

Orientational correlations in polyisoprene/poly(vinylethylene) mixtures

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I.r. dichroism measurements were used to study the orientation in stretched networks of *cis*-1,4-polyisoprene (PIP) containing atactic poly(vinylethylene) (PVE). When both components are part of a network, their relaxation behaviour and equilibrium orientation are essentially identical. In blends of crosslinked PIP with linear PVE, the orientation of the latter is reduced relative to that of the former; however, the PVE retains an equilibrium orientation by virtue of its presence in the strained network. Consistent with earlier results on isotropic crystallization of PIP in this blend, strain induced crystallization evidently entraps some of the amorphous PVE when it is high in molecular weight, thus enhancing the extent of orientational coupling. In amorphous networks, the coupling is dependent on the degree to which the PVE chains can be accommodated within the network mesh; hence, coupling is enhanced for lower molecular weight PVE in less crosslinked PIP. The addition of diluent weakens the coupling in a manner consistent with the excluded volume origin of the interchain interactions.

(Keywords: orientation; *cis*-1,4-polyisoprene; poly(vinylethylene); networks)

INTRODUCTION

The classical depiction of orientation in a crosslinked rubber is that of chains responding independently to stresses conveyed through the network junctions. The orientation reflects the configurational entropy and intramolecular conformational energy of the network strands. However, it is now recognized that intermolecular interactions also contribute to chain orientation. This effect can be seen directly in deformed networks containing unattached probe molecules¹⁻⁶. The orientational correlations arise from steric effects; excluded volume interactions induce orientation of segments residing in proximity to oriented segments⁷⁻¹¹. Such coupling is only locally effective, as evidenced by the retention of isotropic coil dimensions in chains exhibiting orientational coupling^{3,12}. Anisotropic intermolecular forces may also augment the interchain interaction^{13,14}.

In a miscible polymer blend co-operativity in the relaxation of the components may be anticipated due to the specific (chemical) interactions commonly associated with miscibility between high polymers^{15,16}. Orientational coupling in some polymer mixtures has been ascribed specifically to the presence of specific interactions, although in similarly interacting polymer/solvent mixtures no coupling was observed¹⁷. Notwithstanding such orientational correlations, the dynamics of the components in a miscible blend can diverge due to differences in their local friction coefficients and intrinsic relaxation behaviours¹⁸⁻²². Co-operativity of the low frequency motions and equilibrium orientation can be enhanced by simultaneous crosslinking of the components of a miscible blend. Attempts to achieve this with immiscible polymers is the basis of interpenetrating polymer network technology²³.

This paper describes orientational relaxation in miscible blends of PIP and PVE. Miscibility exists despite an absence of specific interactions; the system is a nearly ideal mixture of high polymers²⁴⁻²⁷. PIP networks containing linear PVE, as well as simultaneously crosslinked blends, were studied using FTi.r. spectroscopy. The technique is non-intrusive and requires no labelling, with the dichroic ratio, R , of an i.r. absorption band providing a measure of the second moment of the orientation function.

EXPERIMENTAL

The PIP was natural rubber (SMR-L, a high purity grade of *Hevea brasiliensis*). The atactic PVE, obtained from the Firestone Tire and Rubber Co., was 96% 1,2-polybutadiene ($M_n = 134\,000$; $M_w/M_n = 1.1$) or 93% 1,2-polybutadiene ($M_n = 23\,000$; $M_w/M_n = 1.2$). Various compositions (Table 1) were prepared by mixing the PIP and PVE on an unheated two-roll mill. Thin films ($< 100\ \mu\text{m}$) were then cured using dicumyl peroxide. Consistent with the retention of a homogeneous morphology after crosslinking, the samples remained transparent and exhibited single glass transitions in d.s.c. measurements.

Table 1 Blends with simultaneously crosslinked components

Sample designation	PIP (wt%)	N_c^a
PIP	100	266
PIP90	90	144
PIP80	80	124
PIP50	50	74

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^a Using equation (2)

In these blends, the junction functionality is uncertain due to chain reaction accompanying free radical crosslinking of the PVE. Hence, the crosslink densities were estimated from measurements of equilibrium mechanical stress. The two extremes in elastic behaviour correspond to phantom networks, comprised of volumeless chains able to pass freely through one another, and affine networks, whose strands each deform in direct proportion to displacement of the macroscopic continuum²⁸. These models provide a lower and upper limit, respectively, on the number of monomer units between crosslinks, N_c , at least in so far as the effect of the surrounding chains is limited to constraining the network junctions and not the strands connecting the junctions²⁹. The relationship for a perfect (no chain ends) phantom network is²⁸:

$$N_c = \frac{[1 - (2/\phi)]\rho kT(\lambda - \lambda^{-2})}{m\sigma} \quad (1)$$

in which λ is the equilibrium extension ratio at an engineering stress equal to σ and ϕ is the crosslink junction functionality. The molecular weight of the monomer unit, m , is 68 and 54 g mol⁻¹ for PIP and PVE, respectively, while the respective mass densities, ρ , are 0.93 and 0.88 g cm⁻³. An upper limit for N_c is estimated from the assumption of affine network behaviour, whereby²⁸:

$$N_c = \frac{\rho RT(\lambda - \lambda^{-2})}{m\sigma} \quad (2)$$

The actual N_c values of the networks lie between the values calculated from equation (2) (given in *Table 1*) and the smaller values (by a factor of 0.5 for $\phi=4$) obtained from equation (1).

Since peroxide crosslinking of pure 1,4-polyisoprene yields tetrafunctional crosslinks³⁰, in the absence of PVE the crosslink density of PIP networks can be deduced from the Wood equation³¹ assuming complete reaction of the dicumyl peroxide. A series of pure PIP films of varying crosslink density were prepared by incorporating various levels of dicumyl peroxide (0.5–1.5 wt%), then curing for 30 min at 151°C. The N_c values for these networks determined using the Wood equation are given in *Table 2*. Some of these films were then immersed for 30 days in hexane solutions of PIP (6 and 13 wt% for

the high and low molecular weight PVE, respectively), followed by washing with hexane and vacuum drying. This procedure yielded 9 ± 2 wt% of absorbed PVE in the crosslinked PIP. After washing no PVE was apparent on the film surface. Where subsequent addition of paraffin was desired, samples were soaked in paraffin and then washed again.

For networks comprised of co-crosslinked PIP and PVE, films were stretched manually at room temperature to various elongations, the latter determined from fiducial marks. The PIP networks containing linear PVE were dead-weighted to a constant stress of 0.84 MPa.

FTi.r. spectra were obtained using a Perkin-Elmer 1800 spectrometer with a Spectra Tech polarizing filter. Sixteen scans were averaged at 2 cm⁻¹ resolution in single beam mode. The spectra were analysed by fitting Lorentzian line shapes to the absorption bands of interest. The absorption spectra of the blends were the linear combination of the spectra of the pure components, with no new bands or changes in the shape or frequency. This is a consequence of the absence of specific interactions in the blend^{26,27}. The results for the co-crosslinked specimens represent the average of at least seven individual measurements. The R values were determined as the ratio of the integral absorbance for a band measured with radiation polarized parallel and perpendicular, respectively, to the stretching direction. The 909 cm⁻¹ resonance of PVE (vinyl C–H₂ out of plane deformation^{32–34}) and the dispersion at 836 cm⁻¹ in the spectrum of PIP (C–H out of plane bending^{32–34}) were utilized. Absorbancies were in the range of 0.5–0.9.

RESULTS

Co-crosslinked blends

The measured orientations are expressed in terms of the Hermans orientation function, f , describing the second moment of the orientation function of the chains with respect to the stretching direction³⁵:

$$f \equiv \frac{1}{2}(3\langle \cos^2 \theta \rangle - 1) = \frac{(R-1)}{(R+2)} \left/ \frac{(R_0-1)}{(R_0+2)} \right. \quad (3)$$

where θ is the angle between the chain axis and the stretch direction and R_0 is the dichroic ratio for perfect orientation, i.e.

$$R_0 = 2 \cot^2 \alpha \quad (4)$$

The angle, α , between the transition moment vector of the vibration and the chain axis is taken to be 68° for the vibrational band of PIP at 836 cm⁻¹ (ref. 36), and 33° for the PVE 909 cm⁻¹ resonance.

Figure 1 shows the equilibrium orientation measured at various elongations for PIP networks both neat and in a blend (PIP90) in which both components were simultaneously crosslinked. The orientation of the co-crosslinked PVE parallels that of the PIP. At the lower strains blending increases the orientation of the PIP relative to pure PIP at the same strain. This is an artifact of its higher crosslink density in the latter. As shown in *Table 1*, under constant crosslinking conditions the crosslink density increases in proportion to the concentration of PVE. This dependence of PIP crosslink density on PVE concentration is a consequence of the different peroxide reactivities of the PIP and PVE³⁰. In PIP a stable tertiary radical is formed, with termination usually

Table 2 Orientational coupling results for PIP networks with absorbed linear PVA

PIP network		Linear PVE						PIP crystallinity ^c (%)
N_c	R_G^a	%	R_G	f_{PIP}^b	f_{PVE}^b	ϵ		
1050	89	11	52 ^d	0.147	0.032	0.22	10.4	
050	89	11	120 ^e	0.138	0.047	0.34	8.3	
288	47	11	52 ^d	0.128	0.027	0.21	5.6	
288	47	10	120 ^e	0.128	0.032	0.25	4.0	
118	30	10	52 ^d	0.120	0.024	0.20	0	
118	30	9	120 ^e	0.121	0.017	0.14	0	
74	24	8	52 ^d	0.112	0.021	0.19	0	
74	24	7	120 ^e	0.112	0.012	0.11	0	

^a Using equation (6)

^b At equilibrium for $\sigma = 8.84$ MPa

^c Calculated from 844 cm⁻¹ FTi.r. band (see ref. 31)

^d $N_c = 426$

^e $N_c = 2730$

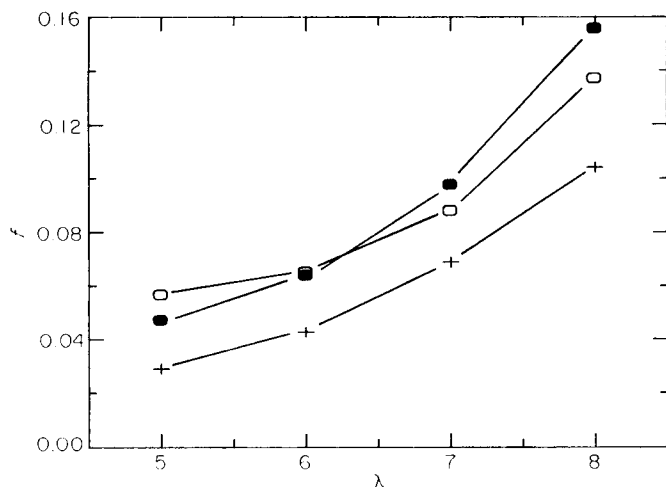


Figure 1 Hermans orientation function, f , measured at mechanical equilibrium for neat PIP (●) and blended (PIP90, ○), along with f of PVE (+) in the latter

occurring by combination to form tetrafunctional crosslinks. In PVE, on the other hand, the free radical formed at the vinyl carbon rapidly propagates with minimal termination. As a result the concentration of free radicals relative to the PIP content increases with PVE concentration, since the latter consumes a negligible quantity of free radicals while being incorporated into the network. The higher crosslink density of PIP in blends with PVE effects higher orientation at the lower macroscopic strains.

At $\lambda > 6$ the situation reverses, with the orientation of neat PIP exceeding that measured for PIP90. This is due to the more extensive crystallization of PIP when neat. For example, at $\lambda = 8$ the pure PIP is 18% crystalline versus only 12% crystallinity in the PIP90 (ref. 37). The suppression of the crystallization in the blend is due both to the presence of the non-crystallizing PVE and to the effect of higher crosslinking *per se*. Strain induced crystallization causes a marked increase in the segment orientation^{38,39}, with the magnitude of the increase paralleling the degree of crystallinity. Hence at higher strains the effect of a lower crosslink density in the neat PIP is compensated for by the enhanced crystallization, leading to greater PIP orientation in the PIP100.

The longest relaxation time of the networks (i.e. the time required for R to attain its equilibrium value) increases with increase of the draw ratio. This retardation is also due to crystallization^{38,39}, which provides a mechanism for stress reduction beyond that due to viscoelastic relaxation. At a given strain the equilibrium times were comparable for the PIP and the non-crystallizing PVE. Co-operativity of the relaxation behaviour in other miscible blends has been ascribed to specific interactions^{15,16}. Since the present mixtures are strictly van der Waals liquids^{26,27}, there is no specific interaction between the PIP and PVE. At much shorter time-scales than observable herein, corresponding to local segmental motion, the PIP and PVE components do exhibit different dynamics and temperature dependencies⁴⁰. This behaviour has been attributed to differences in their respective local friction coefficients¹⁹. The similarity of the orientational relaxations at the longer times studied herein reflects a co-operativity arising from covalent bonding and physical interpenetration

of the two simultaneously crosslinked polymers. The effect of such interactions on the relaxation is manifested only at longer times corresponding to longer length scale motions.

PIP networks containing linear PVE

In samples in which the PIP was crosslinked prior to addition of the PVE, the relaxation behaviour is quite different from that of the co-crosslinked mixtures. The components of the co-cured blends relax coincidentally, with equivalent periods of stress relaxation required for attainment of equilibrium R values. In the blends comprised of a PIP network containing linear (unattached) PVE chains, while the relaxation of the PIP is virtually identical to that observed for neat PIP networks of equivalent crosslink density, the PVE relaxes significantly faster. This result is unsurprising, since the linear chains have more degrees of freedom and hence greater mobility than the network strands.

The linear PVE does not, however, relax to isotropy (Table 2). The presence of an oriented PIP network induces stable orientation of the PVE, indicating that intermolecular correlations are providing a mechanism for orientation other than by stress transferred through the crosslink junctions. The strength of the orientational coupling can be characterized by the ratio of the respective Hermans orientation functions¹²:

$$\epsilon = \frac{f_{\text{PVE}}}{f_{\text{PIP}}} \quad (5)$$

The magnitude of this orientational coupling factor measured for the blends is displayed in Figure 2. Note that the value chosen for α in order to calculate f will alter ϵ only by a constant multiplicative factor.

As seen in Table 2 and Figure 2, at the lower crosslink densities, crystallization of the PIP upon stretching enhances the orientation of both the PIP and the PVE. It has previously been found that³⁷ in these blends PVE of this molecular weight becomes entrapped between the lamella of the crystallizing PIP. Such entrapment was not observed, however, for the lower molecular weight

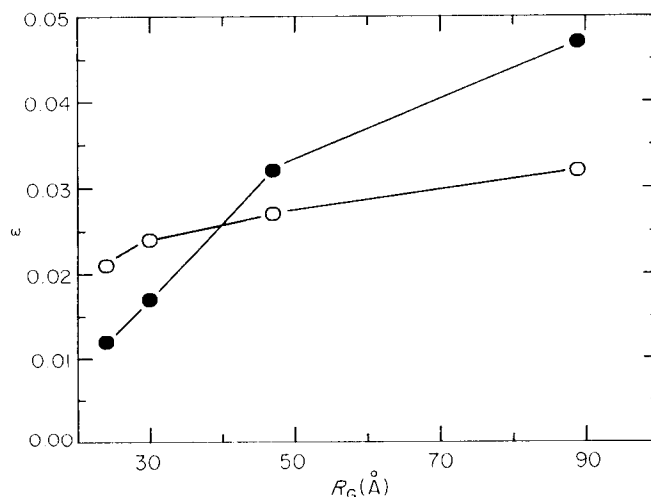


Figure 2 Equilibrium orientational coupling parameter, ϵ , measured at a constant stress of 0.84 MPa for low (○) and high (●) molecular weight PVE in PIP networks of varying crosslink density. The latter is connoted by the radius of gyration, R_G , calculated for the network strand length (Table 2). The R_G values for the PVE were 52 and 120 Å, respectively

PVE³⁷. The higher orientation of the high molecular weight PVE in the semicrystalline PIP may be ascribed herein to such entrapment.

Higher crosslink densities ($N_c = 118$ and 74 in Table 2) suppress the crystallization of the PIP, with a consequent reduction in orientation of both the network and the linear component. In the absence of crystallinity the relaxation of orientation is more nearly complete for the higher molecular weight PVE, while in the semicrystalline blends this dependence of the orientational coupling on chain length is reversed. The coupling of n-alkyl probes dissolved in PIP networks has been reported to increase linearly with the length of the probe chain⁴. On the other hand, in crosslinked poly(dimethylsiloxane) containing deuterated linear chains, the orientation of the latter was found to be independent of their molecular weight³. However, the molecular weights used in both of these earlier studies did not exceed the molecular weight between crosslinks of the network chains.

The orientational coupling for both PVEs is affected by the N_c of the PIP. A direct influence of crosslink density on the strength of the orientational coupling reflects steric constraints imposed by the junctions. The convergence of network chains at a crosslinkage causes some exclusion of PVE. Topological constraints on PVE chains in the vicinity of a junction will reduce their average alignment with respect to the extension direction. This effect is most significant when the network strand length becomes comparable in size to the probe molecules.

From the N_c for the crosslinked PIP (obtained from the Wood equation³¹) the radius of gyration, R_G , of the network strands in the unstrained state can be estimated using⁴¹:

$$R_G^2 = nC_\infty l_0^2 N_c / 6 \quad (6)$$

where n represents the number of backbone bonds per chain unit, l_0 is the average bond length and C_∞ is the characteristic ratio of the chain. For PIP $C_\infty = 5.3$, $l_0 = 1.47 \text{ \AA}$ (ref. 42), and $n = 4$, giving values of R_G for the three crosslink densities in Table 2 in the range of 24–89 Å. Using equation (6) for the higher molecular weight PVE, with N_c now representing the degree of polymerization and taking $C_\infty = 6.6$, $l_0 = 1.54 \text{ \AA}$ (ref. 42), and $n = 2$, the R_G is calculated to be 120 Å. Thus, even the most lightly crosslinked network has a mesh size significantly less than that of the high molecular weight PVE. The decreasing ability of the network strands to accommodate the PVE occasions the reduction in orientational coupling with increased crosslink density in the amorphous networks (Figure 2). This effect is weaker, but still observable, for networks containing the low molecular weight PVE, given its significantly smaller coil size ($R_G = 52 \text{ \AA}$).

The addition of diluent to a network will alleviate the competition for space among segments and thus reduce the orientational coupling⁹. Any interchain enthalpic interactions giving rise to orientation will also be diminished by the presence of solvent¹³. When the volume fraction of PVE in the PIP network was reduced to 87% by the addition of paraffin oil, the equilibrium orientation of the PVE became immeasurably low at the highest achievable sample elongations. An expression for the effect of diluent on the orientation coupling has been derived using a lattice model to calculate the entropy of

packing⁹:

$$\varepsilon = \left(\frac{0.078xv}{1 - xv/x_a} \right) \quad (7)$$

where v is the volume fraction of polymer. The chain axial ratio, x , is a measure of the degree of chain flexibility and x_a is the value of the chain axial ratio above which the system becomes anisotropic^{43,44}. This critical degree of chain flexibility has been calculated⁹ to be 10.98. From the experimental result that at $v = 0.87$ ε is reduced to zero, an upper bound on the axial ratio of the PVE molecule can be deduced. The result, $x < 5.8$, is consistent with the flexible chain character of PVE.

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