INTERACTIONS IN A MISCIBLE POLYMER BLEND*

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INTRODUCTION

The immiscible nature of most polymer mixtures has not inhibited their exploitation to achieve new and useful materials[1]. This immiscibility is a consequence of the limited increase in positional disorder which accompanies mixing, so that even a small positive mixing enthalpy will bring about phase separation. In the absence of any chemical reaction between the respective chain units (*e.g.*, hydrogen bonding, complex formation, or charge transfer), the intermolecular forces are van der Waals type interactions. From the Lorentz–Berthelot combining rule, it can be seen that the interaction energy will have a magnitude equal to the geometric mean of the depth of the potential for the pure components[2],

$$\epsilon_{12} = (\epsilon_{11} \cdot \epsilon_{22})^{1/2}. \tag{1}$$

Accordingly, the forces between unlike species must be weaker (reduced stability) than those between like contacts. If the magnitude of the corresponding endotherm exceeds the free energy decrease resulting from the combinatory entropy, the system will be immiscible. Specifically, for miscibility to occur over the entire composition range, the Flory interaction parameter, χ, for the polymer repeat units must be less than a critical value that is a measure of this combinatory entropy[3,4]

$$\chi^* = 1/2N_1\left\{1 + \left(\frac{N_1\nu_1}{N_2\nu_2}\right)^{1/2}\right\}^2 \tag{2}$$

where ν represents the volume of the chain statistical segment and N is the number of statistical units per chain.

Polymer blends with endothermic heats of mixing (*i.e.*, $\chi > 0$) can only be obtained, therefore, if the molecular weights of the polymers are low (*e.g.*, typically $<10^3$), thereby increasing χ^*, or if the dispersive interaction energy is negligibly different for the blend as for the components. This latter case would result from a similarity in the polarizability of the respective chain subunits of the two species.

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EXPERIMENTAL

The *cis*-1,4-polyisoprene (PIP) and the atactic poly(vinylethylenes) (PVE) used in this study are described elsewhere[5,6]. The syndiotactic poly(vinylethylene), from the Japan Synthetic Rubber Co., was 92% 1,2-polybutadiene with a molecular weight of approximately 100 000 according to the manufacturer.

For adhesion measurements, blend samples were prepared by mixing the PIP/PVE on an unheated two-roll mill. After annealing them for one month, peel-test specimens were molded overnight at room temperature against aluminum foil. Details of this test method and factors influencing the obtained results are discussed elsewhere[7].

Blend samples for the other experiments reported herein were prepared by dissolution in pentane at 2% concentration by weight.

Room-temperature Fourier transform infrared spectra were obtained with a Perkin–Elmer Model 1800 spectrophotometer with typically 200 scans taken at 2 cm^{-1} resolution.

Dynamic mechanical measurements were carried out with a modified Rheometrics RMS 7200 and using an automated Rheovibron. The former employed a parallel plate geometry, while the Rheovibron data were obtained in tension.

RESULTS

MISCIBILITY

The equilibrium morphology of a heterogeneous polymer blend is never achieved in practice since the mixing procedure, involving flow induced breakup and coalescence of the phases, is not governed by thermodynamics[8]. Subsequent to mixing, the structure of a multiphase blend may coarsen, but the viscosity of the systems limits this phase separation process. Consequently, a high degree of dispersion (blend compatibility) may reflect either the nature of the mixing procedure or a low interfacial energy. Conclusive assessment of thermodynamic miscibility is most accurately made by observation of spontaneous interdiffusion of a polymer pair, rather than relying on demixing of mechanical or solution blended mixtures. Miscibility is a requirement for such interdiffusion.

The uncured adhesion (tack) between two dissimilar elastomers will be low, with debonding localized at the interface, if the materials are immiscible. This behavior is seen in Figure 1 for PIP plied against PBD. When either PIP or PVE is brought into contact with itself, a significantly higher level of adhesion is observed, limited by the cohesive strength of the material. The time scale for development of this bond strength reflects the self-diffusion constant of the polymer. In Figure 1 it can be observed that when PIP is brought into contact with PVE, the bond strength increases with contact time, ultimately attaining a plateau in adhesion at which debonding is accompanied by large deformation and bulk tearing. The initially separated polymers spontaneously interdiffuse, which is unambiguous evidence for their thermodynamic miscibility.

The rate of interdiffusion between these polymer species will reflect the degree of miscibility of the system[9]. As χ approaches the critical value for phase

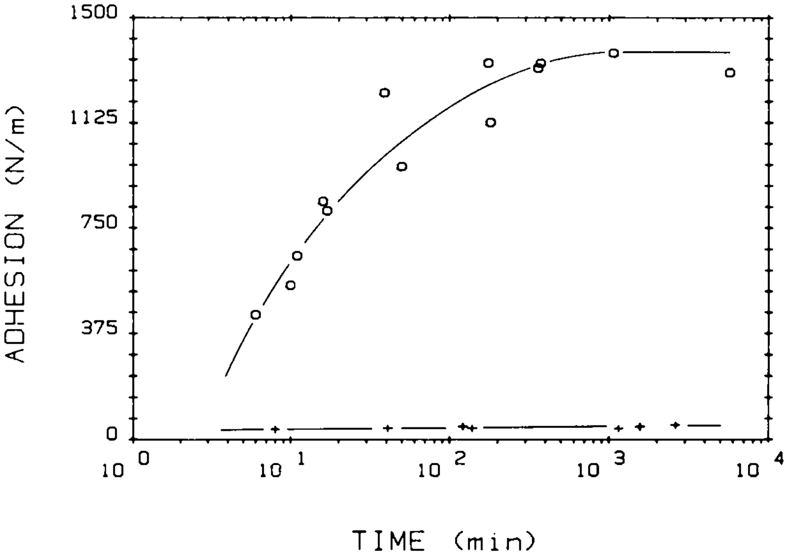

FIG. 1.—The peel adhesion measured as a function of contact time between PVE and PIP (O) and between PBD and PIP (+) respectively. For the former, the mode of failure changes from adhesive to cohesive as the bond strength approaches the plateau corresponding due to the bulk cohesive strength. The peel adhesion of PIP to itself (measured to be 1200 N/m) exhibited no time dependence due to the rapidity of the interdiffusion. In the case of autoadhesion of the PVE, testing after 17 min contact time resulted in destruction of the test specimens, indicating a lower limit of 1800 N/M for the cohesive strength. The slower buildup of adhesion reflects the smaller selfdiffusion constant due to a higher T_g.

separation, "thermodynamic slowing down" of the interdiffusion will occur[10]. The rate at which the peel adhesion increases between the PIP and PVE in Figure 1 is governed by the magnitude of this difference ($\chi - \chi^*$), and, since the composition about a given chain will depend on the extent of its interdiffusion, the rate of this non-Fickian diffusion will also reflect any composition dependence of either χ[11] or the diffusion constant[9].

The occurrence of interdiffusion demonstrates that χ for the PIP/PVE mixture must be less than χ^*. This critical value can be evaluated from Equation (2). In applying this, it is noted that there is a dispersion of chain lengths in the materials employed. Using the weight averages as an approximation[12], the critical value obtained is $\chi^* = 0.0004$. This value of the interaction parameter is expectedly low; only a small unfavorable heat of mixing would be sufficient to overcome the combinatory entropy favoring mixing. What is unexpected is that the interaction parameter for a polymer pair of different chemical composition could be less than 0.0004 in the absence of specific interactions.

FTIR SPECTRA

Any chemical interaction (*e.g.*, hydrogen bonding, complex formation, or charge transfer) occurring between unlike chains in a miscible blend, or the conformational changes induced by such interaction, can effect perturbation of the vibrational transitions accompanying infrared absorption or Raman scattering from the blend. Although the spectral changes are not necessarily expected to be large, in accordance with the magnitude of the intramolecular forces governing these transitions relative to the weak intermolecular potential, there exists substantial evidence for distortion of the infrared spectra of miscible polymer mixtures[13-18]. It has also been shown, moreover, that even interaction energies which make a negligible contribution to the free energy of mixing, in comparison to that from the combinatorial entropy, can nevertheless effect measurable "solvent" shifts in the IR spectrum[19]. If miscible blending of PIP and PVE transpires without specific interactions, the infrared spectra of the blends are expected, therefore, to correspond to the appropriate sum of the components' absorption spectra.

Displayed in Figure 2 are the respective FTIR spectra of pure PIP, pure PVE, a 1:1 blend of these polymers, and the calculated spectrum of the latter minus the sum of the former two. In using IR difference spectra to judge the occurrence of chemical interaction between dissimilar polymer molecules, the possibility exists for the appearance of artifacts in the calculated spectrum, particularly, for example, when a difference exists in the magnitude of the real part of the refractive index of the two polymer species. These optical effects can yield anomalous peaks and distorted absorption bands in the mixture which are unrelated to any chemical shifts[20]. The absence of significant structure in the difference spectrum in Figure 2 indicates that the blend FTIR spectrum is essentially the linear combination of the components' respective absorptions. This type of

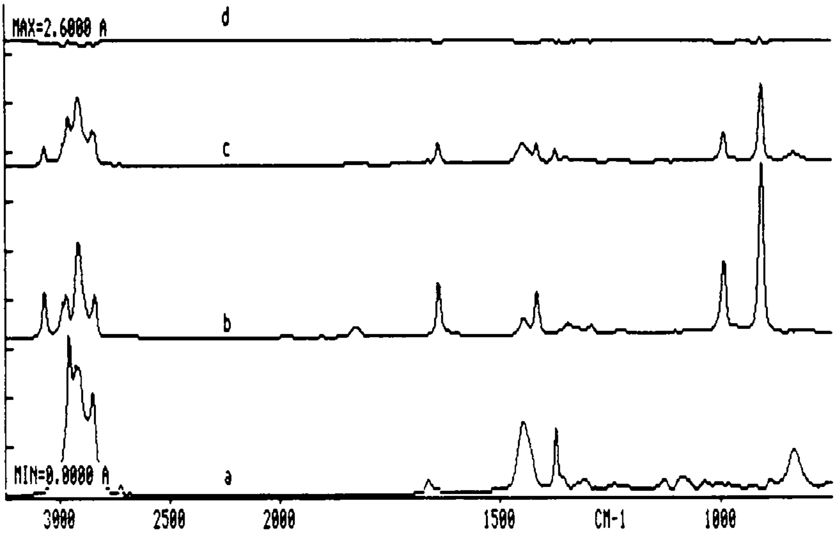

FIG. 2.—The FTIR spectra of (a) PIP, (b) PVE, and (c) a 1:1 blend, along with (d) the calculated difference spectrum. The abscissa is expressed in wavenumbers and the ordinate scale in relative absorbance units.

result has often been taken to demonstrate blend heterogeneity. For the PIP/PVE system, however, the absence of chemical reaction between the polymer species demonstrates that the miscibility is arising only from the combinatory entropy of mixing[5].

Since any spectral perturbations due to specific interactions might be weak, difference spectra were obtained for blends containing 5% of one component in the other. Since the local monomer concentration due to a given polymer chain is small relative to the concentration of monomers from all chains (by roughly a factor proportional to the square root of the degree of polymerization[4]), a chain present in a nineteen-fold excess of the other component will be exposed to a predominance of unlike contacts. Any interaction induced alterations of the vibrational spectrum should accordingly be magnified. Listed in Table I are five absorption bands of PVE that do not overlap intense bands in the PIP spectrum, along with two bands of PIP that are largely separated in frequency from strong PVE absorptions. The difference spectra of these bands for a 19:1 dilution of the PVE in PIP are compared to the corresponding spectral regions measured for pure PVE. The shape, breadth and the frequency of the respective infrared bands are virtually unchanged after blending. No shoulders or new peaks are present in the difference spectra. The results of measurement of difference spectra obtained from the PIP diluted nineteen-fold with PVE are also detailed in Table I. No suggestion of any chemically induced perturbation of the FTIR spectrum can be observed. These results are particularly persuasive in view of the errors inherent in obtaining difference spectra at high dilution, whereby the results represent small differences in the subtracted spectra and any errors associated with the latter will accordingly be magnified[13,20]. The difference spectra provide a clear indication that the PIP/PVE system is a unique example of a miscible high-polymer blend in which the intermolecular forces between

TABLE I

FREQUENCY AND BREADTH OF FTIR BANDS MEASURED FROM THE PURE POLYMERS AND FROM BLENDS

		Neat		Blended[d]	
Polymer	Assignment[a]	Freq.[b]	FWHM[c]	Freq.[b]	FWHM[c]
PVE	CH_2 of $CH_2{=}CH$ out of plane def.	909	13	909	12
PVE	CH_2 of $CH_2{=}CH$ out of plane def.	994	14	994	14
PVE	$C{=}C$ stretch	1641	10	1641	11
PVE	$CH_2{=}CH$ overtone	1827	26	1829	24
PVE	CH of $CH_2{=}CH$ stretch	3074	24	3074	24
PIP	CH of $C(CH_3){=}CH$ out of plane def.	837	36	837	38
PIP	CH_3 symmetric def.	1376	8	1376	8

[a] References 21–23.

[b] Frequency (in wavenumbers) of maximum absorption.

[c] Full width of band at half maximum intensity (in wavenumbers).

[d] Mixture with 5% concentration by weight of the indicated species.

chemically distinct species are limited to van der Waals type interactions; moreover, fortuitous near equivalence of the dispersion forces between like and unlike contacts results in an interaction parameter of negligible magnitude.

This similarity in the van der Waals interaction densities of PVE and PIP is not obvious from mere inspection of the chemical structures. It can be observed that similarity in structure does not produce miscibility in PVE/PBD or PIP/PBD blends at high molecular weight. When only dispersive forces are active in a mixture, solubility parameters can be employed to calculate the interaction parameter according to[24]

$$\chi_{12} = (\nu_1/RT)(\delta_1 - \delta_2)^2. \tag{3}$$

Estimates of the solubility parameter are often obtained by assuming additivity of the polarizabilities of the groups comprising the molecule[25,26]. This approach has the practical limitation that, when miscibility is entropically driven, the low magnitude of the interaction parameter ($0 < \chi < 0.0004$ in the present case) requires accuracy in its determination far exceeding the reliability of the available solubility parameter data. A more serious failing of the group additivity approach is its neglect of the effect of stereoisomerism on χ. Anisotropy of the polarizability can influence the van der Waals energy and the magnitude of the corresponding mixing enthalpy. This effect can be observed in blends of syndiotactic PVE with PIP. The spatial arrangement of the pendant vinyl groups in this isomer of PVE sufficiently reduces the interaction energy so as to bring about phase separation in this system (see Figure 3), whereas atactic PVE of the same molecular weight is miscible with PIP.

In a blend in which one of the components is crystallizable, the thermodynamic stability conferred upon the liquid by formation of a miscible blend re-

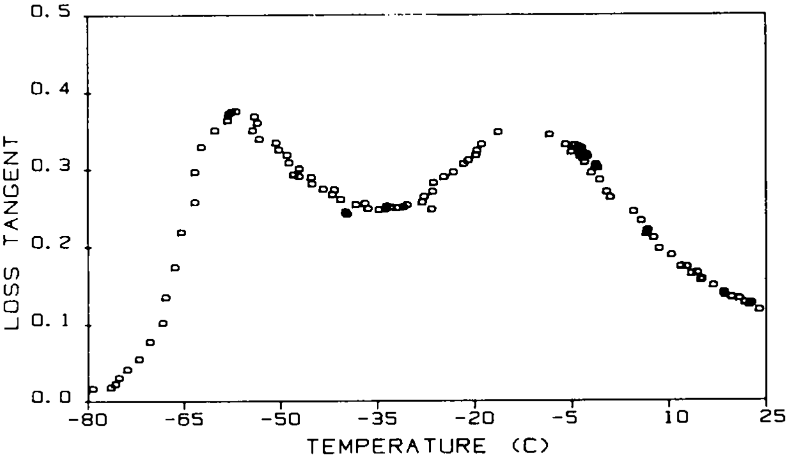

FIG. 3.—The dynamic loss tangent measured in tension for a 50/50 blend by weight of PIP and syndiotactic PVE. This morphology is heterogeneous, as evidenced by distinct glass transitions for the two components, indicating that the change in stereochemical arrangement of the pendent vinyl group reduces the magnitude of the van der Waals interactions sufficient to effect immiscibility.

duces the relative stability of the crystalline state and thus lowers the equilibrium melting point. If the crystals formed in the blend are identical to those formed in the pure melt, then in principle, one can gain a measure of χ from the extent of the melting point suppression. Crystallization of PIP in blends with atactic PVE has resulted in crystals whose melting temperature was equal to that of the crystalline phase of pure PIP within the precision of the measurements[5]. This finding is in keeping with the very low magnitude of the Flory interaction parameter inferred above.

DYNAMICAL MECHANICAL BEHAVIOR

The frequency dependence of the storage, G', and loss, G'', dynamic shear moduli of the series of PIP/PVE blends are displayed in Figures 4 and 5. The most striking change in mechanical behavior with composition is the location of the viscoelastic spectrum on the frequency scale. The transition zone can be seen to transpire at increasingly higher frequency as the relative abundance of PIP in the blend is increased, reflecting the composition dependence of the glass-transition temperature. The temperature at which a miscible blend changes from a glass to the liquid state is intermediate between the T_g's of the blend components. By requiring that, at the glass transition temperature, the molar

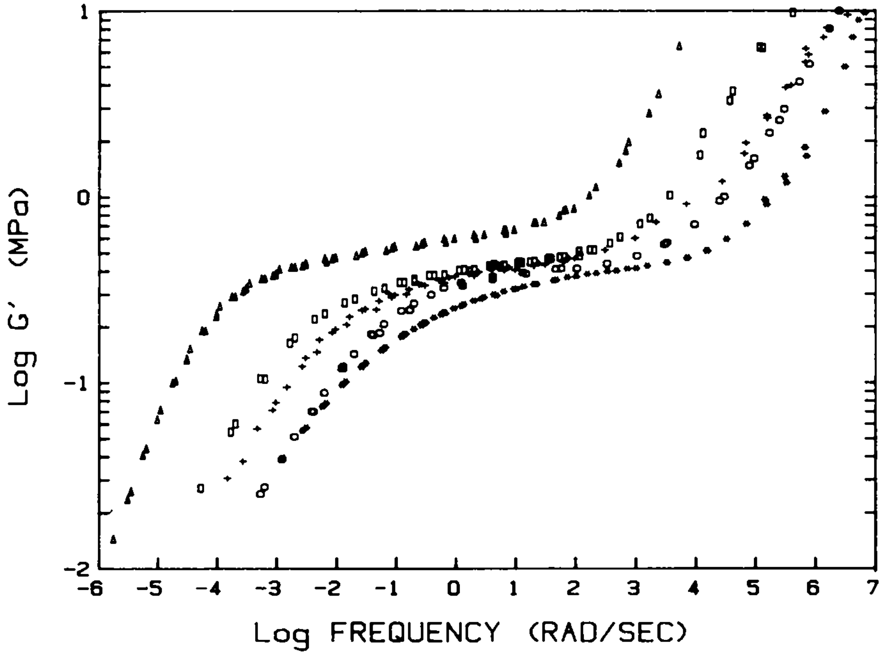

FIG. 4.—Storage modulus measured in shear and expressed as a function of the WLF shifted frequency for PIP blended with 0% (•), 20% (○), 50% (+), 80% (□), and 100% (△) PVE. The moduli have been multiplied by the ratio of the product of the reference temperature (298°K) and the density at the reference temperature to the product of the temperature of measurement and the corresponding density.

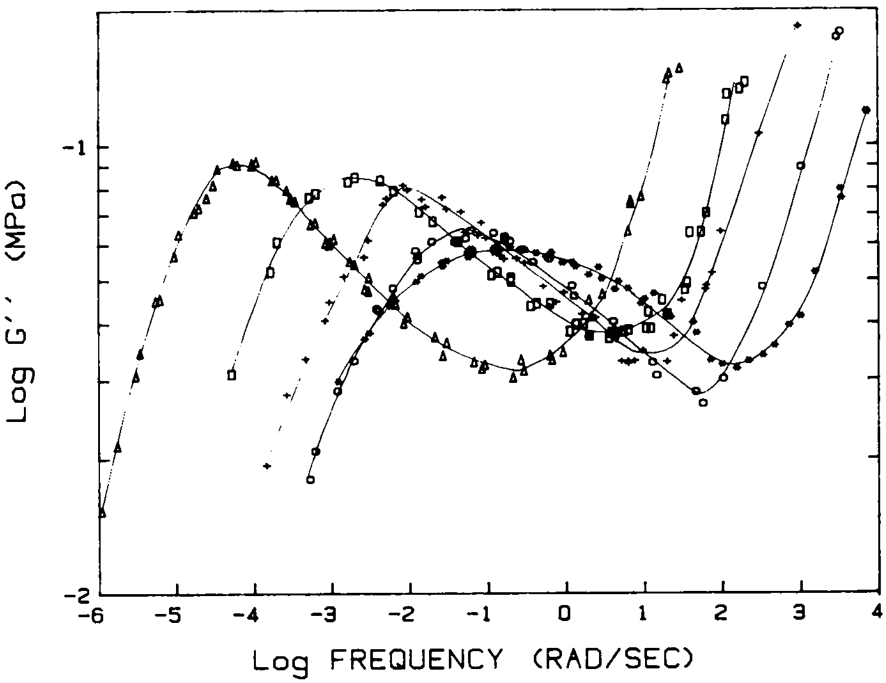

FIG. 5.—Loss shear modulus results after time-temperature superpositioning for the PIP/PVE blends with 0% (•), 20% (O), 50% (+), 80% (□), and 100% (Δ) PVE. The high-frequency portion of the glass-transition region has been omitted to allow expansion of the overlapping data on the terminal side of the plateau region.

entropy of the glassy and liquid states are equal, an expression for the glass-transition temperature of a miscible blend with a random arrangement of the chain units can be obtained[27],

$$T_g = \exp\left[\frac{\rho_1\phi_1\Delta C_{p_1}\ln T_{g_1} + \rho_2\phi_2\Delta C_{p_2}\ln T_{g_2}}{\rho_1\phi_1\Delta C_{p_1} + \rho_2\phi_2\Delta C_{p_2}}\right], \quad (4)$$

where ρ is the density of a given component and the heat capacities, ΔC_p, are assumed to be temperature independent. In blends in which specific interactions exist between the components, although a single blend T_g is observed, it is found to be less than that predicted by Equation (4) due to local orientation effects promoted by the interaction[28]. The agreement illustrated in Figure 6 suggests random mixing of the PIP/PVE, consistent with an absence of interactions (*i.e.*, $\chi \geq 0$).

The time scale for which the glass to liquid transition occurs at a given temperature is determined largely by the magnitude of the monomeric friction coefficient characterizing the local mobility of a chain subunit. The frictional drag exerted by neighboring chains depends both on the available free volume as well as the nature of the intermolecular potential. Since the latter is demonstrated by invariance of the infrared spectra to be unaltered upon blending

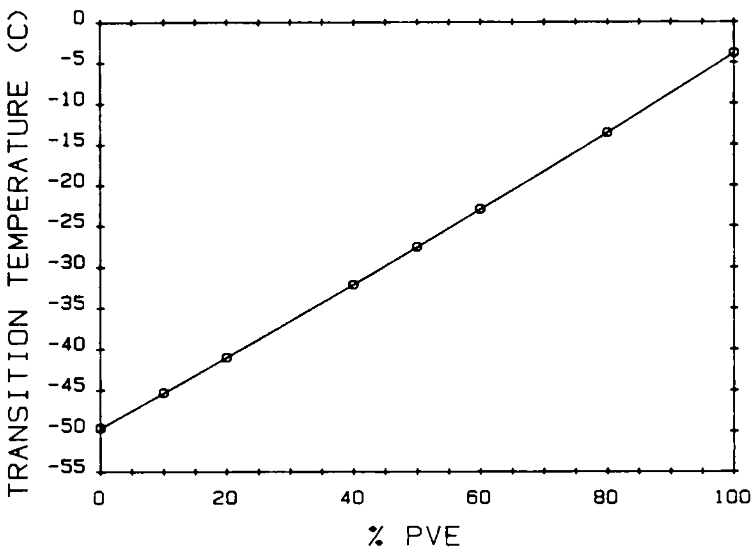

Fig. 6.—Comparison for the PIP/PVE blends of the composition dependence of the temperature of the maximum in the dynamic loss tangent measured in tension with the T_g calculated using Equation (4).

of PVE and PIP, the change in local friction constant is due only to the change in free volume with mixing. In the PVE/PIP mixtures, where the miscibility is only an entropy effect, the composition dependence of f_0 is governed directly by the composition dependence of the glass transition.

A plateau in the storage modulus is observed in Figure 4, corresponding to a pseudoequilibrium modulus, G_N^0, resulting from the transitory network of entanglement couplings. It has been shown for these blends that the entanglement density varies monotonically across the composition range[6]. Of course, since entanglements simply reflect the uncrossability of chain contours, nearly athermal mixing can not be expected to significantly alter these topological features. The maximum in the loss modulus observed in the low frequency region of Figure 5 defines a characteristic time, w_T^{-1}, associated with disengagement of a chain from the "tube" of entanglement constraints. Over the range of compositions, this terminal relaxation time is observed to vary at room temperature from several seconds for pure PIP up to a few hours for the PVE (Table II). This large variation of the terminal relaxation time has been shown to reflect almost solely the local chain mobility[6].

For miscible blends exhibiting negligible interaction energies, chain configurations will be unchanged from in the pure melts, which, in conjunction with the equivalence of the intermolecular potentials, causes the composition dependence of the rheological properties to be dominated by the changes with free volume of the local friction coefficient. While miscible blending of two polymers can in some instances effect a net contraction of the system[29,30], for the PIP/PVE mixtures it is observed that the room temperature density increases

TABLE II

VISCOELASTIC DATA FOR PIP/PVE BLENDS

% PIP	w_T^{-1}, s	G_N^0, MPa	η_0, MPa·s
100	7.4	0.28	2.1
80	15.9	0.31	4.9
50	119	0.39	46
20	493	0.41	200
0	12 200	0.44	5400

linearly with PIP content (Figure 7). This absence of a maximum in the density–composition curve is expected in the absence of specific interactions.

The rheology of a polymer blend is expected to reflect, in some fashion, the constituents present. For example, the densification and greater cohesive energy density observed in polymer blends exhibiting exothermic heats of mixing can, in principle, augment mechanical properties[31]. Entropically driven blends such as the PIP/PVE mixture, on the other hand, experience neither densification nor a change in the intermolecular interaction. In block copolymers, the viscosity and modulus are found to markedly decrease in magnitude at the upper critical solution temperature due to dissolution of the ordered supramolecular structure associated with the phase separated morphology[32,33]; however, there is no corresponding discontinuity in the mechanical properties of homopolymer blends in the vicinity of a critical solution temperature. The molecular property most significantly modified by changes in composition of a blend of PIP with PVE is

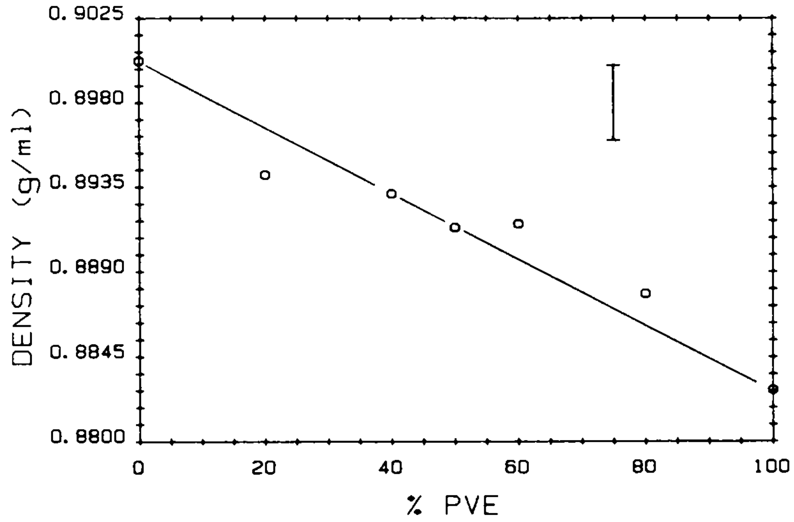

FIG. 7.—The density measured at room temperature for the series of PIP/PVE blends.

the monomeric friction coefficient[6]. Since nearly athermal mixing will always be accompanied by negligible alterations in the configuration of the polymer chains and an unchanged intermolecular potential, the rheology of such mixtures can be expected to be a compromise of the component properties without significant synergistic or novel features.

Much effort has been expended on development of "mixing rules" which might enable prediction of the composition dependence of polymer blend properties[1,34]. One general[1,34] approach is based on series ($n = 1$) and parallel ($n = -1$) representations of blend properties in terms of the component properties, which for the viscosity can be written as

$$\eta_{12}^n = \phi_1 \eta_1^n + \phi_2 \eta_2^n, \tag{5}$$

where ϕ_i refers to the volume fraction of the ith species in the mixture. The limiting viscosity in the terminal region of the viscoelastic spectrum can be obtained from the relation[6,35],

$$\eta_0 = G_N^0 / w_T, \tag{6}$$

and these results are displayed in Table II. From comparison with the blend viscosities calculated using Equation (5), it is seen in Figure 8 that, although the experimental results can be roughly approximated by taking the exponent to be a fitting parameter, these "mixing rules" at best only provide approximate limits on the properties to be expected for the mixtures.

Extension of a series model to second order might be expected to provide more accurate agreement with experimentally measured blend properties,

$$\eta_{12} = \phi_1 \eta_1 + \phi_2 \eta_2 + x_{12} \phi_1 \phi_2 . \tag{7}$$

From application of an expression of this form to results on the glassy modulus of polymer blends, it has been suggested that a positive crossterm (*i.e.*, $x_{12} > 0$) can be a criterion for polymer miscibility[31]. The zero shear viscosity of the PIP/PVE blends, as discussed above, is primarily determined by the magnitude of f_0, whose composition dependence is a result of the differences in free volume available at the reference temperature as the blend composition is varied. Using the result for the $\phi_1 = \phi_2 = 0.5$ sample, the coefficient of the crossterm is calculated to be negative ($x_{12} < 0$), ostensibly implying blend heterogeneity. In fact, however, Equation (7) is completely incapable of describing the viscosity results displayed in Figure 8, even to the limited extent of at least predicting blend viscosities that are greater than zero. Any success in applying empirical expressions such as this to the description of blend properties is more related to the broader functionality provided by the extra "interaction" term, than to a more accurate consideration of the relevant physics.

It has been stated that the Cole plot (*i.e.*, the storage modulus as a function of the loss modulus) for a miscible blend is invariant to changes in the relative abundance of the blend components, while for heterogeneous polymer mixtures, such invariance is not observed[36]. Although, if accurate, it suggests that a blend's Cole plot can be used to assess miscibility, clearly no theoretical basis exists for the expectation that a composition independence of the relationship between G' and G'' should accompany miscibility. The average molecular weight of a

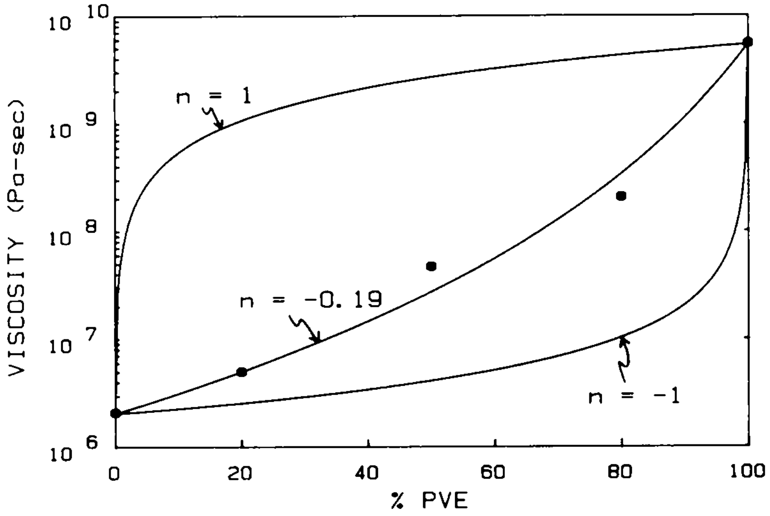

FIG. 8.—Viscosity in the limit of zero-shear rate for the PVE/PIP compositions from the data in Figure 4 using Equation (6). The solid curves represent, respectively, the upper ($n = 1$) and lower ($n = -1$) bounds, and the viscosities calculated using a best-fit value of $n = -0.19$, predicted by Equation (5) from the pure-component viscosities. The logarithmic rule of mixtures[34] would correspond to a linear interpolation between the pure-component viscosities.

miscible blend will usually change as the relative amounts of the components change, and this will alter the shape of the Cole plot (for example, by modifying the depth of the minimum in the ratio of G'' to G'[35]). Also, since the monomeric friction coefficient varies with blend composition, the different f_0 dependence of the storage and loss moduli in the terminal region[35] requires changes in shape of the Cole plot with composition. For the PVE/PIP mixtures, the measured storage moduli were not found to be any unique function of the corresponding loss moduli as the blend composition was altered. Clearly, Cole plots have no general utility in the assessment of morphological homogeneity. At most, it can be concluded that when the individual components of a blend have similar rheological properties, the rheology of the blend itself may be sufficiently insensitive to changes in composition such that the measured Cole plots appear equivalent within the experimental precision; however, it is not obvious that this statement must be restricted to blends which are miscible.

SUMMARY

Characterization of blends of atactic poly(vinylethylene) with *cis*-1,4-polyisoprene provides unique insights into the factors governing the properties of polymer mixtures. While studies of polymer blends have heretofore focussed on systems in which chemical reaction between the components enabled miscibility, any properties arising from the blending of PVE with PIP are not a result of greater cohesive energy density or densification. It is also interesting to consider the different crosslinking reactivity of the main-chain unsaturation in PIP *versus* that of the pendant vinyl group of PVE, which can give rise to interesting network properties. These will be the subject of a subsequent communication.

While it is clear that the Flory interaction parameter for these blends must be non-negative, direct determination of its magnitude is best accomplished through measurement of small-angle neutron scattering[4]. Currently deuterated polybutadienes of varying microstructure are being synthesized to enable such experiments to be carried out, and thereby allow the effect of vinyl level on the miscibility and phase behavior to be quantified.

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