Rheology and Properties of EPDM/BR Blends with or Without a Homogenizing Agent or a Coupling Agent

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SYNOPSIS

Rheology, dynamic mechanical properties, mechanical properties, and morphology of ethylene–propylene–diene rubber/butadiene rubber (EPDM/BR) blends with or without a homogenizing agent or a coupling agent were investigated. AAHR (a mixture of aliphatic and aromatic hydrocarbon resins) was used as a homogenizing agent and bis(3-triethoxysilyl propyl)tetrasulfide (TESPT) was used as a coupling agent. The dynamic mechanical analysis and the morphological studies revealed that EPDM and BR were incompatible and the addition of AAHR was very effective to plasticize the EPDM/BR blend and enhance the compatibility between EPDM and BR. It was found that the addition of an AAHR increased the amounts of bound rubbers and, hence, the vulcanizate properties such as tear strength and fatigue resistance of the EPDM/BR blends were improved. The blends of maleic anhydride-grafted EPDM and BR were also prepared and the properties were compared. The dynamic mechanical analysis and the morphological studies revealed that the addition of TESPT increased the weight of bound rubbers and provided better dispersion of carbon black, resulting in good mechanical properties such as tear strength and fatigue resistance of the vulcanized EPDM/BR blends. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Polymer blends have been intensively studied because of their theoretical and practical importance.[1-3] Among the blends widely investigated in rubber industries are natural rubber (NR)/styrene–butadiene rubber (SBR), NR/butadiene rubber (BR), and NR/BR/SBR.[4-10] Recently, the use of ethylene–propylene–diene rubber (EPDM) has attracted much interest to improve poor performances of other rubbers by blending, since EPDM has excellent outdoor properties such as good resistance to oxygen and ozone.[11-13] Dunn and Wall[14] blended EPDM and BR with NR to develop suitable materials for damping engine mounts having balanced properties of low oxidation degradation and high resilience. However, the poor compatibility of EPDM with other high diene rubber (IR and BR) limits the more versatile uses for

blends. Thus, several attempts have been made to improve the poor compatibility of EPDM with one of such high diene rubbers by introducing functional groups into the EPDM backbone. For instance, Coran[15] modified EPDM by grafting maleic anhydride (MAH) onto EPDM to obtain blends with high diene rubbers having improved tear strength and impact strength.

The term, "homogenizing agent," has been defined in rubber industries as a blend of low molecular weight polymeric resins of different polarities to promote the rapid homogenization of polymers of different molecular weight, viscosity, and polarity.[16] Since the rubber compounds or the rubber/rubber blends are generally very complicated systems containing so many rubber additives, the gross segregation of phases is one of major problems confronted with in final properties and processing. Sometimes, plasticizers perform the function to make mixtures of immiscible polymer blends or polymer compounds more stable by adhering strongly to the original components of the mixtures. Plasticizers, however,

Table I   Materials in This Work

Material	Description	Source
EPDM	Ethylene propylene diene rubber (E/P: 57/43 by mol %, ENB 2.3%)	Kumho E.P.
BR	cis-1,4-Polybutadiene rubber (cis: 98%)	Kumho Petrochem.
Carbon black	N351	Lucky
ZnO	Zinc oxide	Hanil
Process oil	Aromatic oil (A#2)	Michang
Stearic acid	Acid No. 200	Lucky
S	Sulfur	Miyong
NS	N-tert-butyl-2-benzothiazole sulfenamide	AKZO
AAHR	Mixture of aliphatic and aromatic hydrocarbon resins	B.A.S.F.
TESPT	Bis(3-triethoxysilyl propyl)tetrasulfide	Degussa
MBTS	Dibenzothiazyl disulfide	Dongyang
MAH	Maleic anhydride	Showa Ether

have the disadvantage of being prone to migration and bloom.[17,18] To overcome the migration problem, the use of homogenizing agents consisting of blends of low molecular weight polymeric resins of different polarities has been recommended.

Meanwhile, coupling agents are described as those materials which are specifically added to a rubber compound to form a physical or chemical bonding with inorganic fillers and to improve the dispersion properties of those fillers and allow the compound to have good mechanical properties.[19,20] Holland[21] reported that the coupling agent, N-4-nitroso-N-methylaniline, was effective in styrene–butadiene rubber (SBR) or butyl rubber (IIR). It has been known that the nitrodiamine-type coupling agent forms a chemical bonding with carbon black by producing biradicals during intensive mixing, which is effective to improve the dispersion of carbon black in the rubber matrix and to reduce the energy loss in the rubber–carbon black interface.[20] Another important type of coupling agent is an organosilane to form a bonding in the interface of silica and rubber.[22] Thus, several attempts have been made to improve the poor dispersion properties of those fillers as well as the compatibility of EPDM with one of such high diene rubbers by adding coupling agents into the blend matrix.

The objective of this work was to investigate the effect of a homogenizing agent on the compatibility and the properties of the EPDM/BR blends and the effect of the addition of a coupling agent on the dispersion properties of the EPDM/BR blends. For comparison, the compatibility and the vulcanizate

properties of the blends of BR with a graft copolymer of maleic anhydride (MAH) onto EPDM (EPDM-g-MAH) were also investigated.

EXPERIMENTAL

Materials

The materials used in this work are listed in Table I. The EPDM (M_n = 116,000, M_w = 313,700) having ethylidene norbonene (ENB) as a termonomer and BR having 98% of cis contents are all commercially available grades. The homogenizing agent, AAHR, a B.A.S.F. product, is a mixture of aliphatic and aromatic resins of the chemical structures in Scheme I. The EPDM-g-MAH was prepared by reacting EPDM with 2.0 phr of maleic anhydride (MAH) in the presence of 0.2 phr dibenzothiazyl disulfide (MBTS) in a Banbury mixer under the processing condition of 40 rpm at 230°C for 3 min.[23,24] The grafting of MAH onto EPDM was also identified on their FTIR spectra. The grafting of MAH onto EPDM was also proved by the increases in the gel contents (39.6%) and in the molecular weights of the graft copolymers (M_n = 127,700, M_w = 363,100). Bis(3-triethoxysilyl propyl)tetrasulfide (TESPT), developed by the Sumitomo Chemical Co. was used as a coupling agent.

Preparation of Blends

Unfilled EPDM/BR binary blends were prepared in a Haake-Buchler System 40 Brabender by mixing

Aliphatic resin

(a)

Aromatic resin

(b)

R = H, C_4H_9, C_8H_{17}, etc.
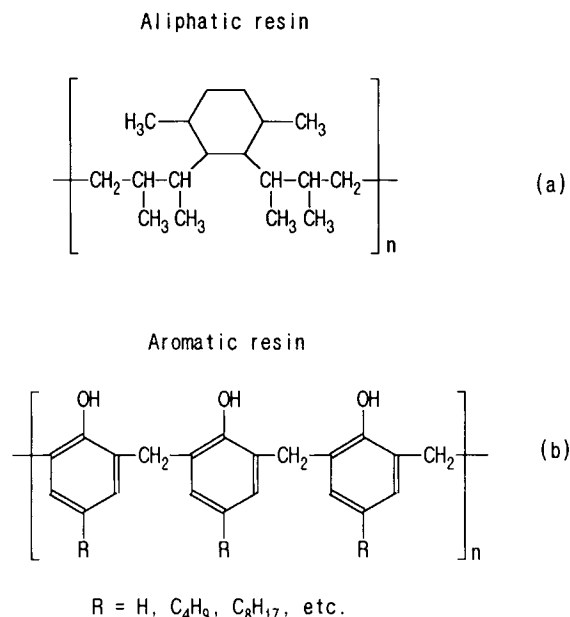
Scheme I Chemical structure of AAHR, a mixture of
(a) aliphatic resin and (b) aromatic phenolic resin.

rubbers for 30 min at 100°C. The polymer ratios
were 75/25, 50/50, and 25/75 EPDM/BR by weight.
Mixing of the carbon black-filled compounds was
done in a Banbury mixer using conventional mixing
procedures by two stages: In the first stage (without
curatives), masterbatch blends of EPDM (or
EPDM-g-MAH) and BR were prepared by mixing
the rubbers with 40 phr of carbon black for 6 min
at 155°C, 40 rpm rotor speed. Two EPDM/BR mas-
terbatch blends, one from the unmodified EPDM
and one from the maleic anhydride-modified EPDM,
were prepared. In the second stage, stocks for vul-
canization and evaluation were prepared from each
of the EPDM/BR and the EPDM-g-MAH/BR
masterbatch blends by the addition of other ingre-
dients such as sulfur and zinc oxide on a 6 × 12 in.
two-roll mill at 100°C for 5 min. Curing was done
in a thermofluid press. The test recipes are given in
Table II.

A masterbatch containing 2 phr sulfur, 5 phr zinc
oxide, 1 phr NS, and 10 phr process oil was used in
all experiments pertaining to blend polymers.
EPDM/BR blends containing AAHR or TESPT,
designated as EPDM/BR/AAHR or EPDM/BR/
TESPT ternary blends, were also prepared using
different ingredient contents as shown in Table II.

Measurements and Physical Testing

Molecular weight was determined by a gel perme-
ation chromatography (GPC; Waters 150C) at 140°C
using 1,2,4-trichlorobenzene (TCB) as an effluent.
IR spectra were taken on an attenuated total reflec-
tance FTIR spectroscopy (Bruker IFS 85). Thirty-
two scans were signal-averaged. Rheological prop-
erties of the unvulcanized blends were measured at
100°C by a capillary rheometer (Monsanto process-
ability tester). The dimension of a capillary was 1.5
mm in diameter with the L/D ratio of 20. The glass
transition temperature was measured using a differ-
ential scanning calorimeter (DSC; Perkin-Elmer
DSC7) at a heating rate of 20°C/min in nitrogen.

Dynamic mechanical properties were measured
using a dynamic mechanical analyzer (GABO
Eplexor-150N) at the frequency of 11 Hz with the
amplitude strain of 0.25%. The stress-relaxation
properties were measured by a dynamic stress re-
laxometer (DSR, BF Goodrich).[25] Morphology ob-
servations were done using transmission electron
microscopy (JEM-2000FX TEM). Samples were
microtomed and stained with osmium tetraoxide.
Cure characteristics, which include scorch time, cure
rate, and torque values, were measured over a 12
min period at 180°C using a Monsanto oscillating-
disc rheometer (Monsanto rheometer R-100) ac-
cording to ASTM Method D1084.

Tear strength was determined according to
ASTM D624 using a Die C specimen. The fatigue
resistance was measured at room temperature using
a fatigue-to-fail tester (Monsanto). Dumbell-shaped
samples of 5 × 76 mm size were subjected to the
cyclic tension with 124% of elongation at the rate
of 95 cycles/min. The number of cycles to show fail-
ure in the samples was taken as the fatigue-resis-
tance data.

For the determination of bound rubber contents,
0.2 g of samples with thickness below 0.5 mm were
dissolved in 100 mL of toluene at room temperature
for 10 days. After filteration, the bound rubber con-
tents (B) were determined from the change in weight
of samples before and after dissolving in toluene with
the following relationship:

$$B(\%) = \frac{R}{I} \times T - F$$

where B is the bound rubber content (%); R, the
weight residue (g) after dissolving in toluene; I, the
initial sample weight (g); T, the total filler content
(phr); and F, the inorganic filler content (phr).

Gel contents (%) of EPDM-g-MAH's were de-
termined from the ratio of weight residue, after 0.1
g of samples (caged in a cube of 100 mesh steel-wire
screen) had been placed in 100 mL of benzene for

40 h and dried under reduced pressure, to the initial sample weight. For the determination of the carbon black dispersion, samples of 5 × 3 mm size were attached to a microtome by rubber cement and freezed in liquid nitrogen. The carbon black dispersion was determined visually using an optical microscope (Optiphot Biological Microscope, Nikon) with a graticule in the eyepiece (ASTM D2663, Method B). The % black dispersed down to a given agglomerate size was derived from the number of total squares covered by black and the black volume loading.[26]

Figure 1   Melt viscosities vs. apparent shear rate of the EPDM/BR blend: (a) EPDM/BR (100/0); (b) EPDM/BR (75/25); (c) EPDM/BR (50/50); (d) EPDM/BR (25/75); (e) EPDM/BR (0/100).

RESULTS AND DISCUSSION

Rheological Properties and Cure Characteristics

Figure 1 shows the melt viscosity of the unvulcanized EPDM/BR blends with various polymer ratios as a function of apparent shear rate. One can see that the rheological behaviors show typical power-law behaviors for all the blends. The melt viscosity increased with increasing EPDM contents. Figure 2 shows the comparison of the rheological behaviors of the AAHR- or TESPT-added EPDM/BR ternary blend as well as of the EPDM-g-MAH/BR blend
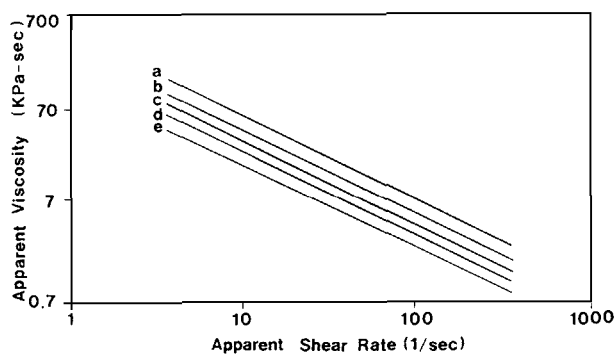
with that of the EPDM/BR blend having the same polymer ratios of 75/25 EPDM/BR by weight. It is seen that the addition of AAHR decreased the melt viscosity of the EPDM/BR blends, meaning that the AAHR functioned as a lubricant for the blends. Even though little is known about the actual basic mechanism of the homogenizing effect of AAHR, the lubricant function of the AAHR can be explained as follows: The AAHR is a blend of aliphatic and aromatic resins of differing polarities; aliphatic res-

Table II   Recipes of Rubber Compounds

Exp. No.	Rubber Ratio	Ingredient (phr)
a	EPDM/BR(100/0)	—[a]
b	EPDM/BR(75/25)	—
c	EPDM/BR(50/50)	—
d	EPDM/BR(25/75)	—
e	EPDM/BR(0/100)	—
f	EPDM/BR(75/25)	N351(40), AAHR (10 phr)[b]
g	EPDM/BR(50/50)	"
h	EPDM/BR(25/75)	"
i	EPDM/BR(75/25)	N351(30), silica(15) TESPT(3.75)[c]
j	EPDM/BR(50/50)	"
k	EPDM-g-MAH/BR(100/0)	—[a]
l	EPDM-g-MAH/BR(75/25)	—
m	EPDM-g-MAH/BR(50/50)	—
n	EPDM-g-MAH/BR(25/75)	—

[a] A masterbatch containing 40 phr N351 carbon black, 2 phr sulfur, 5 phr zinc oxide, 1 phr NS, and 10 phr process oil were used in all experiments pertaining to blend polymers, unless otherwise specified.

[b] The amount of AAHR was fixed at 10 phr based on the total amount of EPDM and BR mixtures. The formulations were the same as the recipes of (a)–(e) except that they contain 10 phr of AAHR.

[c] A masterbatch containing 100 phr polymer mixtures, 2 phr sulfur, 5 phr zinc oxide, 1 phr NS, 2 phr of stearic acid, and 10 phr process oil was used in all experiments pertaining to blend polymers. The amount of TESPT was fixed at 3.75 phr based on the total amount of EPDM and BR mixtures. The formulations were the same as the receipes of (a)–(e) except that they contain 30 phr of N351, 15 phr of silica, and 3.75 phr of TESPT, instead of 40 phr N351 carbon blank.
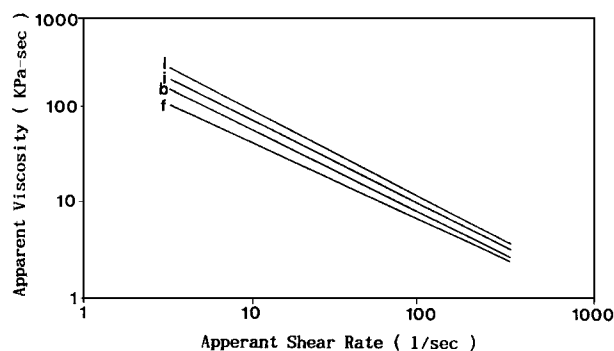
Figure 2   Melt viscosities vs. apparent shear rate of the EPDM/BR blends: (b) EPDM/BR; (f) EPDM/BR/ AAHR; (i) EPDM/BR/TESPT; (l) EPDM-g-MAH/BR. The polymer ratios of EPDM to BR are 75/25 by weight.

ins are nonpolar, whereas aromatic resins are very polar. In polymer blending, this mixture of polarities gives a true solvating effect in wetting out two component polymers, here EPDM and BR. At the same time, their polymeric nature ensures that they have a high viscosity at mixing temperatures which maintains high shear during mixing. This latter effect can be useful in improving the breakdown, incorporation, and dispersion of carbon blacks, fillers, and crumb in compounds. This effect optimizes dispersion and processability through more efficient mixing. A consistent and faster mixing time can be achieved. Their general effect is, therefore, to give a more efficient mixing action which leads to improved processability.

The comparison of the rheological behaviors of the unvulcanized EPDM/BR/TESPT ternaty blend with that of the EPDM/BR blend indicates, however, that the EPDM/BR/TESPT ternary blend exhibits higher melt viscosity than that of the EPDM/BR blends. The result implies that the silane-type TESPT is an effective coupling agent for silica for EPDM/BR blends due to the buildup of silica-to-rubber bonds.[22,27] Scheme II illustrates the possible chemical reaction between the silica and TESPT and the buildup of silica-to-rubber bonds.

The EPDM-g-MAH/BR blend, however, exhibited higher viscosity than both the AAHR-added EPDM/BR ternary blend and the EPDM/BR binary blend. The result may be ascribed to the higher gel contents and molecular weight of the graft copolymer. The rheographs of the EPDM/BR masterbatch blends with different polymer ratios are shown in Figure 3. It is seen that the EPDM-rich blends exhibit higher torques and lower cure rates than do the BR-rich blends, as can be expected from

the viscosity behavior in Figure 1. Figure 4 illustrates the effect of the addition of AAHR on the curing characteristics of the EPDM/BR masterbatch blend of 75/25 composition by weight. The cure rate was not changed significantly but the scorch time became longer when AAHR was added. The result may be related to the reduced melt viscosity and, hence, the improved processability when AAHR was added.

It is seen that the EPDM/BR/TESPT ternary blend exhibits higher torque and a faster cure rate than that of the EPDM/BR blends without the coupling agent, as can be expected from the viscosity behavior in Figure 2. The effect of coupling agents on the curing properties of EPDM/BR blends is more clearly seen in the blend having the 50/50 composition, as shown in Figure 5. The scorch time became shorter when the coupling agent, TESPT, was added. The result may be related to the increasing of melt viscosity when the coupling agents were added. In the case of the EPDM/BR/TESPT blend, the scorch time became shorter and the cure rate became faster when compared to the EPDM/BR blend.

Moreover, it should be noted that in case of the EPDM-g-MAH/BR blends the scorch time became shorter and the cure rate became faster when compared to both the EPDM/BR blend and the EPDM/ BR/AAHR ternary blend. The result implies that there might exist co-cure characteristics in the EPDM-g-MAH/BR blends plausibly because of the presence of the functional group, MAH, in the graft copolymer to induce the *in situ* formation of compatibilizing interchain copolymers of EPDM and BR. The *in situ* formation of interchain copolymers of EPDM and BR could be expected as shown in Scheme III, although more concrete data are needed to draw conclusions.

Dynamic Properties

The elastic moduli of EPDM/BR masterbatch blends with different polymer ratios are illustrated in Figure 6 as a function of temperature. The modulus increased with EPDM contents. Figure 7 compares the moduli of the EPDM-g-MAH/BR blend and the AAHR- or TESPT-added EPDM/BR blend as well as the EPDM/BR blend having the same polymer ratios of 50/50 by weight. A significant difference was not observed in the elastic modulus behavior among them, except the slight decrease in modulus over the lower-temperature ranges, say, between -20 and $-60°C$, for the AAHR-added EPDM/BR blend. The slight decrease in modulus

Modification reaction with TESPT

TESPT / Silica intermediate

Build-up of filler-to-rubber bonds

(Rubber: EPDM and/or BR)
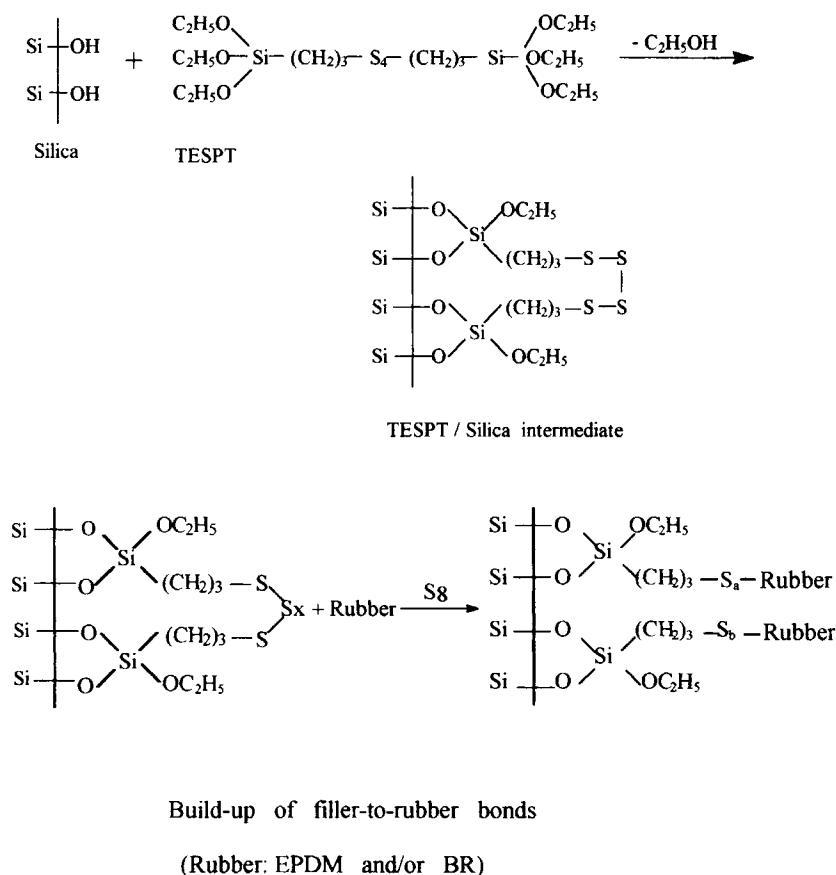
Scheme II Possible chemical reaction between the silica and TESPT and the buildup of silica-to-rubber bonds.

for the EPDM/BR/AAHR blend may be related to the plasticizing effect of AAHR for the EPDM and BR, taking it into consideration that the ternary blend having the polymer ratio of 50/50 EPDM/BR exhibits similar modulus behavior as that of the BR-rich blends (compare Figs. 6 and 7).

Figure 8 shows the tan δ vs. temperature curves of EPDM/BR blends with different polymer ratios. The location of the peak in the tan δ–temperature curve corresponds to the glass transition temperature (T_g) of the polymer. As expected, EPDM and BR were incompatible and they showed two separate T_g's. The plasticizing function of AAHR for the EPDM/BR blend can be seen, however, from the tan δ behavior in Figure 9. In Figure 9, one can see that when AAHR or TESPT was added to the EPDM/BR blend of 50/50 composition by weight

the maximum point of tan δ, i.e., T_g, of EPDM shifted downward to that of BR. The result means that the AAHR acted as a lubricant for the EPDM/BR blend. It is also interesting to note that the TESPT acted also as a plasticizer for EPDM and BR as well as a coupling agent to the buildup of silica-to-rubber bonds.[27] No clear shift of T_g was observed, however, in the case of the EPDM-g-MAH/BR blend having the same polymer ratio.

Table III shows the stress-relaxation properties of the blends. In this table, the maximum torque (TM, in joules) was taken as the torque when for 0.035 radian of rotor deflection the samples, preheated at 100°C for 1 min, were subjected to the load of 2.21 kN for 0.005 s. The sig-2 (in joule s) and the stress-relaxation time (λ, in s) denote that the summation of torques recorded up to 2 s and the
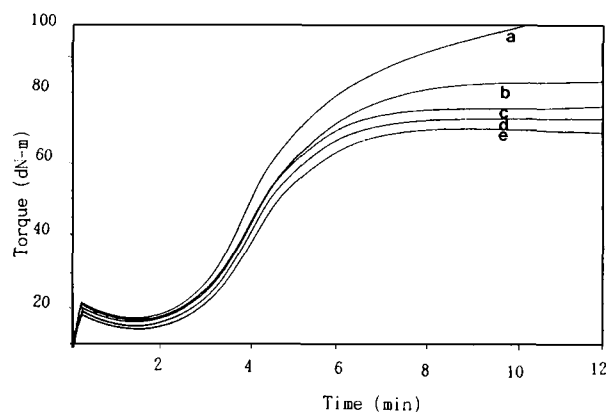
Figure 3 Rheograph of the EPDM/BR blends with different polymer ratios: (a) EPDM/BR (100/0); (b) EPDM/BR (75/25); (c) EPDM/BR (50/50); (d) EPDM/BR (25/75); (e) EPDM/BR (0/100).

Figure 4 Rheographs of various EPDM/BR blends: (b) EPDM/BR; (f) EPDM/BR/AAHR; (i) EPDM/BR/TESPT; (l) EPDM-g-MAH/BR. The polymer ratios of EPDM to BR are 75/25 by weight.

time elapsed from the origin until the torque reduces up to 13.5% of the TM, respectively. In case of the EPDM/BR blends, all the stress-relaxation data increased with increasing EPDM contents due to the increases in the melt viscosity and elasticity. In Table III, however, the AAHR-added EPDM/BR blends showed decreased TMs and relaxation times due to the plasticizing effect of AAHR when compared to EPDM/BR blends without AAHR, regardless of polymer ratios.

In Table III, however, the EPDM/BR/TESPT ternary blend showed higher maximum torques (TMs) and relaxation times (λ) due to the coupling agent, regardless of polymer ratios. The increases of the stress-relaxation data for both polymer ratios of 75/25 and 50/50 may be due in part to the improved dispersion characteristics of carbon black for the blends by the coupling between rubber and carbon black and thus inhibiting the Brownian motion of the rubber molecules.[19,28]

The increases of the stress-relaxation data in case of the EPDM-g-MAH/BR blends for both polymer ratios of 75/25 and 50/50 may be due in part to the reduced molecular mobilities resulting from the co-cure characteristics for the blends, as already discussed in Figure 5.

Morphology

Figure 10 shows the morphology of the carbon black-filled EPDM/BR masterbatch blends having various polymer ratios. In these TEM micrographs, the domain consisting of carbon black agglomerates is the BR phase, because the high diene rubberlike BR has
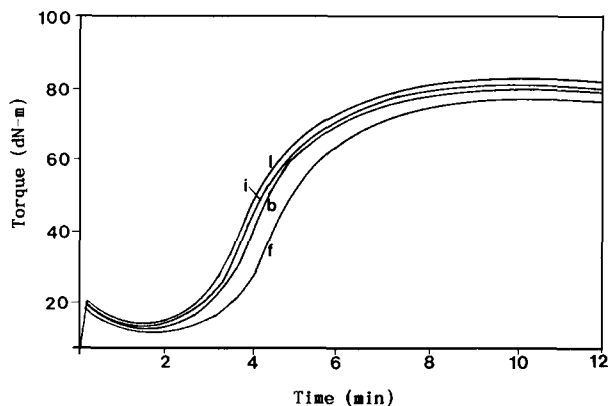
a much larger affinity with carbon black than does a saturated elastomer like EPDM. EPDM and BR showed gross phase separation. The morphology in Figure 11, however, shows clearly the enhanced compatibility of EPDM and BR in the presence of AAHR. In the TEM micrographs of EPDM/BR blends of 75/25 composition by weight, the BR phase of large domain size is dispersed in the EPDM matrix for the EPDM/BR blend, but the size of BR domain reduces significantly when AAHR or TESPT was added to the EPDM and BR binary blend.

In the previous sections, the dynamic mechanical properties as well as the rheological properties showed that the AAHR acted as a plasticizer for the EPDM/BR blend. It should be noted that, however,
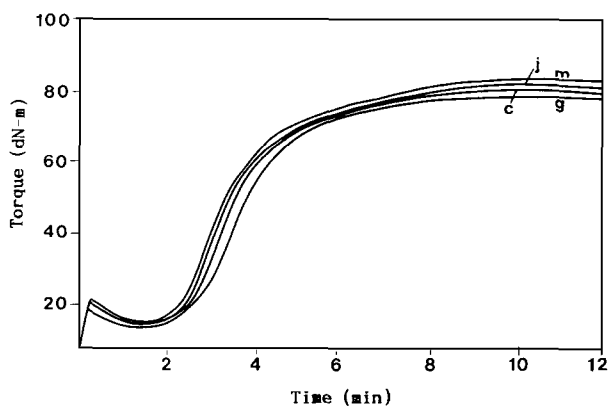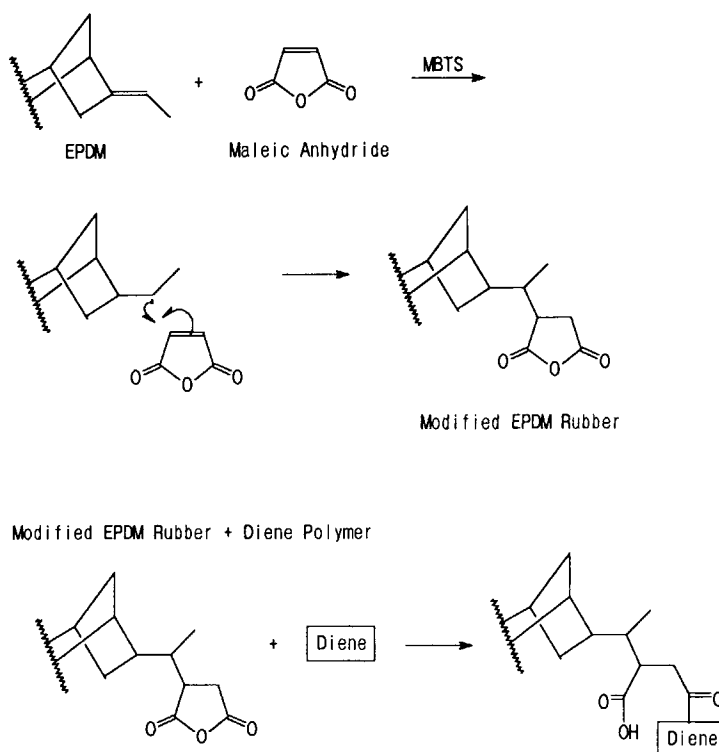

Figure 5 Rheographs of various EPDM/BR blends: (c) EPDM/BR; (g) EPDM/BR/AAHR; (j) EPDM/BR/TESPT; (m) EPDM-g-MAH/BR. The polymer ratio of EPDM to BR is 50/50 by weight.

Scheme III   Possible *in situ* formation of interchain copolymers of EPDM-g-MAH and diene rubber (BR).

the homogenizing agent, AAHR, might be also considered as a "compatibilizer" for the EPDM/BR blend as well as a lubricant, based on the morphological features in Figures 10 and 11, even though the nature of the compatibilization is not clearly understood at the moment. Compatibilizers have

been commonly used to enhance the compatibility of incompatible polymer blends, where the compatibilizers, often referred to as "interfacial agents," are defined as certain polymeric species to be able to improve interfacial adhesion between otherwise gross-phase-separated polymer pairs by reducing the interfacial energy between the phases.[29-31]
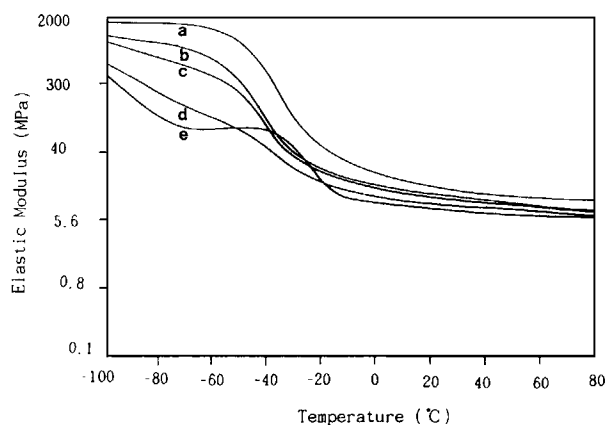

Figure 6   Elastic modulus of EPDM/BR blends with different polymer ratios as a function of temperature: (a) EPDM/BR (100/0); (b) EPDM/BR (75/25); (c) EPDM/ BR (50/50); (d) EPDM/BR (25/75); (e) EPDM/BR (0/ 100).
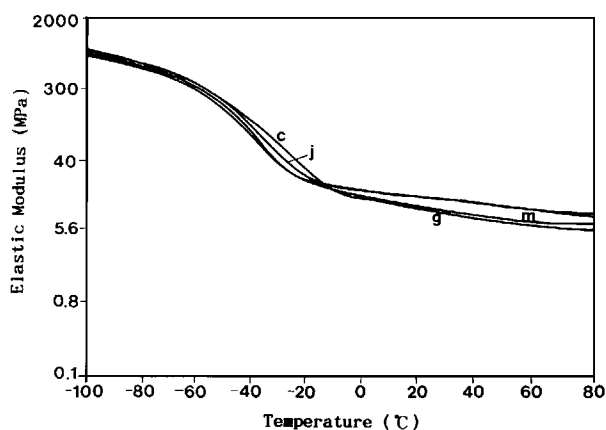

Figure 7   Elastic modulus of EPDM/BR blends as a function of temperature: (c) EPDM/BR; (g) EPDM/BR/ AAHR; (j) EPDM/BR/TESPT; (m) EPDM-g-MAH/BR. The polymer ratios of EPDM to BR are 50/50 by weight.
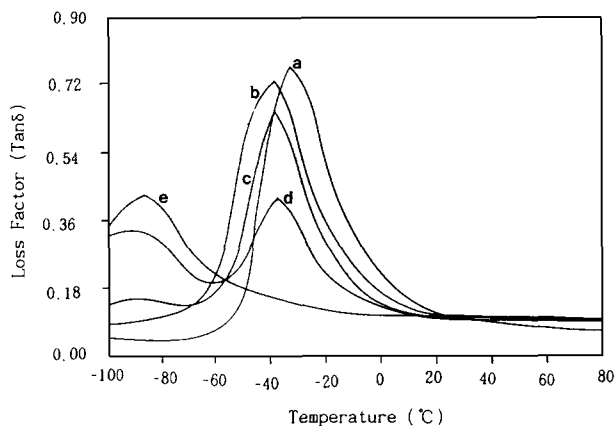
Figure 8   Tan δ of EPDM/BR blends with different polymer ratios as a function of temperature: (a) EPDM/BR (100/0); (b) EPDM/BR (75/25); (c) EPDM/BR (50/50); (d) EPDM/BR (25/75); (e) EPDM/BR (0/100).

The morphology in Figure 11 also shows clearly the enhanced compatibility of EPDM and BR in the presence of TESPT. Also, in the TEM imcrograph of EPDM/BR blends of 50/50 composition by weight, shown in Figure 12, the BR phase of a large domain size is dispersed in the EPDM matrix for the EPDM/BR blend, but the size of the BR domain reduces significantly when TESPT was added to the EPDM and BR binary blend. The EPDM/BR/TESPT blend shows finer domain morphology than does the EPDM/BR blend. Thus, one can conclude that the addition of TESPT to the EPDM/BR blend is effective to enhance the compatibility between EPDM and BR.

The EPDM-g-MAH/BR blend shows finer domain morphology than does the EPDM/BR blend but less finer morphology than does the EPDM/BR/AAHR ternary blend. Thus, one can conclude that the addition of AAHR to the EPDM/BR blend is more effective to enhance the compatibility between EPDM and BR than is the modification of EPDM by grafting MAH onto EPDM backbone.

Vulcanizate Properties

Table IV shows the bound rubber contents for the EPDM/BR blends. It is seen that the bound rubber contents increase with increasing BR contents, because BR has better carbon black dispersion than does EPDM. The carbon black dispersion is summarized in Table V. The % carbon black dispersion increases as BR contents increase for the EPDM/BR blends. The high carbon black dispersion of BR is ascribed to its flexible molecular chain structure.[32]

Note that the dispersions are higher in the order EPDM/BR/AAHR ternary blend > EPDM/BR/TESPT ternary blend > EPDM-g-MAH/BR blend > EPDM/BR blend, regardless of the polymer ratios.

Table IV also shows the bound rubber contents and the tear strength of the AAHR- or TESPT-added EPDM/BR blends and the EPDM-g-MAH/BR blends. The tear strength of the blends increased with increasing bound rubber contents, resulting from better carbon black dispersion and, hence, a better reinforcing effect of carbon black. The higher tear strength of EPDM/BR blends in the presence of AAHR should be noted, since the addition of AAHR not only improved the processability but also enhanced the vulcanizate properties of the EPDM/BR blends.

The higher tear strength of EPDM/BR blends in the presence of TESPT should be also noted, since the addition of TESPT enhanced the vulcanizate properties of the EPDM/BR blends. The higher tear strength for the EPDM/BR/TESPT blend is due to the coupling effect of TESPT with carbon black by forming biradicals during intensive mixing and then increasing bound rubber contents.

Of interest is the fact that the EPDM-g-MAH/BR blends showed higher tear strength when compared to that of the AAHR-added EPDM/BR blends, although they did not have higher bound rubber contents. The result may be ascribed to the combined effects of the high molecular weight and gel contents of the MAH-grafted EPDM and the co-cure characteristics of the EPDM-g-MAH/BR blends.
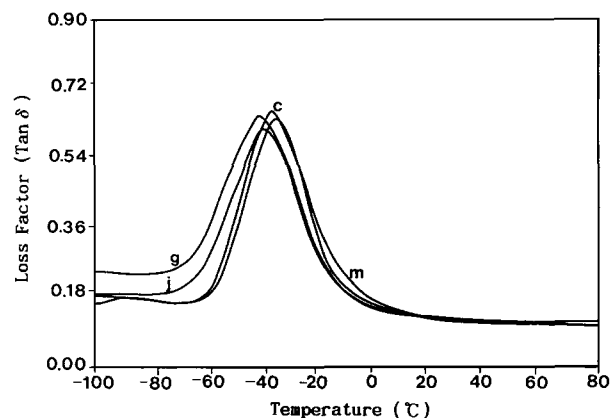

Figure 9   Tan δ of EPDM/BR blends as a function of temperature: (c) EPDM/BR; (g) EPDM/BR/AAHR; (j) EPDM/BR/TESPT; (m) EPDM-g-MAH/BR. The polymer ratios of EPDM to BR are 50/50 by weight.

Table III   Stress-relaxation Data of Various EPDM/BR Blends

Polymer Ratio	TM (joule)	Sig-2 (joule s)	λ (s)[a]
EPDM/BR(100/0)	25.88	13.90	950
EPDM/BR(75/25)	23.28	13.33	899
EPDM/BR(50/50)	19.66	12.43	891
EPDM/BR(25/75)	19.32	11.64	799
EPDM/BR(0/100)	17.97	10.06	681
EPDM/BR(75/25)/AAHR[b]	22.04	12.43	662
EPDM/BR(50/50)/AAHR[b]	18.65	10.06	594
EPDM/BR(75/25)/TESPT[c]	24.19	16.61	1370
EPDM/BR(50/50)/TESPT[c]	22.26	15.93	1351
EPDM-g-MAH/BR(75/25)	23.96	16.27	1069
EPDM-g-MAH/BR(50/50)	21.81	14.24	933

[a] TM: maximum torque for 0.035 radian of rotor deflection when samples were subjected to the load of 2.21 kN for 0.005 s. Sig-2: summation of torques recorded up to 2 s. λ: stress relaxation time.
[b] The amount of AAHR was fixed at 10 phr based on the total amount of EPDM and BR mixtures.
[c] The amount of TESPT was fixed at 3.75 phr based on the total amount of EPDM and BR mixtures.

The fatigue properties of blends are summarized also in Table IV. The trends in the fatigue properties of the blends was the same as in the tear strength, i.e., the BR-rich blends showed higher fatigue resistance than that of the EPDM-rich blends and the addition of AAHR increased the fatigue properties of EPDM/BR blends due to the increased bound rubber contents. The higher fatigue resistance of the EPDM-g-MAH/BR blends was also noted, as in the case of tear strength.

CONCLUSIONS

In this work, studies were made on the effect of the addition of a homogenizing agent and a coupling agent for the carbon black and/or silica-filled EPDM/BR blends on the compatibility and the vulcanizate properties of EPDM/BR blends. AAHR, a B.A.S.F. product of a mixture of aliphatic and aromatic hydrocarbon resins, was used for a homogenizing agent. TESPT was used as a coupling
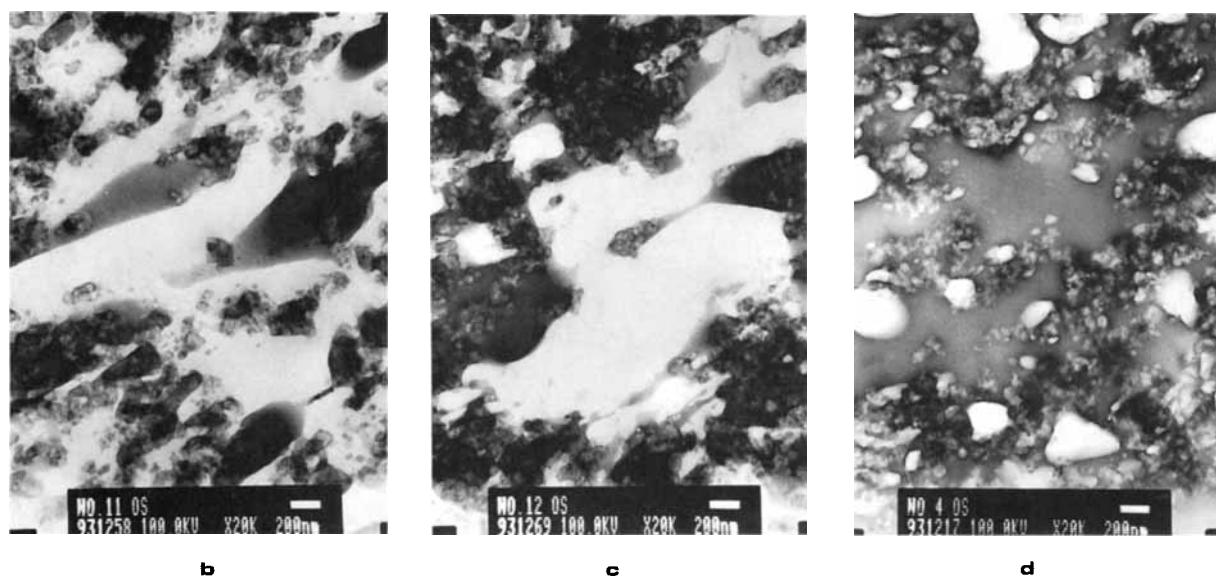

b   c   d

Figure 10   TEM micrographs of the EPDM/BR blends with different polymer ratios: (b) EPDM/BR (75/25); (c) EPDM/BR (50/50); (d) EPDM/BR (25/75).
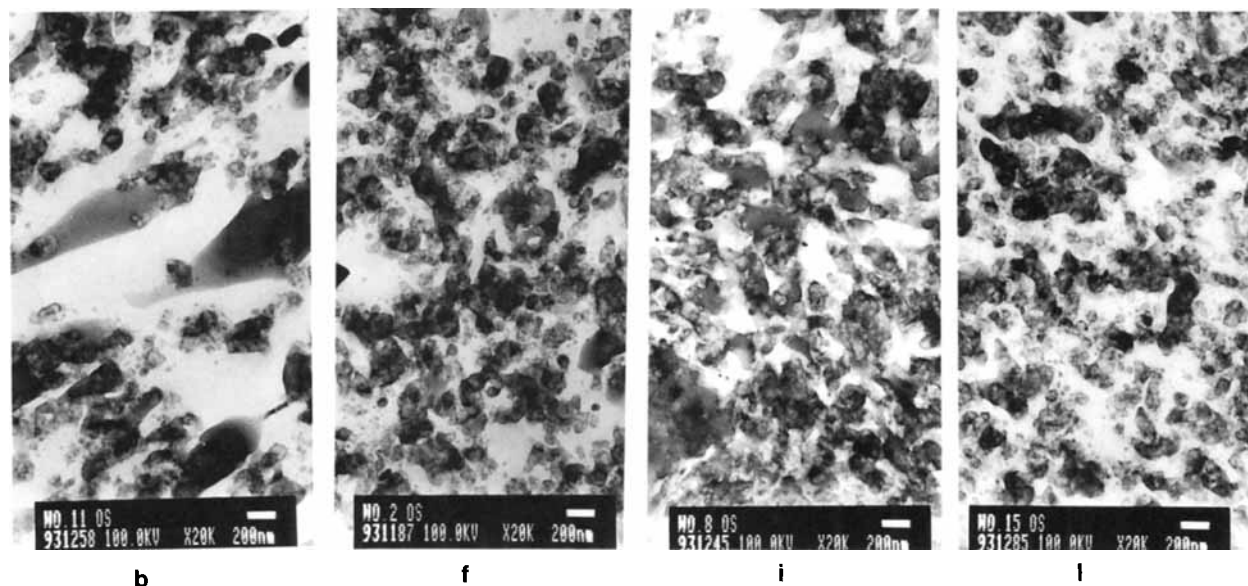
Figure 11   TEM micrographs of the EPDM/BR blends with different polymer ratios:
(b) EPDM/BR; (f) EPDM/BR/AAHR; (i) EPDM/BR/TESPT; (l) EPDM-g-MAH/BR.
The polymer ratios of EPDM to BR are 75/25 by weight.

agent. For comparison, the compatibility and the properties of the blends of BR with EPDM-g-MAH were also investigated, which have been prepared for this work. It was found that the melt viscosity, elastic modulus, and tan δ were increased with increasing EPDM contents. The rheological and the dynamic mechanical measurements along with the

morphology revealed that the AAHR acted as a plasticizer for the EPDM/BR blend and the addition of AAHR is effective to enhance the compatibility between EPDM and BR. It was also found that the addition of AAHR is more effective to lubricate the EPDM/BR blend as well as to improve the compatibility of the blend than is the grafting
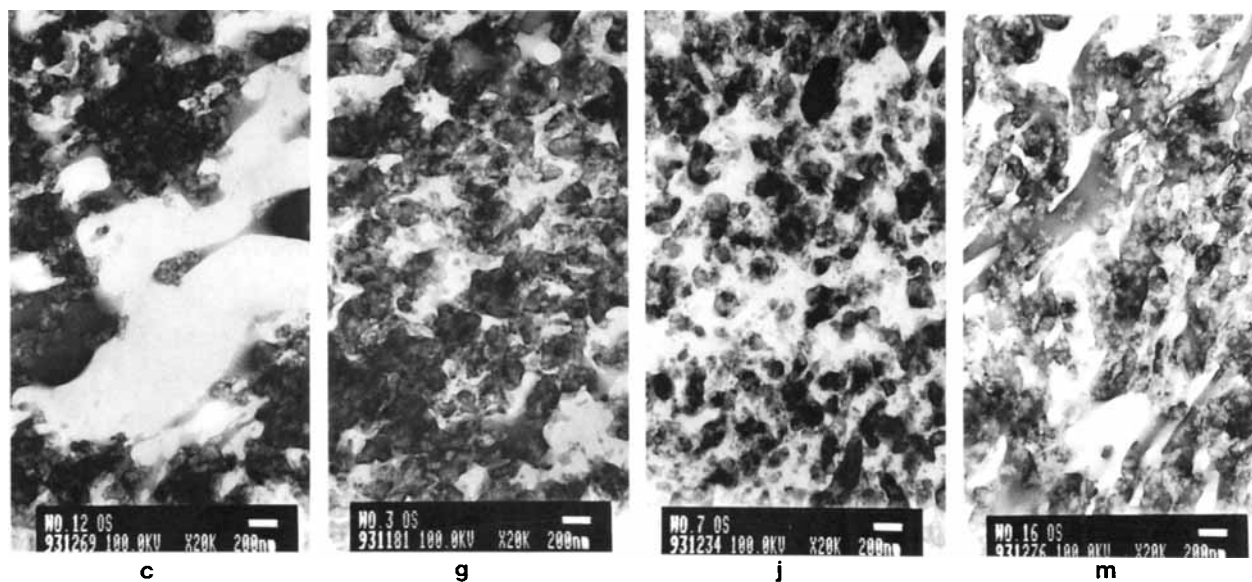

Figure 12   TEM micrographs of the EPDM/BR blends with different polymer ratios:
(c) EPDM/BR; (g) EPDM/BR/AAHR; (j) EPDM/BR/TESPT; (m) EPDM-g-MAH/BR.
The polymer ratios of EPDM to BR are 50/50 by weight.

Table IV   Bound Rubber Contents, Tear Strength, and Fatigue-to-failure Data of Various EPDM/BR Blends

Polymer Ratio	Bound Rubber Contents (%)	Tear Strength (Nm)	Fatigue to Failure (cycle)
EPDM/BR(100/0)	13.3	2.72	124,500
EPDM/BR(75/25)	14.2	2.65	168,100
EPDM/BR(50/50)	14.5	2.55	340,500
EPDM/BR(25/75)	15.2	2.50	466,600
EPDM/BR(0/100)	15.9	2.46	787,600
EPDM/BR(75/25)/AAHR[a]	15.0	3.14	195,000
EPDM/BR(50/50)/AAHR[a]	16.2	2.94	389,400
EPDM/BR(75/25)/TESPT[b]	22.8	3.23	200,100
EPDM/BR(50/50)/TESPT[b]	22.7	3.34	392,400
EPDM-g-MAH/BR(75/25)	14.8	3.33	200,300
EPDM-g-MAH/BR(50/50)	15.1	3.04	398,500

[a] The amount of AAHR was fixed at 10 phr based on the total amount of EPDM and BR mixtures.
[b] The amount of TESPT was fixed at 3.75 phr based on the total amount of EPDM and BR mixtures.

of MAH onto EPDM. The weight percent of bound rubber was increased with increasing BR contents. The addition of AAHR increased the amounts of bound rubbers and thus the vulcanizate properties of the EPDM/BR blends. It was also found that there exists co-cure characteristics in the EPDM-g-MAH/BR blends.

The rheological and the dynamic mechanical measurements along with the morphology revealed that the addition of TESPT is also effective to enhance the compatibility between EPDM and BR. It was found that the addition of TESPT increased

the amounts of bound rubbers and, thus, the vulcanizate properties of the EPDM/BR blends.

Table V   Carbon Black Dispersion of Various EPDM/BR Blends

Polymer Ratio	Carbon Black Dispersion (%)
EPDM/BR(100/0)	90.0
EPDM/BR(75/25)	92.2
EPDM/BR(50/50)	94.9
EPDM/BR(25/75)	98.2
EPDM/BR(0/100)	98.8
EPDM/BR(75/25)/AAHR[a]	97.4
EPDM/BR(50/50)/AAHR[a]	98.0
EPDM/BR(75/25)/TESPT[b]	96.0
EPDM/BR(50/50)/TESPT[b]	96.6
EPDM-g-MAH/BR(75/25)	95.2
EPDM-g-MAH/BR(50/50)	95.6

[a] The amount of AAHR was fixed at 10 phr based on the total amount of EPDM and BR mixtures.
[b] The amount of TESPT was fixed at 3.75 phr based on the total amount of EPDM and BR mixtures.

REFERENCES

1. D. R. Paul and S. Newman, in *Polymer Blends*, Academic Press, New York, 1978, Vols. I and II.
2. L. A. Utracki, *Polymer Alloys and Blends Thermodynamics and Rheology*, Hanser, New York, 1989.
3. O. Olabishi, L. M. Robinson, and M. T. Shaw, *Polymer–Polymer Miscibility*, Academic Press, New York, 1979.
4. T. Inoue, *Int. Polym. Sci. Technol.*, **14**, 9 (1987).
5. K. Fuhimoto and N. Yoshimura, *Rubb. Chem. Technol.*, **39**, 1109 (1966).
6. K. Shah, K. Min, and J. White, *Polym. Eng. Sci.*, **28**, 1277 (1988).
7. M. H. Walters and D. N. Keyte, *Rubb. Chem. Technol.*, **35**, 62 (1962).
8. D. J. Zanig, F. L. Magnus, W. L. Hsu, A. F. Halasa, and M. E. Testa, *Rubb. Chem. Technol.*, **66**(4), 538 (1993).
9. C. M. Roland, *Rubb. Chem. Technol.*, **62**(4), 456 (1989).
10. C. M. Roland and C. A. Trask, *Rubb. Chem. Technol.*, **62**, 896 (1989).
11. R. D. Allen, *J. Elastom. Plat.*, **15**, 19 (1983).
12. C. S. Ha and S. C. Kim, *J. Appl. Polym. Sci.*, **37**, 317 (1989).
13. E. N. Kresge, *Rubb. Chem. Technol.*, **64**(3), 469 (1991).
14. J. R. Dumn and D. W. Wall, Paper No. 48, presented at the meeting of the Rubber Division, American

Chemical Society, Las Vegas, NV, May 27–June 1, 1990.

15. A. Y. Coran, *Act. Chem.*, **5**, 95 (1991).
16. Schill & Seilacher GmbH & Co., Technical Information No. 68, Hamburg, Germany, 1989.
17. A. Rudin, *The Elements of Polymer Science and Engineering—An Introductory Text for Engineers and Chemists*, Academic Press, New York, 1982, p. 456.
18. R. Gachter and H. Muller, *Plastics Additives Handbook*, 2nd ed., Hanser, Munich, 1984, Chap. 5.
19. W. F. Watson, *Ind. Eng. Chem.*, **47**, 1281 (1955).
20. T. Yamaguchi, I. Kurimoto, K. Ohashi, and T. Oita, Paper No. 59, presented at the 134th Rubber Division Meeting of the American Chemical Society, Cincinnati, OH, Oct. 18, 1988.
21. L. W. Holland, U.S. Pat. 2,315,855 (1940).
22. S. Wolff, presented at the First France–German Rubber Symposium, Alsame, France, Nov. 14–16, 1985.
23. M. Xanthos, *Polym. Eng. Sci.*, **28**, 1392 (1988).

24. R. Holsti-Miettinen and J. Seppala, *Polym. Eng. Sci.*, **32**, 868 (1992).
25. E. R. Harrell, R. P. Porter, and N. Nakajima, *Rubb. Chem. Technol.*, **64**(2), 254 (1991).
26. G. R. Hammed, *Rubb. Chem. Technol.*, **55**, 151 (1981).
27. S. Wolff, *Rubb. Chem. Technol.*, **55**, 967 (1982).
28. J. A. Ayala, W. M. Hass, F. D. Kistler, and G. A. Joyce, *Rubb. Chem. Technol.*, **64**, 19 (1990).
29. D. R. Paul, C. E. Locke, and C. E. Vinson, *Polym. Eng. Sci.*, **13**, 202 (1973).
30. C. E. Locke and D. R. Paul, *J. Appl. Polym. Sci.*, **17**, 2597 (1973).
31. D. R. Paul, C. E. Locke, and C. E. Vinson, *Polym. Eng. Sci.*, **12**(3), 157 (1972).
32. W. M. Hess, *Rubb. Chem. Technol.*, **64**(3), 386 (1991).