

Green Strength Enhancement in BIIR/Olefin Copolymer Compounds

Andy H. Tsou, Ilan Duvdevani, Sudhin Datta

Baytown Technology and Engineering Complex, ExxonMobil Chemical Company, Baytown, Texas

Received 6 February 2006; accepted 12 April 2006

DOI 10.1002/app.24745

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Improved green strength of halobutyl at elevated temperatures was obtained via blending with semi-crystalline polymers. For such improvement, a judicious selection of olefin copolymers, such as ethylene-propylene, ethylene-butene, or ethylene-octene copolymers, as blend components has to be made. Green strength enhancement was found to increase with increasing compatibility between bromobutyl (BIIR) and the olefin copolymer. Increased compatibility may be estimated by chain dimension similarity in a dilute solution between polyisobutylene and the olefin copolymer. For the most compatible olefin copolymer examined, a propylene elastomer, a phase percolation threshold was found at 0.13 volume fraction of the copolymer. This threshold value is lower than the theoretical limit of 0.156 for spherical phase domains. Based on the morphological

examination by tapping phase AFM, it was found that this propylene elastomer crystallizes around the carbon black filler agglomerates to form nonspherical and high-aspect-ratio dispersed phases. Its phase anisotropy may contribute to its lower phase percolation threshold in BIIR compounds. Model innerliner compounds of BIIR containing 10–20 phr of such a propylene elastomer in place of natural rubber were shown to have excellent room-temperature and improved elevated-temperature strengths, good aging resistance, and excellent impermeability without significant increases in relaxation time. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 4447–4459, 2006

Key words: bromobutyl; butyl; green strength; olefin copolymer; phase continuity; AFM; innerliner compounds

INTRODUCTION

Isobutylene-based polymers have excellent air impermeability, strength, and elasticity that allow their extensive usage in tire innertubes and innerliners. However, their green strength properties are defensive to those of natural rubber (NR), particularly at elevated temperatures. Green strength is a term denoting the strength, cohesiveness, dimensional stability, and extensibility of rubber compounds before they are vulcanized or cured. Compounds refer to mixtures of polymer/rubber blends, curatives, processing oils, and fillers. Green properties are important in fabricating rubber articles from green compounds, especially for rubber composites such as tires. They are also essential in processing extruded items, such as innertubes, and molded articles, such as pharmaceutical stoppers.

Halogenated isobutylene-based polymers, especially brominated butyl rubbers (bromobutyl or BIIR), are the primary rubbers in most tire liners. The term butyl rubber (IIR) as employed here refers to a vulcanizable rubbery copolymer of isobutylene and isoprene. During the manufacturing process of tires, an

inner layer of a bromobutyl compound prior to curing is laminated with other layers of rubber compounds (green tire carcass) into a cylinder. These cylindrical tire laminated composites are stretched subsequently into precured tires with a donut shape. At room temperature, optimized green bromobutyl compounds have adequate strengths to sustain the stretching without formation of microvoids or cracks. However, during the hot summer months, tire-manufacturing plants without proper air conditioning or ventilation could have ambient temperatures exceeding 40°C. Lower strengths and extensibility of bromobutyl compounds at such elevated temperatures introduce susceptibility in innerliners to pinhole defects during tire building in a hot environment. Therefore, warm temperature green strength enhancement in bromobutyl innerliners is required for tire plants that may operate at warmer ambient temperature.

Blending of isobutylene-based polymers with NR is a common industrial practice for raising green strength of isobutylene-based polymer compounds. NR is known to crystallize upon extension and has very high molecular weight fractions, both of which are responsible for its high green strength.¹ Unstrained NR has a maximum degree of crystallinity of about 25% and an equilibrium melting temperature of over 40°C.¹ However, its high air permeability limits NR content that can be incorporated into the blends. Heat stability of cured NR/BIIR compounds is also compromised because of

Correspondence to: A. H. Tsou (andy.h.tsou@exxonmobil.com).

the presence of high unsaturations on the NR backbones. In general, a minimum of 20–25 phr (parts per hundred of polymer) by weight of NR is required for adequate warm temperature green strength. To compensate the increase in air permeability in NR/BIIR blends, thicker innerliners are thus required to maintain the same air retention ability of BIIR innerliners. The corresponding increases in material usage (because of the increase in thickness) and in tire weight are not desirable for tire cost and performance, not to mention the compromise in aging resistance. Hence, a better solution to enhance BIIR warm-temperature green strength is desired.

The star-branched bromobutyl (BrSBB) is a brominated copolymer of isobutylene and isoprene (IIR) that contains 10–15% chains in stars.² Stars are linear IIR chains terminated onto the midblock of a styrene-butadiene-styrene (SBS) block copolymer branching agent. The very high molecular weight of the star-branched fraction, along with a reduction in the molecular weight of the major fraction, contributes to an increase in green strength without adversely affecting the relaxation process. However, despite the higher room-temperature strength of the star-branched butyl when compared with that of bromobutyl, it still does not have adequate warm temperature green strength. Blending bromobutyl with olefinic semicrystalline polymers (SCP) is an alternative approach to improve the warm-temperature green strength of bromobutyl compounds. But there are limitations to the melting temperature range, glass transition temperature, crystallinity, and amount of these SCP that could be employed.

The requirement for the presence of crystals for strength enhancement at 40°C or higher and the need to process green rubber compounds below dictate the melting temperature range for a suitable SCP to be 40–90°C. The glass transition temperature of this SCP is preferred to be lower than 20°C, most preferably less than 0°C, for adequate low temperature mobility and good cold flexibility. Polyolefin copolymers could be selected, based on comonomer contents, that have the right melting and glass transition temperatures. In addition, these copolymers have excellent extensibility, $\gg 800\%$, and strengths at temperatures greater than 40°C perfectly suited for warm green strength enhancement in blends with bromobutyl. Metallocene catalysts, instead of Ziegler–Natta catalysts, are preferred for their catalytic ability to randomly incorporate comonomers into the backbone, which in turn, produce olefin copolymers with relatively uniform melting temperatures, even when high comonomer contents, $\gg 5$ wt %, are present.³ The broad composition distribution introduced into an olefin copolymer catalyzed by a traditional Ziegler–Natta catalyst leads to an olefin copolymer with multiple melting temperatures that could not satisfy the narrow melting temperature range defined for this application.

Based on our experimental data, blending with high crystallinity SCP, with over 30% crystallinity, raises the stiffness, low temperature brittleness, and relaxation times of their blends with bromobutyl, which are not desirable in tire liner applications. Amounts of crystallinity in these olefin copolymers are therefore preferred to be below 30%. For polyolefin copolymers, this crystallinity constraint is not in conflict with the melting temperature range specified above. In fact, it further narrows comonomer composition ranges in these copolymers. These olefin copolymers with their low crystallinity are, in general, slightly more air permeable than bromobutyl, but are less permeable than NR. Blend amounts of these olefin copolymers in bromobutyl compounds for liner applications should still be kept at a minimum to minimize the expected debits in air permeability, stiffness, brittleness, and relaxation time. However, to realize the enhancement in warm green strength of bromobutyl compounds by adding these olefin copolymers, sufficient amounts of these copolymers are required to obtain phase continuity. The presence of a cocontinuous morphology allows the olefin copolymer blend component to carry the load in parallel with bromobutyl and thereby raises green strengths and extension. A proper selection of the olefin copolymer with an optimal composition allows one to arrive at phase co-continuity with a minimal addition of this copolymer in bromobutyl compounds.

PHASE NETWORKING

Blends of immiscible polymers exhibit various types of morphologies depending on composition, on the viscoelastic properties of individual blend components, and on the mixing process.^{4,5} In general, at low compositions, 20 volume %, the minor polymer component is dispersed in a continuous phase of the major polymer component, in which the shape of the dispersed phase can be spherical, ellipsoidal, fibrillar, or lamellar.^{6–9} Theoretically, percolation occurs when the volume fraction of monodispersed spherical domains is equal to 0.156,¹⁰ which is in reasonable agreement with experimental data for blends with spherical phase domains.¹¹ Above this threshold concentration, the formation of more continuous dispersed phase is obtained because of coalescence and coarsening. Further increase in the amount of dispersed phase will lead to phase inversion at which a cocontinuous structure is formed.^{12–14}

The increase in the aspect ratio of the phase domain was found to decrease the percolation threshold experimentally¹¹ in agreement with percolation theory.¹⁵ The nonspherical dispersion shape was commonly derived by shear or elongational flow of polymer blends. Bromobutyl compounds for tire liner applications contain carbon black (CB) fillers at about 60 phr (part per hundred of polymers). When olefin copolymers are blended in bromobutyl compounds, crystallization of

TABLE I
 g' Values of PIB, Olefin Copolymers Evaluated, and iPP

Polymer	Description	g'
PIB	Homopolymer	0.387
SCP1	Ethylene-propylene (12 wt % C2), propylene elastomer	0.613
SCP2	EXACT 4033, ethylene-butene (23 wt % C4)	0.860
SCP3	EXACT 8201, ethylene-octene (28 wt % C8)	0.824
PP	Isotactic polypropylene	0.560
PE	Linear polyethylene reference	1.0

these polymers is expected around CB particles after cooling from the processing temperature probably because of the thermal gradient established between CB and the bromobutyl matrix.¹⁶ Provided that the interfacial tensions between these olefin copolymers and bromobutyl are low, these copolymers could adopt the high aspect-ratio shape of CB filler agglomerates. This suggests that a low percolation threshold, lower than the theoretical limit for spherical domains, for phase networking could be established in bromobutyl compounds using olefin copolymers with low interfacial tensions. If the interfacial tensions between olefin copolymers and bromobutyl are high, these copolymers could still crystallize around filler agglomerates, but instead, would collapse into spherical shape surrounding fillers to minimize interfacial areas. In summary, an olefin copolymer that could enhance the warm green strength of bromobutyl at a minimal amount to avoid significant compromises in bromobutyl permeability, processability, and low temperature flex is one that has a melting temperature between 40 and 90°C, and a crystallinity less than 30%, and is highly compatible, but not miscible, with bromobutyl.

MATERIAL SELECTION

Polyisobutylene (PIB) was found to be miscible with only a few polyolefins at room temperature. Ethylene-butene copolymers with 52–78 wt % of butene is an example for miscibility with PIB.¹⁷ However, this composition range for butene is not available commercially for ethylene-butene copolymers. In addition, these copolymers are either amorphous or contain low polybutene crystallinity. Commercially available ethylene-butene copolymers have densities greater than 0.88 or butene contents less than 30 wt %. Ethylene-octene copolymers that are available commercially have densities greater than 0.868 or octene contents less than 40 wt %.

As described earlier, it is important to identify immiscible olefin copolymers that are most compatible with bromobutyl to lower their phase percolation threshold values. There are various theories to de-

scribe thermodynamic interactions for saturated hydrocarbon polymer blends. To utilize these theories in estimating compatibility in butyl/olefin copolymer blends, fully saturated PIB, instead of bromobutyl, is used. This may not be a bad assumption since the isoprene content in bromobutyl is limited to 2 mol % and the bromine content is about 2 wt %. Although the solubility parameter approach based on regular solution theory has been applied successfully in evaluating miscibility and compatibility in polyolefin blends,^{18,19} blends of PIB and olefin copolymers were, unfortunately, found to not follow the solution theory.¹⁷ Hence, the method based on conformational asymmetry^{20–22} will be used in this study to estimate the compatibility in PIB/olefin copolymer blends. In accordance with this conformational theory for nearly athermal blends, the match in volumetric radii of gyration between two blend components assures their miscibility. Instead of using radius of gyration of an individual polymer component measured from its bulk or unperturbed state, an approximation was proposed to investigate blend miscibility based on component's radius of gyration measured in a dilute solution at 135°C. A good solvent, such as trichlorobenzene, is used instead of a theta solvent. A perturbed dimension of a polymer coil, instead of its unperturbed dimension in a theta solvent, is measured in a good solvent that accounts for the polymer-solvent interactions. This approximation based on polymer coil dimensions measured in dilute solutions, nonetheless,

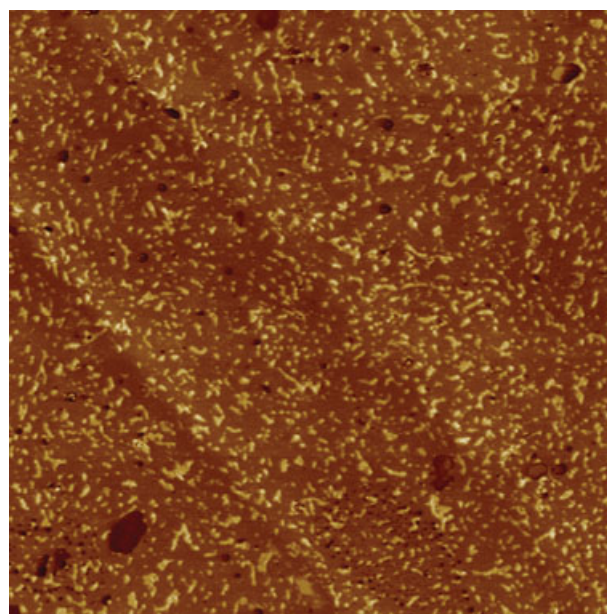


Figure 1 Tapping phase AFM 10 μm by 10 μm image of a 20/80 SCP1/BIIR blend. (Dark brown phase is the BIIR whereas the light yellow phase is the SCP1. The black domains are oil contaminants.) [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE II
Thermal Properties, Crystallinities, and Molecular Weights of Olefin Copolymers Evaluated

Name	T_m (°C)	X_c (%)	M_n	M_w
SCP1	70	20	94,000	173,000
SCP2	58	19	57,000	123,000
SCP3	74	21	37,000	104,000

has been demonstrated to be very useful in estimating polyolefin blend miscibility.

To provide a relative quantitative measure of dilute solution radii of gyration, the solution method employs the plot between the logarithm of radius of gyration and the logarithm of molecular weight for a given polymer obtained from GPC-MALLS (gel permeation chromatography-multiple angle laser light scattering).²³ Using the log-log linear line for a linear polyethylene as a reference, weight-average of deviations in radius of gyration, expressed in ratios, at all molecular weights was calculated for the polymer studied. This weight-average deviation from radii of gyration of polyethylene is denoted as g' . Comparing weight averages between blend components, better compatibility between components is expected with closer match in their g' values. g' Values for PIB and olefin copolymers investigated in this study are listed in Table I. These olefin copolymers were selected for their availability, melting temperatures, and crystallinities. All of these olefin copolymers were prepared through the use of discrete metallocene catalysts. As indicated in Table I, PIB has a very small radius of gyration, which is the reason for its low permeability. The propylene-ethylene copolymer, denoted as propylene elastomer, has the lowest radius of gyration among the three olefin copolymers examined and is expected to be the most compatible with butyl or bromobutyl from among these copolymers.

PROPYLENE ELASTOMERS

Propylene elastomers are commercially available as semicrystalline, elastomeric copolymers composed pre-

dominantly of propylene with limited amounts of ethylene. An example of these products is VistamaxxTM specialty elastomers from ExxonMobil Chemical Company, in which ethylene constitutes less than 20% of the total mass of each polymer chain. The placement of the propylene units within the propylene elastomer chain is predominantly in a stereoregular isotactic manner, leading to isotactic propylene crystallinity. The successful synthesis of these elastomers, which requires both intramolecular control of the tacticity of the inserted propylene units and intermolecular control of the composition of the polymer, is only possible through the use of discrete metallocene catalysts. The combination of these catalysts with a solution polymerization process enables detailed control of the polymer characteristics, which define the properties of the polymer.

The presence of a limited amount of the isotactic propylene crystallinity renders the propylene elastomers as thermoplastic elastomers. The polypropylene crystalline domains in P-E elastomers act as network points (physical crosslinks) at room temperature. However, these junction points can be removed at higher temperatures to provide ease of processing for the material. The extent of crystallinity, which plays a critical role in determining the final physical properties, is attenuated by errors in the stereoregular placement of propylene monomers as well as by incorporation of ethylene in the chain backbone. These two sources of structural defects limit the average length of isotactic propylene runs, and consequently lower the crystalline content of the polymer. Typically, the heat of fusion is depressed to between 5 and 40 J/g. This range of crystallinity for P-E elastomers also sets bounds for both the elasticity and elastic recovery of these materials.

As indicated in Table I, SCP1, or propylene elastomer, is expected to be more compatible with PIB and other isobutylene-based copolymers. One of the measures of compatibility is the interfacial tension. Attempts have been made to determine the interfacial tension between propylene elastomer and bromobutyl through small-amplitude oscillatory shear flow mea-

TABLE III
Compound Formulations for SBB Blends

Ingredients ^a	SBB-1	SBB-2	SBB-3	SBB-4	SBB-5	SBB-6
BrSBB 6222	100	90	85	83	80	70
SCP1	0	10	15	17	20	30
Flexon 876	5	5	5	5	5	5
Struktol 40MS	5	5	5	5	5	5
N660 CB	60	60	60	60	60	60
1068 Resin	4	4	4	4	4	4
Stearic Acid	2	2	2	2	2	2
MgO	0.15	0.15	0.15	0.15	0.15	0.15
Cure-ZnO	3	3	3	3	3	3
Cure-S	0.5	0.5	0.5	0.5	0.5	0.5
Cure-MBTS	1.5	1.5	1.5	1.5	1.5	1.5

^a Details of the function for listed additive package would be found elsewhere.³¹

TABLE VI
Mechanical Properties of Pressed Green BrSBB Compounds

Properties	SBB-1	SBB-2	SBB-3	SBB-4	SBB-5	SBB-6
Vol % of SCP1	0	7.3	10.9	12.3	14.5	21.6
RT, 100% mod. ^a	0.368	0.540	0.634	0.648	0.791	1.087
RT, t_{75} ^b	2.022	2.306	2.591	2.676	3.834	>8
40°C, 100% mod.	0.242	0.321	0.386	0.397	0.471	0.648
40°C, t_{75}	0.539	0.572	0.538	0.556	1.049	>8
40°C, Break ^c	328	323	393	363	445	880

RT, room temperature.

^a 100% mod., 100% modulus in MPa.

^b t_{75} , time to 75% peak stress delay in minutes.

^c Break, elongation to break in %.

EXPERIMENTAL

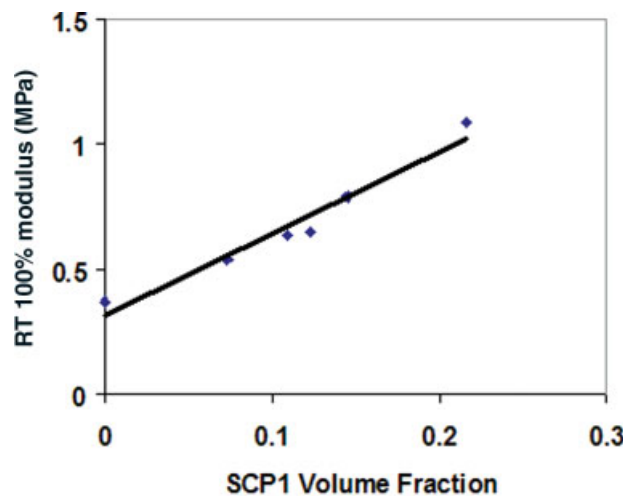
Materials

Bromobutyls, BIIR 2222, 2235, 2255, having 32 ML (Mooney Viscosity), 39 ML, and 46 ML, respectively, and BrSBB 6222 and MDB 86-6, brominated star-branched butyls with 32 ML and 40 ML, respectively, were the five bromobutyls evaluated in this study. SCP1 was an experimental grade produced in a pilot plant and both SCP2 and SCP3 commercial grades. Based on the DSC (differential scanning calorimetry) measurements at 10°C/min scan rate, thermal properties of these three olefin copolymers are tabulated in Table II. Their molecular weights and distributions as measured by GPC are also listed in Table II. All bromobutyls and SCPs are available from ExxonMobil Chemical Company. All Mooney values were measured at 125°C according to ASTM D 1646.

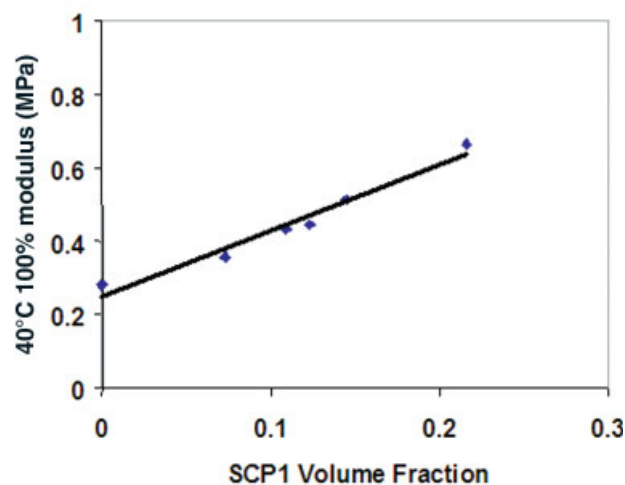
Blending and compounding

Compounds of BrSBB and SCP1 based on a model tire liner formulation with varying BrSBB/SCP1 ratios as listed in Table III were mixed using a 1.5-L Banbury internal mixer at 100 rpm and a 160°C dump temperature. Green strengths of these compounds were measured at room temperature and at 40°C using rubber pads that were calendared and molded at 100°C. To evaluate the thermal treatment effects, green strengths and cured compound strengths of these compounds at 40°C were also measured for green compounds without pressing/calendaring and cured compounds after curing at 160°C from 1 to 30 min, respectively. Curing was performed at 160°C for all compounds with optimal times determined based on cure curves measured from a cure rheometer (Alpha Instrument ODR 2000). Cure times thus obtained for these compounds are around 30 min. Air permeability values of cured samples were determined at 30 and 65°C using an air permeability tester. Tensile properties at room temperature of cured compounds before and after aging were also measured. The aging condition used was 48 h at 120°C.

Based on density values for all the ingredients employed in these compounds, volume fractions of SCP1 in SBB-2 to SBB-6 are 7.3, 10.9, 12.3, 14.5, and



(a)



(b)

Figure 2 Moduli of BrSBB green compounds at room temperature (RT) (a) and at 40°C (b) as functions of SCP1 volume fraction. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

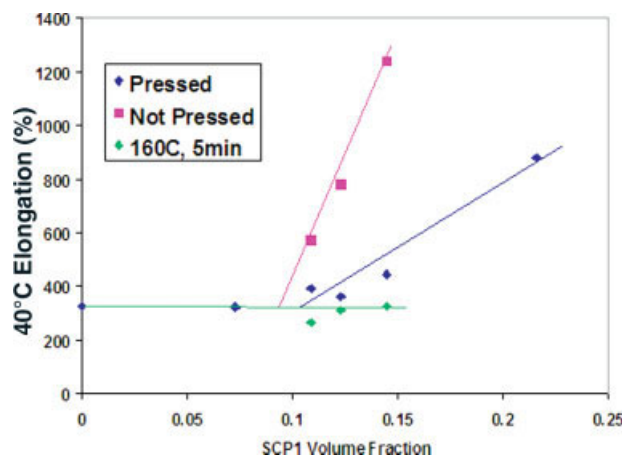


Figure 3 Strains to break of BrSBB green and cured compounds at 40°C as a function of SCP1 volume fraction. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

21.6%, respectively. It was found that phase percolation threshold for SCP1 in these BrSBB compound is less than 20 phr. Using almost the same additive package with the exception of doubling the paraffinic oil (Flexon 876) content (see Table IV), BIIR compounds were prepared using 20 phr of NR, SCP1, SCP2, and SCP3 for understanding the phase compatibility effects on green strength enhancement. The same mixing condition, same as that for BrSBB compounds, was applied to mix these compounds. Green strengths of BIIR compounds were measured at room temperature and at 50°C using rubber pads that were calendared and pressed at 100°C. Procedures for preparing cured compounds and for measuring their properties are the same as that for BrSBB compounds. Volume fractions of NR, SCP1, SCP2, and SCP3 in these com-

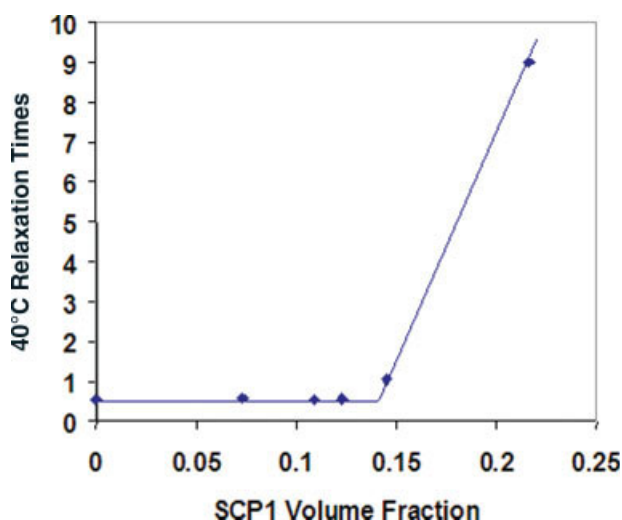


Figure 4 Times to 75% peak stress decay of BrSBB green compounds at 40°C as a function of SCP1 volume fraction. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

pounds are 13.2, 13.7, 13.7, and 14%, respectively. It is interesting to point out that the minimum of 20–25 phr of NR required for adequate warm temperature green strength enhancement commonly employed in the tire industry corresponds to 13–17 vol % for a typical liner formulation. This volume fraction range straddles the theoretic percolation threshold of 15.6% for spherical domains.

A third series of innerliner compounds were mixed in a Banbury internal mixer as shown in Table V to evaluate the effects of SCP1 addition on innerliner green strength, processability, and curing behavior. Mechanical properties, before and after thermal aging, and air permeability values of these cured innerliner compounds were also determined. Capillary flow of these innerliner compounds was measured using a Monsanto Processability Tester (MPT) instrument (Alpha Technologies) at 100°C. SCP1 was introduced at levels of either 15 or 20 phr and NR was added at 25 phr. Oil was blended in at 0, 5, or 10 phr and CB was used at 60, 70, or 80 phr. Green properties of the compounds were measured at room temperature and at 50°C. All tests were carried on in triplicates, with the median value being reported.

Morphology evaluation

For AFM morphology analysis, all green and cured compounds and the blend were cryo-faced at -150°C in a Reichert cryogenic microtome using a diamond

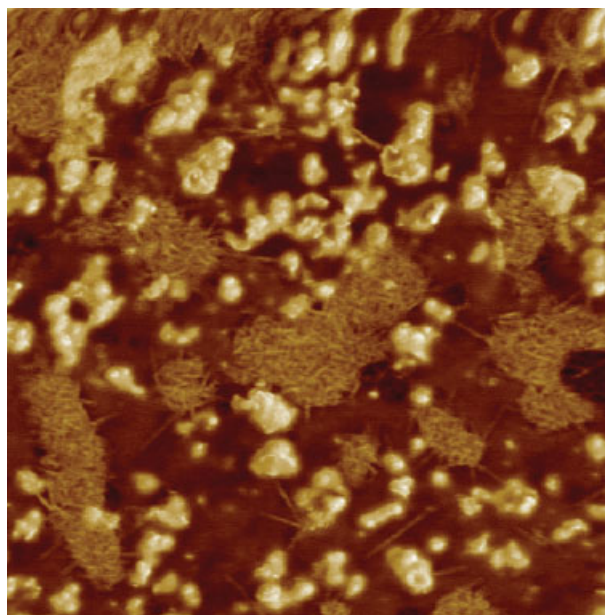


Figure 5 Crystallization of SCP1 around CB fillers in a green BrSBB compound. (2 μm by 2 μm tapping phase AFM image; white/yellow particles – CB, brown phase – BrSBB, dark yellow crystalline phase – SCP1, black phase – oil.) [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

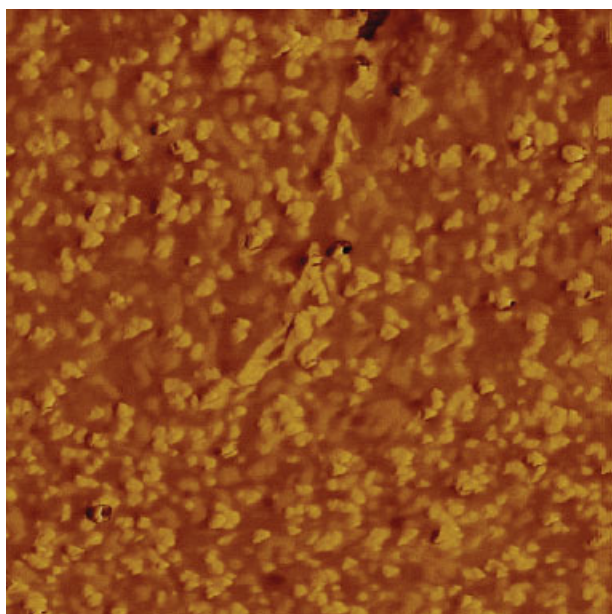


Figure 6 Tapping phase AFM morphology of SBB-5 after mixing without pressing (5 μm by 5 μm). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

knife. To prevent moisture condensation onto the sample surface while warming them to room temperature, the samples were stored in a nitrogen-purged desiccator immediately after cryofacing. The faced samples were then mounted in a miniature vice for AFM analysis within 24 h. Because of the tackiness and deformability of green compounds, it was found

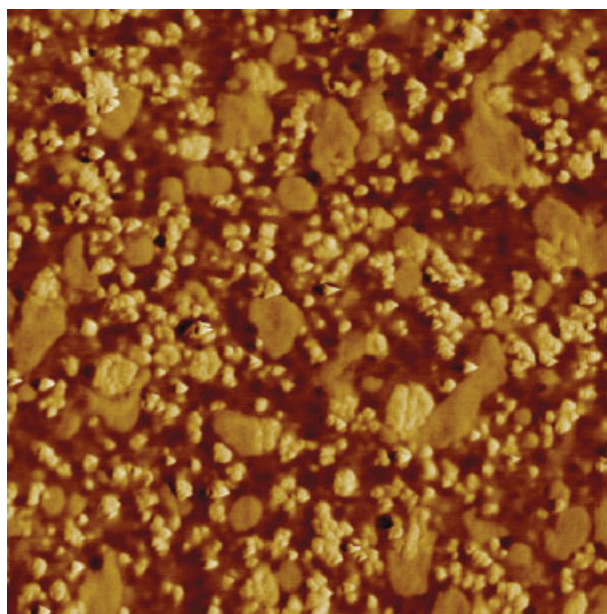


Figure 8 Tapping phase AFM morphology of SBB-5 after curing for 1 min at 160°C (5 μm by 5 μm). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

that most stable surfaces during tapping analysis were obtained by cryofacing the sample the second time after it was cryofaced and stored overnight. These green compound samples were then mounted immediately after the second cryofacing for AFM analysis. Tapping phase AFM analyses were performed using a Digital Instrument Dimension 3000 instrument, which was

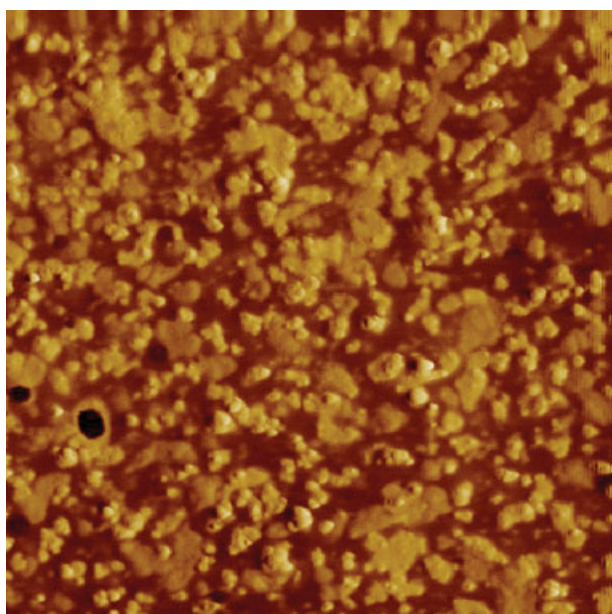


Figure 7 Tapping phase AFM morphology of SBB-5 after pressing for 5 min at 100°C (5 μm by 5 μm). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

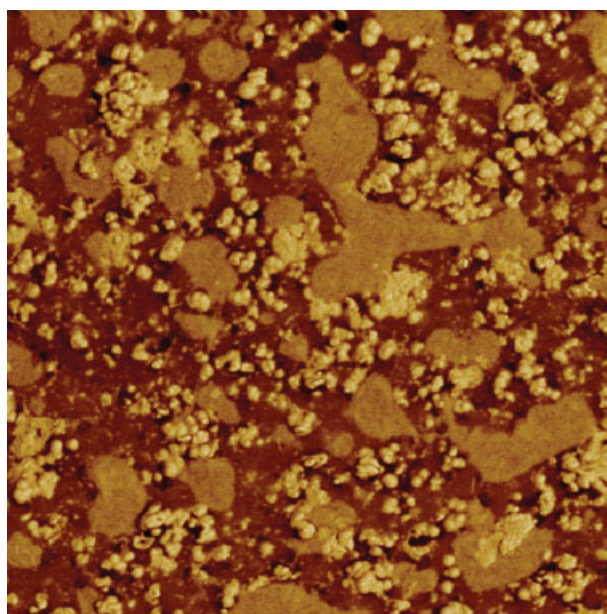


Figure 9 Tapping phase AFM morphology of SBB-5 after curing for 30 min at 160°C (4 μm by 4 μm). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE VII
Properties of Cured BrSBB Compounds

Properties	SBB-1	SBB-2	SBB-3	SBB-4	SBB-5	SBB-6
Vol % of SCP1	0	7.3	10.9	12.3	14.5	21.6
Permeability ^a , 30°C	1.7	1.9	1.9	2.1	2.2	2.6
Permeability, 65°C	11.3	13.6	14.4	15.2	15.9	19.3
RT, 100% mod.	1.65	2.16	2.5	2.7	2.78	3.23
RT, break	626	603	578	577	618	604
RT, 100% mod., aged	2.68	3.35	3.4	3.61	3.64	4.04
RT, break, aged	527	495	467	492	522	497
Shore A hardness	56.5	63.5	67.5	69.1	69.9	76.7
Hardness, aged	47.7	65.1	65.5	71.1	72.3	70.5

RT, room temperature.

^a Permeability unit is ml (mM/m²) (760 mm Hg) (hr).

operated under ambient conditions. A FESP tip with a resonant frequency of 60–70 kHz was used. Tapping phase contrast arises from variations in mechanical properties between the phases in the presence of conservative and dissipative tip-sample interactions as discussed earlier.²⁸ AFM phase images of all specimens were converted into a TIFF format and processed using PHOTOSHOPTM (Adobe Systems).

RESULTS AND DISCUSSION

Properties and morphologies of green BrSBB compounds

Green tensile properties of BrSBB compounds with varying SCP1 contents are listed in Table VI. The 100% modulus is a measure of the green strength whereas the t_{75} is a measure of the relaxation time. Increases in modulus and in relaxation times, both at room temperature and at 40°C, and increase in break elongation values at 40°C with SCP1 contents are indicated. Enhancements in green strength and elongation at 40°C are realized with the addition of SCP1, although the rise in relaxation time is not desirable at room temperature. The exact values of green strength, elongation, and relaxation time required for tire liner construction at 40°C or above depend on tire design and tire fabrication method.

As shown in Figure 2, a linear increase in modulus was found in BrSBB green compounds with increasing SCP1 volume fraction. However, a phase percola-

tion or a phase transition characteristic is revealed from the curves showing the dependence of break strain and of relaxation time on SCP1 volume fraction (see Figs. 3 and 4). The relaxation time values shown in Figure 4 are times required for a given compound to relax out 75% of its initial stress after 100% extension. The solid-diamond curves in Figure 3 represent the elongation to break values of calendared and pressed green compounds listed in Table VI and of a 5-min cured compound. All curves demonstrate the classical characteristic of percolation curves that show property dependence on volume fraction by $(\phi - \phi_c)^\beta$, where ϕ_c is the percolation threshold and β is the exponent. In general, the value of β depends on property measured²⁹ and is 1.7–2.0 for electrical conductivity.³⁰ Based on the curves in Figures 3 and 4, the percolation threshold is between 0.12 and 0.14. This value is lower than the theoretical threshold of 0.156 for spherical domains. As shown in Figure 5, SCP1 crystallizes around CB filler aggregates in a BrSBB green compound and has high aspect ratio phase shapes. This elongated phase shape in SCP1 may explain its lower phase percolation threshold.

To measure the green tensile properties of these BrSBB compounds, they were calendared and pressed at 100°C to provide smooth and uniform testing pads. As shown by tapping phase AFM morphologies in Figures 6–9, the thermal treatment for pressing and the further curing coarsen and coalesce SCP1 phases. In addition, SCP1 phases withdraw from CB and form

TABLE VIII
Mechanical Properties of Pressed Green BIIR Compounds

Properties	BIIR-1	BIIR-2	BIIR-3	BIIR-4	BIIR-5	BIIR-6
Vol % of blend	0	0	13.2	13.7	13.7	14.0
RT, 100% mod.	0.31	0.38	0.29	0.53	0.53	0.56
50°C, 100% mod.	0.22	0.21	0.21	0.33	0.35	0.31
50°C, t_{75}	0.524	0.546	0.507	0.932	1.098	3.252
50°C, break	258	340	304	280	349	1133

RT, room temperature.

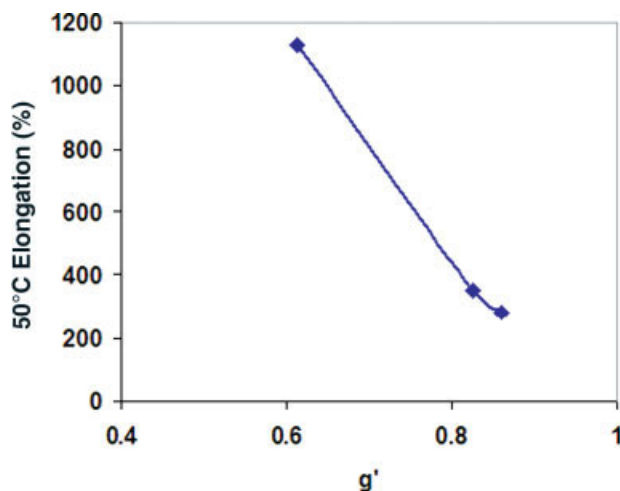


Figure 10 Strains to break of BIIR green compounds containing 20 phr of olefin copolymers at 50°C as a function of the olefin copolymer's solution chain dimension measured by g' . [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

isolated domains. Therefore, it is expected that the phase percolation threshold value be affected by thermal treatment. As shown in Figure 3, the phase percolation threshold moves from around 0.09 for unpressed compounds to 0.11 for pressed compounds to possibly the theoretical value of 0.16 for cured compounds. The actual green strength required during tire construction is the strength of calendared compounds. The coalescence and coarsening of SCP1 phases during curing may be beneficial for cured compound properties. Low temperature flexibility, ductility, and flex fatigue resistance for a tire liner require good low temperature properties of BrSBB compounds. Low temperature properties of SCP1 are defensive when compared with that of bromobutyl. By removing the SCP1 phase continuity in cured compounds, cured properties would be dominated by BrSBB, with SCP1 being present essentially as fillers, which would not compromise the low temperature properties in cured liner compounds.

Cured properties of BrSBB compounds

Mechanical properties and permeabilities of cured BrSBB compounds are tabulated in Table VII. For good tire liner performance, low permeability, low modulus, and high elongation of a cured liner are preferred. With an increase in SCP1 content, the first two properties are compromised. However, the elongation to break is not much changed in the cured compound and the increase in elongation as indicated in green compounds with the addition of SCP1 is not observed in cured compounds. This lack of enhancement in extensibility confirms the finding of the removal of SCP1 phase continuity through phase coalescence and coarsening during curing. Because of the reduction in required properties for liner performance, the addition of SCP1 to a BrSBB compound for its green strength improvement should be kept to a minimum. The increase in modulus and the reduction in elongation are commonly observed in aged butyl compounds because of the continuous crosslinking in butyl with age. As indicated in Table VII, addition of SCP1 does not affect the aging degradation behavior in BrSBB compounds.

Green strength and cured properties of BIIR compounds

Mechanical properties of pressed green BIIR compounds are listed in Table VIII. BrSBB was shown to have slightly better green tensile properties than that of BIIR. Addition of NR also brings in some improvement in BIIR green properties. Comparing the compounds that have SCP1, SCP2, and SCP3 blend components, the improvement, especially in extensibility, is enhanced with increasing compatibility as suggested from Table I. In Figure 10, the increase in elongation of BIIR compounds with 20 phr of olefin copolymer added is shown to increase with a reduction in g' , or with a suggested improvement in compatibility. NR is known to be quite compatible with isobutylene-based polymers. However, its relative compatibility with BIIR with reference to SCP cannot be measured

TABLE IX
Properties of Cured BIIR Compounds

Properties	BIIR-1	BIIR-2	BIIR-3	BIIR-4	BIIR-5	BIIR-6
Vol % of blend	0	0	13.2	13.7	13.7	14.0
Permeability, 30°C	1.7	1.9	2.8	2.5	2.9	2.9
RT, 100% mod.	1.3	1.5	1.4	1.9	1.9	2.0
RT, break	687	599	628	633	661	716
RT, 100% mod., aged	2.0	2.5	2.0	2.8	2.9	2.8
RT, break, aged	572	467	506	530	519	590
Hardness	54	57	54	64	64	67
Hardness, aged	58	63	59	68	69	72

RT, room temperature.

TABLE X
Room Temperature and 50°C Green Strengths of Innerliner Compounds

	1	2	3	4	5	6	7	8	9	10	11	12	13
Room temperature													
Green strength (100%) (MPa)	0.255	0.304	0.313	0.289	0.808	0.672	0.526	0.639	0.740	0.450	0.530	0.643	0.330
t_{75} on peak (min)	1.170	2.307	3.042	1.308	8.000	8.000	4.702	6.553	8.000	2.914	3.078	4.638	–
t_{75} on strain endpoint (min)	1.387	2.658	3.430	1.681	8.000	8.000	6.022	8.000	8.000	4.410	3.763	6.630	4.060
50°C													
Green strength (100%) (MPa)	0.172	0.206	0.220	0.191	0.457	0.360	0.289	0.352	0.396	0.268	0.312	0.369	0.180
t_{75} on peak (min)	0.540	0.825	1.478	0.752	3.862	4.991	2.426	2.621	3.580	1.686	1.436	0.985	1.520
Elongation (%)	264	338	406	369	510	1016	838	521	471	341	282	326	493

by g' because of its chain polarity preventing the usage of the conformation asymmetry theory on which g' equivalence for compatibility is based. Mechanical properties and air permeability values of BIIR-cured compounds were also measured. As discussed in the previous section for cured BrSBB compounds, increases in permeability and modulus are found in cured BIIR compounds containing 20 phr of NR, SCP1, SCP2, and SCP3 (see Table IX). No improvements or erosions in aging resistance are indicated in BIIR compounds with the addition of these blend compounds.

Green strengths and cured properties of innerliner compounds

The room temperature green strengths of innerliner compounds are tabulated in Table X. All compounds that contain SCP1 have higher green strength. Sample 1, the lowest molecular weight bromobutyl, and Sample 4, the BrSBB, relax the fastest. As shown in Table

X, the relative ranking of 50°C green strength in these compounds is similar to that of room temperature. A large increase in elongation to break at 50°C is shown for all compounds containing SCP1. This higher elongation at 50°C in a bromobutyl/SCP1 innerliner compound allows it to be shaped and stretched during tire building without losing its integrity. The corresponding higher green strength also helps to reduce deformation during processing.

Capillary viscosity values and die swell amounts of innerliner compounds measured by the MPT are listed in Table XI. Lower die swells at high shear rates are indicated in innerliner compounds containing SCP1. These lower die swell values correspond to reduced elasticity during processing and suggest improved processability during innerliner compound shaping operations. Viscosity values are also lowered with the addition of SCP1, which acts as a plasticizer at 100°C. No significant changes in cure behavior could be found with the addition of SCP1 in these innerliner compounds. Physical properties of cured

TABLE XI
Rheological Properties of Innerliner Compounds

	1	2	3	4	5	6	7	8	9	10	11	12	13
36 s ⁻¹ Shear rate													
Viscosity (kPa s)	5.41	5.91	6.1	5.43	6.17	5.5	4.53	4.93	5.2	4.91	5.05	5.43	4.18
Run die swell (%)	12	12.5	12.7	12.5	11.8	13.2	13.4	11	10.2	11.5	8.8	7.4	10.5
Relax die swell (%)	16.1	15.7	15.2	16.1	18.4	18.3	16.9	14	13.7	16.2	13.7	11.7	12.9
178 s ⁻¹ Shear rate													
Viscosity (kPa s)	1.52	1.59	1.62	1.54	2.07	1.82	1.54	1.71	1.88	1.61	1.72	1.93	1.45
Run die swell (%)	15.2	14.9	15.7	13.5	13.2	14.0	14.7	13.5	10.2	11.5	9.6	8.0	10.5
Relax die swell (%)	20.6	22.7	25.2	21.2	18.3	24.7	21.0	18.4	21.2	20.3	15.4	15.1	13.4
538 s ⁻¹ Shear rate													
Viscosity (kPa s)	0.63	0.69	0.72	0.65	0.85	0.75	0.64	0.7	0.77	0.67	0.71	0.8	0.62
Run die swell (%)	20.6	22.5	24.7	20.6	15.6	17.6	18.3	16.1	15.2	16.1	13.7	11.8	14.2
Relax die swell (%)	27.4	28.1	31.1	25.9	25.2	27.1	23.0	20.8	21.3	21.7	19.8	14.7	16.9
1079 s ⁻¹ Shear rate													
Viscosity (kPa s)	0.40	0.47	0.51	0.42	0.53	0.46	0.38	0.42	0.47	0.40	0.43	0.49	0.37
Run die swell (%)	28.3	29.3	30.3	25.9	22.3	20.3	23.0	20.0	18.8	18.6	17.9	14.6	16.8
Relax die swell (%)	33.7	39.1	40.4	33.0	29.6	28.3	29.4	24.5	25.0	27.4	24.2	21.3	22.3

TABLE XII
Tensile Properties and Hardness Values of Innerliner Compounds, and Their Air Permeability Values

	1	2	3	4	5	6	7	8	9	10	11	12	13
Tensile not aged (MPa)													
100% Mod.	1.198	1.282	1.331	1.29	2.751	2.32	1.94	2.377	2.948	1.768	2.101	2.745	2.99
200% Mod.	2.554	2.754	3.006	2.875	5.401	4.343	3.658	4.586	5.618	3.565	4.3	5.576	6.76
300% Mod.	4.277	4.682	5.057	4.782	7.924	6.485	5.552	6.785	7.846	5.523	6.57	7.891	10.10
Stress at break (MPa)	10.927	10.926	11.52	9.878	11.123	10.32	10.75	9.89	9.725	9.955	9.472	9.493	12.2
Strain at break (%)	824	746	731	713	608	617	702	592	533	650	567	495	387
Shore A hardness	55.1	54.9	52.7	56.1	73.1	71.1	66.1	72.9	72.7	62.9	67.3	67.7	66.5
Air permeability at 30°C	NM	NM	NM	2.2	1.9	2.4	2.9	2.8	2.7	2.7	2.7	2.5	4.5
Air permeability at 65°C	NM	NM	NM	13.6	14.0	16.6	19.5	18.5	18.3	18.1	17.9	17.0	25.5

innerliner compounds are tabulated in Table XII. With the addition of SCP1, the hardness of an innerliner compound increases but with less relative changes in cured properties after aging. In addition, permeability is lowered significantly with reducing processing oil amount. An increase in CB amount could only lower the permeability slightly in these compounds. Considering that SCP1 has low viscosity, it could be added in place of processing oil, leading to a reduction in air permeability of an innerliner compound without compromises in its processability.

CONCLUSIONS

The conventional practice of adding NR to improve green strengths of bromobutyl compounds results in increased permeability. Judicious selection of olefin copolymers, such as ethylene-propylene, ethylene-butene, or ethylene-octene copolymers, as blend components could also provide green strength enhancement at elevated temperatures with a lower debit in permeability. For the three olefin copolymers evaluated, this enhancement increases with increasing compatibility between a given olefin copolymer and bromobutyl, as estimated based on the measured chain dimension similarity in a diluted solution between PIB and the olefin copolymer. For the most compatible copolymer examined, SCP1, a propylene elastomer, a phase percolation threshold was found at 0.13 volume fraction of SCP1 in pressed and calendared pads of BrSBB/SCP1 compounds. This threshold value was determined based on the sudden increases in high-temperature extensibility and stress relaxation time with increasing SCP1 content. It is lower than the theoretical limit of 0.156 for monodispersed spherical phase domains. From tapping phase AFM examination of BrSBB/SCP1 morphologies, it was found that SCP1 crystallizes around the CB filler agglomerates and forms nonspherical and high-aspect-ratio dispersed phases. Phase anisotropy in SCP1 may have

contributed to its lower phase percolation threshold in SBB compounds.

Coarsening and coalescence of SCP1 phases were observed in BrSBB compounds with thermal treatments from tapping phase AFM micrographs. Initial fine and elongated SCP1 domains around the filler agglomerates after mixing were converted to large and more spherical phases isolated away from fillers with each heat exposure step, from calendaring to curing. The gradual removal of SCP1 phase anisotropy with heat treatments may account for the observed increase in percolation threshold value with each thermal step. In a cured BrSBB compound containing 20 phr SCP1, dispersed SCP1 phase domains in BrSBB matrix were realized instead of the connected phases of SCP1 seen in its green state. Unfavorable increases in permeability and in modulus were present in cured BrSBB/SCP1 compounds with an increase in SCP1 content. Therefore, the amount of SCP1 added needs to be kept at a minimum. Innerliner compounds of BIIR, containing 10–20 phr of SCP1 in place of NR and some of the processing oils, were shown to have excellent room-temperature and improved elevated-temperature green strengths, good aging resistance, and excellent impermeability without significant increases in relaxation time.

We thank Dave Lohse, Thomas Sun, and Bryan Chapman for fruitful discussions on polymer compatibility. We also thank Thomas Sun for providing GPC-MALLS data. Experimental efforts provided by Connie Qian, Regina Netherly, and Jo Caraway are greatly appreciated.

References

- Subramaniam, A. In *Rubber Technology*, 3rd ed.; Morton, M., Ed.; Kluwer: Boston, 1999; Chapter 6.
- Powers, K. W.; Wang, H. C.; Hardy, D. C.; Fusco, J. V. U.S. Pat. 5,071,913 (1991).
- Chum, S. P.; Kao, C. I.; Knight, G. W. In *Metallocene-Based Polyolefins*; Scheirs, J.; Kaminsky, W., Eds.; Wiley: New York, 2000; Vol. 1, Chapter 12.

4. Paul, D. R.; Newman, S., Eds. *Polymer Blends* (2 vols.); Academic Press: New York, 1978.
5. Utracki, L. A. *Polymer Alloys and Blends: Thermodynamics and Rheology*; Hanser: Munich, 1990.
6. Barentsen, W. M.; Heikens, D. *Polymer* 1973, 14, 579.
7. Heikens, D.; Barentsen, W. M. *Polymer* 1977, 18, 69.
8. Favis, B. D.; Therrien, D. *Polymer* 1991, 32, 1474.
9. Gonzalez-Munez, R.; Favis, B. D.; Carreau, P. J.; Lavallee, C. *Polym Eng Sci* 1993, 33, 851.
10. Stauffer, D. *Introduction to Percolation Theory*; Taylor and Francis: London, 1985.
11. Lyngaae-Jorgensen, J.; Utracki, L. A. *Mackormol Chem Macromol Symp* 1991, 48/49, 189.
12. Avgeropoulos, G. N.; Weissert, F. C.; Biddison, P. H.; Bohm, G. G. A. *Rubber Chem Technol* 1976, 49, 93.
13. Metelkin, V. I.; Blekht, V. S. *Kolloidn Zh* 1984, 46, 476.
14. Utracki, L. A. *J Rheol* 1991, 35, 1615.
15. McLachlan, D. S.; Blaszkiewicz, M.; Newnham, R. E. *J Am Ceram Soc* 1990, 73, 2187.
16. Wilkes, G. Personal communication, 1999.
17. Krishnamoorti, R.; Graessley, W. W.; Fetters, L. J.; Garner, R. T.; Lohse, D. J. *Macromolecules* 1995, 28, 1252.
18. Krishnamoorti, R.; Graessley, W. W.; Balsara, N. P.; Lohse, D. J. *Macromolecules* 1994, 27, 3073.
19. Han, S. J.; Condo, P. D.; Lohse, D. J. Internal Report, 1997.
20. Bates, F. S.; Schulz, M. F.; Rosedale, J. H.; Almdal, K. *Macromolecules* 1992, 25, 5547.
21. Bates, F. S.; Fredrickson, G. H. *Macromolecules* 1994, 27, 1065.
22. Fredrickson, G. H.; Liu, A. J.; Bates, F. S. *Macromolecules* 1994, 27, 2503.
23. Sun, T.; Brant, P.; Chance, R. R.; Graessley, W. W. *Macromolecules* 2001, 34, 6812.
24. Palierne, J. F. *Rheol Acta* 1990, 29, 204.
25. Vukov, R. *Rubber Chem Technol* 1984, 57, 284.
26. Taylor, G. I. *Proc R Soc London Ser A* 1932, 138, 41.
27. Taylor, G. I. *Proc R Soc London Ser A* 1934, 146, 501.
28. Tsou, A. H.; Waddell, W. H. *Kautsch Gummi Kunstst* 2002, 55, 382.
29. Zallen, R. *The Physics of Amorphous Solids*; Wiley: New York, 1983; Chapter 4.
30. Chapoy, L. L. *J Chem Phys* 1986, 84, 1530.
31. Morton, M., Ed. *Rubber Technology*, 3rd ed.; Kluwer: Boston, 1999.