

polymer communications

Lattice expansion during polyisoprene crystallization from blends

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Crystallization of *cis*-1,4-polyisoprene (PIP) in blends with atactic poly(vinylethylene) (PVE) is found to be accompanied by entrapment of the amorphous PVE within the crystalline lattice. As determined from wide angle X-ray diffraction measurements, this entrapment causes an expansion of the PIP unit cell. Such mixing within the crystalline phase is usually associated with chain isomorphism, whereby structurally similar blend components cocrystallize. In the present case, the amorphous PVE is literally entrapped as a defect in the crystal. This is in addition to its interlamellar entrapment observed in an earlier study.

(Keywords: crystallization; blends; polyisoprene; natural rubber; poly(vinylethylene); polybutadiene)

Introduction

The crystallization behaviour in *cis*-1,4-polyisoprene (PIP) has been studied by many investigators¹⁻⁹. This behaviour is altered in a very interesting fashion when the polymer is blended with atactic poly(vinylethylene) (PVE). Since the polymers are thermodynamically miscible¹⁰⁻¹³, changes in the rate of PIP crystallization are both expected and observed^{14,15}. It has also been found that the ultimate extent of crystallization is reduced by blending, but, strangely, the amount of suppression is independent of PVE concentration¹⁵. In blends containing from 5 to 50% of PVE, the degree of crystallinity attained by the PIP is equivalent, although less than that of pure PIP.

PIP crystallizes through lamellar growth into radial spherulites²⁻⁴ of two morphologically different forms: the more stable α -lamella and the slower forming β -lamella^{4,8}. The α -lamellar crystals, which grow in the direction of the *a* crystal axis, predominate in pure PIP. The β -lamella, associated with crystal growth along the *b* axis direction, occur only at low levels in pure PIP. In blends with PVE, the concentration-independent suppression of PIP crystallization is accompanied by preferential development of the β -lamellar form¹⁵. The tendency to form the thermodynamically less stable β -lamella has been ascribed to the ability of this crystal morphology to more readily incorporate the non-crystallizing PVE into the fold plane at the crystal surface¹⁵. An earlier investigation¹⁴ showed that the PVE is not entirely able to disentangle from the crystallizing chains of the polyisoprene. Hence, crystallization in the presence of molecularly dispersed PVE results in some interlamellar entrapment of the non-crystallizing component, with a consequent termination of crystal growth.

The better accommodation of amorphous PVE chains at the fold surface of the β -lamella biases the crystal morphology in a similar manner as seen for 'synthetic' natural rubber (that is, PIP containing some *trans* chain units). There is a defect energy associated with incorporation of the *trans* isomers into the lattice, hence

they are largely rejected from the crystal. Their accumulation at the fold surface engenders formation of the β -lamella. The interpretation of PIP's crystallization behaviour in blends with PVE¹⁵ similarly assumes that crystallization is restricted because PVE cannot be readily incorporated into the PIP unit cell. Since the PVE is atactic, it is incapable of crystallizing itself. The purpose of the present study was to determine whether, along with its interlamellar entrapment, any PVE is actually included within the crystalline lattice. This phenomenon is of particular interest for blends of PIP and PVE, given the anomalies in crystallization behaviour already observed^{14,15}.

Experimental

The PIP was natural rubber (SMR-L grade *Hevea brasiliensis*). The atactic, linear PVE, obtained from the Firestone Tire and Rubber Co., was 96% 1,2-polybutadiene ($M_n = 134\,000$ and $M_w/M_n = 1.1$). Blends containing 10 and 20 wt% PVE were prepared by dissolution in cyclohexane and vacuum drying at 60°C. Films (15 × 15 × 1.0 mm) of neat and blended PIP were annealed at $-25 \pm 1^\circ\text{C}$ for 49 days using a thermostatted dry-ice box. It was previously determined¹⁵ that crystallization in this blend reaches a maximum of ~33% crystallinity after 40 days at this temperature. All samples were quenched in liquid nitrogen upon completion of the -25°C annealing. Wide-angle X-ray diffraction (WAXD) measurements were obtained after annealing, with the samples maintained at $-25 \pm 5^\circ\text{C}$ (which is about 25°C below the melting point¹⁵), using an aluminium holder cooled by a continuous flow of isopropanol/dry ice. A Rigaku RU-200B rotating anode with Ni filtered Cu K α radiation (50 kV and 200 mA) was utilized. A 1° dispersion slit, a 0.15 mm (~0.05°) receiving slit, and a 1° scatter slit collectively defined the X-ray beam. Diffraction intensities were obtained at $10^\circ \leq 2\theta \leq 25^\circ$ using a $1.0^\circ \text{ min}^{-1}$ scan rate with a 0.02° sampling interval. Reported results are the average of three consecutive scans.

Results and discussion

The unit cell of PIP is either orthorhombic or monoclinic^{6,16-19}. The small difference in the β angle of

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the two Bravais lattices does not significantly affect the lattice parameters⁹; the more symmetrical orthorhombic unit cell is assumed herein. The (2 0 0), (1 2 0) and (2 0 1) reflections (corresponding to diffraction at $2\theta = 14.8, 21.7$ and 18.3° , respectively) were used to calculate the unit cell dimensions. X-ray diffraction patterns of neat PIP and blends containing 10 and 20% PVE are shown in Figure 1. For the mixtures, the shift of the peaks toward smaller scattering angles indicates dilation of the unit cell. Table 1 lists the angles of the peak maxima for the samples, along with the calculated lattice parameters a , b and c . In comparison to neat PIP, the unit cell volume increases by approximately 50 \AA^3 (a 5% expansion) for the blend with 20% PVE. This indicates that PVE is being incorporated into the unit cell during the course of PIP crystallization, a rare event in polymer blends in which only one component is crystallizable.

Inclusion of foreign entities and a consequent expansion of the unit cell is well known in metals and

inorganic salts, and even occurs in diamond²⁰. Randomly situated inclusions disrupt the regularity of the crystal lattice, causing displacement of neighbouring atoms away from the defect. The consequence is an increase in the measured unit cell volume. The effect on the X-ray scattering is analogous to distortion due to thermal motion^{21,22}.

In polymers, defect inclusion is well known for random copolymers in which at least one chain unit is crystallizable. Two extremes in crystal morphology can be envisaged²³: (i) complete rejection of the non-crystallizing chain unit, which is difficult in copolymers; and (ii) complete incorporation of the non-crystallizing units, whereby the amorphous and crystal phases have the same composition. Such uniform inclusion is precluded at high comonomer content, since significant distortion of the unit cell would reduce the fusion enthalpy and hence the degree of crystallinity.

Comonomer inclusion is known for polyisoprene

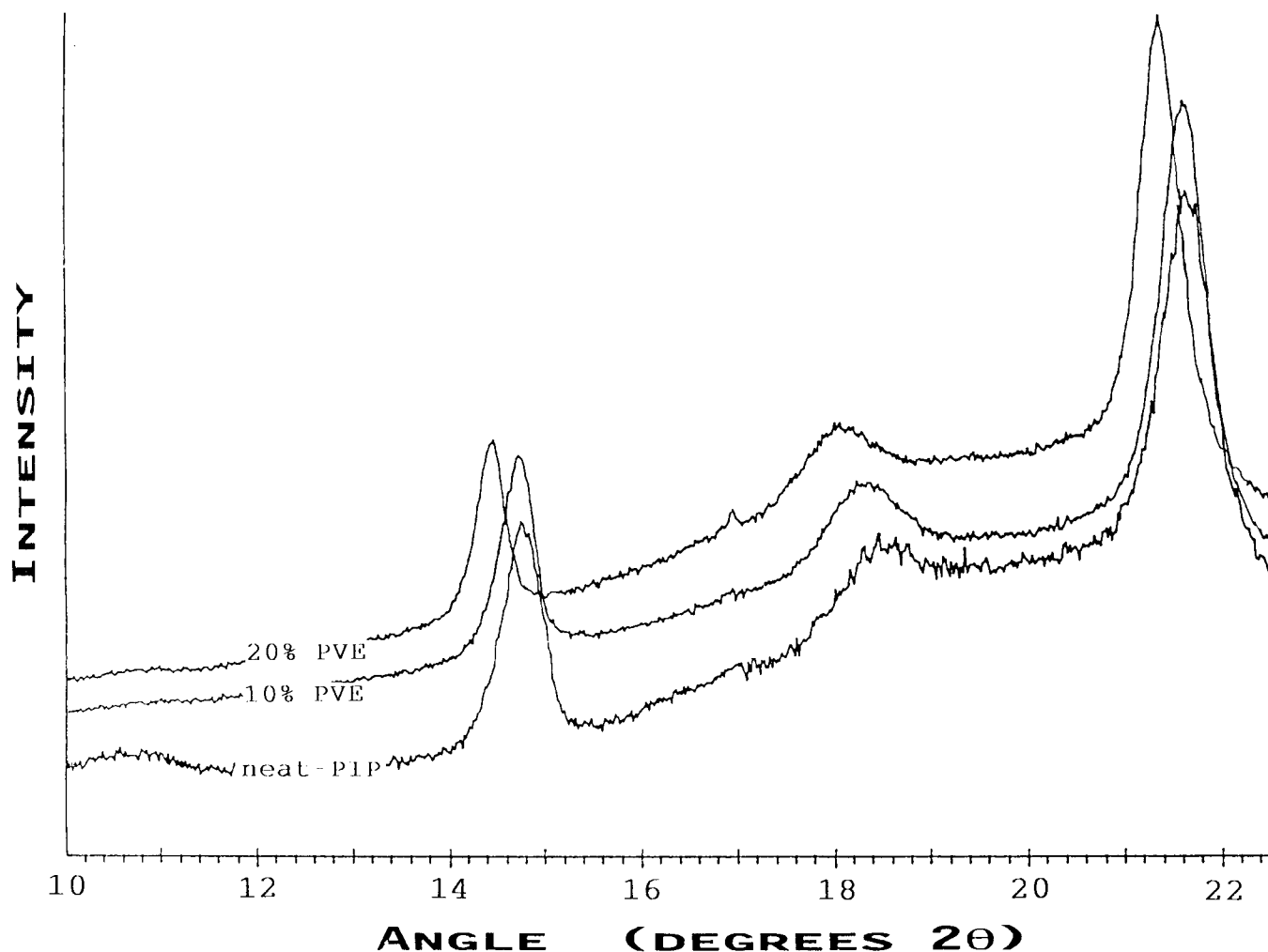


Figure 1 X-ray diffraction intensities measured for PIP crystallized neat and in blends with PVE

Table 1 Lattice parameters and unit cell volumes for PIP

PVE (%)	Diffraction angle (deg)			Lattice parameter (nm)			Unit cell volume (nm ³)	Unit cell expansion (%)
	2 0 0	1 2 0	2 0 1	a	b	c		
0	14.976	21.686	18.387	1.1974	0.8723	0.8150	0.851	—
10	14.766	21.640	18.282	1.1998	0.8741	0.8253	0.866	1.6
20	14.455	21.370	18.024	1.2255	0.8840	0.8261	0.895	4.9

crystallization. Along with the elevated level of β -lamella, some inclusion of *trans* units occurs during crystallization of predominantly *cis*-1,4-polyisoprene³, altering the lattice dimensions. A more interesting case is the crystallization of epoxidized polyisoprene (i.e. random copolymers of 2-methyl-1,2-epoxy-1,4-butanediyl and 2-methyl-1-butenylene). Both geometric factors and hydrogen bonding apparently result in a low defect energy; consequently, crystallization of the isoprene units is accompanied by substantial inclusion of the epoxidized chain units⁹. This allows the remarkable result that even at 50 mol% epoxidation, the degree of crystallinity is virtually unchanged relative to the pure *cis*-1,4-polyisoprene⁹. Inclusion of the epoxide groups is accompanied by significant expansion of the unit cell, of similar magnitude ($\sim 8\%$) to that observed herein. The unit cell distortion increases with concentration of the non-crystallizing units, even though the degree of crystallinity does not change.

The inclusion observed herein is distinctly different from that arising in copolymers, in that the units comprising the defect are not covalently bonded to the crystallizing stems. The usual result in polymer blends is complete rejection; crystallization is accompanied by segregation, with no inclusion²⁴⁻²⁸. For example, in polyethylene containing short alkyl branches, some inclusion of the latter occurs^{22,29}; in contrast, when blends of linear and branched polyethylene are crystallized, the two isomers form physically distinct crystals³⁰⁻³². Only in blends whose components form unit cells of nearly equivalent size has mixing within the crystalline phase been found. This requires similar repeat unit lengths and comparable dimensions normal to the chain. Such 'chain isomorphism'³³ is rarely observed; examples include blends of poly(vinyl fluoride) and poly(vinylidene fluoride)³⁴, isotactic polystyrene mixed with polystyrene/polymethylstyrene copolymer³³, poly(vinyl isopropyl ether) blended with poly(vinyl butyl ether)³⁵ and, a trivial example, blends of linear, high density polyethylene with linear, low density polyethylene (which differ only by the presence of a methyl at every fifth carbon in the latter)³⁶.

The inclusion of atactic PVE within the PIP crystal lattice is a very unusual instance of mixing within the crystal phase without isomorphism. The phenomenon is made possible by (i) the absence of specific interactions (i.e. chemical reaction) in this mixture¹¹, which minimizes the excess enthalpy associated with the adjustments in segment orientation necessary to form a crystalline array; (ii) the remarkable equivalence in van der Waals energies of PVE and PIP^{12,13} which, geometric effects notwithstanding, facilitates inclusion of PVE units by minimizing the contribution to the defect energy from diminution of the van der Waals bonding; and (iii) the low mobility of PVE, whose neat glass transition temperature ($T_g = -1^\circ\text{C}$, ref. 15) is much higher than the crystallization temperature (and, of course, the T_g of the PIP). Consequently, crystallization outpaces segregation, entrapping the PVE within the crystal phase, as well as within the lamella¹⁵.

While comonomer inclusion can exist at equilibrium, generally its extent is governed by kinetic factors^{37,38}; thus, defects are entrapped in a literal sense. This situation is the usual one for copolymers and the only one possible for blends. The inclusion of PVE probably does not reflect an equilibrium partitioning, since given

the absence of specific interactions, there is only a weak driving force for mixing¹². Thus, in principle, the inclusion should suppress the crystalline melting point. Any such depression, however, is evidently less than the experimental precision ($\pm 0.5^\circ$)^{14,15}. While the extent of inclusion increases with the content of PVE, the degree of PIP crystallization is independent of PVE concentration¹⁵. From this we infer that neither the latter effect, nor the associated interlamellar entrapment¹⁵, is related to the inclusion of PVE within the crystal lattice.

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