The Korean Journal of Rheology,
Vol. 7, No. 1, April 1995 pp. 60-67

〈연구논문〉

EPDM/BR 블렌드의 물성에 미치는 커플링결합제의 영향

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(1995년 3월 22일 접수)

Effects of Coupling Agents on the Properties of EPDM/BR Blends

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(Received March 22, 1995)

요 약

EPDM/BR 블렌드의 물성에 미치는 커플링결합제의 영향을 조사하였다. N,N'-(bis(2-methyl-2-nitropropyl))- 1,6-diamino hexane) (MNPDH) 와 bis(3-triethoxysilyl propyl)- tetrasulfide (TESPT)의 두 가지 종류의 커플링결합제를 사용하였다. EPDM/BR 블렌드 및 EPDM/BR/MNPDH 또는 EPDM/BR/TESPT 블렌드의 용융점도, 탄성률 및 tan δ 를 모세관 점도계, 동적점탄성장치, 및 동적응력 완화측정장치로 조사하였다. 동적점탄성 및 형태학적 연구 결과 MNPDH 또는 TESPT를 첨가할 경우 결합고무 함량이 증가하고 카본블랙의 분산성이 좋아져 가황된 EPDM/BR 블렌드의 인열강도 및 내피로성 등의 물성이 향상되었다.

Abstract—Effects of coupling agents on the properties of EPDM/BR blends were investigated. Two kinds of coupling agents were used: N,N'-(bis(2-methyl-2-nitropropyl))- 1,6-diamino hexane) (MNPDH) and bis(3-triethoxysilyl propyl)- tetrasulfide (TESPT). The melt viscosity of the EPDM/BR blends in the unvulcanized state and the elastic modulus and tan δ of the vulcanized EPDM/BR blends with or without coupling agents were measured using capillary rheometer, dynamic mechanical analyzer and dynamic stress relaxometer. The dynamic mechanical analysis and the morphological studies revealed that the addition of MNPDH or 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.

1. INTRODUCTION

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[1,2].

Howland[3] reported the coupling agent, N-4-nitroso-N-methyl aniline was effective in styrene-butadiene rubber (SBR) or butyl rubber (IIR). It has been known that the nitro diamine 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[2]. Another important type of coupling agent is an organosilane to form a bonding in the interface of silica and rubber[4].

Meanwhile, polymer blends have been intensively studied because of their theoretical and practical importances[5-7]. Among the blends widely investigated in rubber industries are natural rubber(NR)/SBR, NR/butadiene rubber(BR), NR/BR/SBR, etc[8-14]. Recently, the use of ethylene-propylene-diene rubber(EPDM) has been 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[14-17]. Dunn and Wall[18] 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 dispersion properties of fillers such as carbon black or silica in the matrix of the blends of EPDM with other high diene rubbers such as synthetic isoprene rubber(IR) and BR limits the more versatile uses for blends. 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. Particularly, the incompatibility of EPDM and BR has limited the more versatile uses of the EPDM/BR blends in rubber industries.

Recently, two novel coupling agents were developed commercially; N,N'-(bis(2-methyl-2-nitropropyl))-1,6-diamino hexane (MNPDH) by Sumitomo Chem. Co. and bis(3-triethoxysilyl propyl)- tetrasulfide (TESPT) by Degussa Chem. Co. The objective of this work is to investigate the effect of the addition of the new coupling agents, MNPDH and TESPT, on the dispersion properties of fillers as well as the compatibility and the properties of the EPDM/BR blends. To our knowledge, no paper, however, has been published as yet on the new coupling agents in rubber blend systems, especially EPDM/BR blend, since they are still under testing for commercial applications.

Table 1. Materials used in this work

Ingredient	Description	Supplier
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-benzothiazyl sulfenamide	AKZO
TESPT	bis(3-triethoxysilyl propyl)-tetrasulfide	Degussa
MNPDH	N,N'-(bis(2-methyl-2-nitropropyl))-1,6-diamino hexane)	Sumitomo

2. Experimental

2.1. Materials

The materials used in this work is listed in Table 1. The EPDM having ethylidene norbornene(ENB) as a termonomer and BR having 98 % of cis contents are all commercially available grades. Two kinds of coupling agent were used; N,N'-(bis(2-methyl-2-nitropropyl))-1,6-diamino hexane (MNPDH; Sumitomo) and bis(3-triethoxysilyl propyl)- tetrasulfide (TESPT; Degussa).

2.2. Preparation of blends

In order to investigate the effect of the addition of the coupling agent, MNPDH or TESPT, on the rheological properties of EPDM/BR blends, the EPDM/BR blends with or without coupling agents were prepared in a Banbury mixer(BR Lab. Farrel Co.) by mechanical mixing. The ratios of EPDM/BR blend were 75/25 and 50/50 by weight. Mixing of the carbon-black filled compounds was carried out in a Banbury mixer using conventional two

Table 2. Rubber compounds containing various ingredient

Exp. No.	Polymer Ratio	Ingredient (phr)[a]
a	EPDM/BR(75/25)	N351(40)
b	EPDM/BR(50/50)	〃
c	EPDM/BR(75/25)	N351(30), silica(15), TESPT(3.75)[b]
d	EPDM/BR(50/50)	〃
e	EPDM/BR(75/25)	N351(30), silica(15), MNPDH(3.75)[b]
f	EPDM/BR(50/50)	〃

[a] 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.

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

step mixing procedures: In the first stage(without curatives), EPDM/BR masterbatch blends were prepared by mixing these rubbers with 40 phr of carbon black for 6 minutes at 155℃, 40 rpm rotor speed. In the second stage, stocks for vulcanization and evaluation were prepared from the EPDM/BR masterbatch blends by the addition of other ingredients such as sulfur and zinc oxide using 6"×12" two-roll mill at 100℃ for 5 minutes. Curing was done in a thermo-fluid press. Rubber compounds used in this study are given in Table 2. To see the effect of coupling agents MNPDH or TESPT, on the vulcanizate properties of carbon black and silica filled EPDM/BR blends, EPDM/BR blends containing MNPDH or TESPT, designated as EPDM/BR/MNPDH or EPDM/BR/TESPT ternary blends, were prepared using different ingredient content.

2.3. Measurements and Physical Testing

Rheological properties were measured at 100℃ by a capillary rheometer(Monsanto Processability tester). The dimension of a capillary was 1.5 mm in diameter with the L/D ratio of 20. Dynamic mechanical properties were measured using a dynamic mechanical analyzer(GABO Eplexor-150 N) at the frequency of 11 Hz with the amplitude strain of 0.25 %. The stress relaxation properties were measured by a dynamic stress relaxometer (DSR, BF.Goodrich)[19]. Morphology observations 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 12 minutes at 180℃ using a Monsanto oscillating-disc rheometer (Monsanto Rheometer R-100) according 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 cycle/min. The number of cycles to show failure in samples was taken as the fatigue resistance data.

For the determination of bound rubber contents, 0.2 g of samples with the thickness of below 0.5 mm were dissolved in 100 ml of toluene at room temperature for 10 days. After filteration, the bound rubber contents(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 weight residue(g) after dissolving in toluene, I initial sample weight(g), T total filler content(phr), and F inorganic filler content(phr).

For the determination of the carbon black dispersion, samples of 5×3×3 mm size were attached to microtome by a rubber cement and freezed in liquid nitrogen. The carbon black dispersion was determined visually using optical microscope(Optiphot Biological Microscope, Nikon) with a graticule in the eyepiece (ASTM D 2663, Method B). The % black dispersed down to a given aggregate size was derived from the number of total squares covered by black and the black volume loading[20].

3. Results and Discussion

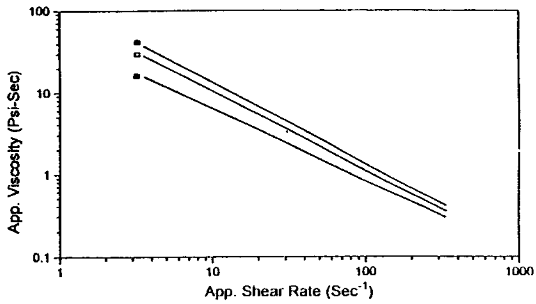


Fig. 1. Melt viscosities vs. apparent shear rate of (a) EPDM/BR, (c)EPDM/BR/TESPT, and (e)EPDM /BR/ MNPDH blends (The polymer ratio of EPDM to BR is 75/25 by weight).

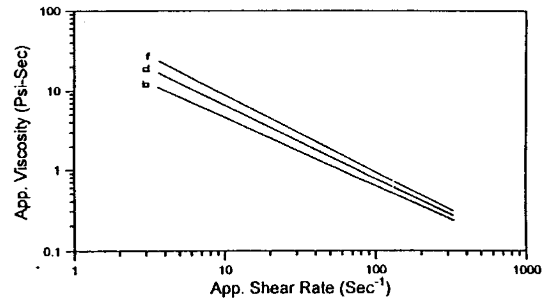


Fig. 2. Melt viscosities vs. apparent shear rate of (b)EPDM/BR, (d)EPDM/BR/TESPT, and (f) EPDM/BR/MNPDH blends (The polymer ratio of EPDM to BR is 50/50 by weight).

3.1. Rheological Properties of Unvulcanized Blends and Cure Characteristics

Fig. 1 shows the melt viscosity in the unvulcanized state of the 75/25 EPDM/BR blends with or without coupling agents as a function of apparent shear rate. One can see that the rheological behaviors show typical power-law behaviors for all the blends. The comparison of the rheological behaviors of the unvulcanized EPDM/BR/MNPDH or EPDM/BR/TESPT ternary blend with that of the EPDM/BR blend indicates that the EPDM/BR/MNPDH and EPDM/BR/ TESPT ternary blends exhibit higher melt viscosity than that of the EPDM/BR blends. It should be noted that the EPDM/BR/TESPT blend exhibited lower viscosity than the EPDM/BR/MNPDH blend. The result implies that the silane type TESPT is more effective coupling agent for silica than the nitro amine type coupling agent, MNPDH for EPDM/ BR blends due to the buildup of silica-to-rubber bonds[4, 21], and MNPDH is a good dispersing agent for carbon black but not effective for silica. The same results were observed for the EPDM/ BR blends having the blend composition of 50/50 by weight, as shown in Fig. 2. The rheographs of the EPDM/BR masterbatch blends with different coupling agents are shown in Fig. 3. It is seen that the EPDM/BR/MNPDH ternary blends exhibit higher torques and faster cure rates than the EPDM/BR/TESPT blends as well as the EPDM/ BR blends without coupling agents, as can be expected from the viscosity behavior in Fig. 3. 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 Fig. 4. The scorch time became shorter when the coupling agent, MNPDH or TESPT was added. The result may be related to the increasing of melt viscosity when the coupling agents were added. It should be noted, however, that in case of the EPDM/BR/MNPDH blends the scorch time became shorter and the cure rate became faster when compared to both the EPDM/BR blend and the EPDM/BR/TESPT ternary blends. The result may be due to the amine group of MNPDH, which can presumably accelerate the vulcanization of the rubbers.

3.2. Dynamic Properties

Fig. 5 compares the moduli of the EPDM/BR blend and the EPDM/BR/MNPDH or EPDM/ BR/TESPT blend having the same polymer ratios of 50/50 by weight. No significant differences were observed in the elastic modulus behavior among them. Fig. 6 shows the tan δ vs. temperature curves of EPDM/BR blends of 50/50 composition by weight with or without different coupling agents. The location of the peak in the tan δ temperature curve corresponds to the glass transition temperature(Tg) of the polymer. As expected, EPDM and BR were incompatible and they showed two separate Tg's. In Fig. 6, it is interesting to note that when TESPT was added to the EPDM/BR blend, the maximum point of tan δ, i.e. Tg, of EPDM shifted downward to that of BR. No clear shift of Tg was observed, however,

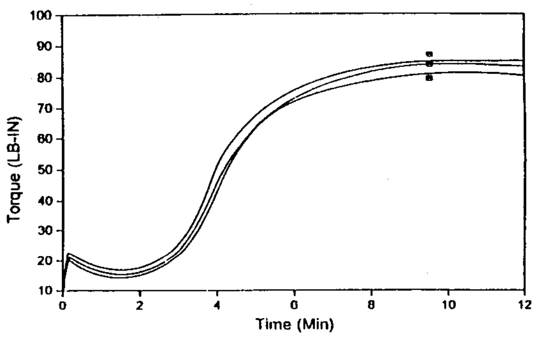


Fig. 3. Rheographs of various EPDM/BR blends; (a) EPDM/BR, (c)EPDM/BR/TESPT, and (e) EPDM/BR/MNPDH blends(The polymer ratio of EPDM to BR is 75/25 by weight).

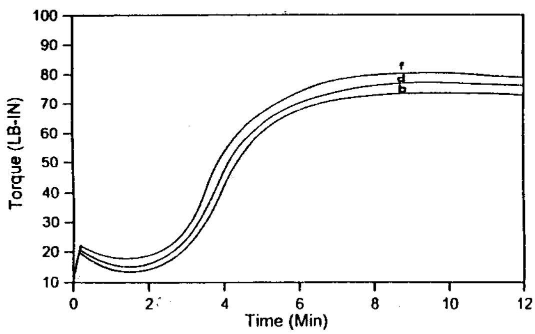


Fig. 4. Rheographs of various EPDM/BR blends; (b) EPDM/BR, (d)EPDM/BR/TESPT, and (f) EPDM/BR/MNPDH blends(The polymer ratio of EPDM to BR is 50/50 by weight).

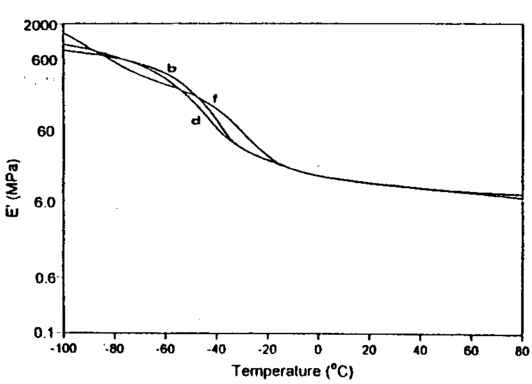


Fig. 5. Elastic modulus of EPDM/BR blends as a function of temperature; (b)EPDM/BR, (d) EPDM/BR/TESPT, and (f)EPDM/BR/MNPDH blends(The polymer ratios of EPDM to BR are 50/50 by weight).

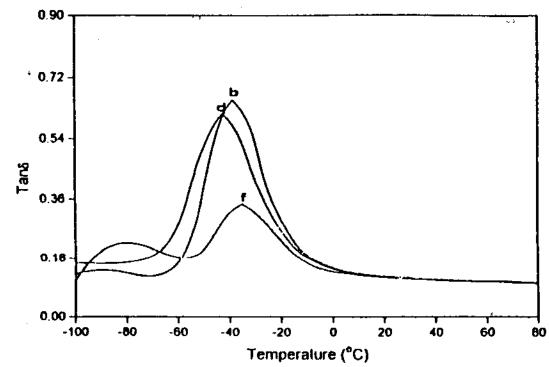


Fig. 6. Tan δ of EPDM/BR blends as a function of temperature; (b)EPDM/BR, (d)EPDM/BR/TESPT, and (f)EPDM/BR/MNPDH blends (The polymer ratios of EPDM to BR are 50/50 by weight).

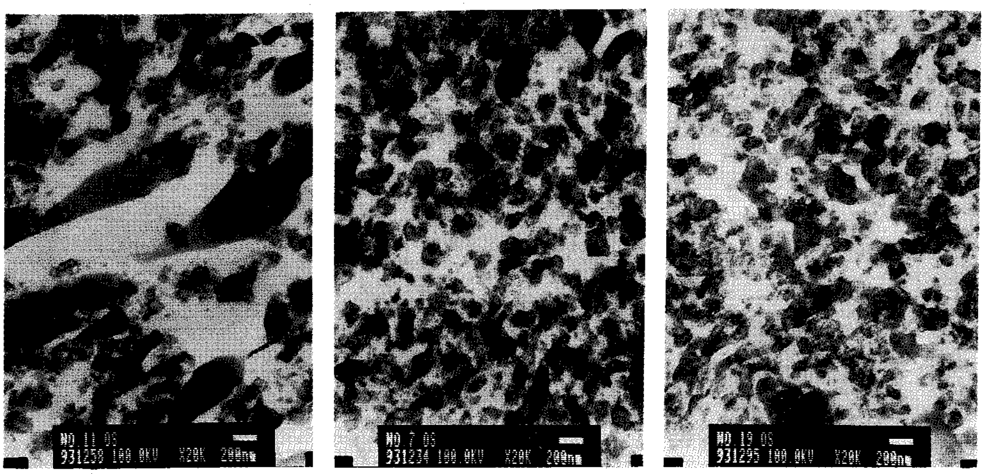
Table 3. Stress relaxation data of various EPDM/BR blends

Polymer Ratio	TM(joule)[a]	Sig-2(joule sec)[a]	λ (sec)[a]
EPDM/BR(75/25)	23.28	13.33	899
EPDM/BR(50/50)	19.66	12.43	891
EPDM/BR(75/25)/ TESPT[b]	24.19	16.61	1370
EPDM/BR(75/25)/ MNPDH[b]	24.30	17.17	1430
EPDM/BR(50/50)/ TESPT[b]	22.26	15.93	1351
EPDM/BR(50/50)/	22.83	14.35	1400

[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 sec, Sig-2 : Integral torque(Summation of torques recorded up to 2 sec), λ : stress relaxation time.
[b] The amount of TESPT or MNPDH was fixed at 3.75 phr based on the total amount of EPDM and BR mixtures.

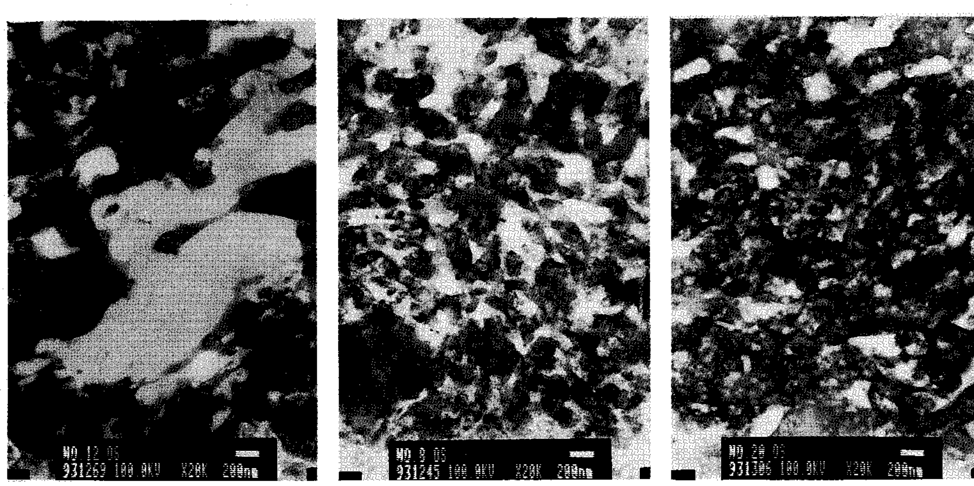
in the case of the EPDM/BR blend and EPDM/BR/MNPDH having the same polymer ratio. The result means that the TEPST acted also as a compatibilizer to improve the compatibility of EPDM and BR as well as a coupling agent to buildup of silica-to-rubber bonds[21].

Table 3 shows the stress relaxation properties of blends. In case of the EPDM/BR blends, the stress relaxation data were higher as EPDM contents were higher due to the increases in the melt viscosity and elasticity. In Table 3, however, the EPDM/BR/TESPT and EPDM/BR/MNPDH ternary blends showed higher maximum torques (TM's) and relaxation times(λ) due to the cou-



(a) (c) (e)

Fig. 7. TEM micrographs of various EPDM/BR blends. (a)EPDM/BR, (c)EPDM/BR/TESPT, and (e)EPDM/BR/MNPDH blends (The polymer ratios of EPDM to BR are 75/25 by weight).



(b) (d) (f)

Fig. 8. TEM micrographs of various EPDM/BR blends. (b)EPDM/BR, (d)EPDM/BR/TESPT, and (f)EPDM/BR/MNPDH blends(The polymer ratios of EPDM to BR are 50/50 by weight).

pling effect of MNPDH or TESPT when compared to EPDM/BR blends without either of the coupling agents, regardless of kinds of coupling agents as well as 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 coupling between rubber and carbon black and thus inhibiting the Brownian motion of the rubber molecules[1, 22]. The higher TM or stress relaxation time for the EPDM/BR/MNPDH blends compared to those for the EPDM/BR/TESPT blends proves the speculation, since MNPDH is a preferential coupling agent for carbon black. It was reported that MNPDH biradicals can react with carbon black to yield the carbon black-to-rubber bonds.

3.3. Morphology

Fig. 7 shows the morphology of the EPDM/

Table 4. Bound rubber contents, tear strength, and fatigue-to-failure data of various EPDM/BR blends

Polymer Ratio	bound rubber contents(%)	tear strength (N m)	fatigue to failure (cycle)
EPDM/BR(75/25)	14.2	2.65	168,080
EPDM/BR(50/50)	14.5	2.55	340,460
EPDM/BR(75/25)/TESPT[(b)]	22.8	3.23	200,100
EPDM/BR(75/25)/MNPDH[(b)]	21.1	3.44	218,900
EPDM/BR(50/50)/TESPT[(b)]	22.7	3.34	392,400
EPDM/BR(50/50)/MNPDH[(b)]	24.2	2.94	403,800

(b) The amount of MNPDH or TESPT was fixed at 3.75 phr based on the total amount of EPDM and BR mixtures.

Table 5. Carbon black dispersion of various EPDM/BR blends

Polymer Ratio	carbon black dispersion(%)
EPDM/BR(75/25)	92.2
EPDM/BR(50/50)	94.9
EPDM/BR(75/25)/TESPT[(b)]	96.0
EPDM/BR(75/25)/MNPDH[(b)]	96.5
EPDM/BR(50/50)/TESPT[(b)]	96.6
EPDM/BR(50/50)/MNPDH[(b)]	97.1

(b) The amount of MNPDH or TESPT was fixed at 3.75 phr based on the total amount of EPDM and BR mixtures.

BR/TESPT and EPDM/BR/MNPDH blends as well as EPDM/BR masterbatch blends having the blend composition of 75/25 by weight. In these TEM micrographs, the domain consisting of carbon black aggregate is BR phase, because the high diene rubber like BR has much larger affinity with carbon black than the saturated elastomer like EPDM. EPDM and BR showed gross phase separation. The morphology in Fig. 7 shows clearly the enhanced compatibility of EPDM and BR in the presence of MNPDH or TESPT. Also in the TEM micrographs of EPDM/BR blends of 50/50 composition by weight, shown in Fig. 8, BR phase of large domain size is dispersed in EPDM matrix for the EPDM/BR blend but the size of BR domain reduces significantly when MNPDH or TESPT has been added to the EPDM and BR binary blend. The EPDM/BR/MNPDH blend shows finer domain morphology than the EPDM/BR blend but less finer morphology than the EPDM/BR/TESPT ternary blend. Thus, one can conclude that the addition of TESPT or MNPDH to the EPDM/BR blend is effective to enhance the compatibility between EPDM and BR and the effect of TESPT is more prominent.

3.4. Vulcanizate Properties

Table 4 shows the bound rubber contents for the EPDM/BR blends. It is seen that the bound rubber contents are higher when BR contents are higher, because BR has better carbon black dispersion than EPDM does. The carbon black dispersion is summarized in Table 5. The % carbon black dispersion becomes higher as BR contents are higher for the EPDM/BR blends. The high carbon black dispersion of BR is ascribed to its flexible molecular chain structure[23]. Note that the dispersions are higher in the order EPDM/BR/MNPDH ternary blend EPDM/BR/TESPT blend EPDM/BR blend, regardless of the polymer ratios.

Table 4 also shows the bound rubber contents and the tear strength of the EPDM/BR/MNPDH or EPDM/BR/TESPT and EDPM/BR blends. The higher tear strength of EPDM/BR blends in the presence of MNPDH or TESPT should be noted, since the addition of MNPDH or TESPT enhanced the vulcanizate properties of the EPDM/BR blends. The high tear strength for the EPDM/BR/MNPDH and EPDM/BR/TESPT blends are due to the coupling effect of MNPDH with carbon black by forming biradicals during intensive mixing and then increasing bound rubber contents.

The fatigue properties of blends are summarized also in Table 4. The trends in the fatigue properties of the blends was the same as in the tear strength: that is, the BR-rich blends showed higher fatigue resistance than the EPDM-rich blends and the addition of MNPDH or TESPT increased the fatigue properties of EPDM/BR blends due to the increased bound rubber contents.

4. Conclusions

In this work, studies have been made on the effect of the addition of a coupling agent for the carbon black and silica filled EPDM/BR blends on the compatibility and the vulcanizate properties of EPDM/BR blends. MNPDH or TESPT was used as a coupling agent. The rheological and the dynamic mechanical measurements along with the morphology revealed that the addition of TESPT is more effective to enhance the compatibility between EPDM and BR, whereas the addition of MNPDH is more effective to improve the vulcanizate properties of the EPDM/BR blends. It was found that the addition of MNPDH or TESPT increased the amounts of bound rubbers and thus the vulcanizate properties of the EPDM/BR blends.

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