Adhesion Between Dissimilar Polymers. II. Effects of Bonding Temperature and Crosslinking Agent*

M. F. Tse,[1] W. Hu,[1] M. S. Yeganeh,[2] D. Zhang[2]

[1]*ExxonMobil Chemical Company, Baytown, Texas 77520*
[2]*ExxonMobil Research and Engineering Company, Annandale, New Jersey 08801*

ABSTRACT: We study the effects of bonding temperature and crosslinking agent on the adhesion of a crosslinkable BIMS polymer (terpolymer of isobutylene, *p*-bromomethylstyrene, and *p*-methylstyrene) to a crosslinkable diene polymer, such as polyisoprene rubber (IR) or polybutadiene rubber (BR). The strength of adhesion between these two dissimilar polymers, represented by the work of detachment, G_a, is measured by using the T-peel geometry at various test temperatures and separation speeds. Surface-sensitive infrared-visible sum frequency generation (SFG) spectroscopy is used to characterize the surface of BIMS and ensure the existence of crosslinkable species, the *p*-bromomethylstyrene functional group, on this polymer. Time-of-flight secondary ion mass spectroscopy (ToF-SIMS) is utilized to determine the loci of failure of the debonded surfaces and the influence of curative migration, if any, on adhesion. Although a zinc di-2-ethylhexanoate crosslinkable BIMS polymer shows interfacial crosslinking or cocure when bonded to a sulfur crosslinkable diene polymer at 140°C, interfacial cocure does not occur when the bonding temperature is raised to 180°C. On the other hand, if the sulfur crosslinking agent in the diene polymer is replaced by another crosslinking agent, a brominated phenolic resin, interfacial cocure occurs between BIMS and the diene polymer when the bonding temperature is 140, 160, or 180°C. Also, this brominated resin cocures the BIMS and diene polymer phases when these immiscible polymers are blended together in the presence of a metal compound (salt) of carboxylic acid, such as zinc di-2-ethylhexanoate. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 93: 323–335, 2004

Key words: adhesion; crosslinking; interfaces; NMR; rubber

INTRODUCTION

The bonding of a crosslinkable, elastomeric polymer to itself was studied extensively by Gent and coworkers.[1–5] They applied the William–Landel–Ferry (WLF) time–temperature equivalence[6] to peel adhesion data measured at different rates and temperatures to construct a master curve as a means of deducing the intrinsic strength, G_o, of model interfaces between sheets of similar elastomer, interlinked to different degrees by covalent bonds. In one of their studies,[4] they found that G_o is proportional to $(\Delta N)L^{3/2}$, where ΔN and L are the volume density and length of the interlinking molecules of the interface, respectively. In general, when the peel rate is increased and the peel temperature is lowered, the strength of adhesion increases as high as $1000G_o$ due to internal dissipative processes.

In the absence of specific, strong chemical interactions (such as acid-base interactions), two dissimilar polymers have a positive free energy of mixing and hence are thermodynamically immiscible because the heat of mixing is usually positive and the entropy gained upon mixing these dissimilar macromolecules is quite small. Therefore, when a partially immiscible pair of polymers is adhered, interfacial mixing or interdiffusion is limited. This results in an interface with low mechanical strength, especially when the interface is ruptured at low separation speeds and high temperatures. However, if each of these dissimilar polymers is crosslinkable, the interface can be strengthened via interfacial crosslinking (cocure). Interfacial cocure can occur by a common curative if both polymers carry identical functional groups, such as the cocuring of polyisoprene rubber (IR) and polybutadiene rubber (BR) in the presence of a sulfur/accelerator crosslinking system. Interfacial cocure can also occur by direct chemical bonding if the two polymers carry functional groups reactive to each other, such as the cocuring between terpolymer of isobutylene, *p*-bromomethylstyrene, and *p*-methylstyrene (BIMS) and nylon 6,[7] or between BIMS and IR or BR, studied in this work. The chemical reactivity of BIMS by electrophilic additions to olefins, depicted briefly in Figure 1, was investigated by Frěchet et al.[8] by using model compounds as well as appropriate polymers. The mechanism of the addition process involves the initial formation of carbocationic complexes with zinc salts, followed by addition to the double bonds of the
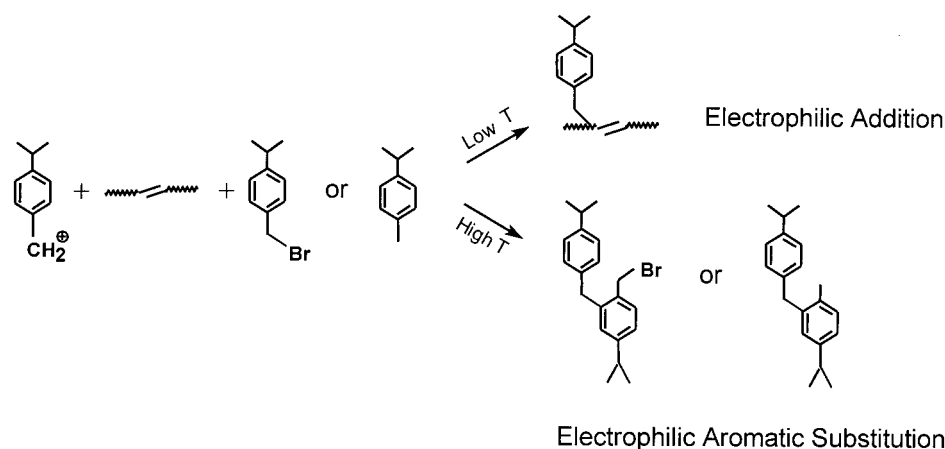
Figure 1 Chemical reactivity of BIMS. T denotes temperature.

olefins. Electrophilic addition of the *p*-bromomethyl-styrene (BrPMS) group to the double bond is more favorable at lower temperatures. On the other hand, the electrophilic aromatic substitution of the BrPMS group to itself or the *p*-methylstyrene (PMS) group is more favorable at higher temperatures. Effects of BIMS composition, carbon black, and benzothiazyl disulfide (MBTS) accelerator on the adhesion of BIMS and diene elastomer (IR or BR) at a bonding temperature of 140°C were discussed previously.[9] It has been found that interfacial cocure does occur between BIMS and either IR or BR. However, addition of carbon black at 45 phr eliminates this interfacial cocure under the conditions studied. Also, when MBTS accelerator is present, the level of BrPMS in the BIMS elastomer determines whether or not interfacial cocure is obtained. In this work, effects of bonding temperature and crosslinking agent (sulfur versus brominated resin) used in the diene polymer on interfacial crosslinking or cocure between BIMS and IR or BR are studied by using T-peel adhesion, sum frequency generation (SFG) spectroscopy, and time-of-flight secondary ion mass spectroscopy (ToF-SIMS) measurements.

Following the approach of Gent et al.,[1–5] peel adhesion measured at different rates and temperatures is used to deduce G_o and assess interfacial cocure. SFG is used to verify the presence of BrPMS groups on the BIMS surface. ToF-SIMS is employed to analyze the fracture surfaces for determining the locus of failure and the mechanism of fracture.

EXPERIMENTAL

Materials

Some abbreviations, symbols, and descriptions of the materials used in this work are shown in Table I. Two BIMS polymers used in this study are described in Table II and Figure 2. The BrPMS and PMS contents were determined from a Varian VXR 300 MHz spectrometer. Molecular weights were measured by gel permeation chromatography (GPC; Waters' Alliance 2690 equipped with UV and DRI detectors), using tetrahydrofuran (THF) as the mobile phase. The BIMS-2 polymer before bromination, labeled as IMS-2, and a polyisobutylene (ExxonMobil Chemical's

TABLE I
Materials and Abbreviations

Abbreviation	Description	Function
BIMS	Isobutylene/*p*-bromomethylstyrene/*p*-methylstyrene terpolymer	Polymer
BR	Polybutadiene rubber	Polymer
Br Resin	SP 1055	Crosslinking agent
IB	Polyisobutylene	Polymer
IIR	Isobutylene/isoprene rubber	Polymer
IMS	Isobutylene/*p*-methylstyrene copolymer	Polymer
IR	Polyisoprene rubber	Polymer
MBTS	Benzothiazyl disulfide	Organic accelerator
	Stearic acid	Accelerator activator
	Sulfur	Crosslinking agent
ZnO	Zinc oxide	Accelerator activator
Zn(OT)$_2$	Zinc di-2-methylhexanoate	Crosslinking agent

TABLE II
Characterization of Polymers

	BrPMS (mol%)	PMS (mol%)	Approximate M_n	Approximate M_w	Approximate M_v
BIMS-1	0.84	5.20	177,000	480,000	—
BIMS-2	1.20	2.50	161,000	400,000	—
IMS-2	0	3.70	161,000	400,000	—
IB	0	0	450,000	1000,000	900,000

VISTANEX® MM L-80), labeled as IB, were also used. The BR used was Budene 1207 elastomer (Goodyear Tire and Rubber Co.), which has ~ 98% *cis*-1,4 content. The IR used was Natsyn 2200 elastomer (Goodyear Tire and Rubber Co.), which has 92% (minimum) *cis*-1,4 content. The N330 carbon black filler has a nitrogen surface area of 83 m²/g and a dibutyl phthalate absorption (DBPA) value of 102 mL/100 g.[10] The brominated phenolic resin, denoted by Br resin throughout this article, was SP 1055 from Schenectady Chemicals. A postulated structure of this resin based on NMR and GPC studies is shown in Figure 3. Because the bromine content is 3.6–4.0 wt %, therefore, not every chain end of this resin molecule is brominated. Also, *n* ~ 4 is only the average number of repeat units. GPC measurement showed that this resin has multimodal molecular weight distribution. DSC glass transition temperature (T_g) of the resin is ~ 48°C.

Recipes of the crosslinkable polymer gum compounds are shown in Table III (numbers expressed in parts by weight). BIMS-1 was crosslinked by zinc di-2-ethylhexanoate (R. T. Vanderbilt Co., Inc.), abbreviated as Zn(OT)₂. IR or BR was crosslinked by sulfur/ZnO/MBTS/stearic acid, sulfur/ZnO/MBTS, or Br resin/ZnO/MBTS. Formulations of the carbon black filled BIMS-1/BR blend compounds are shown in Table IV (numbers expressed in parts by weight).

Mixing and molding

Mixing of the gum compounds was carried out in a two-roll mill (maximum temperature ~ 90°C). Mixing

of the carbon black stocks was carried out in a Banbury mixer. The polymer and the carbon black were mixed first (started at ~ 65°C, mixed for ~ 5 min, and discharged at ~ 150°C), followed by sheeting on a two-roll mill. This mixing and milling process was repeated one more time. At this point, for diene polymers, the mix was returned to the Banbury mixer and curing agents were added (started at ~ 65°C, mixed for ~ 2 min, and discharged at ~ 100°C), followed by sheeting on a two-roll mill. For BIMS-1, the mix was put back on the two-roll mill and the liquid curing agent, Zn(OT)₂, was added. After mixing, each of the formulations in Table II was molded at 140°C for 180 min, which was longer than all the t_{90} values (minutes to 90% of maximum torque) of the compounds measured at 140°C by a moving die rheometer (MDR).[11] At 180°C, Formulations 1–5, 6, and 7 were molded for 12, 60, and 15 min, respectively. The molded pads (thickness ~ 2 mm) were then die cut into appropriate dimensions for solvent swelling and dynamic mechanical measurements.

Solvent swelling measurements

Solvent swelling measurements were carried out in toluene by using a procedure described previously.[12] The average molecular weight between crosslinks, M_c, was calculated from the volume fraction of polymer in the swollen network at equilibrium swelling, V_r, based on the Flory–Rehner equation.[13] Values of χ, the polymer–solvent interaction parameter, used to calculate M_c were χ(IIR-toluene) = 0.557[14]; χ(BR-toluene)

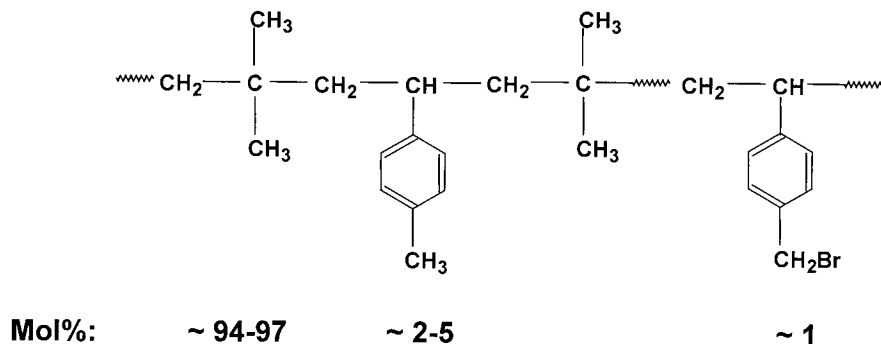Mol%:   ~ 94-97   ~ 2-5   ~ 1
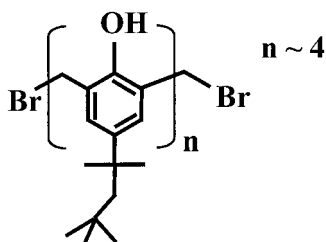
Figure 2 Structure of BIMS polymer.

Figure 3 Postulated structure of Br resin.

= 0.340[15]; and χ(IR-toluene) = 0.393,[14] where IIR denotes isobutylene/isoprene rubber. It was assumed in the calculations that χ(IIR-toluene) = χ(BIMS-toluene) (i.e., we assumed the contribution of the 5.20 mol % PMS in BIMS-1 was negligible). Also, one has to consider that the M_c values in the cured adhesion sample may change because of the transfer of curative/accelerator from one polymer to the other across the interface during the bonding/curing process.[9]

Cured adhesion measurements

The strength of cured adhesion between two adhering polymer layers was determined by the T-peel experiment. Usually, duplicate or triplicate measurements were performed. On the outside, each polymer layer was bonded to a nylon-reinforced rubber backing to prevent the extension of the compound during the peel measurement. Without the backing, the work used to extend both polymers will be included in the peel strength, which does not represent the true adhesion between the polymers. At 140°C bonding temperature, the bonding times were 180 min for the 1/2H (Compound **1** bonded to Compound 2H in Table II), the 1/2L, and the 1/3H bonds, and 120 min for the 1/5 bond. At 160°C bonding temperature, the bonding time was 100 min for the 1/5 bond. At 180°C bonding temperature, the bonding times were 12 min

TABLE IV
Filled BIMS-1/BR Blend Compounds for AFM Studies

	6	7
BIMS-1	50	50
BR	50	50
N330	45	45
Sulfur	1	—
ZnO	1.5	1.5
Zn(OT)$_2$	1.12	1.12
Br resin	—	2
t_{90} @ 180°C, min	26	6
Cure conditions	180°C, 60 min	180°C, 15 min
V_r	0.36	0.38

for the 1/2H, the 1/2L, and the 1/3H bonds, and 45 min for the 1/4 and the 1/5 bonds. Most of the above bonding times were chosen to exceed the t_{90} value of the elastomer layer with a slower cure. The work of detachment (identical to the adhesive fracture energy, G_a, which is equal to twice the peel strength) was calculated from the peel force, F, per unit width, w, of the test specimen:

$$G_a = 2F/w$$

Results of G_a at different separation speeds and temperatures were superimposed by using a reference temperature of 25°C and effective peel rates calculated from the equation below for the shift factor, a_T, given by Ferry as appropriate for polyisobutylene, polyisoprene, or polybutadiene:[6]

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

where T_g is the glass transition temperature, and C_1 and C_2 are the WLF coefficients. Only a horizontal shift along the rate axis was used to achieve superposition.

TABLE III
Crosslinkable Gum Compounds for Adhesion Studies

	1	2H	2L	3H	4	5
BIMS-1	100	—	—	—	—	—
IR	—	100	100	—	100	—
BR	—	—	—	100	—	100
Zn(OT)$_2$	2.23	—	—	—	—	—
Sulfur	—	2	0.32	2	—	—
ZnO	—	3	0.75	3	0.75	0.75
MBTS	—	1	0.8	1	1	1
Stearic acid	—	2	—	2	—	—
Br resin	—	—	—	—	4	4
t_{90} @ 140°C(min)	118	84	129	154		102
$M_c \times 10^{-3}$ (cured @ 140°C, 180 min)	12.0	11.7	41.6	14.9		11.6
t_{90} @ 180°C (min)	37	4	6	10	20	42
$M_c \times 10^{-3}$ (cured @ 180°C, 12 min)	13.6	12.1	64.0	10.9	23.0	5.7

Solid-state NMR measurements

Solid-state NMR measurements were performed in a Bruker DSX 500 spectrometer, with a ^{13}C resonance frequency of 125.76 MHz. A ^{13}C direct polarization/high-power ^{1}H decoupling pulse sequence was used. The spectra were acquired at room temperature. In all the experiments, the recycle delay was 10 s. The BR was primarily *cis-*, with *trans-* and vinyl-population $< 2\%$. The BR population was calculated as the total signal area under the peaks at 130 and 28 ppm, which were assigned to CH and CH_2 in *cis*-polybutadiene, respectively. The BIMS population was calculated as twice the area under the peak at 32 ppm, which was assigned to the CH_3 groups in polyisobutylene. The polyisobutylene population was then converted to the copolymer population according to the mole concentrations of isobutylene, BrPMS, and PMS in the BIMS polymer.

Sum frequency generation spectroscopy

SFG spectroscopy was performed at ExxonMobil SFG-I and designed and assembled at ExxonMobil Laboratories. The generation of the sum frequency photon is forbidden in the bulk of a centrosymmetric material such as polymer films or solid substrates. However, it is allowed at an interface or surface where the inversion symmetry is lifted. This intrinsic property of SFG and its high sensitivity to molecular species, particularly the aromatic ring, make this probe an ideal tool to study BMIS surfaces and interfaces.[16,17] The determination of the existence of the crosslinkable species, BrPMS, on a BIMS surface is complimentary to the identification of the same species via detection of bromine ion using the ToF-SIMS method. In addition, we used SFG to study the crosslinkable species at the buried BIMS/substrate interface, a region that is not accessible to conventional diagnostic tools.

In the investigation reported in this article, the vibrational modes corresponding to the symmetric and asymmetric stretches of CH_3, CH_2, CH, and the aromatic CH were excited by using a tunable infrared laser beam with a photon energy of 2800–3100 cm^{-1}. These excitations were combined with optical transitions, caused by a visible laser beam, to produce SFG resonance signals which are indicative of the surface molecules containing the above functionalities. A schematic of the optical setup is described previously.[18] Briefly, the SFG-I spectrometer contains a nanosecond Spectral Physic Nd : YAG laser and multipass hydrogen Raman shifter. A portion of the output of the doubled-Nd : YAG laser was used as the visible light source. The incident light pulses had a duration of ~ 7 ns and an intensity of ~ 10/cm^2 for both the visible and the infrared beams, which was at least an order of magnitude below the measured sample dam-
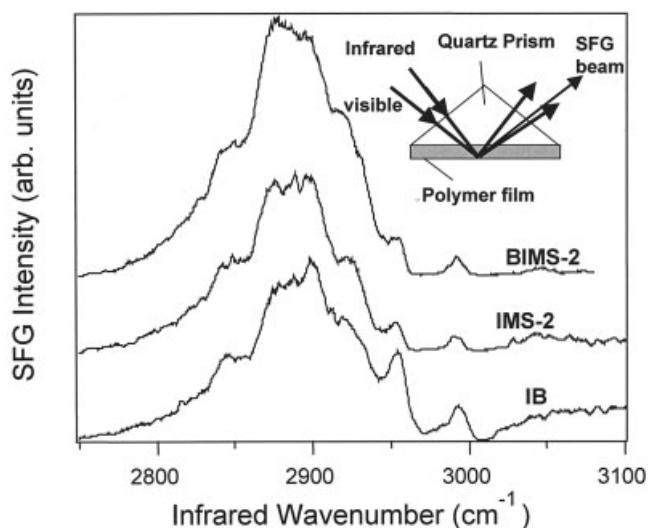

Figure 4 SFG spectrum of the BIMS-2 surface. The SFG spectra of IB and IMS-2 are also shown. Insert: SFG sample geometry.

age threshold. In this investigation, visible, infrared, and SFG beams were set and detected in a P-polarization configuration (i.e., the electric field was in the plane of incidence).

Our sample for the SFG measurement was a ~ 1000 Å polymer film which was spin coated from a hexane solution onto a quartz prism (shown in the insert of Fig. 4). The spin-coated polymer was then heated under vacuum at 70°C for 4 h to eliminate all solvent. The SFG spectra of the polymer surface were collected at room temperature.

Time-of-flight secondary ion mass spectroscopy

ToF-SIMS analysis was performed in the bunched mode by using a Charles Evans and Associates TFS Surface Analyzer equipped with a liquid Ga$^+$ ion source and operated at a pressure of $\sim10^{-6}$ Pa. The 15-keV Ga$^+$ ion beam was bunched into 0.625-ns pulse widths. The bunched Ga$^+$ ion beam was rastered over a 65×65 μm^2 area with a spot size (lateral resolution) of ~ 3–4 μm, and a total ion dose for each analysis $\sim 4 \times 10^{12}$ Ga$^+$/cm^2. All the cured adhesion samples were peeled by hand at a speed of ~ 850 μm/s (2 in./min) immediately before the measurements to minimize contamination of the debonded surfaces. Each of the freshly debonded surfaces of the adhesion specimen was analyzed.

Dynamic mechanical measurements

Isochronal experiments at 1 Hz over a wide range of temperatures were performed with a dynamic mechanical thermal analyzer (DMTA) operated in bending mode (dual cantilever, flat face/small frame ge-
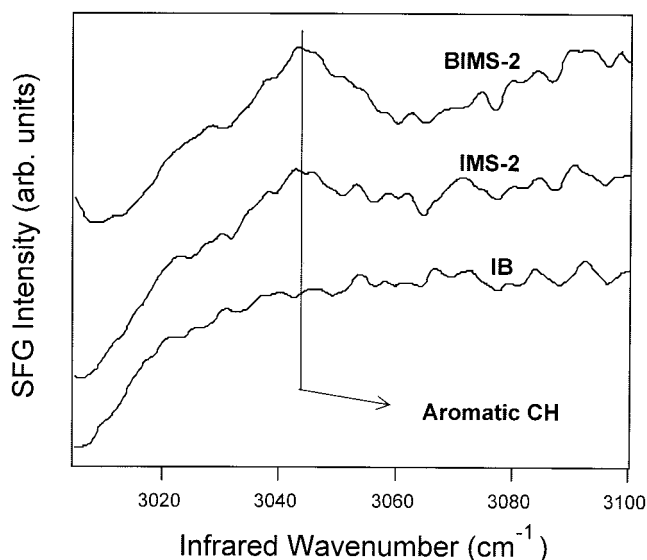
Figure 5 High-resolution SFG spectra of BIMS-2, IMS-2, and IB.

Atomic force microscopy

The morphology of the two filled BIMS/BR blend compounds in Table IV was studied by tapping phase atomic force microscopy (AFM) measurements. Specimens were cryofaced by cooling to $-150°C$ and cutting with diamond knives in a Reichert cryogenic microtome. The faced specimens were mounted in a miniature steel vice for AFM analysis. The AFM mea-

surements were performed in air in a NanoScope Dimension 3000 scanning probe microscope (Digital Instrument) by using a rectangular 225-μm Si cantilever.

RESULTS AND DISCUSSION

Effects of bonding temperature on interfacial adhesion

The main question addressed in this work is whether a crosslinkable BIMS/diene polymer compound, which shows interfacial cocure at a bonding temperature of 140°C, will also show interfacial cocure at a higher bonding temperature, such as 180°C. The polymer compounds used to address this question are described in Table III. Compound **1** is the BIMS-1 compound. Compounds 2H and 2L are high- and low-cure-state IR compounds, respectively, whereas Compound 3H is a high-cure-state BR compound. A compound with a higher cure state shows a smaller M_c value.

To verify the existence of the crosslinkable species, BrPMS, at the surface of the BIMS, SFG spectroscopy was performed at room temperature. Figure 4 shows the SFG spectra generated at the surface of BIMS-2. The SFG spectra of BIMS-2, along with the SFG spectra of IMS-2 (unbrominated polymer) and IB (polyisobutylene), are shown (each performed at the polymer/air interface). The structural features shown below 3000 cm^{-1} are due to various resonance stretches of the CH, CH_2, and CH_3 groups. The high-resolution spectra are also shown in Figure 5 from 3000 to 3100 cm^{-1} for clarification. As expected, IB does not exhibit any structure due to the aromatic CH. However, both IMS-2 and BIMS-2 show a distinct structure at $\sim$ 3045
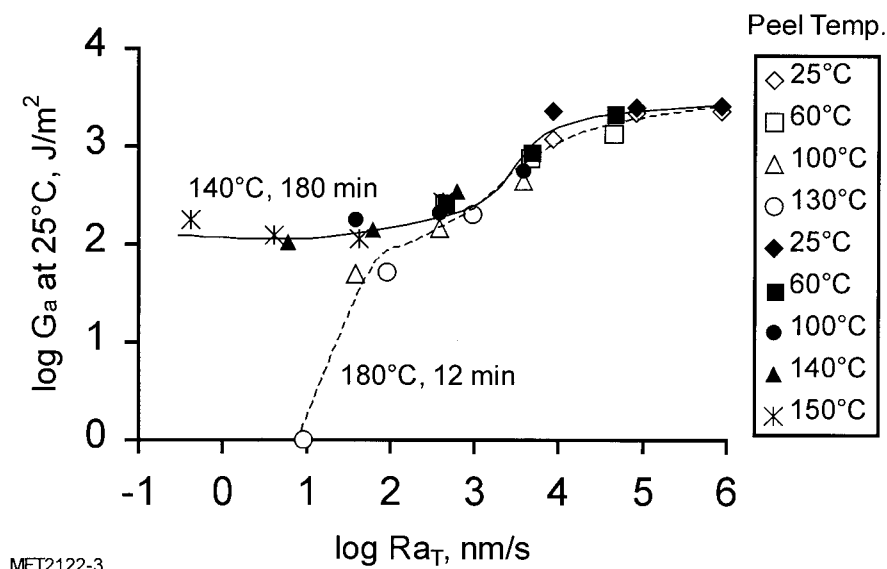

Figure 6 Work of detachment between BIMS-1, Compound **1**, and high-cure-state IR, Compound 2H, at two different bonding temperatures.
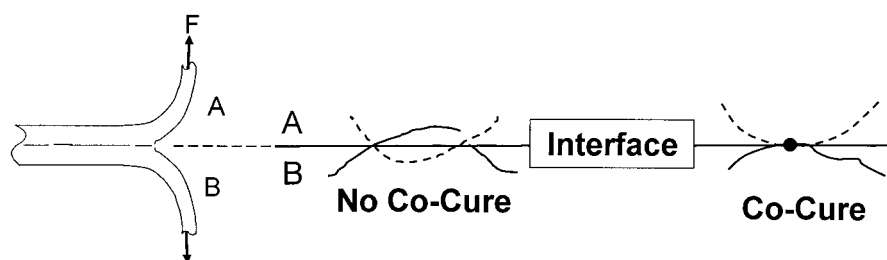
Figure 7 High peel rates can render the entanglement between Chains A and B behave as an interfacial crosslink junction.

cm^{-1} due to the resonance of aromatic CH. This structure shows the existence of PMS at IMS-2. It is also evident from the data that the ~ 3045 cm^{-1} resonance structure is enhanced when the BrPMS is included in the polymer. This is an indication of the existence of BrPMS at the surface of BIMS-2. Despite the difference between BIMS-1 and BIMS-2 (Table II), BrPMS should also exist at the surface of BIMS-1. It should be noted that this structural feature was also detected at higher temperatures. The details of the temperature dependence data will be reported elsewhere.

Figure 6 shows the work of detachment (the measure of cured adhesion), G_a, as a function of the reduced peel separation speed, Ra$_T$, of the BIMS-1 compound bonded to the sulfur/ZnO/MBTS/stearic acid curable IR compound (Compound 2H; high cure state) at a reference temperature of 25°C. The legend in the figure shows the temperatures at which the peel experiments are carried out. One curve corresponds to a bonding temperature of 140°C and the other corresponds to that of 180°C. Clearly, the crosslinkable BIMS-1/IR bond shows interfacial cocure at a bonding temperature of 140°C. This is due to the fact that, under threshold or near-equilibrium conditions (extremely low rates with a peel distance ~ 1 nm in 1 s to eliminate bulk dissipative effects; Figs. 6–7), G_a of the bond between BIMS-1 and IR reaches a plateau, nonzero value, suggesting the existence of interfacial cocure. On the other hand, threshold strength between BIMS-1 and IR bonded at 180°C drops to zero, suggesting the absence of interfacial cocure. Figure 7 emphasizes the concept that, if the rate is high, there is no difference between no cocure and cocure at the interface of the T-peel geometry. This is due to the fact that the entanglement between chain A and chain B at the interface does not have enough time to disentangle and it behaves similar to a cocure junction. Therefore, the force or work, G_a, to detach this entanglement remains high. On the other hand, if the rate is extremely low, the entanglement has enough time to slip. Therefore, the force or G_a is zero when there is no cocure at the interface, but reaches a plateau, nonzero value when cocure exists. A similar behavior was observed for BIMS-1 bonded to both the low-cure-
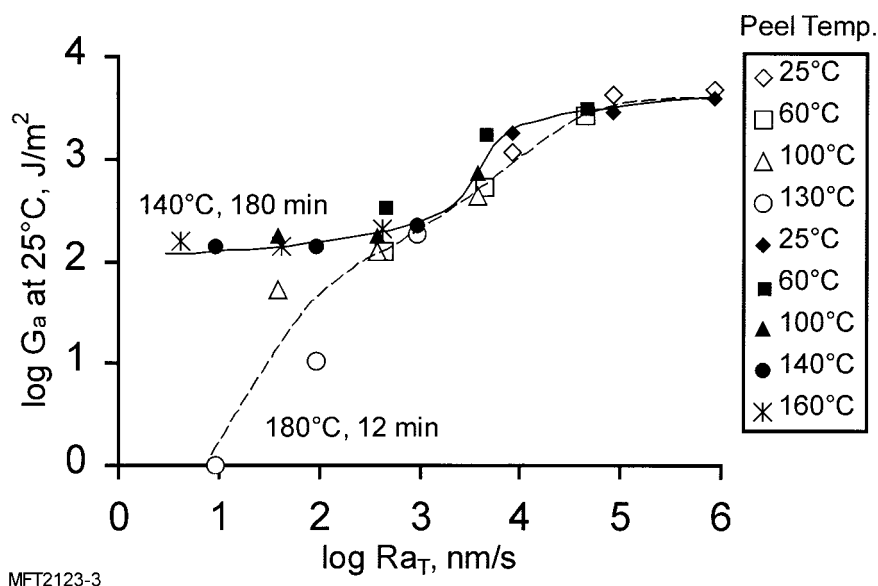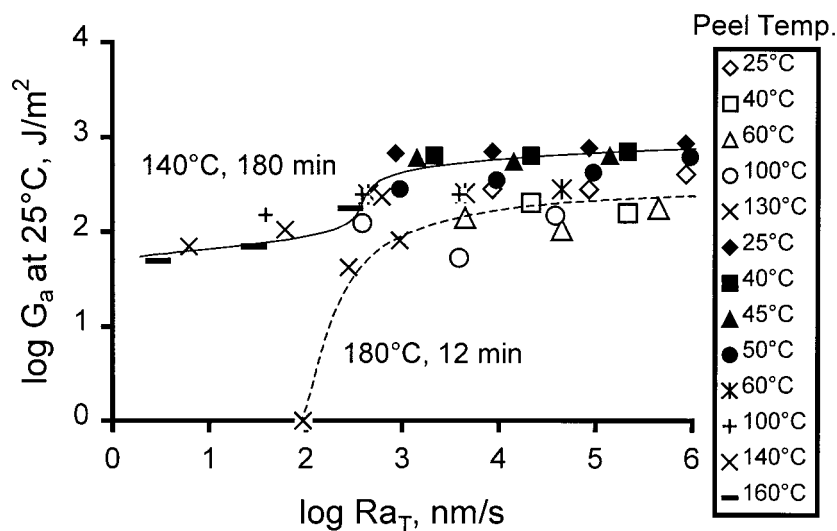

Figure 8 Work of detachment between BIMS-1, Compound **1**, and low-cure-state IR, Compound 2L, at two different bonding temperatures.

Figure 9 Work of detachment between BIMS-1, Compound **1**, and high-cure-state BR, Compound 3H, at two different bonding temperatures.

state IR compound (2L) and the high-cure-state BR compound (3H) (Figs. 8 and 9). These data suggest that a higher bonding temperature is detrimental to interfacial cocure between BIMS and the diene polymer when the crosslinking agent in the latter polymer is sulfur. It is not clear why considerable spread of the data occurs in Figure 9. Overall, the above adhesion results are consistent with the work of Frěchet et al.[8] At low bonding temperatures, reaction of the BrPMS groups in BIMS to the double bonds in BR is more favorable, resulting in interfacial cocure. At high bonding temperatures, reaction of the BrPMS groups

in BIMS to the BrPMS groups in the same polymer is more favorable. Therefore, cocure is less likely to occur.

Following a similar analysis,[9] we examine the ToF-SIMS results obtained from the debonded surfaces of 1 to 2H, 2L, or 3H adhered at 140 and 180°C (Table V). In most cases, we observe the transfer of BIMS to the top layer of the diene polymer side, as shown by the relative signal of BIMS, calculated from the ratio of the areas of the $C_7H_{13}^+$ (97 amu) peak and the $C_2H_3^+$ (27 amu) peak from the ToF-SIMS spectrum.[9] This is consistent with the fact that, when we construct the mas-

TABLE V
ToF-SIMS Analyses of Debonded Surfaces of Cured Adhesion Specimens

|	BIMS, relative signal	Sulfur (ppm)	Surface composition
1/2H (Bonded @ 140°C, 180 min)			
1 Side	2.0338	680	BIMS
2H Side	0.9467	570	IR/BIMS
1/2H (Bonded @ 180°C, 12 min)			
1 Side	1.7293	1540	BIMS
2H Side	0.2364	1650	Zn/Wax[a]; BIMS
1/2L (Bonded @ 140°C, 180 min)			
1 Side	1.3438	3620	BIMS
2L Side	0.0678	4270	IR
1/2L (Bonded @ 180°C, 12 min)			
1 Side	0.2986	220	BIMS/IR
2L Side	0.1296	230	BIMS/IR
1/3H (Bonded @ 140°C, 180 min)			
1 Side	1.7075	1000	BIMS
3H Side	0.2713	5000	BR/BIMS
1/3H (Bonded @ 180°C, 12 min)			
1 Side	1.9982	1550	BIMS
3H Side	0.3385	1400	BIMS/BR

[a] Signal from $Zn(OT)_2$.
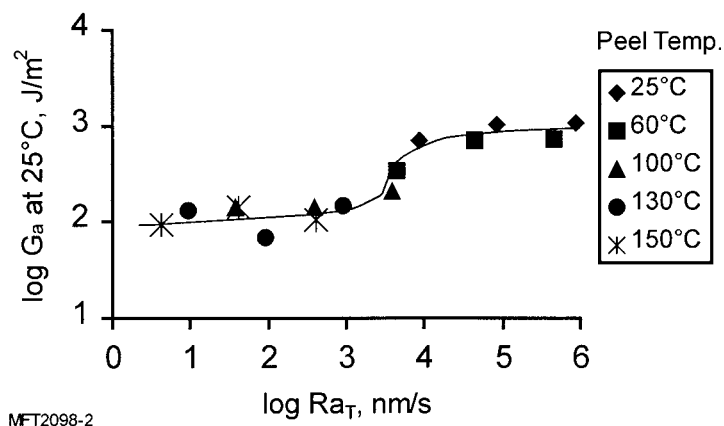
(a)
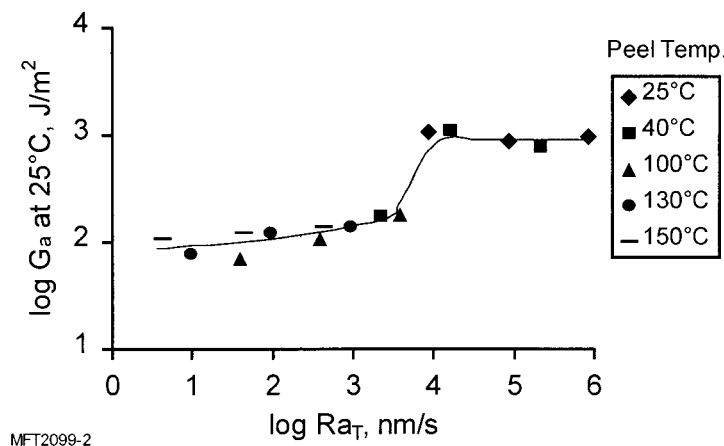
(b)
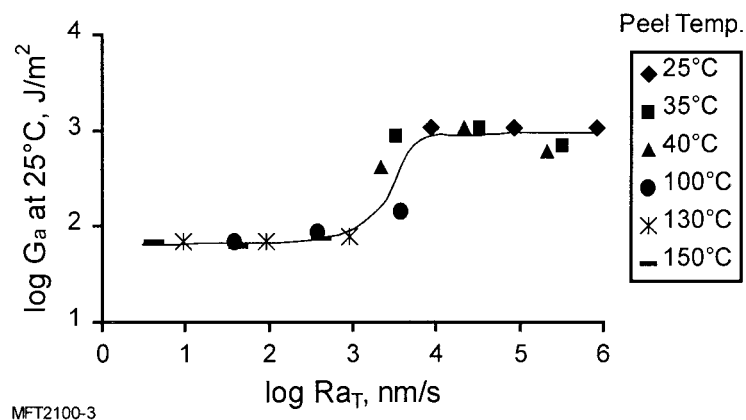
(c)

Figure 10 Work of detachment between BIMS-1 and Br resin/ZnO/MBTS curable BR bonded at (a) 140, (b) 160, and (c) 180°C.
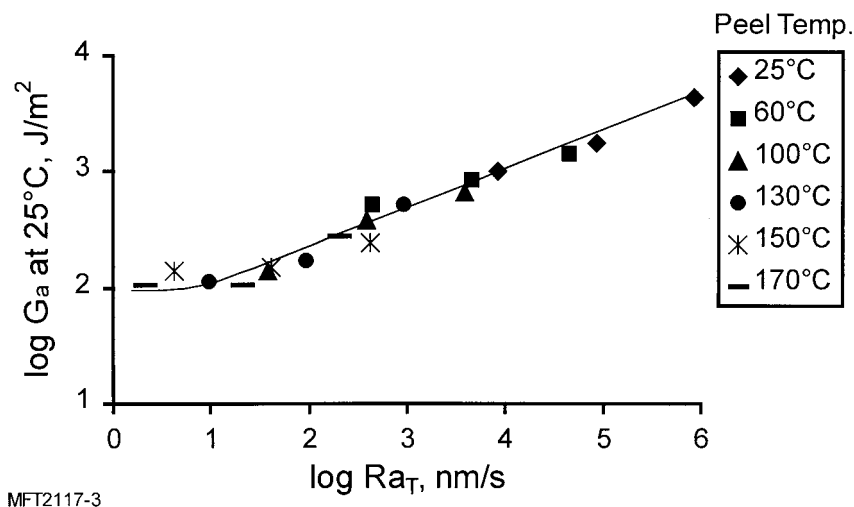
Figure 11 Work of detachment between BIMS-1 and Br resin/ZnO/MBTS curable IR bonded at 180°C.

ter curve of G_a in Figures 6, 8, and 9, we use a_T values of polyisobutylene to calculate the effective peel rates. Also, we observe S^- (32 amu) from the debonded BIMS-1 surface, suggesting that sulfur and/or MBTS from the diene polymer side may transfer to the BIMS-1 side during the bonding/curing process (Table V). The amount of sulfur expressed in ppm is calculated from the areas of the S^- (32 amu) peak and the C^- (12 amu) peak from the ToF-SIMS spectrum.[9]

Effects of Br resin

Figure 10 shows G_a as a function of Ra_T of BIMS-1 (Compound **1**) bonded to the Br resin/ZnO/MBTS curable BR compound (Compound **5**) at 140, 160, and 180°C. Under threshold or near-equilibrium conditions, G_a's of this BIMS/BR bond still show plateau, nonzero values at all bonding temperatures. This suggests the existence of interfacial cocure. Interfacial cocure also occurs when this BIMS-1 compound is bonded to the Br resin/ZnO/MBTS crosslinkable IR compound (Compound **4**) at 180°C (Fig. 11). Therefore, the use of a Br resin appears to eliminate the

bonding temperature effect on interfacial cocure between BIMS-1 and diene polymer perhaps because of the ability of this resin to intercrosslink BIMS-1 and diene polymer at the interface. It is known that diene polymers, such as natural rubber (NR), styrene–butadiene rubber (SBR), and BR, can be vulcanized by the action of a phenolic compound such as the Br resin.[19] The —CH_2—Br group of this resin (Fig. 3) may crosslink BIMS-1 by electrophilic aromatic substitution with the BrPMS group in BIMS-1 in the presence of a metal compound (salt) of carboxylic acid, such as $Zn(OT)_2$.

Cocure of BIMS/BR blend by Br resin

As described above, although a $Zn(OT)_2$ curable BIMS-1 compound shows interfacial cocure when bonded to a sulfur/ZnO/MBTS curable diene polymer compound at 140°C, interfacial cocure does not occur when the bonding temperature is raised to 180°C. On the other hand, when a $Zn(OT)_2$ curable BIMS-1 compound is bonded to a Br resin/ZnO/ MBTS curable diene polymer compound, interfacial

TABLE VI
Interpolymer Crosslinking Between BIMS-1 and BR

	A (Control)	B (Control)	C	D (Control)	E
BIMS-1[a]	11.25	11.25	11.25	11.25	11.25
BR[a]	33.75	33.75	33.75	33.75	33.75
$Zn(OT)_2$	—	0.12	0.12	0.24	0.24
Br resin	1.35	—	1.35	—	1.35
% Unextractable	19.26	48.20	80.39	60.73	88.81
In Unextractable					
BIMS-1/BR Wt. Ratio[b]	0.14	1.11	0.34	0.83	0.38

[a] The originally charged BIMS-1/BR wt. ratio to the mixer is 11.25/33.75 = 0.33.
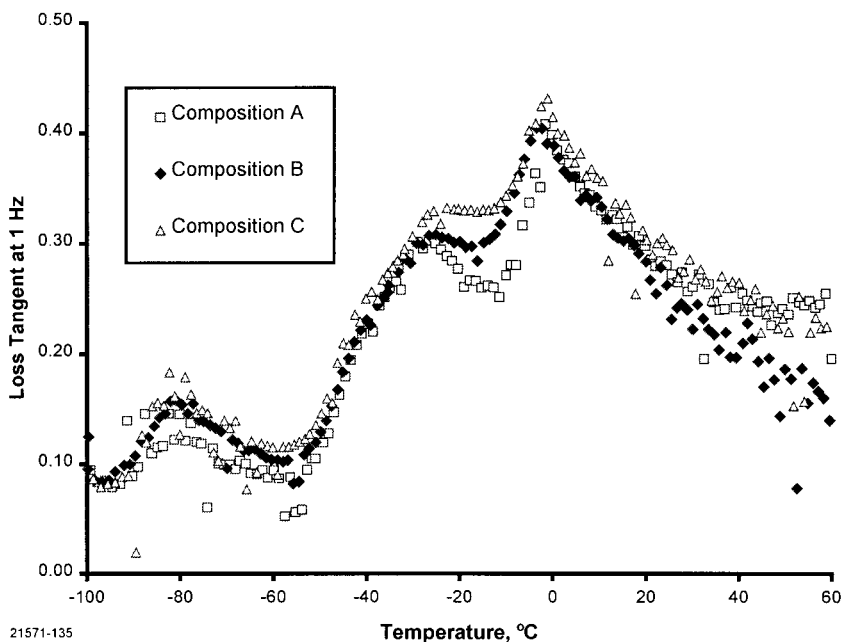[b] Based on solid-state ^{13}C NMR.

Figure 12 Loss tangent at 1 Hz versus temperature for BIMS-1/BR blends.

cocure occurs when the bonding temperature is 140, 160, or 180°C. Therefore, this Br resin seems to cocure BIMS-1 and diene polymer at the interface. Additional experiments are carried out to verify this hypothesis.

Blending of BIMS-1 and BR in the presence of $Zn(OT)_2$, Br resin, or $Zn(OT)_2$ + Br resin is performed as a means of detecting any interpolymer crosslinking (Table VI, where the numbers represent the weights of the ingredients in grams). These blend compositions

are prepared by mixing them in a Brabender mixer at a temperature of 140°C and a rotor speed of 60 rpm. Small pieces of BR are first added together with $Zn(OT)_2$ (if required) to the mixer. After 3 min, small pieces of BIMS together with the Br resin (if required) are added. The blend is then mixed for 5 min and subsequently discharged from the mixer. Several blend compositions with BIMS/BR blend ratio of 25/75 = 0.33 are shown in Table VI. Besides the poly-
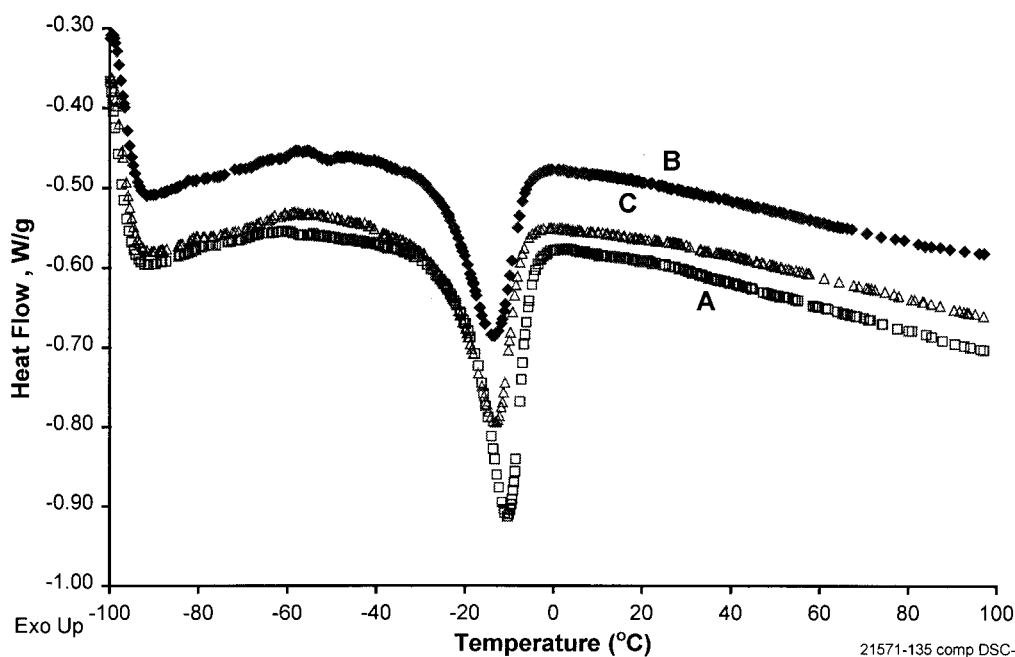

Figure 13 DSC thermograms for BIMS-1/BR blends.

mers, Composition A contains Br resin only, and Compositions B and D contain $Zn(OT)_2$ only, whereas Compositions C and E contain both Br resin and $Zn(OT)_2$.

Each of the above compositions is pressed at 140°C for 15 min and then cut into small pieces. About 1.5 g is loaded in a stainless steel thimble. Extraction in toluene is carried out for 7 days at room temperature. The amount unextractable of each composition is shown in Table VI. Compositions containing either Br resin alone (Composition A) or $Zn(OT)_2$ alone (Compositions B and D) show lower amounts of % unextractable, indicating lower degrees of crosslinking. On the other hand, Compositions C and E containing both Br resin and $Zn(OT)_2$ show higher amounts of % unextractable, indicating higher degrees of crosslinking and evidence of cocure because % unextractables for C and E are higher than a simple addition of the control cases, A + B and A + D, respectively.

The composition of the unextractable material is further characterized by solid-state ^{13}C-NMR. The purpose is to determine the degree of interpolymer (BIMS-1 with BR) or intrapolymer (BIMS-1 with BIMS-1 or BR with BR) crosslinking in each composition. According to Table VI, the originally charged BIMS-1/BR weight ratio to the mixer is 11.25/33.75 = 0.33. BIMS-1/BR blend compositions containing Br resin alone (Control Composition A) and $Zn(OT)_2$ alone (Control Compositions B and D) show lower (0.14) and higher (1.11, 0.83) BIMS-1/BR weight ratios in unextractable compared to the originally charged BIMS-1/BR weight ratio of 0.33. Therefore, the Br resin predominantly performs intrapolymer crosslinking in BR in Control Composition A, whereas $Zn(OT)_2$ predominantly performs intrapolymer crosslinking in BIMS-1 in Control Compositions B and D. On the other hand, BIMS-1/BR blend compositions containing both the Br resin and the $Zn(OT)_2$ (Compositions C and E) show BIMS-1/BR weight ratios in unextractable of 0.34 and 0.38, which are similar to the originally charged BIMS-1/BR weight ratio of 0.33. Therefore, when both the Br resin and the $Zn(OT)_2$ are present in Compositions C and E, interpolymer crosslinking (cocure) occurs between BIMS-1 and BR.

The loss tangents at 1 Hz as a function of temperature for Compositions A–C are shown in Figure 12. We speculate the peak slightly below 0°C corresponds to the crystallization peak of BR. This peak is also observed by running the samples in a modulated DSC (DSC 2910, TA Instruments; 10°C/min heating rate; Fig. 13). The peak at ~ −28°C in Figure 12 corresponds to the damping transition of BIMS.[20] Between these two peaks, the loss tangent is found to be Composition A < Composition B < Composition C. This suggests interpolymer crosslinking between BIMS-1 and BR for the formation of a mixed interfacial region when both Br resin and $Zn(OT)_2$ are present in the
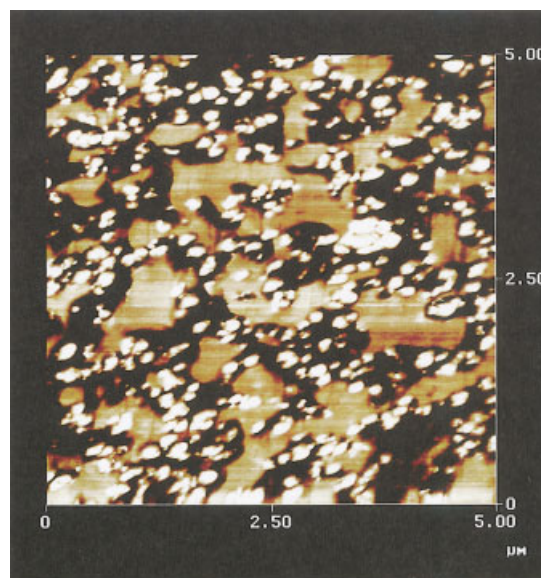
(a)
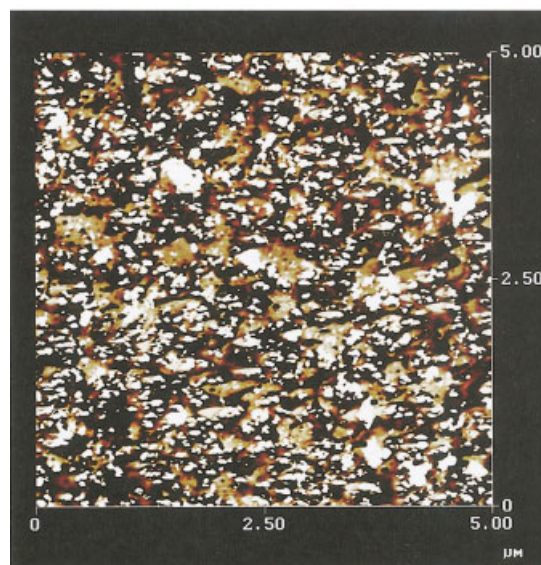
(b)

Figure 14 AFM micrographs of black-filled BIMS-1/BR blend compound crosslinked by (a) sulfur/ZnO/$Zn(OT)_2$ and by (b) Br resin/ZnO/$Zn(OT)_2$.

BIMS-1/BR blends. Another piece of supporting evidence is based on the AFM micrographs of the BIMS-1/BR blend compounds (Table IV; Fig. 14), where the dark, gray (yellow online), and white phases are BR, BIMS-1, and carbon black, respectively. These micrographs reveal that the phase size is more grossly inhomogeneous when the BIMS-1/BR blend compound was crosslinked by the sulfur/ZnO/$Zn(OT)_2$ system than by the Br resin/ZnO/$Zn(OT)_2$ system. The Br resin may cocure part of the BIMS-1 and BR in the blend during mixing or may simply act as an interfacial compatibilizer during masterbatch preparation. If

formed, these cocured BIMS-1/BR molecules act as a compatibilizer for the rest of the BIMS-1 and BR, modifying the nature of the interface between these two polymers. This results in two effects: (1) A lower interfacial energy breaks BIMS-1 and BR phases apart easier; (2) Steric stabilization retards the coalescence of BIMS-1 and BR phases. More likely, (2) is more important not only to decrease phase size, but also to maintain a stable morphology. In summary, the Br resin appears to intercrosslink BIMS-1 and BR in the presence of a metal compound (salt) of carboxylic acid, such as $Zn(OT)_2$.

CONCLUSION

Peel adhesion and ToF-SIMS studies have been performed to characterize interfacial adhesion between BIMS and diene polymer. Although a $Zn(OT)_2$ curable BIMS compound shows interfacial cocure when bonded to a sulfur/ZnO/MBTS curable diene polymer compound at 140°C, interfacial cocure does not occur when the bonding temperature is raised to 180°C. On the other hand, if the sulfur in the diene polymer compound is replaced by a Br resin, interfacial cocure occurs between BIMS and the diene polymer when the bonding temperature is 140, 160, or 180°C. This Br resin also cocures these immiscible BIMS and diene elastomers when they are blended together in the presence of a metal compound (salt) of carboxylic acid, such as $Zn(OT)_2$, as demonstrated by solid-state NMR, dynamic mechanical measurements, and AFM.

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