

Rheological Properties and Compatibility of NR/EPDM and NR/Brominated EPDM Blends

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ABSTRACT: Ethylene-propylene–diene terpolymer (EPDM) was modified by bromination reaction. Blending the resulting brominated EPDM with natural rubber (STR5L) and blending the unmodified EPDM with STR5L at various compositions were carried out. The rheological properties of the blends were investigated using a capillary extrusion. Shear flow curves of the pure rubbers and their blends illustrated the pseudoplastic property as shear thinning behavior with a power law index $n < 1$. True shear viscosity of all blends showed the negative deviation in relation to their additive values. Rheological be-

havior and two T_g 's found from the DSC thermograms at all blend compositions indicated blend incompatibility for both sets of blends. The incompatibility of the vulcanized blends was also found by measuring the spin–spin relaxation time T_2 by pulsed NMR. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 837–847, 2003

Key words: rheology; rubber; compatibility; bromination; power law index

INTRODUCTION

In the rubber industry, rubber blends have been widely used to obtain the best characteristics of each single rubber. Natural rubber vulcanizates have good elasticity and strength properties, whereas they show poor heat and ozone resistance. Blending a suitable amount of low unsaturated ethylene–propylene–diene terpolymer (EPDM) into a diene rubber has been found to improve both heat and ozone resistance.^{1–5} However, the difference in olefin concentration of EPDM and natural rubber resulted in a cure-rate–incompatible blend. This has been recognized to cause both inferior static and dynamic mechanical properties such as poor tensile strength, fatigue resistance, and high hysteresis in the rubber blend.⁶ Consequently, many attempts to improve the properties have been reported to achieve an equivalent cure rate between the two rubbers.^{6–15} For example, grafting of the vulcanization inhibitor, prevulcanization inhibitor (PVI) groups, onto the EPDM was found to reduce the access of the natural rubber (NR) to the cure system.⁷ Improvement of crosslinking distribution and tensile strength was then achieved.^{7,8} Grafting of accelerators onto EPDM has also been reported to be effective in providing cure compatibility.⁶ Maleic anhydride was

grafted and then provided a metal-chelating group on the EPDM by Coran.^{9,10} Carboxylated EPDM and halogenated EPDM were found to increase the number of cure sites resulting in cure compatibility.^{11–15} Most attempts clearly showed a significant improvement in overall properties. However, the properties of blends are also closely related to the state of mixing. The rheological behavior of individual gum rubbers and blends plays an important role in the quality of mixing and compounding, which influences the final product quality. It is therefore important to clarify the miscibility behavior of the rubber blend, which can be studied on the basis of viscoelastic and glass-transition measurements.^{16,17} It was also found that not enough attention has been given to the rheological properties and miscibility of the modified EPDMs and their blends with NR. In this study we have therefore evaluated the rheological properties and compatibility of the brominated EPDM (BEPDM) blend with natural rubber (STR5L) and those blends of the unmodified EPDM with STR5L. Recently there have been some reports of employing a pulsed NMR technique to investigate the crystallization of polymers^{18,19} and polymer blends.^{16,20,21} We then also used the pulsed NMR technique to characterize the compatibility of the blends by measuring the spin–spin relaxation time T_2 of the vulcanized rubber blends.

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EXPERIMENTAL

Materials

The raw materials used in this study were NR (STR5L; Tavorn Industrial Co., Ltd. Thailand) and EPDM (Kel-

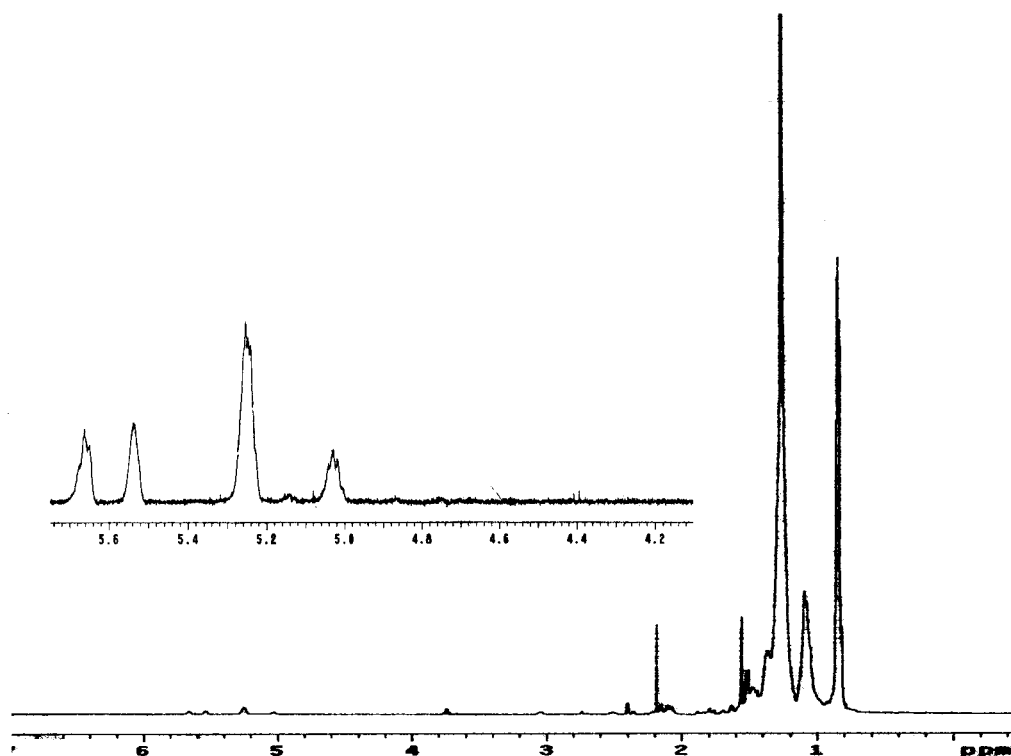


Figure 1 $^1\text{H-NMR}$ spectrum of the original EPDM.

tan 714) with a high ethylidene-2-norbornene (ENB) content of 8% (DSM Elastomers, East Asiatic, Bangkok, Thailand).

Preparation of brominated EPDM

Bromination of the EPDM was carried out by following the work of Yoon et al.¹⁵ as follows. The EPDM (180 g) was first dissolved in 3600 cm^{-3} of chloroform. After having been stirred for 24 h at room temperature, a 2 vol % solution of bromine in chloroform was added. The mixed solution was then stirred to promote the bromination reaction for 2 h at room temperature. The brominated EPDM (BEPDM) product was coagulated in methanol and reprecipitated by toluene/methanol to remove traces of bromine solution. Finally, it was dried in a vacuum oven at 50°C for 72 h. $^1\text{H-NMR}$ spectra of the EPDM rubber before and after the bromination were later recorded on a Varian Unity Inova 500 liquid NMR spectrometer (Varian Associates, Palo Alto, CA) using tetramethylsilane (TMS) as an internal standard. If the molecular weight of the virgin polymer is known, we can then calculate the bromination percentage by combining the MW data with the $^1\text{H-NMR}$ data. It is also easy to analyze bromine by elemental analysis. Unfortunately, we do not have the high-temperature GPC equipment and oxygen combustion flask (Schoniger flask) to conduct the experiments at this time. However, from the reported literature that we followed, the bromine con-

tent (by elemental analysis) could be estimated to be 2.4–2.5 wt %.

Preparation of brominated EPDM/NR and EPDM/NR blends

Blends of BEPDM/NR and EPDM/NR were carried out in a laboratory-sized two-roll mill at a mixing temperature of 60°C . At any blend composition, the higher amount rubber was masticated first and banded on the mill for 2 min. After that the second rubber (small amount) was then mixed and allowed to blend for another 6 min. Finally, the rubber blend was sheeted out and cut into small pieces, ready for rheological and DSC measurements.

Rheological measurements

Rheological properties in terms of shear stress and shear viscosity were studied using a Rosand single-bore capillary rheometer (model RH7, Rosand Precision Ltd., Stoubridge, West Midlands, England). A capillary die of diameter 2 mm, length 32 mm, and 180° entry angle with a length-to-radius (L/R) ratio of 32 was used as a long die. The small pieces of the rubber blends were put in a barrel and initially preheated for 5 min under pressure at approximately 4 MPa to get a compact mass. The excess rubber was then automatically purged and extruded at shear rates in the range of 10 to 1500 s^{-1} and the test temperature of 100°C by

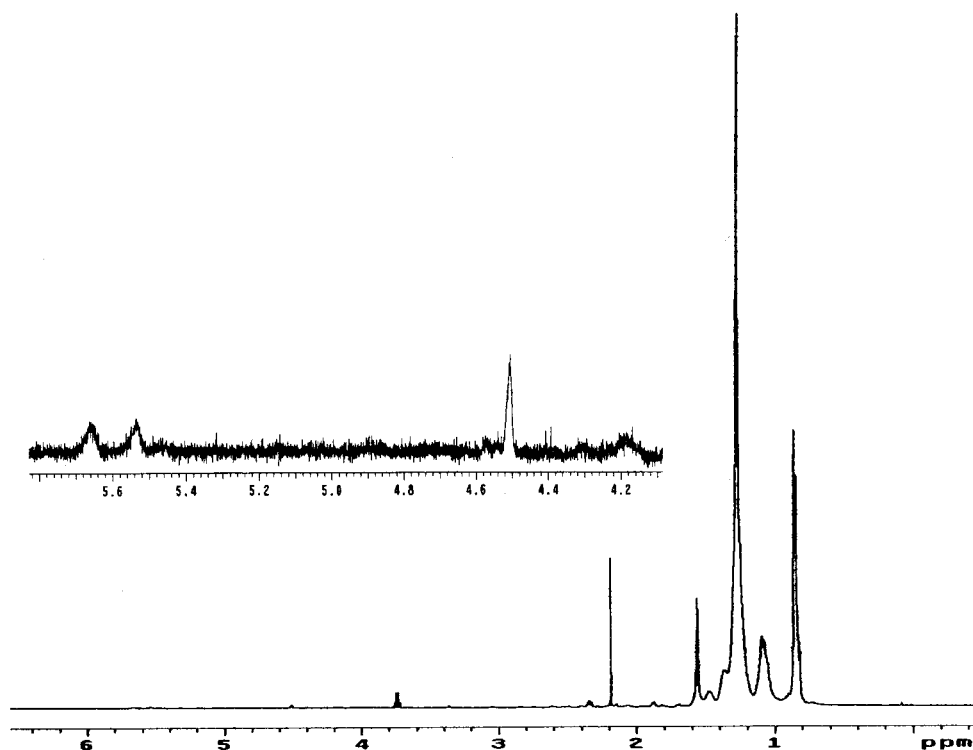


Figure 2 $^1\text{H-NMR}$ spectrum of the brominated EPDM.

a microprocessor-controlled program. During the test, the pressure drop across a capillary channel and melt temperature was captured by a data acquisition system. The apparent values of shear stress, shear rate, and shear viscosity were calculated using the derivation of the Poiseuille law for capillary flow and yields²²:

$$\text{Apparent wall shear stress (Pa): } \tau_{\text{app}} = \frac{R\Delta P}{2L} \quad (1)$$

$$\text{Apparent wall shear rate (s}^{-1}\text{): } \dot{\gamma}_{\text{app}} = \frac{4Q}{\pi R^3} \quad (2)$$

$$\text{Apparent shear viscosity (Pa s): } \eta_{\text{app}} = \frac{\tau_{\text{app}}}{\dot{\gamma}_{\text{app}}} \quad (3)$$

where ΔP is the pressure drop across the channel (Pa), Q is the volumetric flow rate ($\text{m}^3 \text{s}^{-1}$), R is the capillary radius (m), and L is the length of the capillary (m).

The true wall shear stress was obtained using the Bagley correction. This was done by measuring the pressure drop (P_0) on the zero length die ($L/R \cong 0$) with the same die diameter and entrance angle. The true shear stress was then calculated:

$$\text{True wall shear stress (Pa): } \tau_{\text{true}} = \frac{(P_L - P_0) R}{2L} \quad (4)$$

where P_L is the pressure drop across the channel of the long die ($L/R = 32$) (Pa) and P_0 is the pressure drop across the zero length die (Pa).

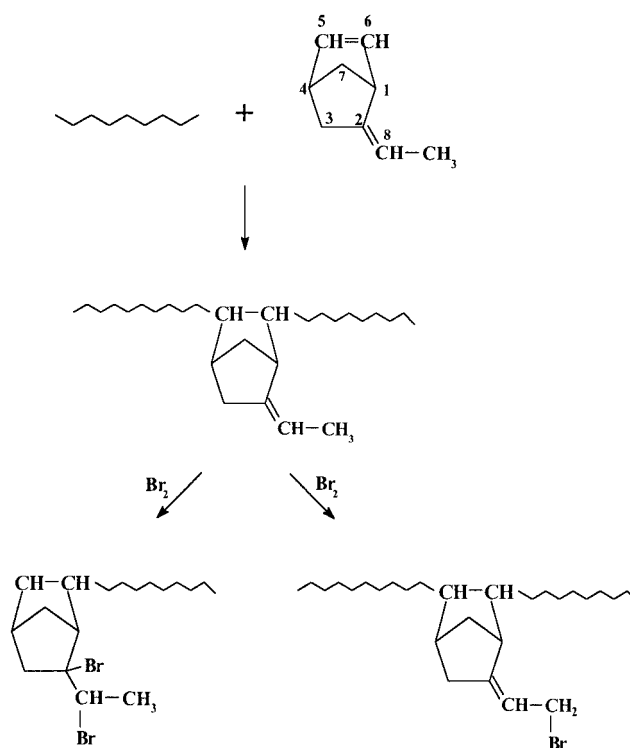


Figure 3 Possible bromination reaction of EPDM.

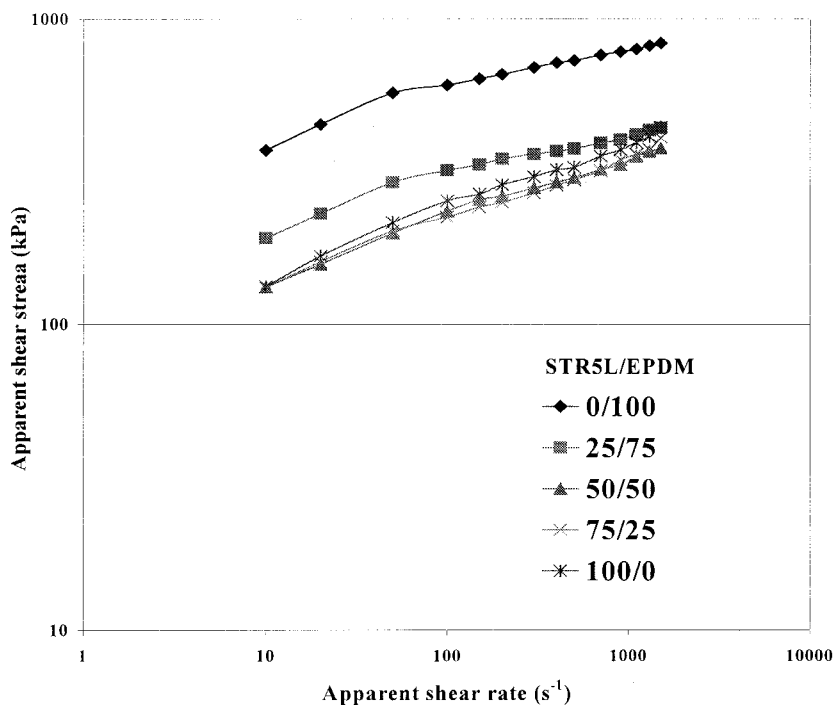


Figure 4 Effect of apparent shear rate on the apparent shear stress of STR5L/EPDM blends at various blend compositions.

The true wall shear rate was obtained by applying the Rabinowitsch correction:

$$\text{True wall shear rate (s}^{-1}\text{): } \dot{\gamma}_{\text{true}} = \frac{3n + 1}{4n} \dot{\gamma}_{\text{app}} \quad (5)$$

where n is the power law index obtained from the slope of the line plots between $\log(\tau_{\text{app}})$ and $\log(\dot{\gamma}_{\text{app}})$.

True shear viscosity was therefore calculated:

$$\text{True shear viscosity (Pa s): } \eta_{\text{true}} = \frac{\tau_{\text{true}}}{\dot{\gamma}_{\text{true}}} \quad (6)$$

Glass-transition temperature measurements

Differential scanning calorimetric (DSC) measurements were made by DSC (QC) 085 Apparatus (Rheometric Scientific, Surrey, UK) in the nitrogen atmosphere at a heating rate of $10^{\circ}\text{C min}^{-1}$. The inflection point of the specific heat change was taken as the glass-transition temperature.

Pulsed NMR measurement

Pulsed NMR equipment (PC-20 model, resonance frequency for proton, 20 MHz; Bruker Instruments, Billerica, MA) was used to determine the spin-spin relaxation time T_2 of the vulcanized rubber blend at room temperature and to analyze related signal intensity. The vulcanized rubber blend sample was prepared by mixing the rubber compound in a two-roll

mill and vulcanizing by compression molding. The same compound formula for all blends was used: zinc oxide, stearic acid, tetramethyl thiuramdisulfide (TMTD), 2-mercaptobenzothiazole (MBT), and sulfur of 5, 2, 1.5, 0.5, and 1.75 phr, respectively.

RESULTS AND DISCUSSION

$^1\text{H-NMR}$ spectra in 10% (w/v) CDCl_3 solution of the original EPDM and after bromination are shown in Figures 1 and 2, respectively. The spectrum of the unmodified EPDM shows two pairs of complex signals between δ 4.9 and 5.7 ppm, attributable to the olefinic protons of the ENB diene monomer unit.²³ Signal characteristics of C(5)–C(6) olefinic hydrogen atoms (Fig. 3) of the unmodified ENB monomer between δ 6.0 and 6.2 ppm cannot be observed. This suggests that ENB was incorporated into the EPDM through the cyclic C(5)–C(6) double bond. After the bromination, the modified EPDM spectrum does not exhibit the two signals between δ 4.9 and 5.3 ppm but the other two signals between δ 5.5 and 5.7 ppm can still be observed with less intensity. This spectrum also shows an addition signal at δ 4.5 ppm, which indicates the bromine attached a C–C single-bond hydrogen atom.²⁴ It is therefore concluded that during the bromination reaction, the bromine atoms can attack the double bond or substitute hydrogen in either the allylic position or the other positions. The probable reaction is shown in Figure 3.

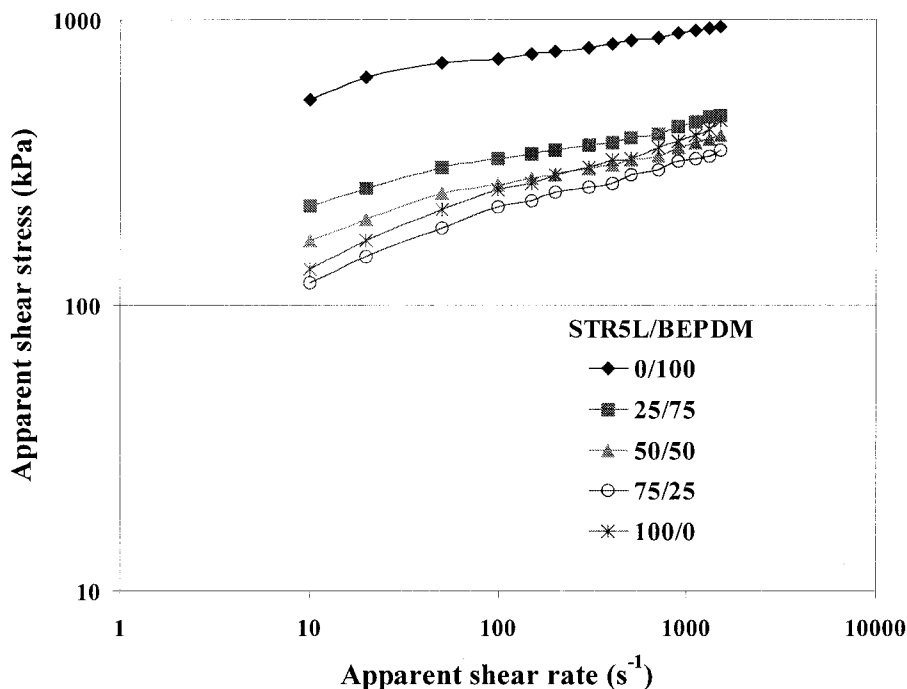


Figure 5 Effect of apparent shear rate on the apparent shear stress of STR5L/BEPDM blends at various blend compositions.

Rheological properties and compatibility

The log–log plots of apparent shear stress versus apparent shear rate for STR5L/EPDM and STR5L/BEPDM blends with various blend compositions are shown in Figures 4 and 5, respectively. Flow curves of all the blends show reasonably straight lines, whose intercept K and slope n correspond to the power law equation (the Ostwald–de Waele equation)²⁵

$$\tau = K(\dot{\gamma})^n \quad (7)$$

where n is the power law index or the flow behavior index, and K is the consistency of flow or viscosity coefficient index. Table I shows the power law index and the consistency of flow of STR5L/EPDM and STR5L/BEPDM blends. The values of n dictate the pseudoplastic nature of STR5L, EPDM, BEPDM, and their blends, given values of $n < 1$. Hence, the apparent viscosity of the two sets of blends decreased as the shear rate increased, as shown in Figures 6 and 7. It can also be seen that for the pure rubbers, BEPDM had the lowest n value and STR5L has the highest n value.

This accounts for the high pseudoplasticity, the highly shear thinning fluid in the modified BEPDM, and the more pluglike profile.²⁶ Consequently, the blends of STR5L/BEPDM tended to have a lower n value at a given blend composition, which increased with increasing levels of STR5L.

Figure 8 shows the plot of apparent shear stress versus apparent shear rate of pure STR5L, EPDM, and BEPDM. It can be seen that the modified EPDM by bromination reaction affects the shear flow property. That is, at a given shear rate, a higher apparent shear stress of pure BEPDM compared to that of EPDM and STR5L was found. The highest shear viscosity of BEPDM was therefore observed at a given apparent shear rate (Fig. 9). It indicates that the bromine substituents on the rubber main chain may increase the chain rigidity of the rubber, consequently increasing the ability to resist flow, whereas STR5L gave the lowest apparent shear viscosity because of its ease in molecular weight breakdown with mastication during sample preparation and with shear force during the capillary flow test.

TABLE I
The Power Law Index (n) and the Consistency of Flow (K) for Various Blend Compositions

NR/EPDM blend	n	K (kPa)	NR/BEPDM blend	n	K (kPa)
0/100	0.14	293.0	0/100	0.10	444.6
25/75	0.15	149.9	25/75	0.14	169.0
50/50	0.20	88.7	50/50	0.16	124.5
75/25	0.21	85.1	75/25	0.20	81.8
100/0	0.22	86.8	100/0	0.22	86.8

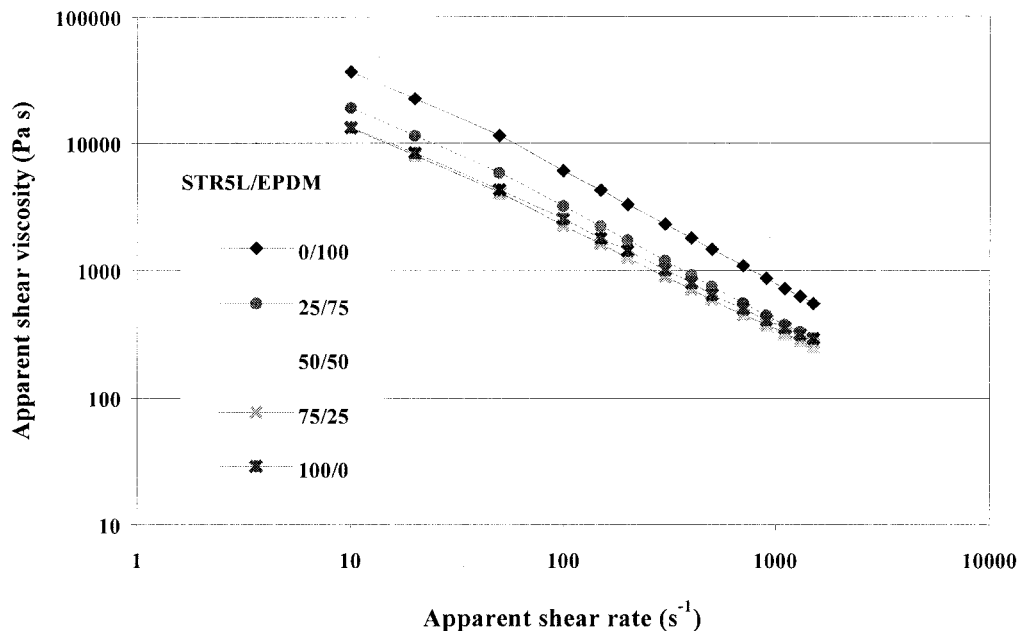


Figure 6 Effect of apparent shear rate on the apparent shear viscosity of STR5L/EPDM blends at various blend compositions.

Figure 10 compares the apparent shear viscosity with the level of EPDM or BEPDM in the blend composition at the apparent shear rates of 50, 150, and 500 s^{-1} . It was found that the apparent shear viscosity of the blends tended to increase with increasing levels of either EPDM or BEPDM attributed to the higher apparent shear viscosity of EPDM and BEPDM. However, at high apparent shear rates,

there was less of a difference in the apparent shear viscosity of the blends with increasing quantities of EPDM and BEPDM.

Generally, the true shear viscosity of a polymeric blend follows the log additive rule²⁷⁻³⁰:

$$\log \eta_B = \sum w_i \log \eta_i \quad (8)$$

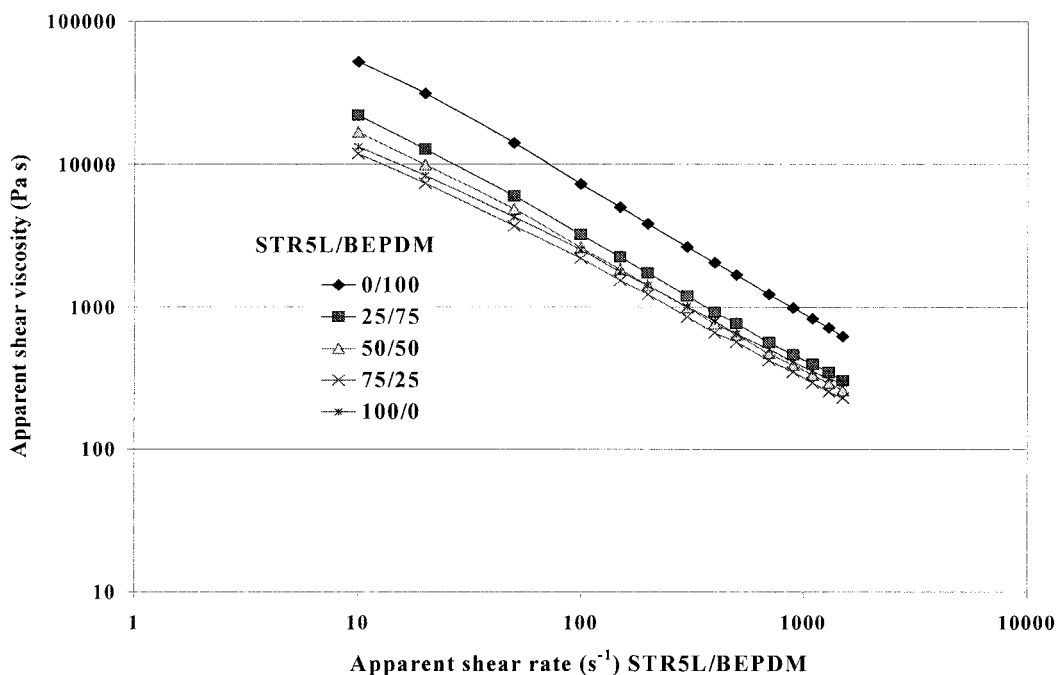


Figure 7 Effect of apparent shear rate on the apparent shear viscosity of STR5L/BEPDM blends at various blend compositions.

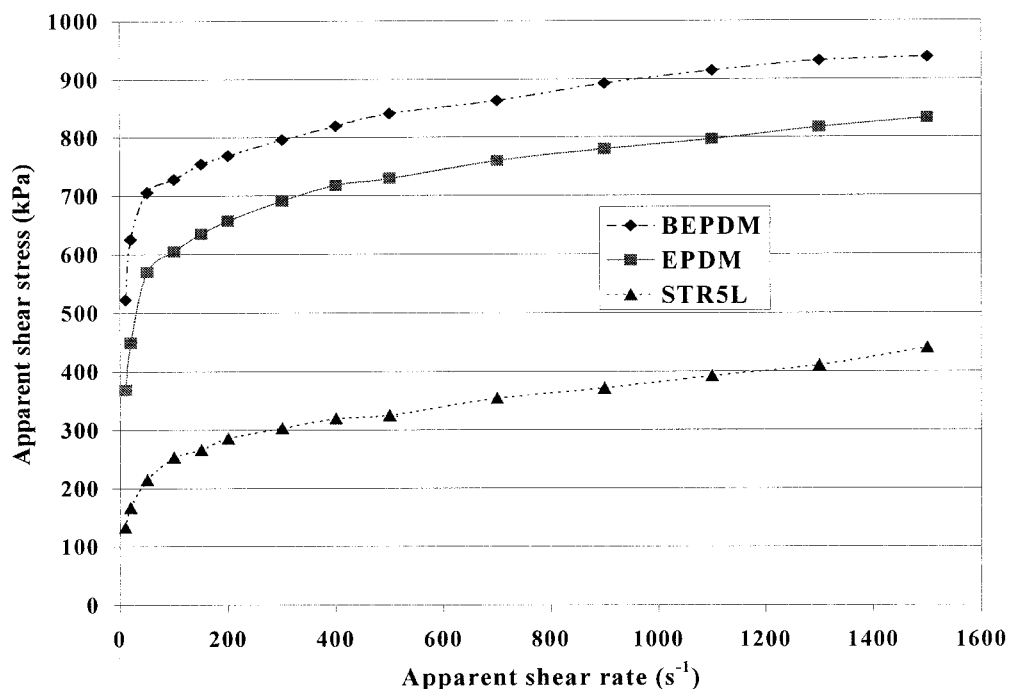


Figure 8 Apparent shear stress of pure STR5L, EPDM, and BEPDM as a function of apparent shear rate.

where η_i and η_B are the true shear viscosity of the i th component and that of the blend, and w_i is the weight fraction of the i th component. For the miscible blends, rheological properties (e.g., viscosity and die swell) show a positive deviation from their additive values, whereas the immiscible blends give a negative deviation in rheological properties.²⁹ In this work, the true shear viscosity of STR5L/EPDM and STR5L/BEPDM

blends in all blend compositions was evaluated and found to be a negative deviation relating to their additive values. It is therefore indicated that the blends of STR5L/EPDM and STR5L/BEPDM were the immiscible blends. It means that there is no specific interaction between the two components of both blends. This may be attributed to the dissimilar, low unsaturated structure of EPDM and the polarity of the

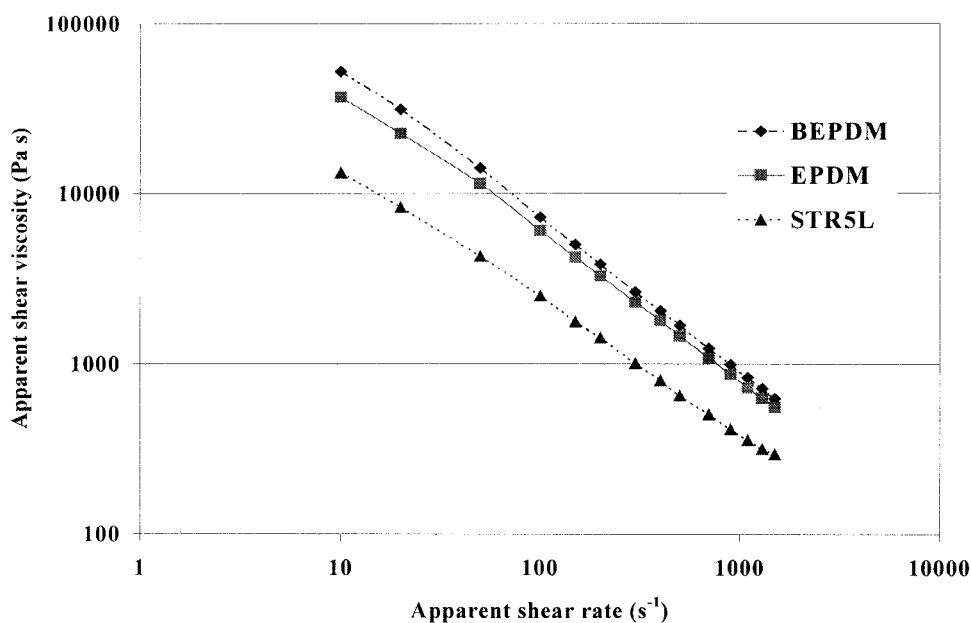


Figure 9 Relationship between apparent shear rate and apparent shear viscosity of pure STR5L, EPDM, and BEPDM.

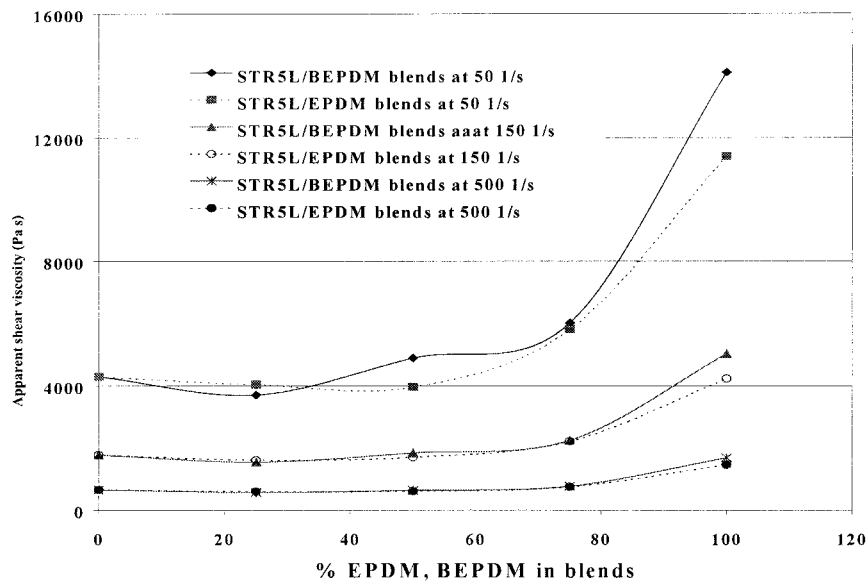


Figure 10 Comparison of apparent shear viscosity at apparent shear rate of 50, 150, and 500 s^{-1} for STR5L blended with various contents of EPDM and BEPDM.

bromine substituents on the BEPDM chains compared to the unsaturated nonpolar structure of natural rubber.

The miscibility behavior of the blends was also investigated based on the glass-transition temperature measured by thermal analyses. Figures 11 and 12 illustrate the DSC thermograms of both blends with various blend compositions. The glass-transition temperature measurements confirmed the rigidity of pure BEPDM because it had a higher glass-transition temperature than that of the unmodified EPDM. Higher glass-transition temperatures of both pure EPDM and BEPDM compared to that of STR5L also support their high ability to resist flow, as discussed above. Two glass transitions were observed at most blend compositions, but those appeared less distinct at the compo-

sition of 75/25 for both STR5L/EPDM and STR5L/BEPDM blends. The glass transition at the higher temperature region is related to EPDM for STR5L/EPDM blends and to BEPDM for those of STR5L/BEPDM blends. The blends of STR5L/EPDM and STR5L/BEPDM are therefore considered to be immiscible because of two glass-transition temperatures in the DSC thermograms.³¹

For pulsed NMR results, Figure 13 illustrates dependency of T_2 and its fractional amount on EPDM content in STR5L/EEPDM blend vulcanizates. The three components of T_2 form the heterogeneous phases in mobility and the fractional amounts in the system. It can also be seen that each T_2 is not heavily dependent on EPDM content. It may indicate that there is no significant difference in the mobility of the crosslinked

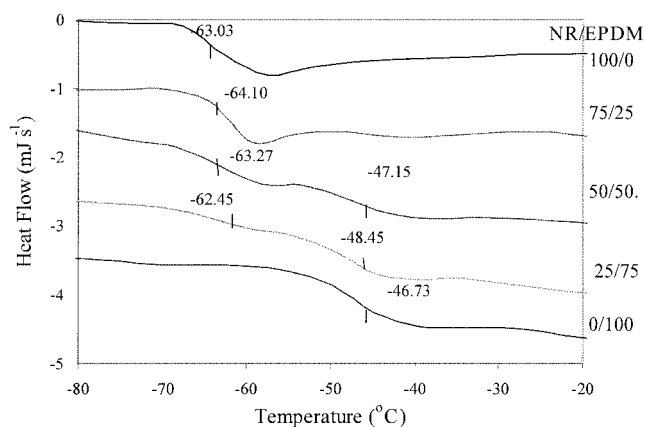


Figure 11 DSC thermograms obtained from various compositions of NR/EPDM.

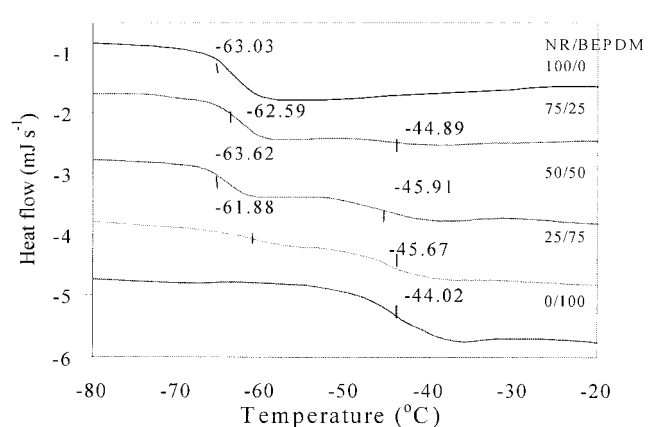


Figure 12 DSC thermograms obtained from various compositions of NR/BEPDM.

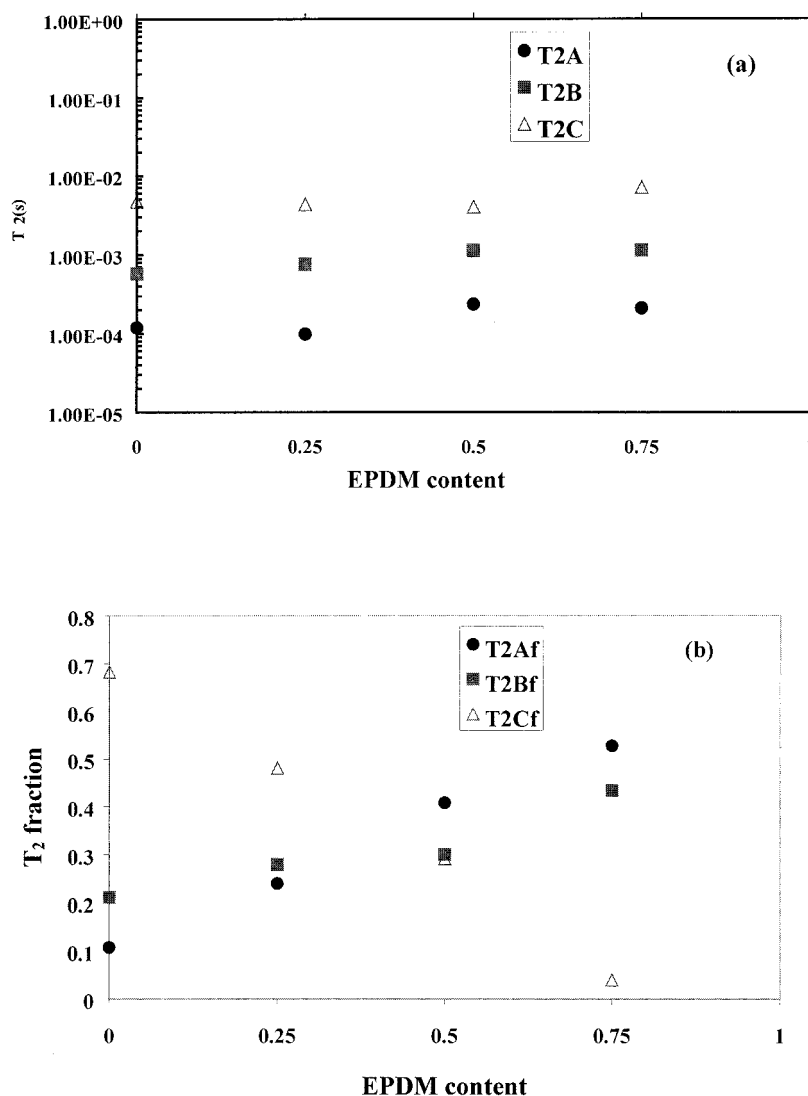


Figure 13 Dependency of T_2 (a) and its fraction (b) on EPDM contents of NR/EPDM blends.

pure rubbers and their blends at any blend ratio. However, the fractional amount of each T_2 component, as shown in Figure 13(b) as T_{2Af} , T_{2Bf} , and T_{2Cf} are dependent on EPDM contents. T_{2Af} and T_{2Bf} increase, whereas T_{2Cf} decreases with increasing EPDM contents. The degree of molecular motion is highest for T_{2C} . Consequently, we can see the highest T_{2C} fraction in the pure STR5L sample. It can be therefore related to STR5L in the blends because it decreases with an increase in EPDM contents. T_{2Af} and T_{2Bf} may therefore be related to EPDM. For the STR5L/BEPDM blends series, the same trend of results is found in Figure 14. An increase in BEPDM contents resulted in increases in T_{2Af} and T_{2Bf} . On the other hand, T_{2Cf} decreases with increasing BEPDM contents whereas STR5L contents decrease. This indicates the multiphase system in both STR5L/EPDM and STR5L/BEPDM blends, and thus they are incompatible.

CONCLUSIONS

Brominated EPDM was successfully prepared and confirmed by $^1\text{H-NMR}$ analysis. Rheological behavior of STR5L/EPDM and STR5L/BEPDM can be represented by a power law index calculated from the slope of log-apparent shear stress against log-apparent shear rate lines. The log additive rule of polymeric blend, viscosity, and glass-transition measurements were used to elucidate the blend compatibility. True shear viscosity of the whole set of blends showed negative deviations with respect to their additive values at all shear rates. The two T_g 's from the DSC thermograms at any blend composition were also obtained. From rheological and thermal analyses it can therefore be concluded that both NR/EPDM and NR/BEPDM blends are thermodynamically incompatible. The three components of spin-spin relaxation time of

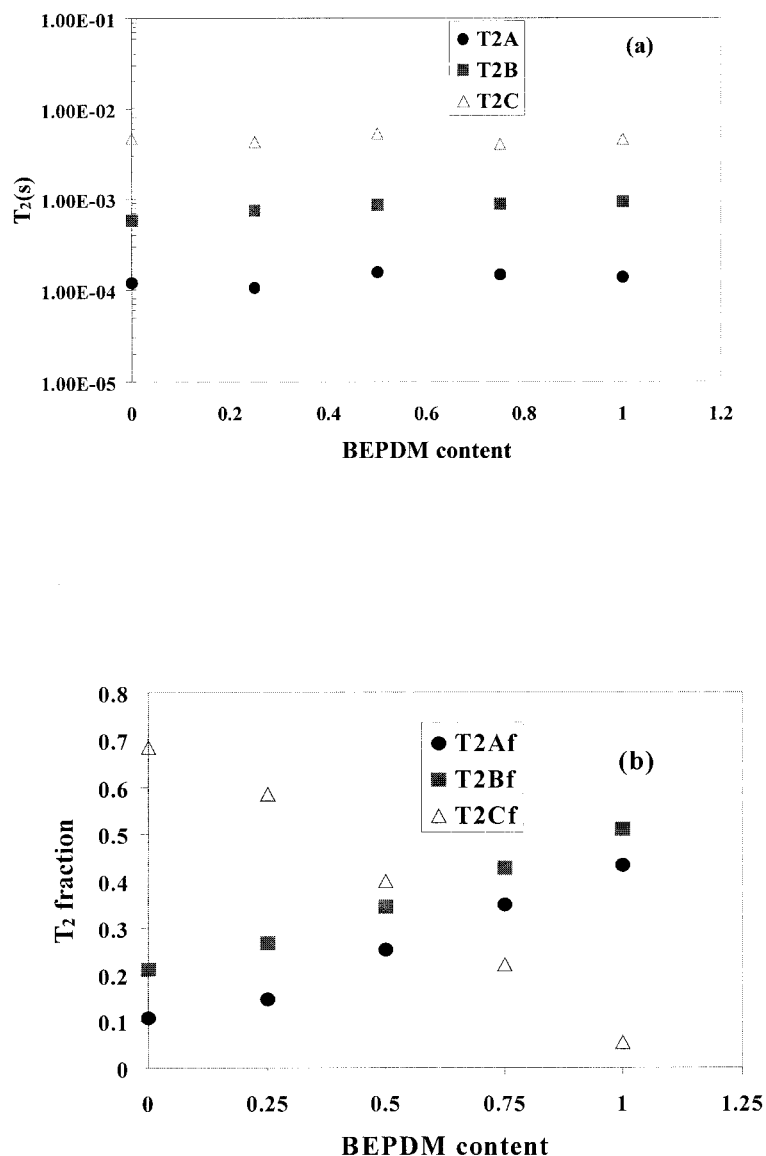


Figure 14 Dependency of T_2 (a) and its fraction (b) on BEPDM contents of NR/BEPDM blends.

the vulcanized blends and each component fraction measured by pulsed NMR depend on EPDM or BEPDM contents also suggested that they are incompatible.

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