Description	Source		
Natural Rubber (NR)	SMR-CV60,	Mardec, Malaysia		
	$ML_{1+4} @ 100°C = 60$			
Ethylene-propylene-diene	KEP-350,	Kumho E. P., Korea		
rubber (EPDM)	ENB type, ML_{1+4} @ 100°C = 83			
trans-Polyoctylene rubber ^a	Vestenamer 8012,	Huls, Germany		
(TOR)	ML_{1} @ 100°C < 10, $M.W_{2}$ = 100,000.	, ,		
	$T = 51^{\circ}C$ $T = -65^{\circ}C$			
	f_m of $G_{1,1}$ of $G_{2,2}$ of $G_{2,1}$			
	Crystalling $@25 \ C = 21\%$			

Table I Rubbers Employed in This Study

due to the emulsification effect by the third component. Also, it was observed that the additions of hydrocarbon resin to BR/EPDM blend¹⁴ and liquid rubbers to NR/EPDM blend^{15,16} enhanced the homogeneity of the blends. In this study, *trans*polyoctenylene rubber (TOR), a low molecular weight polymer expected to be a potential compatibilizer for rubber/rubber blends, was added to the NR/EPDM blend. Based on the usefulness in industrial application, the (70/30) NR/EPDM blend composition was used, and the variations of blend properties such as processing, morphology, ozone resistance, and mechanical properties were investigated.

EXPERIMENTAL

Materials

The rubbers used in this study are natural rubber (NR), ethylene-propylene-diene rubber (EPDM), and *trans*-polyoctylene rubber (TOR). And the characteristics of the rubbers are described in Table I. TOR was added to NR/EPDM (70/30) blends by 0, 5, 10, and 20 phr. The amounts of sulfur and *N*-cyclohexyl-2-benzothiazol sulfenamide (CBS) were varied with TOR so that all blend compositions have the same concentration of curatives. Formulations of the rubber mixtures are shown in Table II.

Preparation of Blends

Mixing was carried out in a Banbury type internal mixer (Haake Polylab 3000) at 60 rpm and at 50°C. The fill factor was 0.7. NR was mastificated for 1 min and then EPDM and TOR were subsequently added. When the mixing torque reached constant value, zinc oxide, stearic acid, and CBS, followed by sulfur, were added. The rubber compound was cured in an electrically heated press (Carver 2518) at 160°C for optimum cure time (t_{95}) , which was determined from an oscillating disk rheometer (Monsanto, R-100).

Measurements of Physical Properties

Crosslinking densities of the blends were characterized by gel percent (%). A small amount of cured rubber sheet, ca. 0.3 g, had been placed in toluene until the weight of the swollen rubber did not increase further. Then the swollen rubbers were dried completely under reduced pressure. The gel content was calculated by the ratio of weight of dried rubber to initial sample weight.

Table II	Formulations of NR/EPDM/TOR	ł
Blends		

		Compound No. (phr)			
	1	2	3	4	
NR	70	70	70	70	
EPDM	30	30	30	30	
TOR	0	5	10	20	
Zinc oxide	5.00	5.25	5.50	6.00	
Stearic acid	1.50	1.58	1.65	1.80	
Sulfur	2.00	2.10	2.20	2.40	
CBS	1.00	1.05	1.10	1.20	

Phase morphology of the cured blends was investigated by scanning electron microscopy (SEM, Akashi, WB-6). A smooth surface was prepared by fracturing the frozen sample with a sharp precut in the liquid nitrogen atmosphere. To enhance the contrast, the fractured surface was exposed to vapor above a 10% methanol solution of bromine for 3–5 h.¹³ Solvent and chemically nonbound bromine were removed completely in a high vacuum chamber before the surface was coated with gold.

The interfacial strength of the adhesion was measured by peeling sheets apart, using a universal testing machine (United Co., STM-10E).¹⁷ The peel specimen was prepared by curing two separately milled rubber sheets at 160°C. To prevent the elongation of the leg during peeling, a backing cloth was applied onto both sheets prior to curing. A strip of 20 mm wide and 2.5 mm thick was cut from the sheet. The test was carried out at a peel rate of 10 mm/min at room temperature. For this geometry, the strength of adhesion (G_a) is given by

$$G_a = 2F/t \tag{1}$$

where t is the width of the bonded interface and F is the measured force.

Ozone resistance of the blends was determined in terms of the critical stress–strain parameter.¹⁸ A test specimen, as shown in Figure 1(a), is prepared in which width varies continuously with length so that the ratio of widths at the ends of the specimen is 2, and the ratio of the length to the average width is 11. The tapered specimen was subjected to a certain stress for 16 h to determine the average extension ratio [Fig. 1(b)]. Then, the specimen were immediately placed in an ozone chamber and left there for 24 h at 40°C. The ozone concentration in the chamber was maintained at 50 pphm. Because the stress on specimen is not uniform along the length of specimen, the ozone cracks appear only in the higher stress region toward the narrow end of tapered specimen [Fig. 1(c)]. After removing the weight, the length from the bottom narrow end to the boundary of cracked region (X_c) and the length of the deformed specimen (L_f) were measured. Critical stress (σ_C), critical strain (ε_C), and critical stored energy density (W_C) is calculated using the following equations, which were derived from the theory of rubber elasticity.

$$\sigma_C = F/[at_C(1 + X_C/L_f)] \tag{2}$$



Figure 1 Geometry for ozone test specimens: (a) original specimen with fiducial marks at the ends of the tapered section. a = 0.6 cm, and $L_o = 10$ cm; (b) specimen under stress; (c) ozone-aged specimen with a cracked zone at the narrow end. X_c is the length of the boundary of the cracked zone, and L_f is the distance between marks.

$$\varepsilon_{C} = [1.42 - 1.42/\lambda_{\rm av}]/[X_{C}/L_{0} - 0.42 + 1.42/\lambda_{\rm av}]$$
(3)

$$W_C = [0.5\sigma_C \varepsilon_C (\lambda_C + 2)] / (\lambda_C^2 + \lambda_C + 1) \qquad (4)$$

where F is applied force, X_c is length to the boundary of the cracked zone, λ_{av} is overall or average extension ratio, a is specimen width at the narrow end (X = 0) before deformation, t_c is the specimen thickness at X_c , and λ_C is $1 + \varepsilon_C$.

The dynamic mechanical properties of vulcanizates were determined by using a dynamic mechanical analyzer (TA Instrument DMA 2980). The sample was subjected to a cyclic tensile stain with the amplitude of 0.1% at the frequency of 10 Hz. The temperature was increased at the heating rate of 2°C/min in the range of -110 to 20°C. The ultimate tensile strength, elongation at break, and modulus were determined using a universal testing machine (United Co., STM-10E) at room temperature with a rate of deformation of 100 mm/min.





Figure 2 Variation of mixing torque and temperature for the the NR/EPDM/TOR blends with time.

RESULTS AND DISCUSSION

Mixing and Curing

Figure 2 shows the variations of torque and temperature of NR/EPDM/TOR blends as a function of mixing time. The mixing torque of blend is decreased by the addition of 5 phr of TOR, but it is not changed significantly by the further addition of TOR. On the contrary, the mixing temperature is continuously decreased with TOR. For example, the mixing temperature of the NR/ EPDM/TOR (70/30/20) blend is ca. 10°C lower than that of the NR/EPDM (70/30) blend. The values of the mixing torque are plotted against the temperature in Figure 3. It can be seen that, under the same temperature condition, the mixing torque decreases with TOR content in the blends. This indicates that TOR acts as a processing aid and reduces the melt viscosity of rubber blends, which consequently decreases the energy consumption and temperature of blends during mixing.

It is also observed that TOR influences vulcanization process of the NR/EPDM blend. The results of Monsanto rheographs of the NR/EPDM/ TOR blends at 160°C are summarized in Table III. Upon the addition of TOR, the rate of crosslinking reaction becomes slower. There is a

Figure 3 Mixing torque vs. mixing temperature for the NR/EPDM/TOR blends.

gradual increase both in $t_{\min+2}$ corresponding to a two-unit rise in torque above the minimum torque, and in t_{95} corresponding to the time to reach optimum cure, depending on the concentration of the TOR. The values of the crosslinking density of all the blend compositions, characterized by gel percent, are more or less the same, as shown in Table III. It is worth noting that the additional amount of curatives is used in the presence of TOR (see Table II). These variations in curing characteristics imply that TOR, having a lower degree of unsaturation than NR, participates in vulcanization reaction and becomes a part of the network structure. In addition, it is to be noted that the maximum torque in the Monsanto rheograph increases with the addition of

Table IIIVulcanization Characteristics ofNR/EPDM/TOR Blends

	Compound No.				
	1	2	3	4	
Gel percent (%)	0.953	0.956	0.960	0.974	
$t_{\min+2}$ (s)	439	484	495	496	
t_{95} (s)	645	708	733	760	
$ au_{\max}$ (Nm)	19.8	20.0	20.9	21.4	





(b)

Figure 4 SEM micrographs of the NR/EPDM/TOR blends: (a) 70/30/0; (b) 70/30/10.

TOR. The maximum torque value of the blend containing 20 phr of TOR is increased by the amount of ca. 10%, whereas the crosslinking density of the blend is slightly increased by an amount of 2%. This is supposed to be associated with the change in network structure.

Morphology

Figure 4(a) and 4(b) exhibit SEM micrographs of the NR/EPDM (70/30) and NR/EPDM/TOR (70/ 30/10) blend vulcanizates, respectively. The lighter phase is NR, which was selectively stained by bromine, and the darker phase is EPDM. It can be seen that the EPDM particles are dispersed into NR matrix in the blend. In the absence of TOR, as shown in Figure 4(a), the dispersed particles are generally large, the size distribution is broad, and the shape of particles are very irregular. The irregular large particles over 20 μ m coexist with spherical small particles below 1 μ m. However, in the case of the NR/EPDM/TOR (70/ 30/10) blend, the dispersed particles become smaller, uniform, and spherical, as can be seen in Figure 4(b).

The improvement in compatibility of the blend may be explained by the following mechanisms. First, it is speculated that TOR, which has a much lower viscosity compared to NR and EPDM (see Table I), may locate at the interface of NR and EPDM phase, because the component with lower viscosity tends to encapsulate the polymer with higher viscosity during mixing. Previous study on the morphology of NBR/EPDM/TOR blend¹³ revealed that TOR is located at the interfacial area between the highly incompatible NBR and EPDM rubbers. Thus, it is highly probable that TOR at the interface region reduces the interfacial tension between the incompatible rubbers, which may facilitate the mixing of the rubber blends.

It is also speculated that interfacial chemical bonding may be created in the presence of TOR during the vulcanization process, which may produce a finer phase morphology in the rubber blends.^{19,20} This conjecture is based on the observation that the interfacial strength between the NR and EPDM layers is increased dramatically in the presence of TOR. Table IV presents the strength of adhesion (G_a) between NR and EPDM layers with or without TOR. In the absence of TOR, the interfacial strength between the rubber layers is quite low, and the torn surface is very smooth, indicating adhesive failure. In contrast, the adhesive strength between NR and EPDM

Table IV Interfacial Strength (G_a) between NR and EPDM Layers

Sheet 2 ^a	$G_a \; ({\rm J/m^2})$	
EPDM	279	
EPDM/TOR (90/10)	1274	
EPDM	1176	
EPDM/TOR (90/10)	1489	
	Sheet 2 ^a EPDM EPDM/TOR (90/10) EPDM EPDM/TOR (90/10)	

^a The formulation employed for each sheet is 100 phr of rubber, 2 phr of sulfur, 1 phr of CBS, 1.5 phr of stearic acid, and 5 phr of zinc oxide.

		Compound No.			
	1	2	3	4	
Critical stress, σ_C (MPa)	0.142	0.180	0.210	0.240	
Critical strain, ε_C (%)	10.15	11.55	12.55	11.25	
Critical stored elastic energy density, W_c (kJ/m ³)	7.350	10.00	12.65	13.06	

Table V Ozone Resistance of NR/EPDM/TOR Blends

layers containing TOR in either layer or both is remarkably increased, and the fracture pattern becomes cohesive.

It should be mentioned that the chemistry of interfacial bonding is not clear at this moment. However, it is conjectured that the interfacial bonding between NR and EPDM may be formed, probably due to the vulcanizability of TOR in the presence of sulfur. That is, during the vulcanization process, TOR located at the interface may be covulcanized with component elastomers, which may lead to the formation of interfacial bonding.

Ozone Resistance

The ozone resistance of the blend was determined quantitatively in terms of critical stress-strain parameters.¹⁸ Table 5 gives the values of critical stress, critical strain, and critical stored elastic energy density of rubber blends required for initiation of an ozone crack. It shows that the values of the critical stress-strain parameters are increased with TOR contents. Because the moduli of the blend vulcanizates are different (as will be shown in Table VI), the critical stored elastic en-

Table VITensile Stress-Strain Behaviors ofNR/EPDM/TOR Blends

		Compound No.			
	1	2	3	4	
100% modulus (MPa)	0.78	0.79	0.89	0.98	
200% modulus (MPa)	1.18	1.20	1.38	1.49	
300% modulus (MPa)	1.76	1.83	2.13	2.26	
Stress at break, σ_b (MPa)	15.34	14.35	12.84	8.07	
Strain at break, ε_b (%)	650	625	585	510	



(a)



(b)

Figure 5 SEM micrographs of surface ozone cracks for the NR/EPDM/TOR blends: (a) 70/30/0; (b) 70/30/10.

ergy density (W_C) is considered to the best criterion for ozone resistance. Based on the values of W_C , the ozone resistance of blend is improved with TOR content. The ozone resistance of the NR/EPDM blend is increased by the amount of 80% upon the addition of 10 phr of TOR. The improvement in ozone resistance for the TORcontaining blend is attributed to the better dispersion of the EPDM particles in the NR matrix, which is aided by TOR. That is, more finely dispersed EPDM particles prohibit the growth of ozone cracks initiated in the NR matrix before the crack grows over the critical length.^{10, 21} Once the ozone crack grows over the critical size, crack



Figure 6 Dynamic storage moduli and tan δ for the NR/EPDM/TOR blends containing different concentrations of TOR.

propagation cannot be stopped by EPDM particles.

Figure 5 are SEM micrographs of the surface of ozone-aged specimens. It can be seen that the ozone cracks propagate in the direction perpendicular to the applied stress without much deviation. NR/EPDM/TOR (70/30/10) blends show shorter cracks than NR/EPDM (70/30) blends, which confirms that crack growths were stopped more effectively by finely dispersed EPDM particles in NR matrix.

Mechanical Properties

Results of stress-strain properties of the blend are shown in Table VI. The tensile modulus of blend is increased gradually, depending upon TOR content, as can be expected from the values of maximum torque in the Monsanto rheograph. However, tensile strength and elongation at break of the blends are decreased in the presence of TOR.

Figure 6 illustrates the dynamic moduli and tan δ of blends over a temperature range of -110 to 20°C. Upon the addition of TOR, dynamic elastic modulus (E') of a blend is increased over the measured temperature range, whereas the hysteresis, determined in terms of tan δ , is not in-

creased. A single tan δ peak is observed, despite the phase-separated structure, which is due to the similarity of the glass transition temperature of the blend components. Such a variation of dynamic property implies that TOR increases rigidity of blend vulcanizates without substantial change in heat buildup under the dynamic stress, which is a useful feature in the application of rubber, especially in tires. Note that lowering the hysteresis of rubber can be achieved in various ways, such as lowering the carbon black loading or increasing the crosslinking density, but these variations inevitably accompany the sacrifice of performance of rubber.²²

Changes in the mechanical properties of the blend upon the addition of TOR are not supposed to arise from the variation of crosslinking density, because the crosslinking densities of all the blend compositions used in this study have similar values (see Table III). Instead, the incorporation of TOR, containing cyclic macromolecules without free chain ends, into the rubber network may change the network structure, which improves the vulcanizate properties, especially dynamic mechanical property.^{23,24}

CONCLUSIONS

- 1. TOR acts as a processing aid and causes a reduction in melt viscosity in the NR/EPDM blend. The participation of TOR in the vulcanization reaction results in the variation of the cure rate and crosslinking density.
- 2. TOR efficiently acts as a compatibilizer in the NR/EPDM blends. The improvement in homogeneity are speculated to be induced by the encapsulation of the low viscosity component, TOR, onto the NR and EPDM phases during mixing, and by formation of interfacial crosslinking during the vulcanization process.
- 3. Fine dispersion of EPDM particles in the NR matrix, which is achieved by the addition of TOR, leads to a significant increase in ozone resistance of the NR/EPDM blend. The NR/EPDM/TOR (70/30/10) blend shows the higher critical stored elastic energy density by the amount of 80%, compared to NR/EPDM (70/30).
- 4. Addition of TOR into the NR/EPDM blend leads to an improvement in dynamic properties and an increase in modulus, with a

slight reduction in tensile strength and elongation at break.

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REFERENCES

- 1. Spenadel, L.; Sutphin, R. L. Rubber Age 1970, 102, 55.
- 2. Mathew, N. M. J Polym Sci Polym Lett 1984, 22, 135.
- Mathew, N. M.; Thomas, K. T.; Philipose, E. Indian J Nat Rubber Res 1988, 1, 8.
- Barnnwal, K. C.; Son, P. N. Rubber Chem Technol 1974, 47, 88.
- Yoon, J. R.; Hashim, A. S.; Kawabata, N.; Kohjiya, S. Rubber World 1996, 20.
- Suma, N.; Joseph, R.; George, K. E. J Appl Polym Sci 1993, 49, 549.
- 7. Coran, A. Y. Rubber Chem Technol 1988, 61, 281.
- Suma, N.; Joseph, R.; Francis, D. J. Kautsch Gummi Kunstst 1990, 43, 1095.
- 9. Coran, A. Y. Rubber Chem Technol 1991, 64, 801.
- 10. Andrews, E. H. Rubber Chem Technol 1967, 40, 635.

- 11. Hamed, G. R. Rubber Chem Technol 1982, 55, 151.
- Setua, D. K.; White, J. L. Kautsch Gummi Kunstst 1991, 44, 542.
- Lohmar, J. Kautsch Gummi Kunstst 1986, 39, 1065.
- 14. Go, J.; Ha, C. J Appl Polym Sci 1996, 62, 509.
- 15. Cesare, F. C. Rubber World 1989, 14.
- Visetsillapanont, A.; Bualek, S. 25A-11, presented at international rubber conference, Kobe, Japan, 1995, p. 67.
- Chun, H.; Gent, A. N. J Polym. Sci Part B Polym Phys 1996, 34, 2223.
- Wilchinsky, Z. W.; Kresge, E. N. Rubber Chem Technol 1974, 47, 895.
- Bauer, R. F.; Dudley, E. A. Rubber Chem Technol 1977, 50, 35.
- Inoue, T.; Shomura, F.; Ougizawa, T.; Miyasaka, K. Rubber Chem Technol 1985, 58, 873.
- 21. Draxler, A. Kaut Gummi Kunstat 1970, 12, 628.
- Roland, C. M. In Handbook of Elastomers; Bhowmick, A. K.; Stephens, H. L., Ed., Marcel Dekker: New York, 1988.
- Draxler, A. Polyalkenylenes in Handbook of Elastomers; Bhowmick, A. K.; Stephens, H. L., Eds.; Marcel Dekker: New York, 1988, p. 661.
- Nedden, K. Z.; Diedrich, K. M.; Huhn, G/ Paper No. 35, presented at the meeting of the Rubber Division, American Chemical Society, Detroit, MI, Oct.17, 1989.