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Heterogeneous networks of polyisoprene/polyvinylethylene

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Abstract

High *cis*, 1,4-polyisoprene (PI) and polyvinylethylene (PVE) form a miscible blend, having a lower critical solution temperature (LCST). Networks of this blend were prepared by crosslinking with organic peroxide or by sulfur vulcanization. The very different reactivity of the two polymers leads to a disparity in the crosslinking, especially for sulfur curing—networks of PI can be formed without substantial reaction of the PVE. When the sulfur vulcanization is carried out at ca. 130 °C or higher (above the LCST), the polymers phase separate, yielding a PI network with PVE domains. Curing at lower temperatures maintains the miscible morphology, and a homogeneous blend network is obtained.

Keywords: Blends; Networks; Vulcanization

1. Introduction

In developing an elastomeric compound, the particular polymer selected for the formulation has minimal effect on the network properties per se. That is, while the chemical structure of the network affects various aspects of performance (e.g., chemical and heat resistance, friction, adhesion, gas permeability, biocompatibility, etc.), the mechanical behavior up through moderate deformations is essentially the same for all flexible-chain polymers. Even the fracture and fatigue properties, in the absence of strain-induced crystallization, are not especially dependent on the polymer. Of course, the chemical structure of the network has an indirect effect, through its influence on the crosslinking reaction.

This situation is quite different for blends, since new factors arise, with possible consequences on the network properties. Most rubber blends are thermodynamically incompatible, and thus phase-separated [1]. A heterogeneous morphology can lead to disparity in the spatial distribution of crosslinks, particularly when the crosslinker has different solubilities in the phases [2,3]. Even for homogenous phase morphologies, however, the relative crosslinking reactivities of the components can potentially affect the network properties. An example of this is bimodal networks, in which short (even oligomeric) chains are mixed with high molecular weight polymer. Forming a network by end-linking such a blend yields bimodal elastomers, which have novel mechanical properties, notably exceptional toughness [4]. Another example is hydrogel blends, formed by sequential crosslinking of the components. These are aqueous networks in which a homogeneous morphology results from the mutual solubility of the components in water. Recently, Gong et al. [5] reported that for hydrogel blends in which the crosslink densities of the components differed by a factor of 40, remarkable improvements in toughness were obtained. Both approaches rely on mixtures of short and long network chains, to yield stiff yet strong composite networks.

Since so few rubber blends are thermodynamically miscible, considerable effort has been expended on obtaining interpenetrating networks of incompatible polymers. The basic approach is to start with a homogenous polymer solution, followed by polymerization of the solvent with simultaneous crosslinking of the components [6,7]. Unfortunately, the kinetics of phase separation is invariably too fast, and phase separated morphologies are obtained. Among the few cases of rubber blends which are thermodynamically miscible, the most interesting is 1,4-polyisoprene (PI) and polyvinylethylene (PVE, or 1,2-polybutadiene). Miscibility of natural rubber and high vinyl

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polybutadiene was first reported by Bartenev and Kongarov [8], and subsequently investigated by various groups [9–12]. Miscibility appears to result from a fortuitous near-equivalence of the polarizabilities (and thus van der Waals energies) of the repeat units for the two materials [13,14]. Although infrared spectroscopy indicates an absence of specific interactions [12], the interaction parameter is negative, implying a lower critical solution temperature (LCST) [13]. The polymer interaction parameter is a measure of all non-combinatorial entropic contributions to the free energy, including those due to non-random mixing or other equation of state effects. For PI mixed with deuterated PVE, the interaction parameter has a temperature dependence given by [13]

$$\chi = 8.31 \times 10^{-3} - 3.6/T \quad (1)$$

which gives an LCST $\cong$430 K. Thus, at least up to typical cure temperatures, the blend morphology is expected to be homogeneous for all proportions of the components, as borne out by experiment [14,15].

The rheology and dynamic properties of uncured blends of PI and PVE have been investigated using various techniques [12,16–19]. The main finding is that the components retain their distinct dynamics, notwithstanding the homogeneous phase morphology. One result of this ‘dynamic heterogeneity’ is very broad glass transitions in the blend [10]. The crystallization behavior [10,20,21] is of particular interest, since strain crystallization underlies the exceptional mechanical properties of natural rubber. Pure *cis*-1,4-polyisoprene crystallizes into α-lamellae, which are the most stable crystalline form. During crystallization from the blend, however, PVE chains are trapped between the lamella, causing preferential development of β-lamellae [20]. The β-lamellae have the same unit cell, but a higher fold-surface free energy, which can better accommodate the PVE at the crystal surface. Synthetic natural rubber, having a lower *cis* content than natural rubber, similarly yields a significant fraction of the β-form. During crystallization of PI from blends, some PVE is also trapped within the crystalline lattice, which results in an expansion of the unit cell [21].

Very little work has been done on crosslinked PI/PVE blends. PI networks with absorbed PVE chains were used to study nematic coupling, whereby an anisotropic probe molecule, such as a polymer chain, is oriented at equilibrium by virtue of its presence in a stretched network [22,23]. For PVE in deformed PI networks, the coupling was greatest for short PVE chains in PI networks having low crosslink density [24]. The onset of strain-induced crystallization caused a marked increase in the orientation of the PVE, consistent with its entrapment within the PI spherulites.

When the components of PI/PVE blends were simultaneously crosslinked using organic peroxides, the main effect of the PVE is to increase the total crosslink density [24]. This is due to the chain reaction accompanying free radical crosslinking of the PVE, leading to crosslinks of high functionality. For neat PI, a stable tertiary radical is formed, with termination usually occurring by combination to form tetrafunctional crosslinks [25].

In this work, networks of PI and PVE were formed either by free-radical crosslinking, which favors the PVE, or by sulfur vulcanization. Since tertiary vinyl carbons do not sulfurize [25], sulfur vulcanization is expected to favor the PI. In this manner, we attempt to make blend networks in which the components have different degrees of crosslinking. The ultimate purpose is to develop better elastomers. However, as described herein, the modification of the chains by the crosslinking, in combination with high cure temperatures (> LCST), can perturb the phase morphology of the blend.

2. Experimental

The PVE had a vinyl content equal to 97.5% per ^{13}C-NMR, and a number average molecular weight of 123 kg/mol (polydispersity =1.03). The PI was 77% *cis* 1,4-, 16% *trans* 1,4-, and 7% 3,4-polyisoprene (^{1}H NMR), with a nominal molecular weight of 500 kg/mol. A EV (‘efficient vulcanization’) cure system was used for sulfur vulcanization (Table 1), yielding predominantly monosulfidic crosslinks. Peroxide crosslinked blends were also prepared, using 0.2 to 0.7 phr of dicumyl peroxide. Cure times and temperatures varied as described below. The cure kinetics were measured using a TA Instruments ARES rheometer (parallel plate geometry: 1–2 mm gap and 12 mm diameter). Swelling experiments were carried out over three days, with cyclohexane as the solvent. FTIR spectra (ThermoElectron 750 ESP spectrometer) were obtained on cast films, typically 30–50 μm thick. The resolution was 1.9 cm^{-1}, with typically 10 scans averaged per spectra. Differential scanning was carried out on a Perkin–Elmer DSC-7, at heating/cooling rates of 10°/min. Mechanical measurements employed an Instron 5500R with a Wallace optical extensometer. Test specimens, 27.5 mm long with a

Table 1
Sulfur-cure formulation

	Phr
cis-1,4-polyisoprene (PI)	50
1,2-polybutadiene (PVE)	50
Zinc oxide	5
Stearic acid	2
N-(1, 3-dimethylbutyl)-N′-phenyl-p-phenylenediamine[a]	2
N-cyclohexylbenzothiazole-2-sulphenamide[b]	3
Tetrabenzylthiuramdisulfide[c]	2
Sulfur	0.3

[a] Santoflex 13® Antidegradant (Flexsys).
[b] Santocure® CBS accelerator (Flexsys).
[c] Perkacit® TBzTD accelerator (Flexsys).

3.8 mm^2 cross-sectional area, were stretched at 250 mm/min.

3. Results

3.1. Sulfur-vulcanized blends

Samples were crosslinked at 130 °C, the highest temperature at which the cure could be reproducibly terminated prior to completion. Swelling data as a function of cure time are displayed in Fig. 1. After 20 min, half the material has gelled, the remainder being soluble; both fractions were analyzed by FTIR. The spectra (Fig. 2) indicate that initially the gel is entirely PI; that is, only the PI crosslinks. The PVE remain unattached and thus entirely comprised the soluble fraction.

As discussed above, initially the components are miscible and thus form a homogenous mixture. However, DSC measurements reveal that this homogeneous morphology is not retained during the early stages of the curing, when only the PI is reacting. As shown in Fig. 3, after 20 min at 130 °C, distinct glass transitions are observed for the soluble and insoluble portions, at respective temperatures corresponding to those of pure PVE and PI. This implies that the elevated cure temperature, which is 27 °C below the LCST of the PI/deuterated PVE blend [13], induces phase separation. Of course, the loss of miscibility is abetted by the chemical changes in the PI (attachment of sulfur) accompanying vulcanization.

To circumvent this, we carried out the curing at a significantly lower temperature, 90 °C. The reaction is greatly retarded at such a low temperature (see Fig. 4), so that extended cure times are required. After 11 h reaction at 90 °C, the gel content was 55%. As determined from the FTIR spectra (Fig. 5), at this stage of the vulcanization the soluble fraction was 60% PVE and 40% PI. Thus, the discrimination between the crosslinking of the components is lost when the blend is cured at a temperature substantially

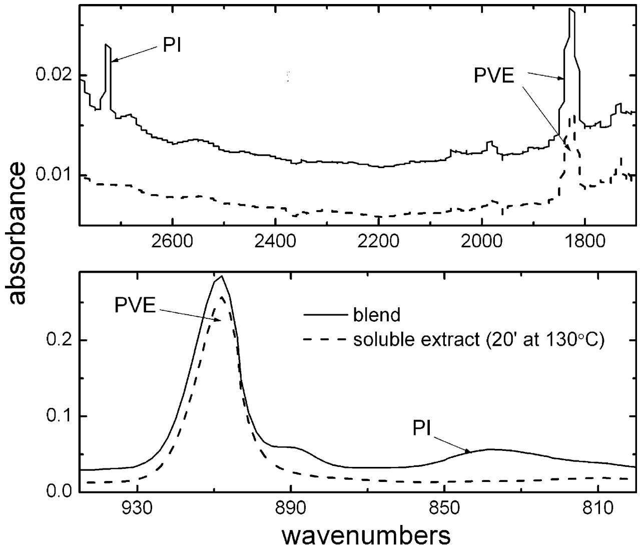

Fig. 2. Infrared absorption of PI/PVE, measured initially (solid line) and after vulcanization 20 min at 130 °C (dashed line), in regions of the spectra at which distinct absorption bands for the two polymers can be resolved. Upper: PVE vinyl overtone band (1837 cm^{-1}) and PI methylene out of plane stretch (2724 cm^{-1}); lower: out of plane deformation of PI vinyl carbon (837 cm^{-1}) and out of plane deformation of PVE vinyl carbon (909 cm^{-1}). Assignments from Ref. [31–35].

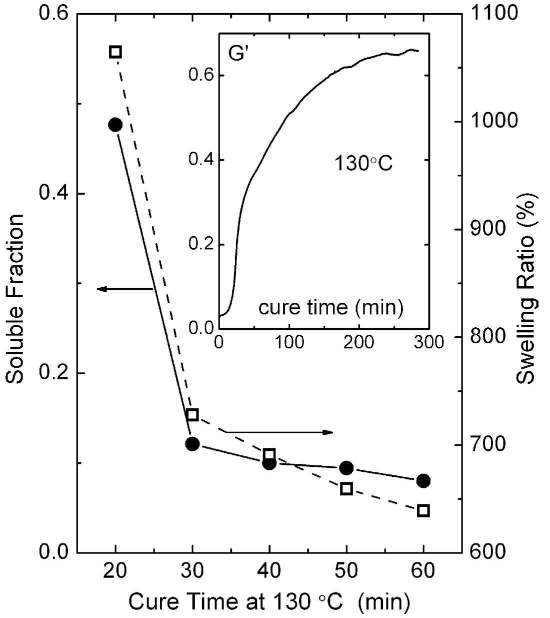

Fig. 1. The soluble fraction (●) and swelling ratio (☐) of the sulfur-cured blend as a function of cure time at 130 °C. The inset shows the cure curve (storage modulus in arbitrary units).

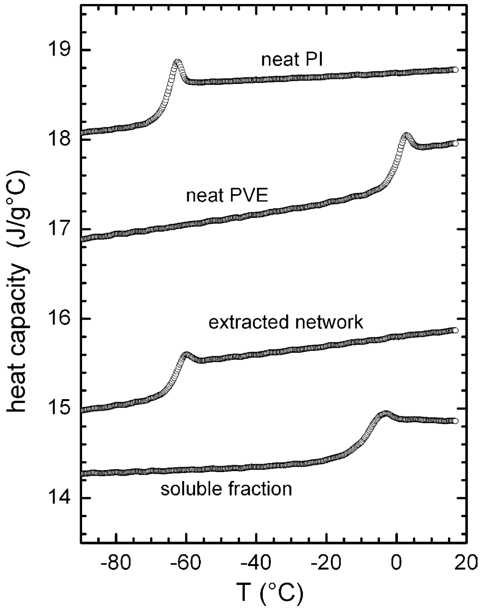

Fig. 3. DSC curves for pure, uncrosslinked components (upper curves) and for the gel and soluble fraction of the S-vulcanized blend, reacted 20 min at 130 °C. The respective transition temperatures for the latter are essentially equal to that of the neat PI ($T_g = -64$ °C) and neat PVE ($T_g = -1$ °C).

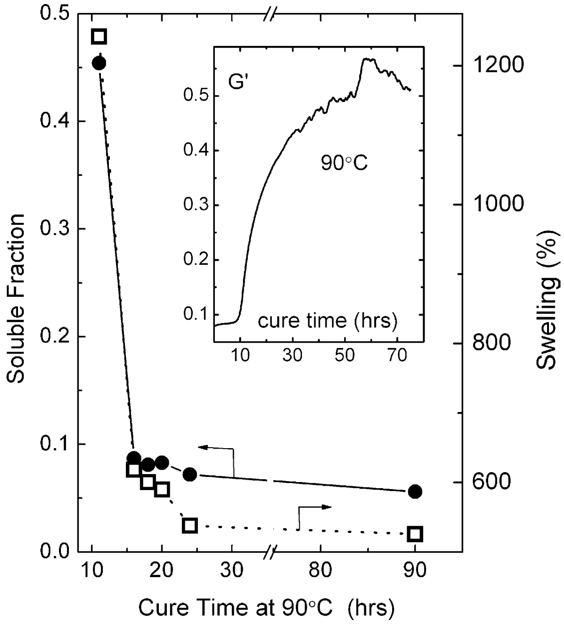

Fig. 4. The soluble fraction (●) and swelling ratio (☐) of the sulfur-cured blend as a function of cure time at 90 °C. The inset shows the cure curve (storage modulus in arbitrary units). Some reversion is apparent at longer time.

below the LCST. The DSC curve for the gel fraction (Fig. 6) exhibits only a single, albeit broad, glass transition, at a temperature intermediate between the T_g of the neat components; that is, the morphology is homogeneous, at least on the length scale probed by heat capacity measurements.

Transmission electron micrographs, obtained on samples fully cured respectively at 95 and 130 °C, are shown in Fig. 7. Curing at the lower temperature (upper panels) gives rise to a very fine structure, on the order of 25 nm or less. Although this is larger than molecular dimensions, it is too small for the components to manifest distinct glass transitions in the DSC measurements. The length scale for segmental relaxation has been measured in glass-formers by various techniques, with results in the range from 1 to 3.5 nm [26–30]. In a blend, this characteristic length is smeared (broadened) due to concentration fluctuations, whereby only a single glass transition is observed. Strictly speaking, however, the blend is phase-separated. The thermodynamic incompatibility is evidently a consequence of the reaction with sulfur, which chemically modifies the polymers. However, the co-crosslinking of the components precludes significant phase separation.

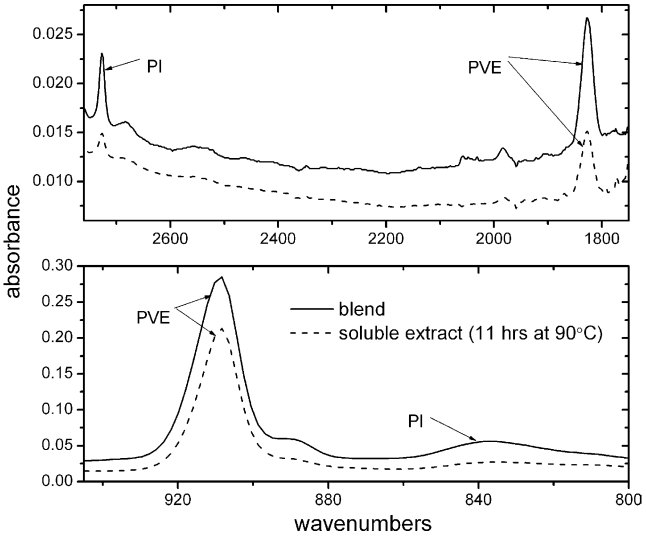

Fig. 5. Infrared absorption of PI/PVE blend, measured initially (solid line) and after 11 h S-vulcanization at 90 °C (dashed line), in regions of the spectra at which distinct absorption bands for the two polymers can be resolved. Upper: PVE vinyl overtone band (1837 cm^{-1}) and PI methylene out of plane stretch (2724 cm^{-1}); lower: out of plane deformation of PI vinyl carbon (837 cm^{-1}) and out of plane deformation of PVE vinyl carbon (909 cm^{-1}). Assignments from Ref. [31–35].

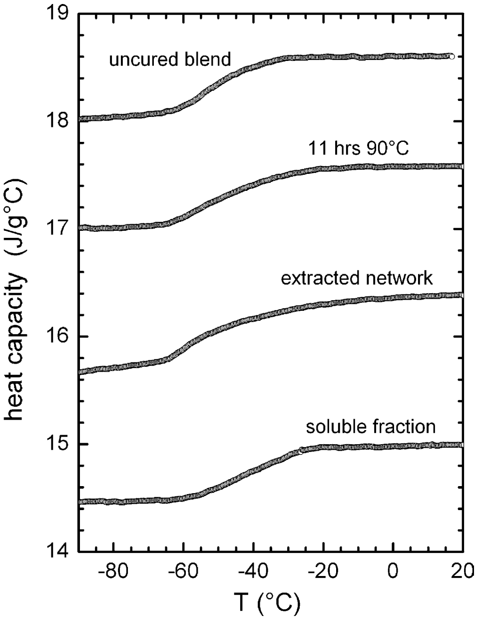

Fig. 6. DSC curves for the uncrosslinked blend (upper curve) and for the gel and the soluble fractions obtained after 11 hrs S-vulcanization at 90 °C. All curves have single, broad glass transitions, at temperatures intermediate to the respective T_g of the neat components.

The situation for the blend cured at higher temperature is quite different. As seen in Fig. 7 (lower panels), the morphology is coarse, with domain sizes on the order of 300 nm. Immiscibility was induced, prior to any reaction of the PVE, because the curing was carried out above the LCST. Phase separation transpired before the PVE was incorporated into the network, and thus large domains were formed.

3.2. Peroxide cured blends

The PI/PVE blend was cured with varying levels of dicumyl peroxide, yielding networks which in all cases had a homogeneous morphology. DSC revealed a single, broad T_g at a temperature close to that of the uncured blend, ca.

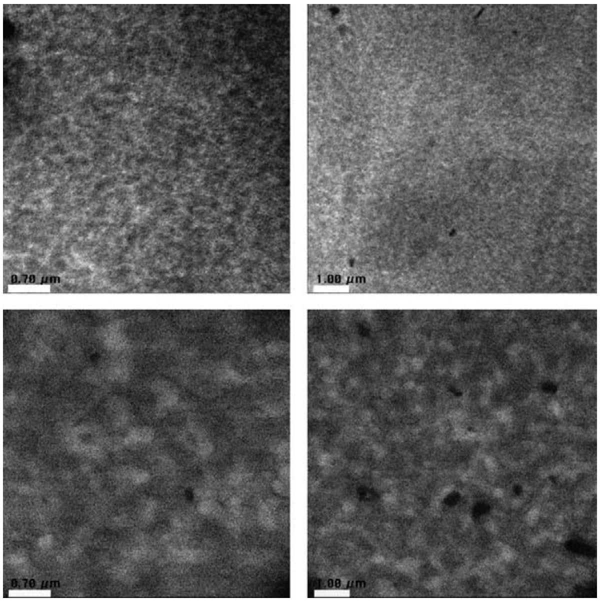

Fig. 7. Transmission electron micrographs of the sulfur-vulcanized blend: (top) cured at 95 °C and (bottom) at 130 °C. Scale bars in lower left corner of each panel correspond to either 0.70 μm (left panels) or 1.0 μm (right panels).

−50 °C. Carbon–carbon bonds resulting from free-radical crosslinking do not change the chemical nature of the polymer chains as much as sulfur vulcanization. This may contribute to maintaining miscibility. In addition, the reaction is quite fast (there is no induction period, as for sulfur curing), which may preclude phase separation.

As previous work had shown [24], the main effect of the PVE is to increase the crosslink density of the PI. Free radical crosslinking of PVE is associated with chain reaction and a high junction functionality, whereas peroxide reaction of PI yields tetrafunctional junctions [25]. This means that in the blend, crosslinks of higher functionality will tend to be enriched in PVE.

3.3. Mechanical properties

An objective of modifying the phase morphology of the blend network is to obtain better mechanical properties. By taking advantage of the disparate crosslinking reactivity of the PI and PVE, potentially tougher rubbers might be obtained, in the manner of bidisperse PDMS networks [4] and hydrogel blends [5]. The present study, intended to permit analysis of the blend morphology, relied on linear polymers, available in limited quantity. Consequently, a full compounding study, in which the optimum blend networks could be developed, was not possible. Available quantities were also inadequate to quantify failure properties, such as strength and fatigue life. Some precursory mechanical measurements were obtained, with more detailed studies intended as future work.

The morphology of the blends was fixed once curing had proceeded past the gel point; for example, DSC results became invariant to thermal (cure) history. Accordingly, after initial vulcanization at either 90 or 130 °C, the blends were cured an additional 20 min at 160 °C to ensure completion of the crosslinking. In Fig. 8 are shown the stress/strain curves for the two S-vulcanized networks. Both exhibit the same modulus (measured essentially at mechanical equilibrium): Young's modulus =0.99 MPa and 100% secant modulus =0.52 MPa. The blend cured at higher temperature has a significantly larger failure strain, associated with higher stress. Neither rubber is particularly high in strength, although there has been no effort to optimize the formulations with regard to mechanical performance. To the extent the presence of the PVE inhibits strain-crystallization of the PI, the putative benefits of a heterogeneous network may be overcome by the loss of this inherent toughening mechanism of *cis*-1,4-polyisoprene.

The poorer response of the network cured at lower temperature is unexpected. A homogeneous morphology would be less affected by poor interfacial crosslinking, which is a common problem with phase-separated rubber blends. Given the long duration of the cure used to produce this homogeneous network, the possibility exists for thermal oxidative aging and/or crosslink reversion. There is some evidence of the latter (see Fig. 4 inset), notwithstanding the use of an EV cure system. This is a technical problem, which can be overcome by using a more stable crosslink system. Anti-reversion agents and post-vulcanization stabilizers are well-known and commercially available.

The peroxide-cured blends have poor mechanical properties. At levels of crosslinking sufficient to achieve even a moderate modulus, the materials are brittle and weak. Included in Fig. 8 is the stress/strain curve for the blend cured with 0.5 phr peroxide. This gives a modulus at low

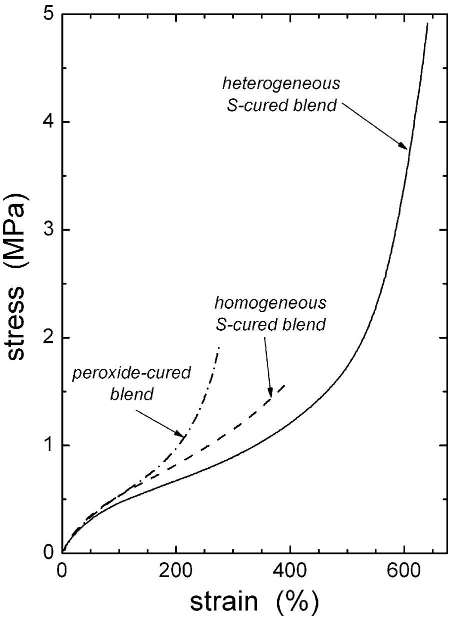

Fig. 8. Engineering stress versus tensile strain for the sulfur and peroxide cured blends.

strains equal to those for the two sulfur-vulcanized blends. Clearly, the peroxide-cured blend is inferior to the S-vulcanized rubber. This is due, at least in part, to the labile nature of the sulfur crosslinks. These are well-known to yield better mechanical performance, due to their capacity to alleviate local stress concentration.

4. Conclusions

By variation of the sulfur vulcanization temperature, the phase morphology of the PI/PVE blend can be controlled. By curing below the LCST, a homogeneous morphology is retained, while higher cure temperatures lead to phase separation. Free-radical crosslinking with organic peroxide always results in a homogeneous blend. Although only a cursory assessment of the mechanical properties was carried out, preliminary indications are that phase separation leads to better performance. The poor performance of the network may be related to the suppression of strain-induced crystallization of the PI. How specific the behavior is to the crosslinking and relative crosslink densities employed herein remains to be investigated.

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