

BIMS/Filler Interactions. II. Effects of Filler Concentration and BIMS Structure

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ABSTRACT: Brominated isobutylene *para*-methylstyrene (BIMS) elastomer is a terpolymer of isobutylene, *para*-methylstyrene (PMS), and *para*-bromomethylstyrene (BrPMS). Viscoelastic measurements have been used to characterize the blends of this BIMS elastomer with different concentrations of a carbon black (CB) filler, N234. Data in the low temperature/high frequency region suggest that N234 at a concentration less than or equal to 15 vol % in BIMS appears not to affect the T_g of BIMS although a slight increase in relaxation time in the transition zone is observed. Also, the effects of BrPMS and PMS contents in BIMS on BIMS/N234 CB interactions have been qualitatively investigated by us-

ing the bound rubber measurements. To assess BIMS/CB interactions with reference to diene rubber/CB interactions, mixing of BIMS with various amounts of a polybutadiene rubber in the presence of CB has been performed. Atomic force microscopy and image processing have been employed to quantify filler phase distributions in these blends for a practical ranking of polymer/CB interactions. Preferential partition of CB in the BIMS or BR phase depends on the BrPMS content in BIMS. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 659–667, 2006

Key words: fillers; morphology; relaxation; rubber

INTRODUCTION

Blends of elastomer and carbon black (CB) and their interactions have been studied extensively in the last 50 years.^{1–3} The CB aggregates in an elastomer tend to agglomerate, especially at high filler concentrations, producing a continuous, chain-like filler structure. There is no direct experimental evidence to determine if this secondary network structure is formed by direct contact between filler aggregates or by a layer of immobilized rubber on the filler surface,² although recently we have speculated that there is a strong mediation of the CB filler network structure by the brominated isobutylene *para*-methylstyrene (BIMS) polymer.⁴ This filler structure or network breaks down or dissociates with increasing dynamic strain amplitude. This was first observed by Warring in 1950⁵ and by Fletcher and Gent in 1953.⁶ In other words, the CB network is very sensitive to an applied strain or deformation. The CB network “breaks” upon deformation. The results are a drop in the storage modulus G' (the total stiffness of the filled polymer is decreased) and a maximum in the loss modulus G'' (the

CB network energy is dissipated as heat). Subsequent dynamic mechanical measurements of Payne^{7–10} and electrical conductivity and dynamic mechanical measurements of Voet et al.^{11–13} further support this concept of filler network. This phenomenon of elastomer/filler blends is also termed as the “Payne effect.” Interestingly, this filler network is “reformed” upon the removal of the strain. Therefore, the reinforcing nature of the filler to the polymer matrix will be retained. It has been postulated that CB contributes mainly to the reinforcement of the polymer/CB blend at strain amplitudes below 6–8% (depending on the type of CB). Payne and Whittaker¹⁴ have observed that HAF CB-filled butyl rubber systems do not show any “Payne effect” if the concentration of this filler is lower or equal to 16.8 vol % and strain is below 0.5%. The “Payne effect” did occur at this filler loading for strains above 0.5%.

Arai and Ferry¹⁵ measured dynamic moduli G' and G'' (0.12–2 Hz) and shear relaxation modulus $G(t)$ (time t up to 10^4 s) on vulcanized and unvulcanized CB-filled styrene/butadiene rubber (SBR) or *cis*-polybutadiene rubber (BR) compounds over a temperature range of –22.5–63°C. The maximum shear strain in the oscillatory deformation was less than 0.5% and in the stress relaxation measurements, 1.5%. The temperature dependence of viscoelastic properties could not be fully described by the horizontal shifts (a_T) of $\log t$ or $\log \omega$, where ω is the frequency. It could, however, be largely described by vertical shifts (b_T) corresponding to uniform temperature dependence of the magnitudes of contributions to modulus from a spectrum

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TABLE I
Viscoelastic and DSC Data of N234-Filled BIMS

N234 content		C_1	C_2 (K)	$\log \tau_{tr}$ (s)	T_g	ΔC_p (J/g/°C)
Phr	Vol %					
0	0	9.3	191	-3.09	-65.8	0.29
5	2.5	9.0	183	-3.13	-66.0	0.31
10	4.9	8.8	177	-3.07	-65.3	0.27
20	9.3	9.2	188	-2.95	-65.0	0.24
35	15	6.5	139	-2.82	-65.9	0.23

of relaxation mechanisms. The temperature dependence of b_T 's followed the van't Hoff equation with values of $\Delta H = 5.9$ – 14.7 kJ/mol, where ΔH is the heat of dissociation, per mole, of contacts between CB aggregates. We observed the failure of the time-temperature equivalence of viscoelasticity of BR/N234 blends due to the continuous crosslinking of the blends during mixing and/or in high temperature measurements.¹⁶

The CB network, under a large strain, is broken down into discontinuous filler subnetworks, which may restrict polymer chain mobility. However, it is postulated that this filler network can be partially reformed, especially in the stress-free state. The rate of reformation is similar to that of small-strain stress relaxation.^{17,18} Only in crosslinked compounds is the network fully recovered, presumably because in these the particles are embedded in a crosslinked matrix and have crosslinked bridges that provide reestablishment of interparticle contacts. On the other hand, in uncrosslinked compounds, the matrix has no crosslinks and the bound rubber on adjacent CB particles may only be entangled.

Bound rubber (solvent extraction), viscoelastic, stress-strain, and NMR measurements were used to identify, differentiate, and scale polymer/filler interactions in BIMS/CB, BIMS/silica, SBR/CB, and SBR/silica composites in Part I of this study. In this work (Part II), first, we want to investigate the viscoelastic behavior of BIMS when loaded with different amounts

of N234 CB in the unvulcanized state. We start with a very low CB concentration (5 phr or 2.5 vol %; Table I). The evolution of the viscoelastic properties of the BIMS/N234 blends with increasing CB concentration (up to 35 phr or 15 vol %; Table I) relative to BIMS will be reported. We attempt to employ viscoelastic behavior as a means of understanding BIMS/N234 interactions. Second, we want to understand the effects of the *para*-bromomethylstyrene (BrPMS) and *para*-methylstyrene (PMS) contents in BIMS on BIMS/N234 interactions. Third, CB-filled blends of BIMS with BR have been prepared. Two BIMSs with different BrPMS levels have been studied. We attempt to observe filler partition in the BIMS and the BR phases of these blends when the BrPMS level in BIMS is varied. A preferential CB partition in one of these polymer phases versus the other polymer phase can be attributed to the strong interactions of this polymer phase with CB.

EXPERIMENTAL

Polymers and fillers

The brominated isobutylene *para*-methylstyrene (BIMS) elastomers used in this study are described in Table II, where an asterisk (*) denotes that no measurements were taken. The wt % and mol % of *para*-methylstyrene (PMS) in each polymer are shown. Actually, the wt % of PMS refers to that of BIMS before bromination. The mol % of PMS, y , was calculated from the wt % of PMS, x , according to the following equation:

$$y = [56x / (118 - 0.62x)] - (\text{mol \% BrPMS})$$

The polybutadiene rubber (BR) used was Budene 1207 elastomer (Goodyear Tire and Rubber, Akron, OH), which had ~98% *cis*-1,4 content. Two CBs were used. N234 has a nitrogen surface area of 126 m²/g and a dibutyl phthalate absorption (DBPA) of 125 mL/100 g, whereas N330 has a smaller nitrogen

TABLE II
Characterization of BIMS Polymers

	BrPMS (mol %)	PMS, wt % (mol %)	Mooney at 125°C	Approximate $M_n \times 10^{-3}$	Approximate $M_w \times 10^{-3}$
BIMS 93-4	1.2	7.5 (2.51)	38	170	420
SIMS 96-3	0.75	7.5 (2.96)	40	170	440
BIMS 89-1	0.75	5.0 (1.69)	35	200	470
BIMS 90-10	1.2	7.5 (2.51)	45	190	460
BIMS 038	0.22	13.6 (6.73)	40.6	*	*
BIMS 048	0.56	13.6 (6.39)	36.6	*	*
BIMS 046	0.77	13.6 (6.18)	41.7	*	*
BIMS 042	0.97	13.6 (5.98)	37.9	*	*
BIMS 96-4	0.85	12.0 (5.23)	40	180	480
BIMS 003	0.45	12.0 (5.63)	40	170	440

surface area of 83 m²/g and a lower DBPA of 102 mL/100 g.¹⁹

Mixing and molding

Mixing of the CB stocks was carried out in a Banbury internal mixer (started at ~65°C, mixed for ~3–5 min, and discharged at ~150°C), followed by sheeting on a two-roll mill to provide a high level of black dispersion. This mixing and milling process was repeated once again. No additives other than the fillers were added.

For viscoelastic measurements in the low temperature/high frequency region, the elastomer and the CB-filled elastomers were molded between two pieces of Teflon-coated aluminum foil at 150°C for 25 min. All these molded pads were then die-cut into appropriate dimensions for viscoelastic measurements.

To evaluate the effects of polymer/filler interactions on filler phase partition in BIMS/BR blend compounds, straight mixing of BIMS 96–4 (0.85 mol % BrPMS, 12.0 wt % PMS) and BR with varying blend ratios were prepared using a Banbury internal mixer.¹⁶ Fifty phr of N330 CB was added 30 s after the polymers were mixed in the Banbury. No processing oil was applied. Blend ratios prepared were 20/80, 40/60, 50/50, 60/40, and 80/20 in BIMS/BR. Curatives used were zinc oxide and stearic acid for BIMS, and sulfur and MBTS (sulfur accelerator, 2-benzothiazyl disulfide) for BR.

The blend compositions of BIMS 003 (0.45 mol % BrPMS, 12.0 wt % PMS) and BR are described elsewhere.²⁰ Blend ratios prepared were 30/70, 40/60, 50/50, 60/40, and 70/30 in BIMS/BR. They were prepared by mixing in a Banbury mixer and on a two-roll mill. The mixing was started at about 65°C. Both polymers were added at the same time followed by the addition of 45 phr of N330. The total mixing time was about 3–5 min and the mix was discharged at about 150°C. Following cooling, the components were mixed again on a two-roll rubber mill during which the curing agent and accelerator were added and uniformly dispersed at a relatively low temperature, about 80–105°C. The BIMS phase was crosslinked by zinc di-2-ethylhexanoate (1.2 phr). The BR phase was crosslinked either by sulfur (0.5 phr) or by a brominated resin (0.5 phr) in the presence of zinc oxide (0.75 phr). The final, green compounds, if required, were sheeted one more time on the two-roll mill. After mixing, all compounds were molded (180°C, 45 min) into pads of ~2 mm thickness.

Viscoelastic and DSC measurements

Isothermal dynamic mechanical experiments (0.1–20 Hz) from –40 to 40°C, at a 10°C increment, were performed in a Rheometrics dynamic mechanical ther-

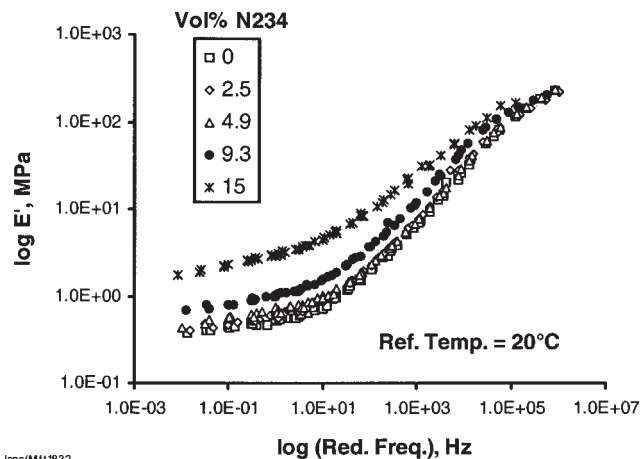


Figure 1 Carbon black raises the low frequency storage modulus of BIMS.

mal analyzer (DMTA Mark II). It was operated in the bending mode (dual cantilever, flat face/small frame geometry) with a maximum strain of about 0.1%. The sample was a 35.0 × 12.8 mm² rectangle with 2 mm thickness, die-cut from the molded specimen. Master curves were obtained by the superposition of the viscoelastic data measured at different temperatures. Both frequency (horizontal) shift factors a_T and modulus (vertical) shift factors b_T were used to achieve superposition.²¹

Thermal characterization of the N234-filled BIMS systems was performed using a Perkin-Elmer Pyris I DSC with subambient capability at a heating rate of 10°C/min.

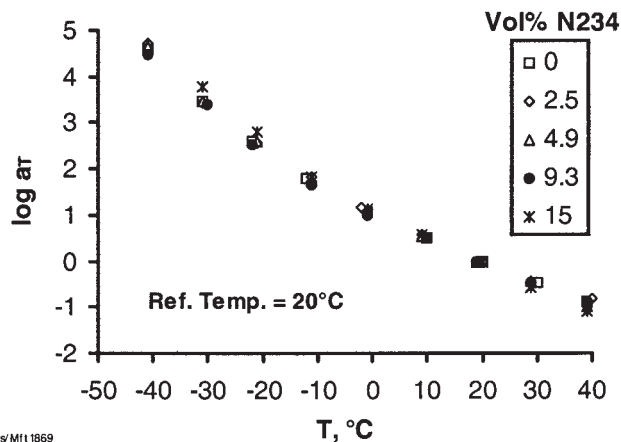
Atomic force microscopy

Tapping phase atomic force microscopy (AFM) and subsequent image processing were employed previously to quantify filler phase distributions in BIMS/BR blends for a practical ranking of polymer/CB interactions. Detailed procedures can be found elsewhere.¹⁶

RESULTS AND DISCUSSION

Low temperature/high frequency viscoelastic properties

Figure 1 shows the master curves of storage modulus E' of the N234-filled BIMS 93–4 systems at different CB volume fractions compared to the neat BIMS elastomer. Loadings of 5, 10, 20, and 35 phr of CB correspond to 2.5, 4.9, 9.3, and 15 vol %, respectively, of N234 in these filled systems (Table I). The reference temperature T_0 used to construct these master curves is 20°C. Each polymer system behaves like a rubbery material at low frequency. Here, CB raises the storage



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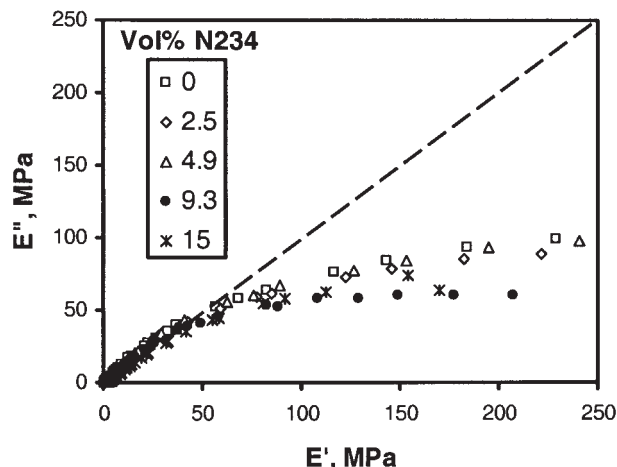
Figure 2 Frequency shift factors a_T 's of BIMS and BIMS/N234 blends show similar temperature dependence.

modulus of BIMS with increasing amount of N234 in the polymer. A strain of 0.1% does not seem to separate CB aggregates at N234 vol % lower than or equal to 15. In other words, there is no "Payne effect" in these filled polymer systems. This agrees with Payne and Whittaker¹⁴ that butyl rubber/CB blends do not show any "Payne effect" if the CB concentration is lower than or equal to 16.8 vol % and the strain is below 0.5%. When the frequency of deformation is increased up to eight decades, each polymer system undergoes a rubbery-to-glassy transition.

Due to the lack of nonlinear "Payne effect," we now focus our discussion on the linear viscoelastic properties of these N234-filled BIMS systems. First, Figure 2 shows the shift factor a_T described by the WLF equation²¹:

$$\log a_T = -C_1(T - T_0)/(C_2 + T - T_0)$$

Shift factors of BIMS and the filled BIMSs show similar temperature dependence with C_1 and C_2 values (Table I) close to the literature values: $C_1 = 9.0$ and $C_2 = 202^\circ\text{C}$ at 25°C for a lightly crosslinked butyl rubber.²¹ Of course, it is also noticed that the filled BIMS containing 15 vol % N234 shows lower C_1 and C_2 values compared to the other polymer systems. This is possibly due to the reason that there is a more restricted motion of the BIMS chains as more BIMS is replaced by CB, with increasing CB loading in these filled polymer composites. On the other hand, previous data in the high temperature/low frequency region suggest that upon addition of small amounts of CB to BIMS, no change in the viscoelastic behavior is observed.⁴ However, increasing the filler loading beyond a critical concentration of filler at around 9 vol % (corresponding to a presumed secondary network formation) leads to the observation of a network-like response.

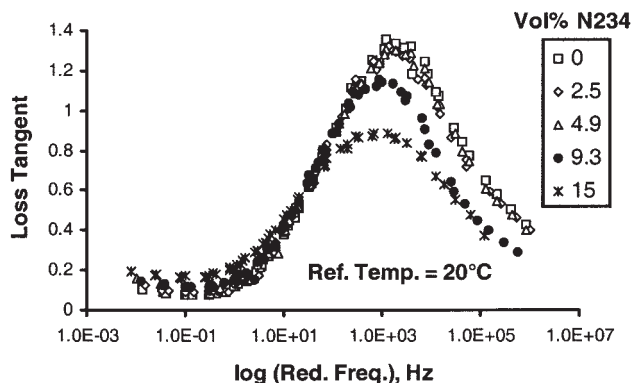


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Figure 3 Storage and loss moduli of N234 filled BIMS obey a single behavior, independent of temperature, frequency, and N234 loading.

Figure 3 shows all the storage and loss modulus data of BIMS and the filled BIMS systems. Overall, the data points appear to obey a single behavior in this linear plot of E'' versus E' linear, independent of temperature, frequency, and N234 loading. The dotted line in Figure 3 represents the line of $E'' = E'$. At low values of E' and E'' , the data points are located more or less on this dotted line, suggesting an equal elastic and viscous characteristics. In other words, N234 CB increases E' and E'' of BIMS to similar amounts at relatively low values of E' . At high values of E' and E'' , E'' appears to reach or approach a plateau value so that the data points are now located below the dotted line; or, stated alternatively, they are in the elastic-dominating region.

Figure 4 shows the master curves of loss tangent δ of these polymer systems. Values of the relaxation time τ_{tr} in the transition zone shown in Table I are



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Figure 4 A very minor increase in relaxation time τ_{tr} in the transition zone with increasing concentration of N234 in BIMS.

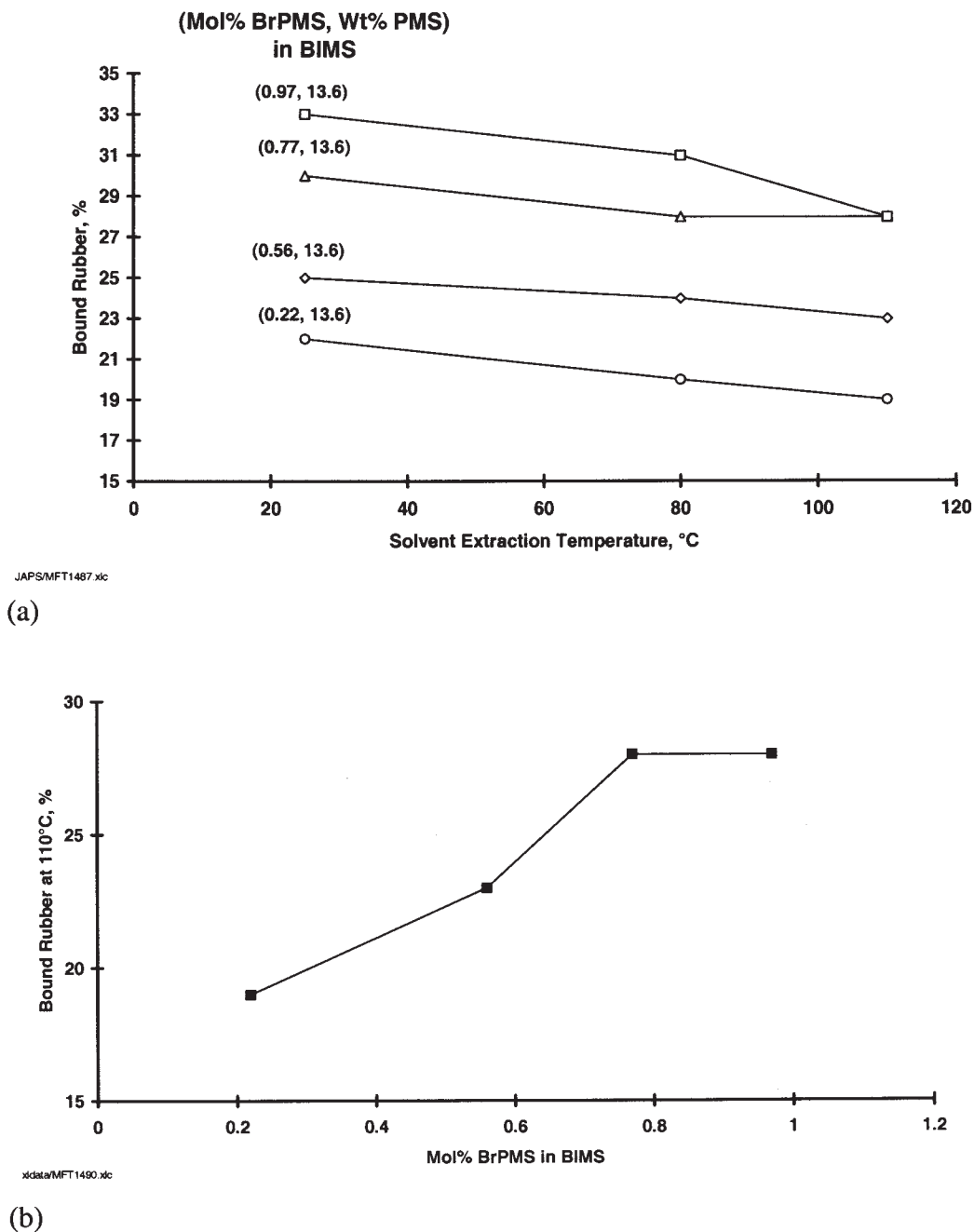


Figure 5 The BIMS polymer with a higher BrPMS content shows stronger interactions with N234.

estimated from the loss tangent peak positions in this figure. There is only a very slight increase in this relaxation time with increasing concentration of N234 in BIMS. This is consistent with the DSC data in the same table that N234 has no significant effect on the T_g of the N234-filled BIMS. The only slight effect is to decrease the difference in the heat capacity C_p when T_g is traversed with increasing N234 loading.

BIMS structural effects

Interactions of BIMS 93-4 with different types of CB are described in Part I of this study. Now we extend

our study to various BIMS polymers (Table II) blended with 50 phr of a given CB, such as N234. The method used to scale polymer/filler interactions is bound rubber measurements because our previous work suggests that they provide useful information for the more temperature-stable polymers, such as BIMS and IMS, compared to BR or IR.¹⁶ The results are shown in Figures 5 and 6.

Figure 5(a) shows the bound rubber as a function of solvent extraction temperature of the blends of various BIMS elastomers (at a constant wt % of PMS but varying mol % of BrPMS) with N234. Figure 5(b) shows the bound rubber at 110°C extraction tempera-

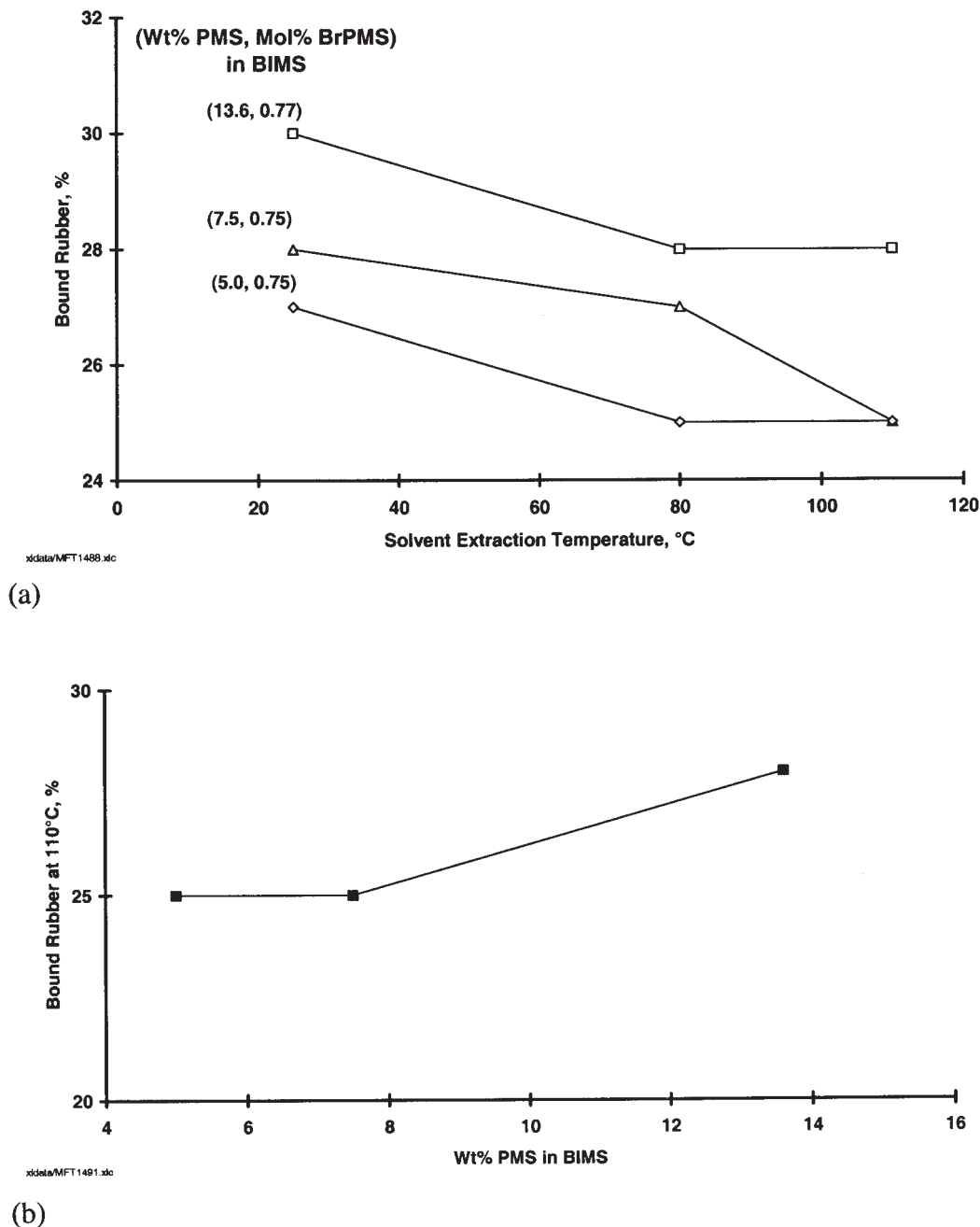


Figure 6 The BIMS polymer with a higher PMS content shows stronger interactions with N234.

ture as a function of mol % of BrPMS in BIMS. The higher the mol % of BrPMS in BIMS, the higher is the bound rubber, suggesting stronger polymer/filler interactions. Figure 6(a) shows the bound rubber as a function of solvent extraction temperature of the blends of various BIMS elastomers (at an approximately constant mol % of BrPMS but varying wt % of PMS) with N234. Figure 6(b) shows the bound rubber at 110°C extraction temperature as a function of wt % of PMS in BIMS. The higher the wt % of PMS in BIMS, the higher is the bound rubber, indicating stronger polymer/filler interactions. Therefore, data in Figures

5 and 6 suggest that both BrPMS and PMS in BIMS promote interactions with CB, but BrPMS has a stronger effect at moderate BrPMS levels.

Filler phase partition

Filler partition in the individual polymer phases was studied by AFM and image processing in the CB-filled blends of BIMS with BR. Essentially two $10 \times 10 \mu\text{m}^2$ AFM images taken at different locations on each cut sample were processed to obtain quantitative image analysis data. Two different BIMSs (BIMS 96-4 and

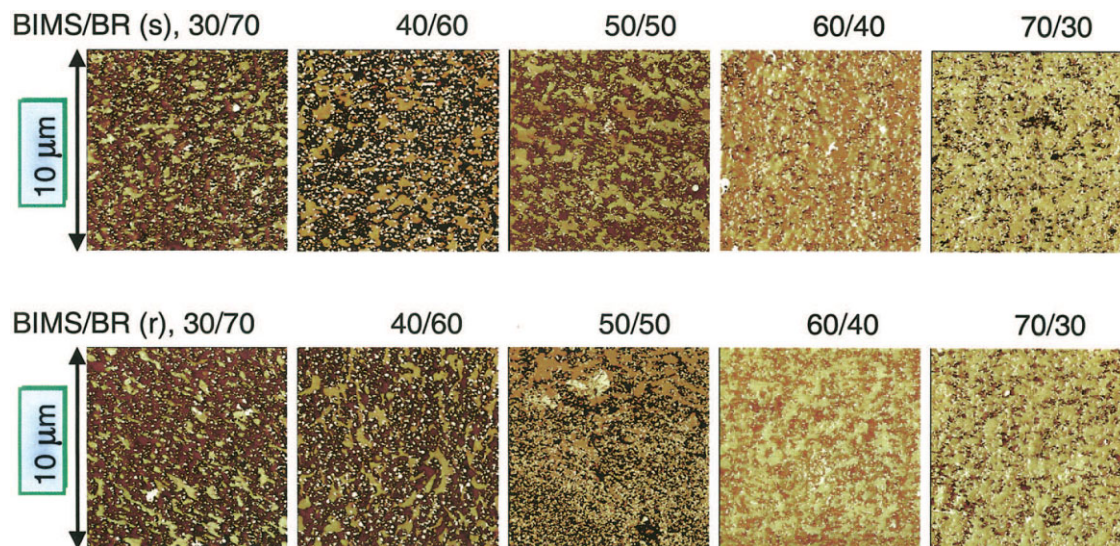


Figure 7 AFM micrographs of CB-filled BIMS 003/BR blends. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

BIMS 003) were used in these blends. As shown in Table II, BIMS 96–4 has a higher level of BrPMS than BIMS 003, but both polymers have very similar levels of PMS. The preferential partition in a particular polymer phase suggests a stronger interaction of CB with that polymer. AFM micrographs for the BIMS 96–4/BR blends were shown elsewhere.¹⁶ AFM micrographs for the BIMS 003/BR blends are shown in Figure 7, where the white particles are carbon blacks, the gray (yellow online) phases are BIMS phases, and the dark phases are BR phases. For BIMS 96–4/BR blends, more CB filler is incorporated into the BIMS phase (see Table III and Fig. 8). The dotted line in the graph (% filler in BIMS *versus* phr BIMS) in Figure 8

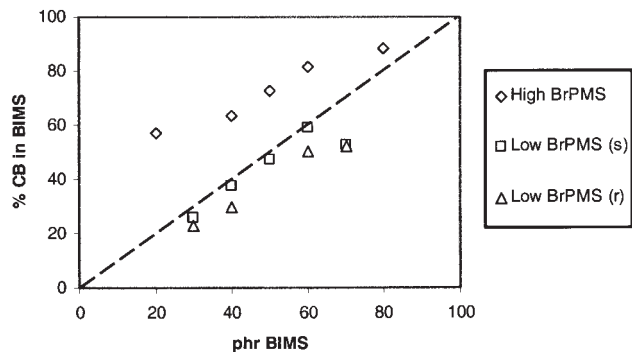
represents the line of equal CB partition in BIMS and BR phases. All the data points from Table III for BIMS 96–4/BR blends are above this dotted line. This suggests that there is preferential filler partition in the BIMS phase at various BIMS/BR blend ratios even though the area coverage of CB in the BIMS phase, calculated by dividing the measured CB % in BIMS by BIMS % in the blend, decreases with increasing BIMS content. This is not surprising because each compound contains a constant amount of CB. A higher BIMS content will result in a lower share of CB per unit wt. of BIMS. Table III also summarizes the AFM results for the BIMS 003/BR blends, where (s) and (r) denote curing in the BR phase of the blends by sulfur

TABLE III
Partitioning of CB in BIMS after Straight Mixing with BR

RIMS/BR blend ratio	Measured CB (%)		Area coverage of CB	
	High-BrPMS BIMS 96–4	Low-BrPMS BIMS 003	High-BrPMS BIMS 96–4 ^a	Low-BrPMS BIMS 003 ^a
20/80	56.9		2.8	
30/70		25.9(s) 22.8(r)		1.3 1.0
40/60	63.3	37.6(s) 30.0(r)	1.6	0.65 0.57
50/50	72.7	47.2(s)	1.5	0.94
60/40	81.3	59.0(s) 50.1(r)	1.4	0.98 0.84
70/30		52.6(s) 52.0(r)		0.75 0.74
80/20	88.1		1.1	

N330-filled compounds (50 phr) of high-BrPMS BIMS 96–4/BR; N330-filled compounds (45 phr) of low-BrPMS BIMS 003/BR.

^a (Measured CB % in BIMS)/(BIMS % in blend).



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Figure 8 Partition of CB in BIMS/BR blends with different compositions.

and brominated resin, respectively. For BIMS 003/BR blends in which the BR phase is crosslinked by sulfur (s), the CB filler is distributed quite uniformly between the two polymer phases. The only exception is the blend with 70 phr PMS, Table III and Figure 8. For BIMS 003/BR blends in which the BR phase is crosslinked by the brominated resin (r), a slightly higher amount of CB filler resides in the BR phase because the data points are below the dotted line at various BIMS/BR blend ratios. This suggests that the CB filler has a slight preference to be partitioned in the BR phase. Therefore, a higher BrPMS level in BIMS is required to attract more CB filler in this phase, consistent with the bound rubber results in Figure 5.

Predicted effects on mechanical properties

It is speculated that results in Figures 5–8 and Part I of this work have important consequences to the mechanical performance, such as ozone resistance, cut growth resistance, cured adhesion, and abrasion resistance of the phase-separated BIMS/BR compounds. A BIMS elastomer with a higher BrPMS and a higher PMS should attract more black in the BIMS phase. The result is a larger BIMS phase volume, which should in turn increase the ozone resistance of the compound.²² However, a larger amount of CB in the BIMS phase will decrease the contour length of network molecular chains L_c of the BIMS phase due to polymer/filler attachments. This results in a decrease in the cut growth resistance of the compound.²³ Therefore, optimum BrPMS and PMS levels in BIMS are necessary to carefully control BIMS phase volume and L_c for a good balance in ozone resistance and cut growth resistance. Results in Figures 5 and 6 should also have one other potentially important implication. If the BIMS phase is ZnO-cured, only one half of the BrPMS functional groups is consumed. The remaining BrPMS groups should be available for interactions with CB. On the other hand, if the BIMS is Duralink- or diamine-cured, all the BrPMS functional groups should

be consumed, where Duralink and diamine have the structures of $\text{Na}^+\text{O}_3\text{S}-\text{S}-\text{CH}_2-(\text{CH}_2)_4-\text{CH}_2-\text{S}-\text{SO}_3^-\text{Na}^+$ and $\text{NH}_2-\text{CH}_2-(\text{CH}_2)_4-\text{CH}_2-\text{NH}_2$, respectively. Of course, it is speculated that the sulfur linkage in Duralink and the nitrogen linkage in diamine can also interact with the CB in BIMS. Therefore, curing chemistry of BIMS/BR compounds may also play an important role in balancing ozone resistance and cut growth resistance regarding BIMS phase volume and L_c . Because both the BrPMS and PMS groups in BIMS interact with CB, this may lower the chemical reactivity of BIMS when bonded to a diene rubber, such as BR or IR.²⁴ We have some experimental evidence, which suggests that the presence of 45 phr CB in both BIMS and BR eliminates the interfacial cocure between these dissimilar polymers.²⁵ This is also true if BR is replaced by IR. Furthermore, we have generated some experimental results on abrasion resistance. It has been found that a more interactive filler (N234 or silica *versus* N660) with BIMS improves the abrasion resistance of the filled BIMS. On the other hand, BR filled with either N234 or N660 shows good abrasion resistance irrespective of the filler type.²⁶ Therefore, the partition of the filler in the BIMS/BR blend should affect the abrasion resistance of the blended compound.

CONCLUSIONS

First, viscoelastic studies have been performed to characterize BIMS containing different concentrations of N234 CB. In the low temperature/high frequency region, N234 concentration ≤ 15 vol % in BIMS does not appear to affect the T_g of BIMS although a slight increase in relaxation time in the transition zone is observed. This is consistent with a previous study in the high temperature/low frequency region.⁴ Therein, no change in the viscoelastic behavior is observed upon addition of small amounts of N234 to BIMS. However, increasing N234 loading beyond a critical concentration leads to the transition of a liquid-like to pseudosolid-like response (corresponding to a presumed secondary network formation). Time-temperature superposition is possible for all the samples, with the frequency shift factor following the WLF behavior. The near independence of the frequency shift factor with the CB concentration suggests that the temperature dependence of the relaxation probed is similar in the filled and unfilled polymers. Second, bound rubber studies suggest that a higher BrPMS and/or PMS content in the BIMS elastomer improve polymer/CB interactions. Third, AFM and image processing indicate that partition of CB in BIMS/BR blends depends on the BrPMS content in the BIMS polymer. If the BrPMS content is higher than a

certain level, preferential partition in the BIMS phase will occur. Of course, a stronger BIMS/CB interaction or more CB partition in BIMS could result in a larger BIMS phase volume, a shorter network chain length between crosslinks L_c in BIMS, and a lower interfacial reactivity of BIMS with a diene polymer (BR or IR). Also, the presence of a filler in BIMS and BR will result in different behaviors in abrasion resistance. Therefore, all the above effects will impact the mechanical properties of the polymer compound.

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