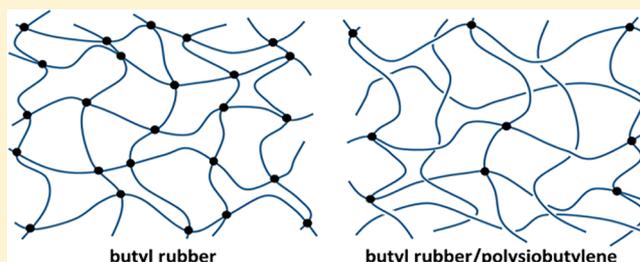


Strength Enhancement in Miscible Blends of Butyl Rubber and Polyisobutylene

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ABSTRACT: The thermodynamic miscibility of polyisobutylene (PIB) with butyl rubber (IIR), a copolymer of isobutene and a few mole % isoprene, was established through observation of spontaneous interdiffusion of the polymers. Networks were prepared from their blend, in which only the IIR component was cross-linked (PIB cannot be cross-linked by sulfur vulcanization or any other method). The blends were significantly stronger (almost 3-fold higher tensile strength) and tougher than neat IIR networks, when compared at equal modulus. This improvement was greater for blends having higher molecular weight PIB. The results show that miscible blends with components having large disparities in their degree of cross-linking (infinite in the present case) circumvent the trade-off between stiffness and strength found for conventional elastomers. The operative mechanism is alleviation of local overstresses by configurational rearrangement of unattached, but entangled, chains. This mechanism is common to other approaches that improve the mechanical properties of networks, such as bimodal networks and hydrogel blends.



INTRODUCTION

For length scales beyond that of the chain repeat unit, the behavior of flexible chain polymers is quite general—elastomers exhibit about the same mechanical response up through moderate strains.¹ The modulus can be varied by adjusting the concentration of cross-links; however, beyond the gel point an increase in modulus entails a decrease in the strength and other failure properties of rubber. This means that for a given polymer there is a compromise between its stiffness and strength. The latter property can be improved by using a different material, for example a polymer with the capacity for strain-induced crystallization. However, the competing effect of cross-linking on modulus and failure properties remains.

A number of methods have been proposed to circumvent this limitation of conventional networks. Interpenetrating polymer networks (IPNs) ideally consist of two homogeneously mixed polymers. Each component is cross-linked subsequent to mixing, and assuming phase separation does not interfere, topological constraints couple the cocontinuous networks.^{2–5} A variation on IPNs is double networks, in which a rubbery network is cross-linked a second time while in a strained state. This imparts permanent orientation⁶ and can lead to increases of both the stiffness and the strength of the elastomer.^{7,8} Bimodal networks, which are end-linked mixtures of high and low molecular weight chains of the same polymer,⁹ also display increased mechanical toughness.^{10,11} The origin of this improvement is uncertain but has been ascribed to a “delegation of responsibilities”,^{9,12} wherein the short network chains augment the modulus and the long ones provide greater extensibility. Particularly when one component is un-cross-linked, superior mechanical properties may be ascribed to the ability of the free chains, coupled to the network via

entanglements, to alleviate local stresses, while the cross-linked component provides mechanical integrity.¹ Hydrogel mixtures,^{13,14} referred to as “double network hydrogels”, are bimodal networks of two chemically different polymers having a large difference in cross-linking, with phase homogeneity achieved by a solvent (e.g., water). These have been shown to yield large increases in toughness and are of great potential for biomedical applications.^{14–16}

The focus of this work is cross-linked blends in which the components are thermodynamically miscible. This differs from IPNs, whose components are usually immiscible, with cross-linking relied on to retain a homogeneous morphology. Although phase segregation is minimized in IPNs, the network is heterogeneous at least on the segmental level.^{4,5} For a network formed from miscible rubbers, there is no driving force for phase separation, so that intimate mixing is inherent. If the components have different cross-linking reactivities, a disparity in cross-link densities can be achieved, potentially conferring the advantages found for bimodal networks.^{9,11–14} This approach, while limited to thermodynamically miscible polymers, can offer the advantages of IPNs and bimodal networks, without the extra processing steps. It also obviates concerns about phase separation, provided the cross-linking *per se* does not significantly affect the thermodynamic compatibility.

Previously two systems based on this concept have been investigated. Ethylene–propylene copolymer mixtures with a random terpolymer of ethylene–propylene–diene yielded

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blend networks having tensile strengths twice those of the neat terpolymer at equal modulus.¹⁷ Thermodynamically miscible blends of 1,4-polyisoprene and poly(vinyl ethylene) showed mechanical properties sensitive to the details of the curing.¹⁸ A homogeneous morphology is achieved only for very slow cross-linking at temperatures below the lower critical solution temperature.

The present work addresses blends of polyisobutylene (PIB) and butyl rubber. The chemical structure of the latter is predominantly polyisobutylene with low levels of an unsaturated comonomer (isoprene), hence the designation IIR (“isobutylene isoprene rubber”). This comonomer enables cross-linking because the PIB is otherwise unreactive.^{19,20} Prior work on this blend found that PIB in a network of IIR increased the self-adhesion (tack).²¹ Some improvements in the tear resistance of IIR were obtained by addition of PIB.²² Herein we first carried out experiments to affirm the thermodynamic miscibility of PIB and IIR by observation of spontaneous interdiffusion of the two polymers. Then blends were prepared and their mechanical properties compared to neat IIR networks as a function of cross-link density. For a given value of the modulus, the strength of the blend is greater, by as much as a factor of 3, than that of IIR. This finding demonstrates a route to better properties for applications involving butyl rubber. There is recent interest in this polymer due to improvements in the ballistic performance of steel armor having IIR as a coating on the front (strike face).²³ This application involves very high strain rates (ca. 10^5 s^{-1}), and preliminary ballistic tests indicate modest improvements from the blend compared to the conventional butyl rubber.

EXPERIMENTAL SECTION

The butyl rubber (from LANXESS Inc.) was a random copolymer of isobutylene and 7.0 mol % isoprene. Its number-average molecular weight was 150 kDa, with a polydispersity ~ 4 and gel content less than 2%. For assessment of miscibility with the PIB, some IIR having lower isoprene content were also used. The polyisobutylene (Oppanol B30 from BASF) had a number-average molecular weight of 73 kDa; for selected experiments, a higher molecular weight ($M_n = 200 \text{ kDa}$) was used as well. The blend was an equal concentration of IIR and PIB; elastomer formulations are given in Table 1. The extent of cross-

Table 1. Formulation

	source	phr ^a
polymer	RB70 (LANXESS Inc.); Oppanol (BASF)	100
stearic acid, zinc salt	(Aldrich)	1
zinc oxide	Akrochem XF-Z zinc oxide (Akrochem)	5
tellurium diethyldithiocarbamate	Ethyl Tellurac (R.T. Vanderbilt)	1.0–10
2-mercaptobenzothiazole	Captax (R.T. Vanderbilt)	0.25–2.5
sulfur	(Akrochem)	0.5–5

^aMass per 100 parts of polymer, which was IIR or 50/50 IIR/PIB.

linking was varied, with the ratio of the curatives fixed (1.0 ethyl tellurac/0.25 captax/0.5 sulfur by weight) for all samples. Mixing of the blend was carried out with a Brabender internal mixer, with curatives added subsequently using a two-roll mill. Curing was done in compression molds at $150 \text{ }^\circ\text{C}$ for 35 min.

Specimens for mechanical testing were typically 80 mm long with a 6 mm^2 cross-sectional area. Uniaxial tension measurements employed an Instron 5500R with optical extensometer; the nominal strain rate was 0.1 s^{-1} unless stated otherwise. Adhesion tests were carried out on

$2.5 \times 15.0 \text{ cm}$ strips, reinforced with a mesh to avoid stretching during the test. A 20 kPa load was applied for 10 min after the strips were brought into contact, followed by annealing without pressure for 5 days (estimated to be a few orders of magnitude longer than the time for diffusion over distances equal to the chain size). Peel-adhesion (180° geometry) was then measured at a nominal strain rate of 0.1 s^{-1} . Dynamic mechanical tests at RT were carried out on an Anton Paar in a parallel plate geometry. The ballistic test followed Mil-Std-662F. We measured the velocity required for 12.7 mm diameter projectiles to penetrate 7.3 mm steel (Mil-A-46100) having 5 mm elastomer coatings on the front surface. The velocity of the projectile was measured with a pair of tandem chronographs.

RESULTS AND DISCUSSION

Achieving a phase morphology that is homogeneous on the segmental level requires the components of the network to be thermodynamically miscible. Although their very similar chemical structures leads to the assumption of miscibility of PIB and IIR,^{21,24} this has never been demonstrated. The usual test is to observe a single glass transition temperature, which would indicate homogeneity down to a length scale of 10 nm or so.¹ However, this method cannot be applied to the present blend, since PIB and IIR have essentially the same T_g ($= -69.5 \text{ }^\circ\text{C}$ by calorimetry). Accordingly, rather than rely on the absence of significant phase segregation of the mixed components, we monitored the spontaneous mixing of two, initially separated, sheets of the materials. Thermodynamic miscibility is a requirement for interdiffusion, although since diffusion rates of high polymers are slow, it is necessary to employ a probe of the morphology that is sensitive to the structure at the interface. The adhesion that develops between plied films reflects the spatial extent of interdiffusion, and for rubbery polymers this melding of the interface transpires over feasible ($<10^5 \text{ s}$) time periods.^{25–27}

Representative adhesion results are shown in Figure 1. The peel force rises until the arms of the test piece are fully extended, followed by steady state tearing at a constant force; the ratio of this force to the sample width is the peel energy (work of detachment).²⁸ The adhesion between the layers attains a value equal to the cohesive strength of the PIB (Table

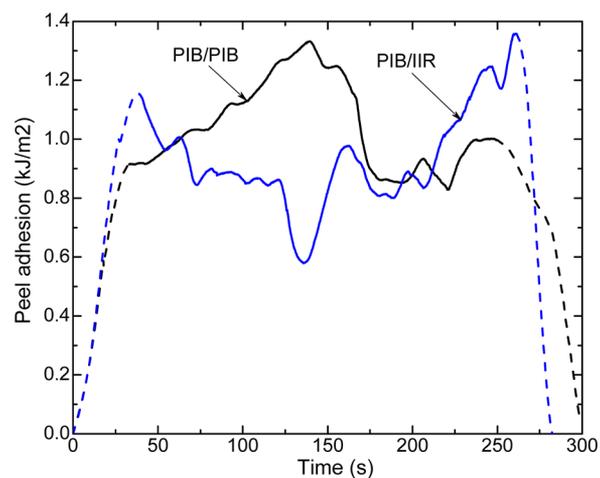


Figure 1. Peel adhesion measured for films of PIB (self-adhesion) and the same polymer contacted with IIR. The adherends were maintained in contact for 5 days prior to the measurement. The levels of adhesion were equal, as governed by the cohesive strength of the lower molecular weight PIB. The mean values of the data denoted by solid lines are listed in Table 2.

2), with separation of the adherends accompanied at that point by substantial deformation, yielding rough, highly deformed

Table 2. Peel Adhesion to PIB

adherend	isoprene (%)	kJ/m ²
PIB	na	1.0 ± 0.15
IIR	2	0.95 ± 0.12
IIR	4	0.82 ± 0.12
IIR	7	0.89 ± 0.16

surfaces. This mode of separation reflects interdiffusion over distances greater than the coil size of the chains, consistent with the thermodynamic miscibility of the PIB and IIR. We repeated these interdiffusion experiments with two IIR polymers having lower isoprene content (and thus more likely miscible with the PIB); the peel adhesion results were the same (Table 2).

Networks were prepared by adding curatives to the mixed components and heating. The miscibility affirmed at room temperature by spontaneous interdiffusion of the polymers does not guarantee their miscibility during vulcanization. However, since the miscibility is due to combinatorial entropy (rather than specific interactions), we expect an upper critical solution temperature and thus a stronger driving force for mixing at the higher temperatures of curing (150 °C). Of course, the chemical alteration of IIR on reaction with sulfur will reduce the components' compatibility, although the affected monomers are the isoprene units, which are chemically distinct even prior to vulcanization. Moreover, segregation is impeded by the formation of the network structure, so that we expect phase homogeneity on a length scale at least as small as that of the network chains.

This network chain length can be estimated from the modulus. Assuming affine motion of the chains¹

$$E = 3\nu RT \quad (1)$$

where E is the tensile modulus, R the gas constant, and ν the concentration of network chains. A phantom network, in which chains are not constrained to deform in proportion to the macroscopic strain, may be more appropriate for cross-linked butyl rubber containing 50% linear PIB. The corresponding equation for a phantom network is¹

$$E = 3 \left(1 - \frac{2}{f} \right) \nu RT \quad (2)$$

in which f is the cross-link functionality (= 4 for the vulcanization used herein). For $E = 0.85$ MPa, which is the midpoint value for the networks, we obtain $0.11 \leq \nu$ (mol/L) ≤ 0.23 . Thus, the molecular weight of the network chains, $M_c = \rho/\nu$ where ρ is the mass density, is ~ 6 kDa. Using a value of 6.6 for the characteristic ratio of PIB,²⁹ the distance between cross-links is estimated to be ca. 6 nm. If phase separation is restricted by the network junctions, this defines an upper bound on the morphological homogeneity. (Note that assuming affine behavior for the network would increase this upper bound by a factor of 2.¹) The lower bound is the chain segment length (<1 nm), which assumes thermodynamic miscibility is retained after cross-linking.

The objective herein is to determine if a homogeneous blend with components having very different cross-link densities exhibits better mechanical properties than a conventional elastomer. Since the modulus and strength of a network are mutually dependent, a series of samples were prepared with

varying degrees of cross-linking. The PIB does not react with sulfur (or to any other cross-linking method), so only the IIR component forms a covalently bonded network. Because of some partitioning of curatives into the PIB, the blends require more sulfur and accelerator to achieve the same modulus as the neat IIR. In Figure 2 are plotted the tensile strengths as a

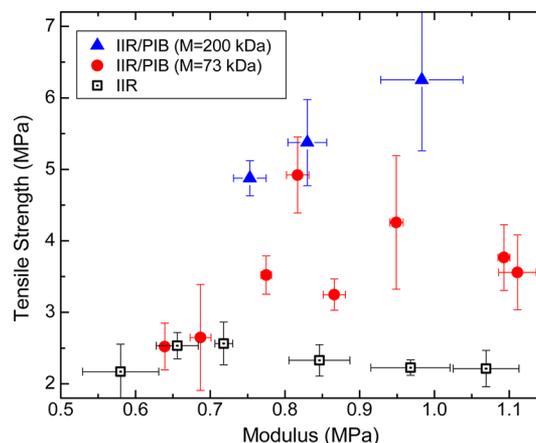


Figure 2. Engineering stress at failure versus the modulus at 100% extension for neat IIR (hollow squares) and 50/50 blends with low (circles) and high (triangles) molecular weight PIB. The nominal strain rate was 0.1 s^{-1} . The data points are the median values, and the error bars are the standard deviations.

function of 100% modulus for IIR and the blend, with the data spanning a range of E from 0.5 to 1.1 MPa (obtained by varying the amount of curative). For a given modulus, the blend exhibits higher tensile strength, by as much as a factor of 2; thus, stronger networks can be achieved without sacrifice of modulus by blending IIR with the miscible, un-cross-linkable PIB.

Figure 3 shows the toughness (area under the stress–strain curve) and failure strain for these samples. Except at very low

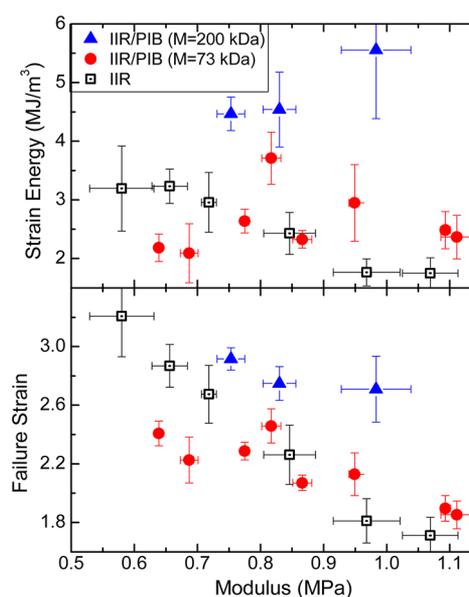


Figure 3. Toughness (top) and failure strain (bottom) as a function of the stress at 100% strain for neat IIR and two blends with PIB. Symbols are the same as in Figure 2.

degrees of cross-linking, both properties are greater for the blend compared to the neat IIR. Of course, the greater extensibility is the primary origin of the higher toughness and strength. This is seen in Figure 4 showing representative

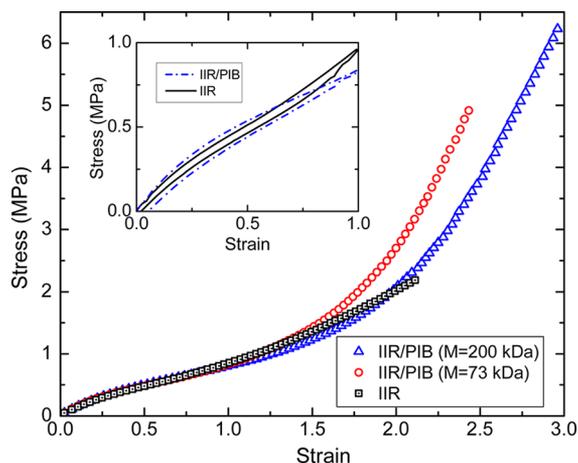


Figure 4. Extension stress–strain curves for the three networks. The inset shows the hysteresis observed on retraction from 100% elongation. Symbols are the same as in Figure 2.

stress–strain curves for the networks. Samples having the same tensile stress through 100% extension deviate significantly at higher strains, leading to the better failure properties for the blends. Included in the figures are data for a 50/50 blend of IIR having a higher molecular weight PIB ($M_n = 200$ kDa). This polymer is about 3 times more entangled with the network chains than the lower molecular weight PIB, and as seen this increases the strength, toughness, and failure strain.

The origin of the improved mechanical properties is the ability of the blend networks to alleviate local overstressing (which is inherent to any randomly cross-linked material), by rearrangement of the unattached chains. The homogeneous morphology of the blend is necessary for the mechanical coupling of the two components, primarily via entanglements but also through nematic interactions.^{30–32} Relaxation of the unattached PIB chains yields larger energy loss in reversing stress–strain measurements. For example, the hysteresis observed during retraction after extending to a strain of 100% is 60% larger for the blend than for the IIR. This loss mechanism, which underlies the greater strength of the blends, also increases the mechanical damping. At ambient temperature at frequencies within the rubbery plateau zone of the viscoelastic spectrum (ca. 10^{-3} – 1 s⁻¹), the dynamic loss modulus and loss tangent for the blend were more than 2-fold higher than for the IIR.

One reflection of the effect on chain orientation of neighboring segments is from the diminution of the elastic stress with increasing tensile strain, as described by constraint models of rubber elasticity.^{33,34} A simple implementation of this idea is the phenomenological Mooney–Rivlin equation³⁵

$$\sigma = (C_1 - C_2/\lambda)(\lambda - \lambda^{-2}) \quad (3)$$

in which σ is the engineering stress, λ is the extension ratio, and C_1 and C_2 are material constants. There have been various attempts to connect the strain-dependent term in eq 3 to the entanglements,¹ with the magnitude of the ratio C_2/C_1 a measure of the topological constraints on the network chains. Thus, in Figure 5 we plot the stress measured at very slow

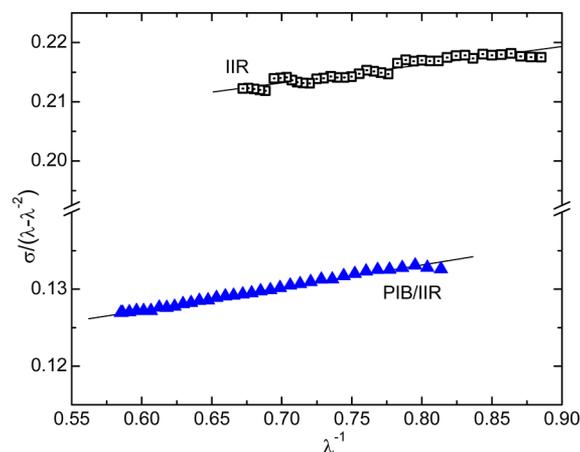


Figure 5. Elastic tensile stress reduced by the strain function of rubber elasticity versus the reciprocal stretch ratio. The fitted curves yield the ratio of the elastic constant $C_2/C_1 = 0.16$ for IIR and 0.27 for the blend (PIB $M_n = 200$ kDa). Note these networks have about the same modulus when measured at the strain rate, ca. 0.1 s⁻¹, used for the data in Figures 2–4.

extension rate ($<10^{-5}$ s⁻¹) for the IIR and the blend network having the higher molecular weight PIB. (For the blend with the lower M_n component, we were unable to achieve reliable mechanical equilibrium data.) The fits of eq 3 yield $C_2/C_1 = 0.16$ and 0.27 for neat IIR and the blend, respectively. This result is unsurprising, as unattached chains certainly have more freedom to change their configuration as the network is stretched. The mobility serves as the mechanism for local stress alleviation and ultimately better mechanical properties. It follows that the unattached PIB chains, which cannot sustain load at sufficiently long times, will provide less strength enhancement at lower rates; this is confirmed by slow strain rate measurements (Table 3).

Table 3. Effect of Strain Rate on Tensile Strength

	nominal strain rate (s ⁻¹)	
	0.001	0.1
IIR	1.4 MPa	2.3 MPa
blend ^a	2.1 MPa	5.4 MPa

^a50/50 IIR and PIB ($M_n = 200$ kDa).

A recently developed application of butyl rubber is as a coating on steel used for armor.²³ The elastomer increases the resistance to ballistic penetration of the steel, with negligible increase in weight. For the uncoated steel the penetration velocity was measured to be 733 m/s. This increases to 803 ± 3 m/s with a neat IIR coating (5 mm thickness) on the strike face; using the blend as the coating, we measured 812 ± 4 m/s. The improvement for the blend is significant, but much less than the factor of 2–3 increase in strength shown in Figure 2. The reason for this is that impact of a bullet compresses the material at very high strain rates (estimated as the ratio of the projectile velocity to coating thickness, $\approx 10^5$ s⁻¹), which means that ballistic penetration may involve the segmental dynamics of the polymer.³⁶ How the network structure, or the blend morphology, affects failure properties involving segmental motion of the network chains remains to be investigated.

CONCLUSIONS

Commercial materials exist that are blends of thermodynamically miscible polymers, although this miscibility *per se* does not guarantee any improvement in performance. In fact, the properties of homogeneous blends are often just an average of the neat component properties. In the approach adopted herein, one component is cross-linked and the other remains a linear polymer; this structural disparity results in different contributions to the mechanical response of the network. The IIR responds elastically, and the un-cross-linked PIB serves as a viscous medium; however, unlike a low molecular weight diluent, the PIB is coupled to the network via topological interactions. As the cross-linked component becomes highly oriented during deformation, in a heterogeneous manner due to the random nature of the network, the PIB chains rearrange over sufficient length scales to alleviate local overstressing. This suppresses propagation of rupture nuclei, delaying macroscopic failure. The result is stronger, tougher elastomers. The mechanism underlying the improvement in the mechanical performance of miscible, heterogeneously cross-linked blends can be considered an example of “delegation of responsibilities”¹²—the more cross-linked component augments the modulus, and the greater configurational freedom of the linear chains of the un-cross-linked component provides greater extensibility. The latter also gives rise to larger mechanical damping (energy loss) for the blend network in comparison to the cross-linked IIR. Heterogeneously cross-linked blend networks have features in common with bimodal networks^{9,11,12} and hydrogel blends;^{13,14} however, these materials require end-linking or the presence of a solvent. Unlike IPNs, thermodynamic miscibility of the blend components herein avoids phase segregation. Indeed, the miscibility of IIR and PIB demonstrated in this work is a crucial aspect of this approach, which can be adopted for existing applications of butyl rubber. Extension to other polymers is straightforward, the requirements being that the components are miscible and have very different susceptibilities to cross-linking.

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Notes

The authors declare no competing financial interest.

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