

Influences of *trans*-Polyoctylene Rubber on the Physical Properties and Phase Morphology of Natural Rubber/Acrylonitrile–Butadiene Rubber Blends

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ABSTRACT: The influence of *trans*-polyoctylene rubber (TOR) on the mechanical properties, glass-transition behavior, and phase morphology of natural rubber (NR)/acrylonitrile–butadiene rubber (NBR) blends was investigated. With an increased TOR level, hardness, tensile modulus, and resilience increased, whereas tensile strength and elongation at break tremendously decreased. According to differential scanning calorimetry and dynamic mechanical analysis, there were two distinct glass-transition temperatures for a 50/50 NR/NBR blend, indicating the strongly incompatible nature of the blend. When the TOR level was

increased, the glass transition of NBR was strongly suppressed. NBR droplets of a few micrometers were uniformly dispersed in the continuous NR phases in the NR/NBR blends. When TOR was added to a 50/50 NR/NBR blend, TOR tended to be located in the NR phase and in some cases was positioned at the interfaces between the NBR and NR phases. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 125–134, 2002

Key words: *trans*-polyoctylene rubber (TOR); natural rubber (NR)/acrylonitrile–butadiene rubber (NBR) blends; phase behavior; physical properties; morphology; transitions

INTRODUCTION

Various rubber blends have been widely used for performance and cost optimization in the rubber industry, including the tire industry.¹ Acrylonitrile–butadiene rubber (NBR) has been widely used for various types of fuels, oil hoses, and seals because its excellent fuel and oil resistance, which comes from the polar functionality of acrylonitrile (AN).² Generally, NBR makes an incompatible blend when it is mixed with other typical rubbers, such as natural rubber (NR), styrene–butadiene copolymer, and polybutadiene rubber (BR), for improved mechanical strength and cost reduction.^{3–5} For the suppression or minimization of such a strongly incompatible nature of rubber blends containing NBR, an appropriate compatibilizer is necessary.

trans-Polyoctylene rubber (TOR) has been suggested as a compatibilizer for incompatible rubber

blends containing polar rubbers such as NBR.^{3,6–11} It can be obtained from 1,3-butadiene via 1,5-cyclooctadiene, which, in turn, is converted into polyoctenamer in the form of mixtures of linear and cyclic macromolecules, as shown in Figure 1.¹⁰ One of the main features of TOR is its crystallizability, which depends on the *cis*–*trans* ratio of the double bonds. Lohmar³ suggested that small amounts of TOR favored the mechanical dispersion of incompatible blends such as NBR/ethylene–propylene–diene terpolymer (EPDM). This was explained by a reduction of the interfacial tension due to the interpositioning of TOR between NBR and EPDM phases. Setua and White^{6,7} also examined the compatibilizing effect of TOR in an EPDM/NBR blend and found that TOR was effective, especially for lower levels of AN. Recently, Chang and coworkers reported that TOR was effective in reducing the scale of phase morphology for NR/EPDM blends⁸ and NBR/EPDM blends.¹¹ However, little attention has been given to making a detailed study of the compatibilization mechanism of TOR in polar–nonpolar rubber blends such as NR/NBR.

In this study, TOR, potentially acting as both a compatibilizer and a rubber component, was added to an incompatible NR/NBR blend in which the blend ratio was set to be 50/50 to maximize the incompatible nature. The cure behavior, various mechanical prop-

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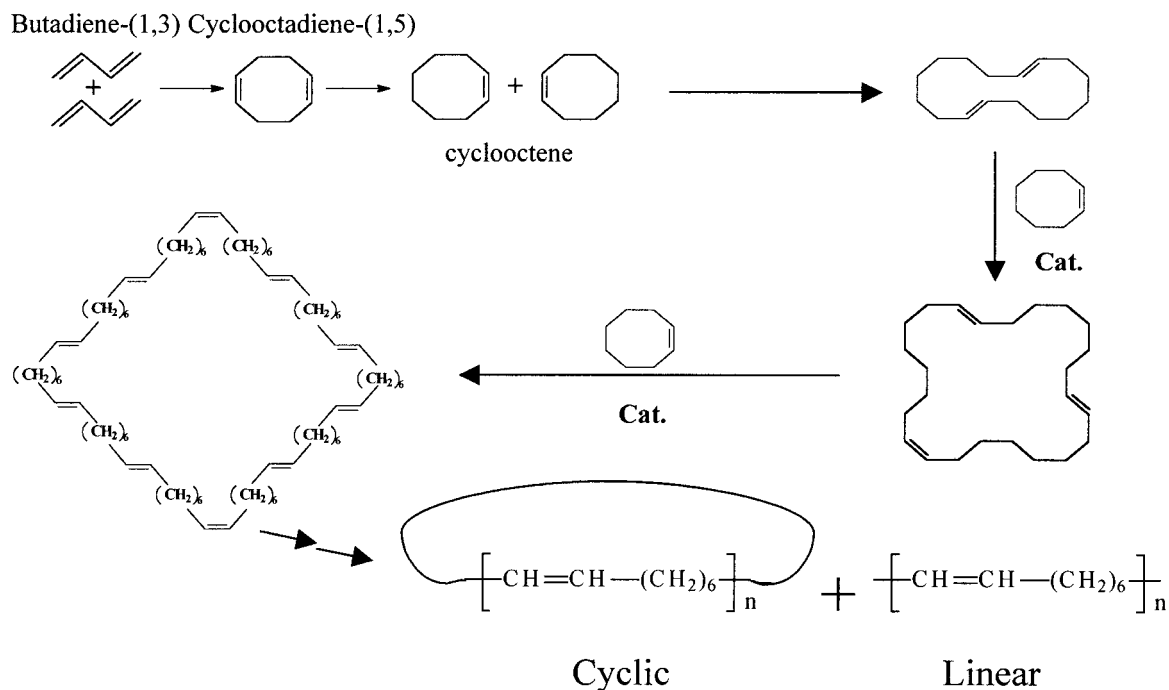


Figure 1 Schematic representation of TOR synthesis.¹⁰

erties, thermal behavior, and morphology were investigated in terms of the TOR loading level.

EXPERIMENTAL

Materials and sample preparation

NR (Standard Malaysian Rubber CV60, Malaysia), NBR (34% AN content; Korea Kumho Petrochemical Co., Korea), and TOR (Degussa AG, Marl, Germany) were selected as the rubber components for this study. The blend ratio of NR/NBR blends was kept constant (50/50) when an incremental amount of TOR as a third rubber component was added, replacing the corresponding portions of NR and NBR, to maximize the

incompatible nature of NR and NBR blends. The same cure system was employed for all the compounds. The remaining additives, including curatives, were selected with grades typical for the rubber industry. Compound recipes, including applied cure conditions, are summarized in Table I.

The mixing of compound ingredients, except for curatives, was performed with an internal mixer (82BR, Farrel Co., CT) at about 150°C for 6 min. The curatives were added with a two-roll mill (M8422AX, Farrel Co.) at about 100°C for 3 min. Vulcanized rubber sheets about 2 mm thick were pressed and vulcanized with an electrically heated press (2518, Carver, United States) at 145°C for a given period of time

TABLE I
Compound Recipes Investigated

Ingredient	NR (phr)	NBR (phr)	TOR (phr)	BLD-0 (phr)	BLD-5 (phr)	BLD-10 (phr)	BLD-20 (phr)	BLD-30 (phr)	BLD-40 (phr)
NR ^a	100	—	—	50	47.5	45	40	35	30
NBR ^b	—	100	—	50	47.5	45	40	35	30
TOR ^c	—	—	100	0	5	10	20	30	40
ZnO	5	5	5	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2	2	2	2
Cure accelerator ^d	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6
Sulfur	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
Cure time at 145°C (min)	55	45	—	45	45	45	50	55	55

^aStandard Malaysian rubber (SMR CV-60).

^bAN content = 34%, Mooney viscosity, $ML_{1+4} > 100^\circ\text{C} = 41$.

^cTOR 8012 grade, $T_g = -65^\circ\text{C}$, $T_m = 54^\circ\text{C}$, cis/trans = 20/80.

^dN-t-Butyl-benzothiazyl sulfenamide.

determined with a torque rheometer (R-100, Monsanto, United States).

Differential scanning calorimetry (DSC) measurements

DSC thermographs were determined for various rubber blends with a differential scanning calorimeter (DSC-7, PerkinElmer, CT) from -100 to 80°C at a heating rate of $10^\circ\text{C}/\text{min}$. The sample weight of each material was adjusted to 10 ± 0.5 mg, and the samples were cut into small pieces before the introduction into DSC. N_2 gas was continuously purged into the sample chamber to prevent any possibility of oxidation.

Measurements of physical properties

Dumbbell-shaped specimens were cut from vulcanized rubber sheets for the measurement of tensile properties. Stress-strain curves were obtained with a tensile tester (6021, Instron, MA) at room temperature and at a crosshead speed of 500 mm/min according to the procedure described in ASTM Standard D 412. The rebound property was measured at room temperature with a steel ball rebound tester (SR-1, MFG Co., OH) according to the procedure described in ASTM Standard D 2632. Dynamic mechanical properties were measured over a wide temperature range from -80 to 80°C with a dynamic mechanical analyzer (Rheovibron DDV-III, Toyo Baldwin, Tokyo, Japan). The frequency and dynamic deformation were set to 11 Hz and 0.1% , respectively, and the measurements were performed according to the procedure described in ASTM Standard D 2231.

Morphology observations

For the determination of the morphological behavior of NR/NBR/TOR blends, the surfaces cryogenically fractured with liquid nitrogen were gold-coated in a vacuum evaporator (Polaron Division, United States) and observed with scanning electron microscopy (SEM; JXA-840, JEOL, Tokyo, Japan). For clearer verification of the NR/NBR morphology, pure NR was stained with OsO_4 according to a previous method,³ and the stained NR was mixed with NBR and TOR for a given ratio with a specially designed mini-internal mixer with 5 mL of free volume (Bau, Seoul, Korea), in which a mixing chamber was composed of a stationary cylinder and a rotating disk and the chamber was surrounded with an electrical heater for temperature control during mixing. The frozen rubber mixture was then sliced into a thin film of about 70 nm or less with a microtome. Then, the microtomed film was observed with transmission electron microscopy (TEM; 300, Phillips, Amsterdam).

TABLE II
Cure Characteristics of NR, NBR, TOR, and Their Blend Compounds at 145°C

Compound	T_{\min} (dN m)	T_{\max} (dN m)	t_2 (min)	t_{90} (min)
NR	7.8	24.4	32.5	44.7
NBR	6.2	29.4	20.5	37.3
TOR	2.2	39.0	72.4	97.4
BLD-0	6.2	27.0	18.6	36.5
BLD-5	6.0	27.3	19.3	36.7
BLD-10	5.9	27.3	20.3	36.7
BLD-20	5.4	28.1	22.3	38.6
BLD-30	4.5	30.4	27.0	43.1
BLD-40	4.4	31.6	30.3	45.5

RESULTS AND DISCUSSION

Physical properties

Table II shows the cure behaviors of various NR/NBR/TOR blend compounds including pure NR, NBR, and TOR at 145°C . Here, T_{\min} and T_{\max} represent the maximum and minimum torque values in the rheometer curve, respectively. t_2 indicates the required time corresponding to a two-unit rise in torque above T_{\min} , and t_{90} indicates the time required to reach an optimum cure. NR, NBR, and TOR showed considerably different cure behaviors because of the differences in their molecular structures. The difference in T_{\max} and T_{\min} , representing the relative degree of crosslinking, was much higher for TOR, and the induction period, t_2 , for the vulcanization reaction was much longer for TOR than for NBR and NR. Therefore, TOR can be crosslinked with a conventional accelerated sulfur vulcanization system.

When equal amounts of NR and NBR were blended (BLD-0), the cure behavior did not seem to follow the intermediate values between the two rubbers, except for T_{\max} . For instance, t_2 and t_{90} values became even smaller than those of NBR. This may have resulted from the differences in the diffusivities of curatives into each rubber phase during mixing and curing processes. It has been reported that the rate of diffusion of sulfur and an accelerator in NBR containing a strongly polar group is lower than that in NR.¹²⁻¹⁴ Therefore, when NR and NBR are mixed in equal amounts in the presence of curatives, the rate of the curatives will be faster for the NR phase than for NBR, resulting in a much higher probability of vulcanization in the NR phase.

With increasing TOR, the rate of the vulcanization reaction (t_2 and t_{90}) became slower because of its longer induction time for the vulcanization reaction. However, T_{\min} decreased and T_{\max} increased with increased TOR content; this indicated a higher degree of crosslinking. The observed tendency comes from the basic characteristics of pure TOR. The observed variations in the cure characteristics imply that TOR

TABLE III
Physical Properties of NR, NBR, and Blend Compounds with TOR

	Compound							
	NR	NBR	BLD-0	BLD-5	BLD-10	BLD-20	BLD-30	BLD-40
Hardness (Shore A)	39	53	47	48	50	55	66	76
Tensile modulus at								
50% (MPa)	0.57	0.95	0.77	0.79	0.89	1.08	1.56	2.09
100% (MPa)	0.83	1.30	1.10	1.13	1.23	1.42	1.87	2.31
200% (MPa)	1.28	1.83	1.60	1.63	1.78	1.99	2.47	2.94
300% (MPa)	1.85	2.37	2.20	2.27	2.53	2.80	3.44	4.09
Tensile strength at break (MPa)	28.4	3.62	26.3	23.7	25.5	21.7	10.5	7.24
Elongation at break (%)	769	417	680	655	653	610	497	429
Rebound (%)	68	18	40	41	43	45	50	57

participates in the vulcanization reaction and becomes a part of a network structure.

Table III shows the physical properties of various rubber compounds. The hardness of pure NBR was much higher than that of pure NR. However, the tensile moduli at various strains, tensile strength and elongation at break, and resilience of pure NR were superior to those of pure NBR. When they were blended in a 50/50 ratio, the values for those properties were between those of pure NR and NBR rubbers. The effect of the TOR level on the properties was noticeably large, as reported previously.^{8,11} For instance, the hardness, tensile modulus, and resilience increased whereas the tensile strength and elongation at break tremendously decreased with the increasing TOR level. Higher values for the modulus and hardness with higher TOR loadings were conjectured from the values of T_{max} , which are shown in Table II. The improved resilience for TOR-loaded blends may arise from the fact that the number of free chain ends, which can cause a hysteresis loss upon deformation, de-

creases when some parts of linear rubbers are replaced with TOR, which contains cyclic macromolecules with no free chain ends

Thermal behavior

For characterization of the transition behavior, DSC thermograms were measured at a heating rate of 10°C/min. The glass-transition temperature (T_g) and melting temperature (T_m) of pure TOR were -65 and 55°C, respectively, as can be seen in Figure 2. As shown in Figure 3(A,B), T_g of pure NR was -64.2°C, which was almost the same as that of TOR, and NBR showed a considerably higher T_g value of -24°C. When the two rubbers were blended in an equal ratio, two distinct transitions were observed at each corresponding transition temperature, -64.5 and -23.6°C, indicating a strongly incompatible nature of the blends [Fig. 3(C)].

Figure 4 shows the effect of the TOR content on the transition behavior of NR/NBR blends. With an in-

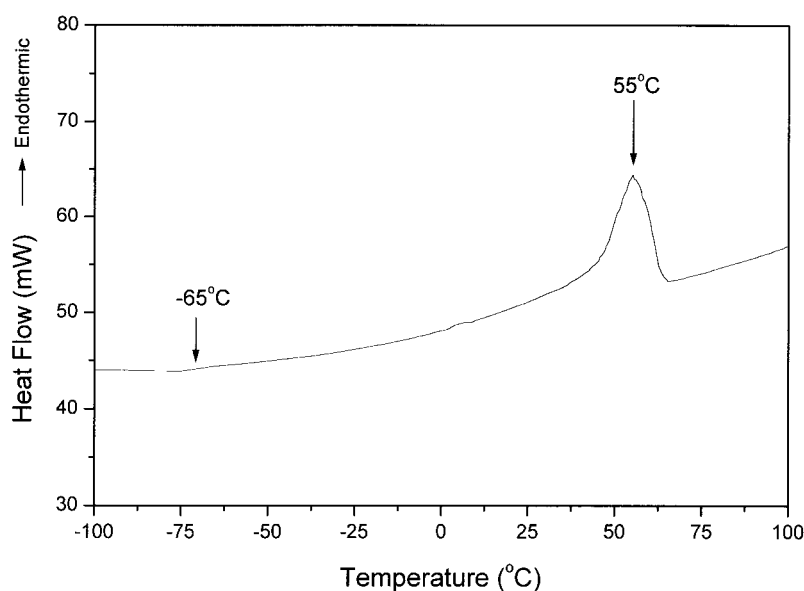


Figure 2 DSC thermograph of pure TOR.

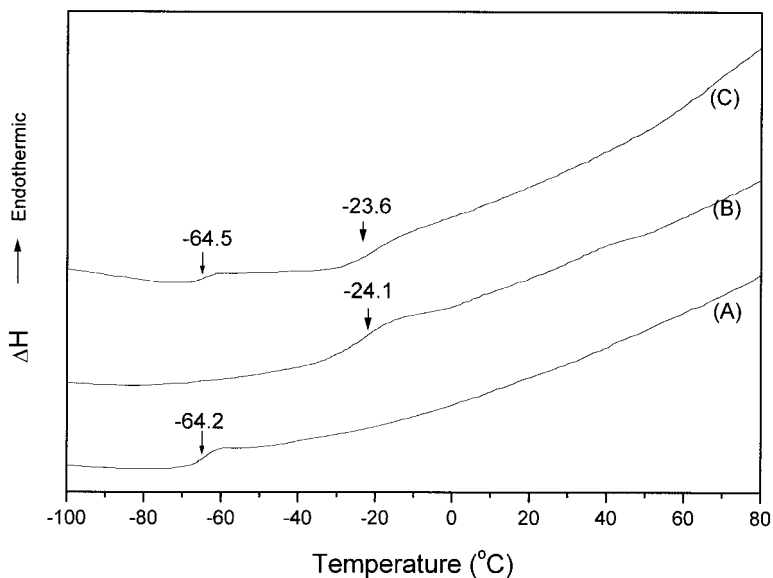


Figure 3 DSC thermographs of (A) pure NR, (B) NBR, and (C) 50/50 NR/NBR.

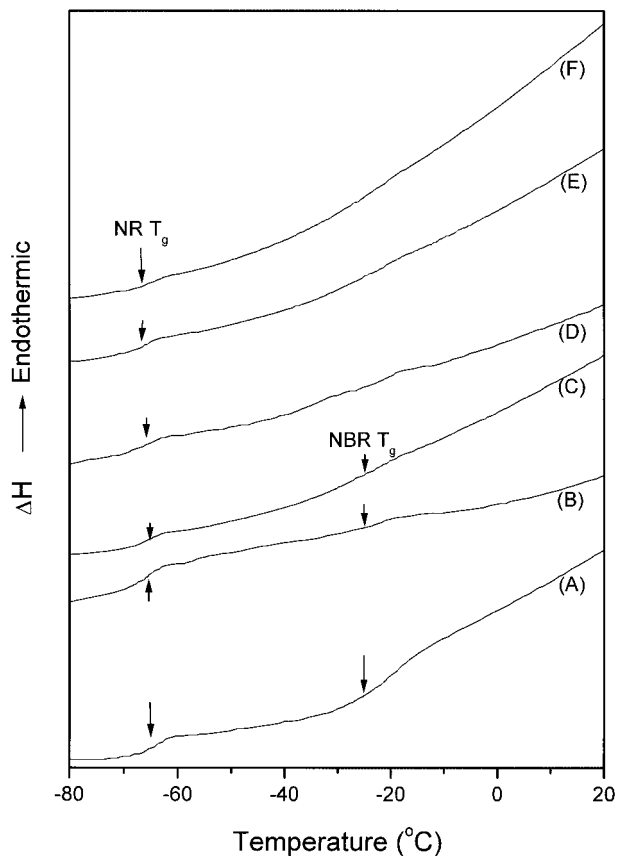


Figure 4 DSC thermographs of various rubber blends: (A) NR/NBR = 50/50, (B) NR/NBR/TOR = 47.5/47.5/5, (C) NR/NBR/TOR = 45/45/10, (D) NR/NBR/TOR = 40/40/20, (E) NR/NBR/TOR = 35/35/30, and (F) NR/NBR/TOR = 30/30/40.

creasing TOR level, the glass-transition behavior of the NBR phase became negligibly small, whereas that of the NR phase was observed throughout the blend ratio ranges used in this study. Moreover, the transition temperatures of both NR and NBR were not affected by TOR addition. It is interesting to note here the strong effect of TOR on the glass-transition behavior of the NBR phase. For confirmation of this interesting result, dynamic mechanical properties, another useful way of verifying the transition behavior, were also investigated over a wide temperature range, from -80 to 80°C , as described in the following section.

Dynamic mechanical properties

Dynamic mechanical properties are most commonly used to characterize polymer blends. In this work, the dynamic modulus (E^*) and $\tan \delta$ were investigated for various rubber blends, and the results are shown in Figures 5–8. As found in the DSC thermographs, two distinct transitions were also observed for a 50/50 NR/NBR blend (Figs. 5 and 6). This again supports the strongly incompatible nature of the two rubbers, NR and NBR. When TOR was added to an NR/NBR blend and its loading level was increased, E^* in the glassy region ($< -60^{\circ}\text{C}$) decreased, whereas E^* in the rubbery region ($> 40^{\circ}\text{C}$) increased slightly, as shown in Figure 7. The transition behaviors of the two rubbers changed considerably differently with increasing TOR levels, as found previously with the DSC results. Again, the NBR transition became extremely small in comparison with that of NR as the amount of TOR was increased. This trend was more clearly observed in $\tan \delta$ curves, as shown in Figure 8. The peak posi-

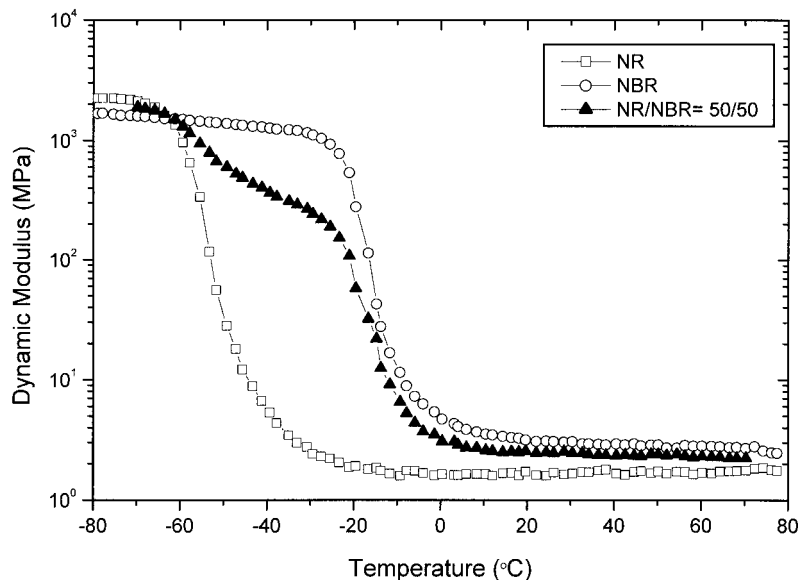


Figure 5 E^* versus temperature for NR, NBR, and 50/50 NR/NBR.

tion, however, was not changed. Generally, when a compatibilizer is introduced to two-component polymer blends and it is effective in compatibilizing the two polymers, at least to a certain degree, the transition peaks tend to move toward the center of two peaks, so that they become closer.

In an attempt to analyze the observed TOR effect in a quantitative manner, the relative peak heights (RPHs) corresponding to NBR and NR glass transitions for each TOR-containing compound with respect to that of a reference compound (NR/NBR blend) without TOR were calculated from the $\tan \delta$ curves in Figure 8, and they are plotted in Figure 9 as a function of the TOR content. The RPH of the NR glass transi-

tion increased somewhat with increased TOR content because the amorphous portion of TOR also showed a transition temperature similar to that of NR, as observed in the previous DSC thermographs (Figs. 2 and 3). However, the RPH for the NBR glass transition linearly decreased with increasing TOR content. An extrapolated content of TOR at a zero level of RPH, indicating no NBR materials in the rubber blends, was found to be only about 50 phr, but NBR was still expected to remain at 25 phr. Therefore, the newly observed strong effect of TOR on the peak height of the transition behavior of NR/NBR blends is very interesting, and there is a clear need to elucidate what causes such transition behavior. To examine

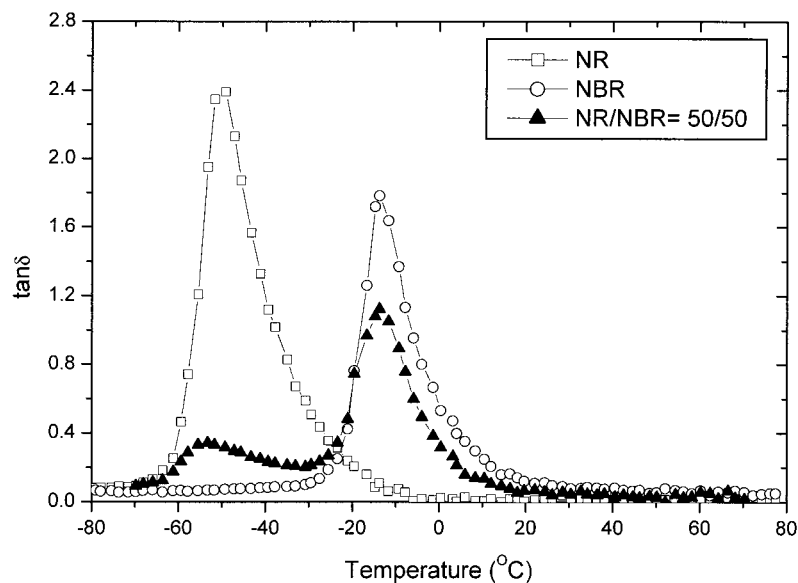


Figure 6 $\tan \delta$ versus temperature for NR, NBR, and 50/50 NR/NBR.

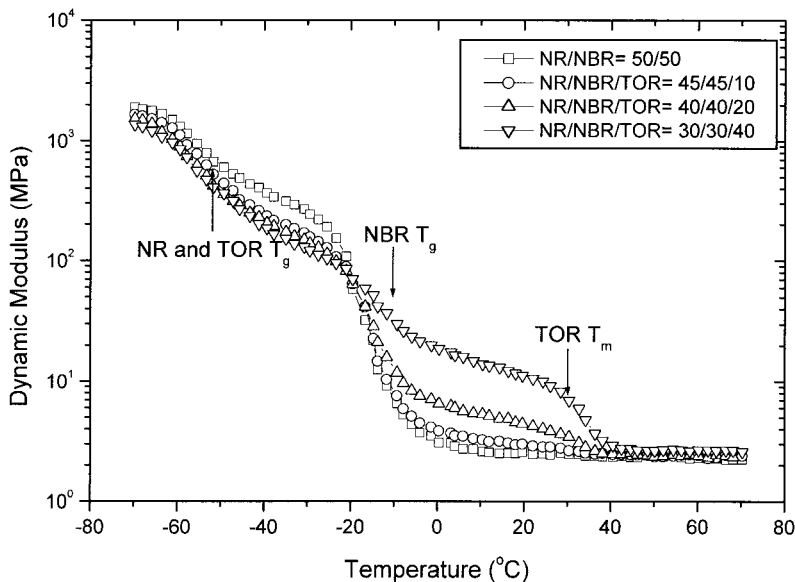


Figure 7 E^* versus temperature for various rubber blends.

such an interesting effect in more detail, we investigated the phase morphology of the blends with SEM and TEM.

Morphology

To study the blend morphology, we investigated via SEM surfaces cryogenically fractured with liquid nitrogen, and the results are shown in Figures 10 and 11. For the NR/NBR blends with blend ratios of 50/50 [Fig. 10(A)] and 80/20 (Fig. 11), numerous droplets of a few micrometers to about 10 μm were evenly dispersed in the continuous matrix. The viscosity ratio between the dispersed phase and the matrix has been

known as one of the most critical variables for controlling blend morphology.¹⁵ Generally, the polymer showing a lower viscosity tends to be the continuous phase. Therefore, NR possibly becomes the continuous phase and NBR becomes the dispersed phase because the viscosity of NR becomes lower on account of a severe mastication effect during mixing.¹⁶ Experimental evidence also supported such a blend morphology for NR/NBR blends.^{4,17} Moreover, the phase morphology was confirmed by TEM in this study (Fig. 12), as described in detail later. When the amount of TOR was increased, the dispersed particles became smaller and well dispersed, and the bright regions became larger, as shown in Figure 10(B–D). Therefore,

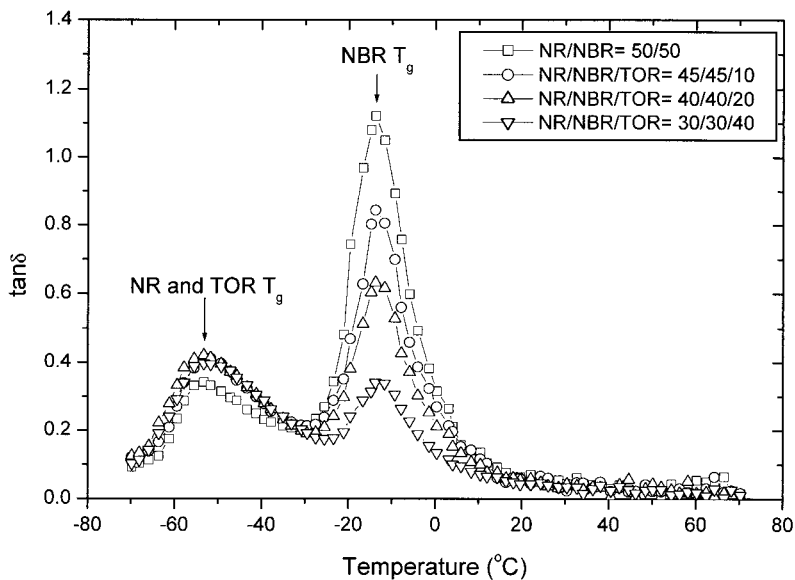


Figure 8 $\tan \delta$ versus temperature for various rubber blends.

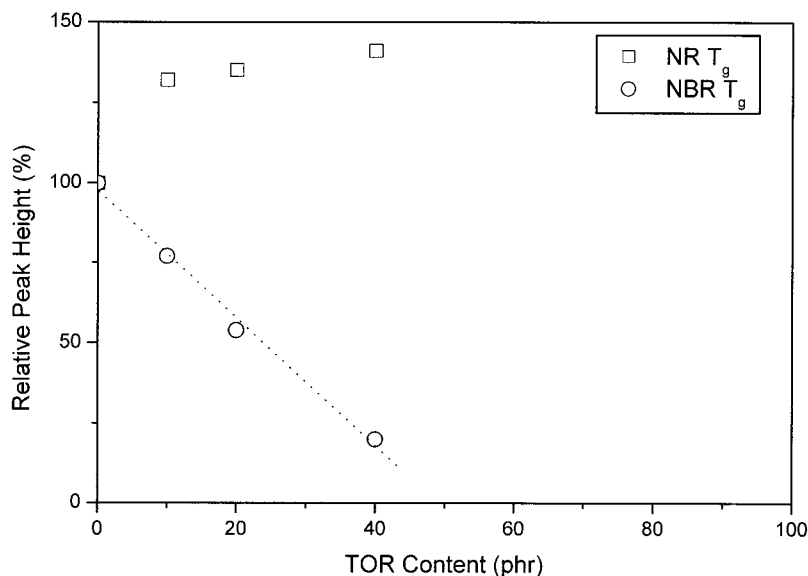


Figure 9 RPH of NR and NBR as a function of the TOR content.

it is conjectured that the bright region indicates the TOR phase. Small holes corresponding to NBR droplets of a few micrometers were observed over the fractured surface, especially on the TOR phase for a highly loaded NR/NBR/TOR blend [Fig. 10(D)].

In an attempt to clarify this interesting blend morphology, NR was stained with OsO_4 , and then mixed with NBR and TOR in a blend ratio of 40/40/20,

respectively. A thin microfilm (ca. 70 nm or less) was then observed with TEM, and the result is shown in Figure 12. The stained dark region of the photograph indicates the NR phase, whereas the gray region indicates the NBR phase, as suggested in the SEM photographs. The remaining bright regions can be imagined to be the TOR phase, as can be surmised from the composition of the blend (NR/NBR/TOR = 40/40/

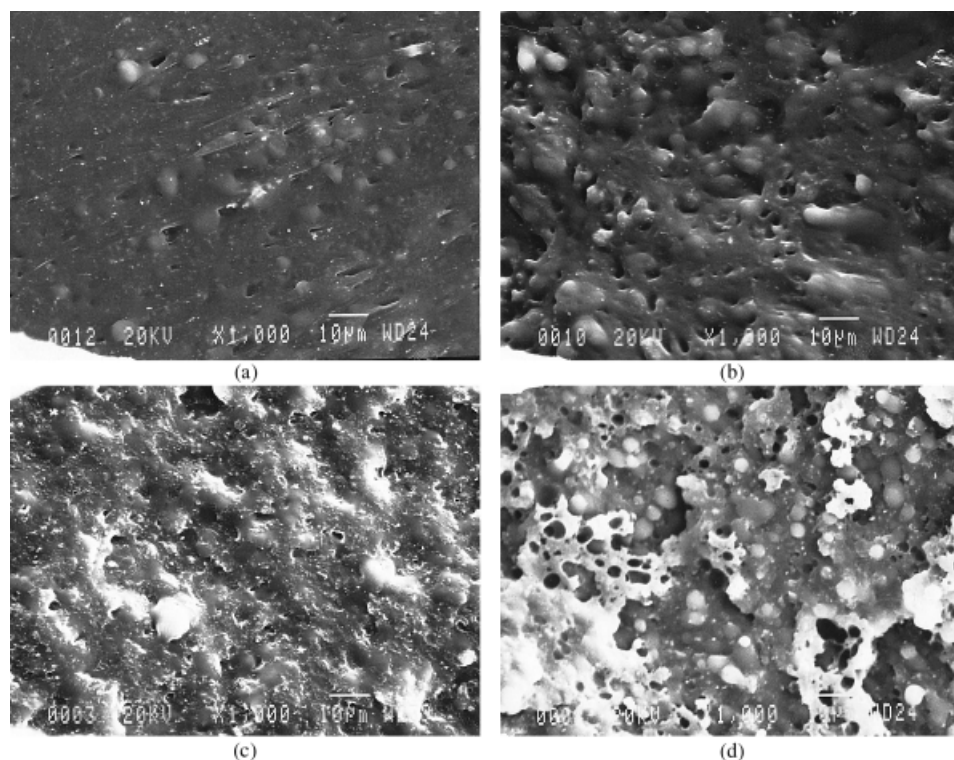


Figure 10 SEM micrographs of various rubber blends: (A) NR/NBR = 50/50, (B) NR/NBR/TOR = 47.5/47.5/5, (C) NR/NBR/TOR = 40/40/20, and (D) NR/NBR/TOR = 30/30/40.

20), and they are located between the NR and NBR phases. A similar trend was also reported for NR/EPDM⁸ and NBR/EPDM³ blends. On the basis of the SEM and TEM micrographs, it is now clear that TOR tends to be located in a nonpolar rubber phase and in some cases at the interfaces between polar–nonpolar rubber blends. This phase morphology can reduce the interfacial tension of highly incompatible rubber blends such as NR/NBR, NR/EPDM, and NBR/EPDM. Therefore, a plausible explanation for the observed strong effect of TOR on the glass transition of NBR is that TOR dispersed in the NR matrix or, in some cases, located at interfaces between NR and NBR can affect the glass-transition behavior of NBR because TOR is still hard enough at the corresponding transition temperature to compress the segmental motion of NBR. However, there is no direct evidence to support this explanation at this moment, and further study is necessary.

CONCLUSIONS

1. With increasing TOR, the rates of the vulcanization reaction (t_2 and t_{90}) of the rubber blends became slower, and T_{\min} decreased, whereas T_{\max} increased. NR generally showed superior mechanical properties, including tensile moduli at various strains, tensile strength and elongation at break, and resilience. When they were blended in a 50/50 blend ratio, the values for those properties were between those of pure NR and NBR rubbers.
2. The TOR loading level strongly affected the physical properties. For instance, the hardness, tensile modulus, and resilience increased but the tensile strength and elongation at break tremendously decreased with an increasing TOR level.

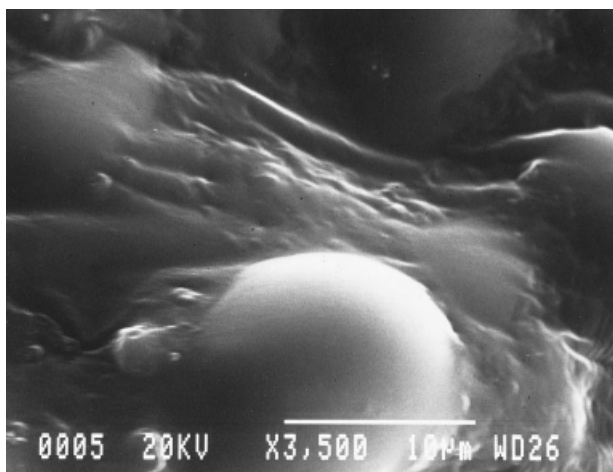


Figure 11 SEM micrograph of an NR/NBR blend (80/20).

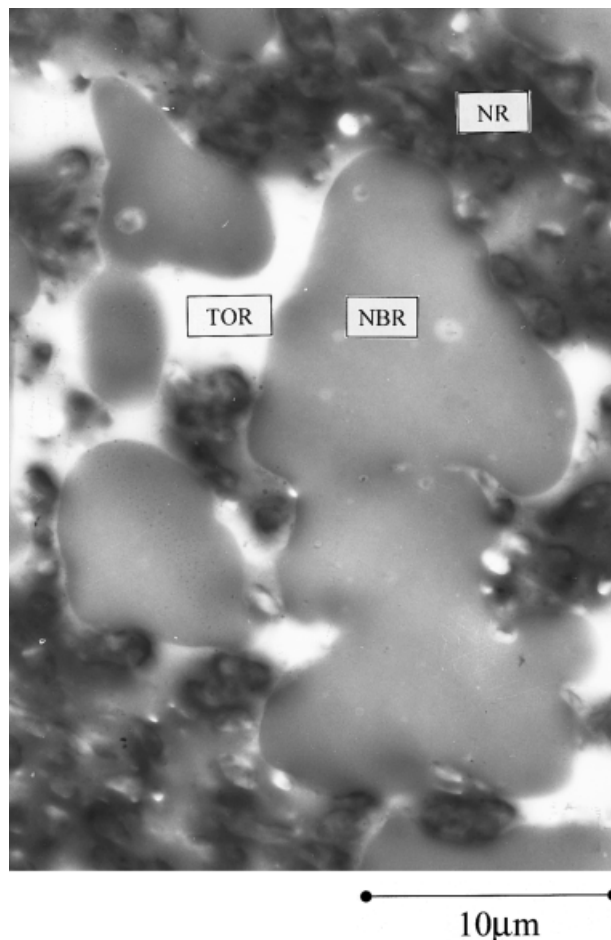


Figure 12 TEM micrograph of an NR/NBR/TOR blend (40/40/20). The NBR phase was stained with OsO_4 .

3. When NR and NBR were blended, two distinct glass transitions, indicating the incompatible nature of the blend, were observed to exist from both DSC thermograms and dynamic mechanical analysis results (E^* and $\tan \delta$). With an increasing TOR level, the glass transition of only the NBR phase became considerably smaller, and no detectable effect was found on T_g .
4. The phase morphology of NR/NBR blends was found to be composed of a few micrometers of NBR droplets and NR continuous phases; this indicated a strongly incompatible nature. When TOR was added to NR/NBR blends, TOR tended to be located in the NR phase and, in some cases, at interfaces between the NR and NBR phases.

REFERENCES

1. McDonel, E. T.; Baranwal, K. C.; Andries, J. C. In *Polymer Blends*; Paul, D. R.; Newman, S., Eds.; Academic: New York, 1978; Vol. 2, Chapter 19.

2. Hamed, G. R. In *Engineering with Rubber*; Gent, A. N., Ed.; Hanser: New York, 1992; Chapter 2.
3. Lohmar, J. *Kautsch Gummi Kunstst* 1986, 39, 1065.
4. Hess, W. M.; Herd, C. R.; Vegvari, P. C. *Rubber Chem Technol* 1993, 66, 329.
5. Brydson, J. A. *Rubber Chemistry*; Applied Science: London, 1978; Chapter 6.
6. Setua, D. K.; White, J. L. *Polym Eng Sci* 1991, 31, 1742.
7. Setua, D. K.; White, J. L. *Kautsch Gummi Kunstst* 1991, 44, 542.
8. Chang, Y.-W.; Shin, Y.-S.; Chun, H.; Nah, C. *J Appl Polym Sci* 1999, 73, 749.
9. Dräxler, A. *Kautsch Gummi Kunstst* 1983, 36, 1037.
10. Product Brochure of Degussa AG.
11. Chang, Y.-W.; Shin, Y. *Elastomer (Korea)* 2000, 35, 149.
12. van Amerongen, G. J. *Rubber Chem Technol* 1964, 37, 1065.
13. Gardiner, J. B. *Rubber Chem Technol* 1968, 41, 1312.
14. Gardiner, J. B. *Rubber Chem Technol* 1969, 42, 1058.
15. Favis, B. D. In *Polymer Blends*; Paul, D. R.; Bucknall, C. B., Eds.; Wiley: New York, 2000; Vol. 1, Chapter 16.
16. Bristow, G. M.; Watson, W. F. In *The Chemistry and Physics of Rubber-Like Substances*; Bateman, L., Ed.; Maclaren & Sons Ltd.: London, 1963; Chapter 14.
17. Scott, C. E.; Callan, J. E.; Hess, W. M. *J Rubber Res Inst Malaysia* 1969, 22, 242.