RUBBER MIXTURES

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CONTENTS

I. INTRODUCTION

Given the economic and technical uncertainties associated with synthesizing new polymeric materials, the utilization of polymer mixtures to achieve a desired combination of properties has obvious attraction. This review describes the factors governing both the morphology and behavior of polymer blends. Although such considerations have broad applicability, the specific focus herein is on those mixtures whose components are elastomeric. Of course this restriction is somewhat arbitrary, since the term elastomer encompasses any amorphous high polymer above its glass-transition temperature. Earlier reviews dealing with rubber mixtures are available[1-3], in addition to a number of general reviews and collected papers on polymer blends and solutions[4-11].

Most solutions and miscible blends result from the increase in positional disorder accompanying mixing. Since this combinatory entropy is small for the blending of high polymers, the overwhelming majority of such blends, including most commercially utilized rubber mixtures, possess phase separated morphologies. For technological utility, the components of a blend need only be compatible to the extent that a satisfactory dispersion can be attained without subsequent spontaneous demixing on a macroscopic scale. The practical application of truly miscible blends is limited; exceptions include polystyrene blended with either poly[oxy-1,4-(2,6-dimethylphenylene)][12] or polyphenylene ether[13], polyetheretherketone with polyethersulfone[14], and polyvinylchloride blends with nitrile rubber[15,16].

II. THERMODYNAMICS

A. SIMPLE (FLORY–HUGGINS) MIXTURES

Miscibility implies that a lower free energy is associated with molecular dispersion of the components than with a phase separated morphology. The free-energy change (excess free energy) accompanying formation of a strictly random two-component mixture can be expressed as[7,17,18]

$$\Delta G_M / kT = V[(\phi_i / V_i N_i) \ln \phi_i + (\phi_j / V_j N_j) \ln \phi_j + \phi_i \phi_j X / V_r], \tag{1}$$

where V is the total volume, and V_i, N_i, and ϕ_i represent the molar volume, degree of polymerization, and the volume fraction of the ith component respectively. V_r is an arbitrary reference volume that can be conveniently taken to equal the root mean square of the respective molar volumes of the components' chain units. The first two terms on the right hand side of Equation (1) correspond to the ideal, or random mixing, entropy. The third term represents the excess enthalpy. This mixing enthalpy is zero for an ideal mixture; that is, a mixture of molecules that have the same size and shape and in which the intermolecular forces between pairs of like segments of each type, as well as between unlike segments, are all equivalent. Such ideality is not expected in practice, and the excess enthalpy due to mixing is described by the Flory–Huggins interaction parameter, X. For regular mixtures, in which mixing transpires without specific (chemical) interaction between the components and with no significant alteration

of liquid-state structure, X is a measure of the changes in contact energies associated with replacing like contacts with unlike contacts:

$$X = (E_{ij} - E_{ii}/2 - E_{jj}/2)/kT. \tag{2}$$

For a regular mixture, this exchange energy is independent of concentration. The proportionality of the enthalpy to the product of the component concentrations in Equation (1) reflects the assumption of random mixing, whereby the number of like and unlike contacts is only a function of the concentration.

The forces between segments in a regular mixture are dispersion interactions (arising from correlation between charge fluctuations). The magnitude of the van der Waals interactions can be described by a series whose leading term corresponds to the well-known London equation for the dispersion energy[19,20]:

$$E_{ij} = -(3/4)I_{ij}P_iP_jr^{-6}, \tag{3}$$

where P_i is the polarizability of the ith molecule or chain unit, separated by r from the jth unit, and I_{ij} is approximately equal to the (assumed equal) ionization potential of the species. From Equations (2) and (3), it is seen that the mixing enthalpy associated with dispersive interactions always favors phase segregation (since $P_i^2 + P_j^2 > 2P_iP_j$, provided $P_i \neq P_j$). This means that the interaction parameter for a blend is positive in the absence of chemical reaction between the components, reflecting a greater attraction between like segments than unlike segments. Miscibility in such a system can only arise from the increased positional disorder of a blend.

The anisotropy of the polarizability can be an important aspect of the thermodynamics of van der Waals mixtures. Bond polarizabilities can be characterized by a component parallel to the bond direction as well as a component transverse to this direction. The dispersion energy will, in general, depend on the spatial orientation of the interacting induced dipoles. Group additivity approaches to the calculation of solubilities and miscibility[21] can be misleading in their consideration of only an average polarizability. The effect of tacticity on miscibility has been observed, not only in polymer mixtures in which the miscibility arises from chemical reaction between the components[22], but also in blends without any specific interactions[23,24].

In strictly van der Waals mixtures, phase separation can be induced by increases in the molar mass of the constituents, since the miscibility is of entropic origin. For high polymers, this combinatory entropy makes a sufficiently small contribution to the free energy such that miscibility is almost always limited to mixtures in which the components chemically interact and thereby effect a negative excess enthalpy. When such specific interactions are present, increases in molecular weight can still effect phase separation if the net X for the system is positive. Blends with strongly exothermic mixing enthalpies, on the other hand, can be expected to remain miscible at the highest of molecular weights.

In Figure 1 is a representative phase diagram illustrating the binodal and spinodal curves. The binodal, defined by equivalence of the chemical potentials, demarcates the regions of miscible and phase separated morphologies on the phase diagram. For mixtures lying only slightly beyond the miscible region, phase separation occurs by a nucleation and growth mechanism. The resulting
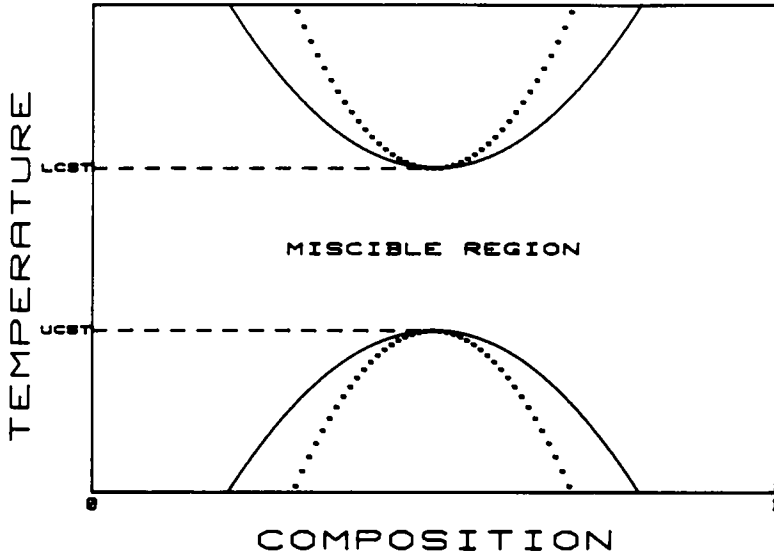
FIG. 1.—The phase diagram as a function of composition for a blend of equal sized polymer chains exhibiting both upper and lower critical solution temperatures, as indicated by the binodal (—) and the spinodal (● ● ●) curves.

phases at equilibrium would contain a portion of both components, although the high viscosity of polymers more usually results in metastable compositions. The spinodal curve represents the limits for such metastable compositions. Spinodal decomposition, referring to spontaneous and unstable development of concentration fluctuations leading to phase separation, occurs when the interaction parameter for a miscible blend becomes greater than some critical magnitude. The spinodal value of the interaction parameter can be obtained by setting the second derivative of the free energy with respect to composition equal to zero. Using Equation (1) for the free energy of mixing,

$$X_{sp} = (V_r/2)[1/V_i N_i \phi_i + 1/V_j N_j \phi_j], \tag{4}$$

where the ϕ now refer to the respective concentrations at a given spinodal temperature. The spinodal point, or minimum on the spinodal curve, defines a value of the interaction parameter below which the system is miscible for all proportions of the components. The composition at the critical point is deduced by equating the third derivative of the free energy with respect to concentration to zero. Again using Equation (1) for a Flory–Huggins mixture, this critical composition is given by

$$\phi_i^* = (V_j N_j)^{1/2}/[(V_i N_i^{1/2}) + (V_j N_j^{1/2})], \tag{5}$$

and, by inserting ϕ^* in Equation (4), the corresponding critical value of the interaction parameter is obtained:

$$X_{cr} = V_r/2[(V_i N_i)^{-1/2} + (V_j N_j)^{-1/2}]^2. \tag{6}$$

Phase separation will result if X exceeds X_{cr}. X is determined by the magnitude of the interaction energy, while X_{cr} is determined by the molecular weights and concentrations of the components. Within the assumptions of lattice theory, for a given pair of polymers, X is fixed, while X_{cr} can be adjusted in principle to control the phase morphology. In regular solutions and mixtures, upper critical solution temperatures (UCST) are expected, since X is inversely proportional to temperature, reflecting the fact that the driving force for miscibility, the contribution of the combinatory entropy to the free energy of mixing, is proportional to temperature.

B. DEVIATIONS FROM SIMPLE MIXTURE BEHAVIOR

When the constituents of a blend chemical interact (*e.g.*, *via* hydrogen bonding, complex formation, or charge transfer) the resulting negative excess enthalpy is favorable to mixing. In fact, the overwhelming majority of miscible high-polymer mixtures are a consequence of such specific interaction. In such mixtures, the inverse dependence on temperature of the interaction parameter predicted by the Flory–Huggins model is not observed, since the magnitude of the interactions is influenced by the available thermal energy. The diminution of specific interactions by increasing thermal agitation can effect phase separation upon increase in temperature. Examples of such lower critical solution temperature (LCST) behavior have been reported[25-29]. In the presence of specific interactions, the interaction parameter is also found to exhibit a concentration dependence[30-37], contrary to the assumption of simple mixture theory.

1. *Equation of state effects.*—The lattice theories on which Equations (1) and (6) are based describe "regular" solutions, in which no chemical interaction transpires and whose volume is the sum of the pure component volumes. Often, however, a difference in liquid structure (free volume) of the components gives rise to an excess volume, with concomitant influence on the mix enthalpy and entropy[4,17,38-41]. The magnitude of these equation of state effects can be gauged from the dissimilarity in the thermal expansion coefficients of the component polymers. Components of different size (loosely speaking, molecules of different size in the direction transverse to the chain) will usually form mixtures having a negative excess volume (a net contraction). Even when the latter is zero, however, the differences in liquid structure can still influence the mixing free energy. Contraction of the mixture will make a negative contribution to both the enthalpy and entropy, with the net effect invariably favoring demixing. Since the negative excess entropy is enhanced by increases in temperature, mixtures of polymers in which significant equation of state effects are operative can exhibit LCST, even in the absence of specific interactions. The same free-volume differences between polymer and solvent can be responsible for the LCST commonly exhibited by polymer solutions[42,43]. The competing effects of the positive combinatory entropy and the negative excess entropy caused by differences in liquid structure can in principle give rise to both upper and lower critical solution temperatures. Of course, if the latter is less than the former, miscibility is not possible at any temperature.

2. *Nonrandom mixing.*—It is well known that the concentration indepen-

dence of the interaction parameter required by the Flory–Huggins model is rarely observed in polymer mixtures when chemical reaction transpires between the components[30-37]. It has recently been reported that the theory also fails to accurately describe the thermodynamics of mixtures of polymer isotopes[44]. Such experimental results are consistent with theoretical predictions that the number of contacts between chain units depends upon the interaction energy[45-48], contrary to the random mixing assumption of the Flory–Huggins model. Local correlation effects, due to chain connectivity and the attractive forces between like contacts, increase the concentration of these contacts at the expense of unlike contacts, and thus serve to extend the bounds of miscibility in polymer blends.

The equation of state theory relates molecular interactions to surface, rather than volume, fractions[4,17,37,38]. If the surface to volume ratio of a component in the blend is concentration dependent (*e.g.*, blending promotes a conformational change or aggregation), the mixing free energy will then have a composition dependence different from that given by Equation (1). A difficulty in the application of this concept is determination of actual surface to volume quantities in blends.

A concentration dependence can be empirically introduced into the interaction parameter by expressing X as a polynomial in the concentration. Since ϕ_i, ϕ_j, and functions thereof are all interdependent, the particular measure of concentration is arbitrary. Using $\phi_i - \phi_j$ gives for the excess free energy[49],

$$G_M/kTV = (V_iN_i)^{-1}\phi_i \ln \phi_i + (V_jN_j)^{-1}\phi_j \ln \phi_j$$
$$+ \phi_i\phi_j[X_0 + X_1(\phi_i - \phi_j) + X_2(\phi_i - \phi_j)^2 + X_3(\phi_i - \phi_j)^3]. \quad (7)$$

If all odd powers are omitted from Equation (7),

$$G_M/kTV = (V_iN_i)^{-1}\phi_i \ln \phi_i + (V_jN_j)^{-1}\phi_j \ln \phi_j + \phi_i\phi_j[X_0 + X_2(\phi_i - \phi_j)^2]. \quad (8)$$

Equation (8) describes the symmetrical model of mixtures[49,50], according to which the mixing free energy is invariant to changes in composition that are symmetrical. If $X_2 \ll X_0$, then the simple Flory–Huggins result is recovered. The spinodal equation for the symmetrical mixture is

$$X_0 + [5(\phi_i - \phi_j)^2 - 8\phi_i\phi_j]X_2 = [(V_iN_i\phi_i)^{-1} + (V_jN_j\phi_j)^{-1}]/2, \quad (9)$$

where

$$X_{sp} = V_r[X_0 + X_2(\phi_i - \phi_j)^2]. \quad (10)$$

From Equation (10), it is seen that if the interaction parameter exhibits a concentration dependence (*i.e.*, $X_2 > 0$), the miscible region of the phase diagram is extended beyond that for a Flory–Huggins mixture. Also, the critical composition for a symmetrical mixture, unlike that of a simple Flory–Huggins blend [Equation (5)], is dependent on the magnitude of the interaction parameter.

III. STRUCTURE DEVELOPMENT

Equilibrium thermodynamics can provide an indication of when miscibility is expected in a polymer mixture. In a blend of immiscible polymers, the mor-

phology is not usually at equilibrium, given the sluggishness of macromolecular diffusion. The structure may be time invariant, however, due to this slow diffusion or because of crosslinking. In the preparation of miscible mixtures, there is a greater likelihood that equilibrium conditions will be obtained, and the consequent morphology is relatively insensitive to the details of the method of blend preparation.

A. PHASE SEPARATION

When a miscible blend becomes slightly unstable by a change in temperature, a metastable condition is obtained whereby the mixture can separate into domains of different composition by a nucleation and growth process; however, complete demixing of the components does not occur. With increasing instability the system will experience growth of composition fluctuations. When the magnitude of these fluctuations exceeds some critical extent, continuous phase separation occurs. This process, spinodal decomposition, is associated with a mixture beyond the spinodal line on the phase diagram, while nucleation and growth is expected when the system exists between the binodal and spinodal curves (see Figure 1). Different morphologies result from these phase separation processes. Much effort has been directed in particular toward understanding the kinetics of the demixing process[51-61].

B. FORMATION OF HETEROGENEOUS BLENDS

Rubber blends can be prepared by a variety of methods, including *in situ* polymerization, by latex or solution blending, and by mechanical mixing. The morphology of immiscible rubber blends is dependent upon the mixing procedure and rheological properties of the blend components and on their degree of compatibility as reflected in the interfacial energy. When components have similar viscosities and concentrations, there is a greater incidence of co-continuity of the phases[62-64]. The usual structure of a heterogeneous blend is a dispersion of one component in a continuous matrix of the other. As seen in Figure 2, the rubber of lower viscosity constitutes the continuous phase, provided it is present at a sufficiently high concentration[62,65]. This is at least plausible, since a more fluid component can readily encapsulate the more viscous phase. The capacity for a component to be highly extended without fracturing under the conditions of mixing increases the likelihood of that component forming a continuous phase. From consideration of the interfacial tension between two phases, it has been suggested that the phase with the larger normal stress function will form the dispersed particles[66]. Correlations have also been reported of the morphology of a blend with the relative magnitude of the interfacial and surface tensions[67]. It seems likely, however, that the viscoelastic stresses developing during polymer processing will usually override any effect of surface energies, at least with regard to domain sizes, if not shapes.

During the mechanical mixing of rubber blends, the dispersed domains are deformed during passage through the high shear regions of the mixing vessel and, under the proper circumstances, will fracture to produce smaller particles. Simultaneously, these flowing particles collide and often coalesce to form larger dispersed domains. The blend morphology obtained represents this competition
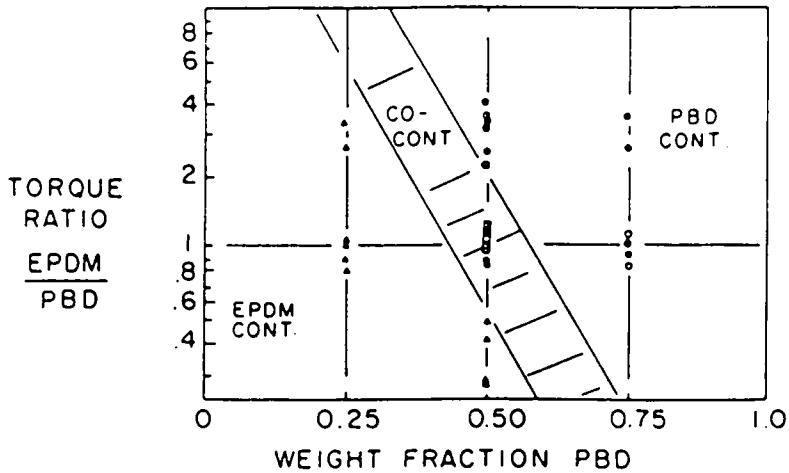
FIG. 2.—The dependence of the phase structure on composition for EPDM/BR blends, at various relative viscosities of the components (as reflected in their Brabender mixing torques)[65].

between dispersion of the rubber particles and their flow-induced coalescence[68-70]. Many studies, both experimental and theoretical, have focussed on the dispersion of fluid particles in a fluid medium[71-84]. The minimum stress necessary to break up a suspended droplet has been shown to be lowest when the viscosities of the two phases approach one another under the prevailing conditions of temperature and deformation rate[65]. Attempts to predict the morphology of rubber blends from consideration of the competition between breakup and coalescence have been made by assuming an energy criterion for particle fracture[68,70]. In fact, breakup is more related to the stress level exerted on the particle by the flowing matrix, and how effectively this stress can sustain particle deformation. The number of particles produced upon breakup is also a strong function of the stress level as well as depending upon the relative viscosities of the components[71]. Experimental studies of particle deformation and breakup invariably focus on single drops in a dilute suspension. In the concentrated systems usually employed in more practical situations, particles are surrounded by their neighbors. This shielding makes it more difficult to disperse domains in practice than results from the laboratory studies would suggest. Moreover, characterization of the material properties is usually based on low strain and/ or steady state data, whereas the fracture of fluid particles clearly involves high deformations and transient behavior.

Although the design of various commercial mixers leads to good distributive mixing and acceptable dispersive mixing, the latter is obtained almost strictly through shear flow[3]. It has long been recognized that dispersion is most effectively accomplished with pure straining flow fields due to the continual stretching of suspended particles[3,71,76,85]. In shear flow, vorticity causes rotation of suspended particles; consequently, the particles alternately experience extension and compression[75,86].

The flow-induced coalescence of the dispersed domains requires their collision, removal of the intervening film through its drainage and fracture, then finally molecular interdiffusion between the droplets. Coalescence has been found to be very extensive both when the viscosity of the suspended particles is much lower than that of the continuous phase[87] as well as when the viscosities are comparable (Figure 3)[69]. As the continuous phase becomes more viscous, the rate of coalescence decreases, although interestingly an increased rate of shearing was found to increase the fraction of interparticle collisions which resulted in coalescence[69]. The net result of flow-induced coalescence in sheared rubber blends is that the ultimate particle size is thereby limited. It is well-recognized that a continuation of the mixing process will cease effecting a finer dispersion[88]. This is, in general, due to the attainment of a steady-state competition between the particle breakup and coalescence processes. Since the stress required to fracture a particle by flow fields increases inversely with the particle size[71,76], the ability of the high-shear regions of the mixing vessel to provide the necessary stress level can also be a limiting factor in the dispersion process.

C. INTERPENETRATING POLYMER NETWORKS

An interpenetrating polymer network (IPN) refers to a blend ostensibly consisting of co-continuous, interlocking networks (catenanes) of the respective constituents[10,11,89]. This interpenetration of network structures may not actually be obtained, so that, in practice, the designation IPN connotes the method of preparation, rather than the actual morphology, of a blend. IPNs can be made simultaneously or sequentially. A simultaneous IPN is formed from the polymerization and crosslinking of premixed monomers or linear prepolymers (the

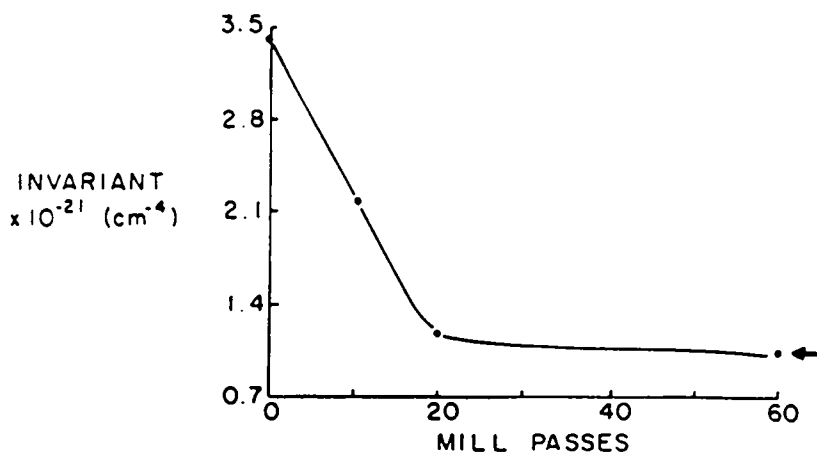FIG. 3.—The reduction in small-angle neutron scattering invariant accompanying mixing of a BR/CR blend on a two-roll mill. The decrease in scattering intensity results from the loss of isotopic purity in the BR domains due to their flow-induced coalescence. The arrow indicates the minimum obtainable scattering intensity, corresponding to complete homogenization of the particles after extensive multiple coalescence[69].

components being miscible at the low initial molecular weights). During network formation, the tendency for phase separation is promoted by the increasing molar mass of the constituents, but, provided the time scale for segregation is long relative to the crosslinking reactions, interpenetrating networks can be achieved. In a sequential IPN, one network is established prior to formation of the second. Phase separation is more extensive than in simultaneous IPNs, but co-continuity can still be achieved. The swelling of a crosslinked rubber with monomer, which is subsequently polymerized and crosslinked, is the most distinct method of preparing a sequential IPN. The term is also applied, however, to blends formed by simply mixing and crosslinking a pair of polymers. Virtually all rubber blends could thus be regarded as IPNs. "Semi-IPN" is often used in reference to an IPN in which one component remains uncrosslinked.

The premise underlying the formation of an IPN is the absence of interference among any polymerization and crosslinking reactions. Actually, such interferences are unavoidable. Grafting between the components often takes place, with consequences for both the morphology (in that it inhibits phase separation) and the properties (e.g., improvement in strength) of IPNs[89-93]. While from the structure of IPN's it is expected that mechanical performance will be additive with regard to the component properties, interlocked networks can confer greater mechanical integrity than a completely phase-separated blend morphology. When a network is formed while swollen with monomer or prepolymer of the second component, the resulting rubbery modulus will be reduced due to the extended configuration of the network chains during their formation, the higher incidence of intrachain crosslinking, and perhaps a lower concentration of topologically trapped entanglements[11,91,94,95].

In addition to much research literature, a number of patents describing the application of IPN technology to rubber–rubber mixtures have appeared[89].

IV. ASSESSMENT OF BLEND MORPHOLOGY

The experimental demonstration of thermodynamic miscibility, as well as the determination of the morphology in a phase separated blend, can be attempted by a variety of methods, the most important of which are described below.

A. INTERDIFFUSION

The observation of interdiffusion between a pair of polymers is an unambiguous demonstration of their thermodynamic miscibility. Of course, the slow rates of diffusion of macromolecules can limit the extent of this spontaneous mixing. It is necessary to employ a probe of the morphology that is sensitive to the structure at the interface between the polymers, since the bulk may remain compositionally pure. Unless the components are exceptionally high molecular weight (the diffusion constant scales with the second power of chain length for linear chains) or are highly branched (long branches suppress reptation and thus greatly retard chain diffusion), the time scales for significant interdiffusion are accessible to experimentation. The rate of interdiffusion be-

tween polymer species can be described by a concentration-dependent coefficient that will vary as[96]

$$D = f(\phi)(X_{sp} - X),\tag{11}$$

where $f(\phi)$ relates the kinetics of the interdiffusion to the respective tracer diffusion coefficients, D^0 (D in the limit of the volume fraction going to zero),

$$f(\phi) = 2\phi(1 - \phi)[D_i^0 N_i \phi + D_j^0 N_j(1 - \phi)].\tag{12}$$

This non-Fickian diffusion will transpire at a rate which reflects the degree of miscibility of the system. As X approaches the critical value defined by Equations (4) or (9) and (10), "thermodynamic slowing down" of the interdiffusion will occur[97]. Although the rate of the interdiffusion reflects the magnitude of the interaction parameter, both the interaction parameter and the glass-transition temperature of a blend may depend on the concentration of the constituents. This will impart an additional composition dependence to D beyond that given in Equation (12).

The adhesion which develops between contacted rubber sheets can directly reflect mutual interdiffusion between them[98]. Displayed in Figure 4 is the uncured adhesion measured as a function of contact time between, respectively, sheets of two immiscible rubbers, two miscible rubbers, and a rubber plied against itself[99]. This adhesion parallels the extent of any interdiffusion of the polymer
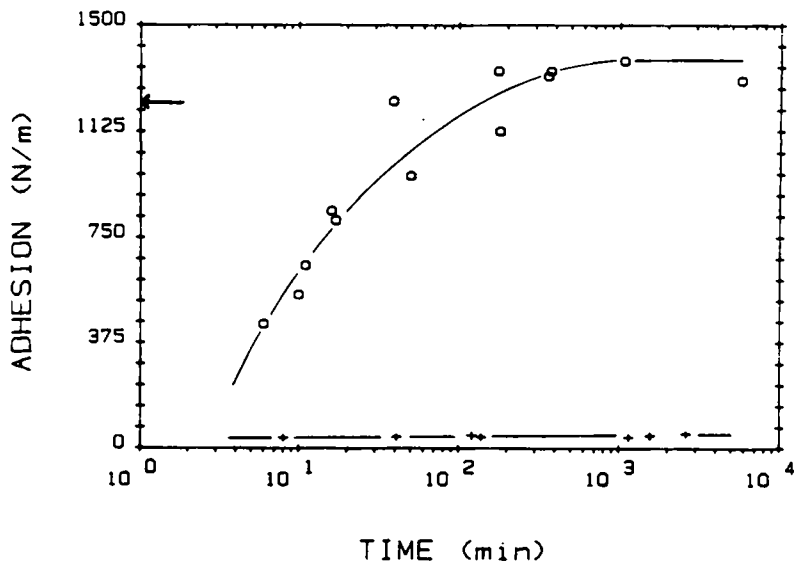
FIG. 4.—The peel adhesion measured as a function of contact time between 1,2-BR and NR (O O O) and between 1,4-BR and NR (+ + +) respectively. For the former, the mode of failure changes from adhesive to cohesive as the bond strength approaches the plateau corresponding to the bulk cohesive strength. The peel adhesion of NR to itself, indicated by the arrow, exhibited no time dependence due to the rapidity of the interdiffusion. In the case of autoadhesion of 1,2-BR, 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.[99].

chains. When interdiffusion takes place, the adhesion will level off at a value limited by the cohesive strength of the materials. This corresponds to chain diffusion over distances roughly equal to the chain coil size. For a typical value for rubber of the self-diffusion coefficient (on the order $0.1 \text{ nm}^2/\text{s}$[100]) and for a radius of gyration, R_g, of 10 nm for the coiled chains, the adhesion should plateau at a level equal to the bulk strength over a time scale, t, of roughly a few seconds

$$t \cong R_g^2/2D. \tag{13}$$

This is less than the time required to make adhesion measurements so that, for example, autoadhesion (tack) measurements are usually time invariant. The magnitude of the adhesion is equal to the cohesive strength of the material, as can be inferred as well from the large deformation and bulk tearing that accompanies separation of the specimens[98,101]. If the contacted sheets are comprised of immiscible rubbers, no interdiffusion occurs. The adhesion, as illustrated in Figure 4, remains low with a strictly adhesive mode of failure. Natural rubber (NR) is miscible with 1,2-polybutadiene (1,2-BR) even at high molecular weights[23,24,99]. As a result, when the NR is brought into contact with 1,2-BR, the initially separated polymers spontaneously interdiffuse. This is clearly reflected in the data in Figure 4 as well as by the nature of the separation mechanism (cohesive tearing from within the sample bulk).

Other means of demonstrating occurrence of any interdiffusion can be employed. When some form of scattering contrast exists between the materials, interdiffusion will enhance the scattering intensity (either x-ray or neutron) measured from the plied sheets. In Figure 5 is shown the magnitude of the small-angle neutron scattering intensity arising due to interdiffusion from layered sheets of cis-1,4-polyisoprene (IR) with deuteriated 1,2-BR[23]. The interdiffusion must proceed over significant distances for measurable scattering intensities to be observed (for the data in Figure 5, the rubber sheets had been maintained in contact for 162 h[23]).

Infrared microdensitometry[102,103] and electron microprobe energy dispersive x-ray analysis[104] have been used to directly characterize concentration profiles of interdiffusing species. Other applicable methods include radiotracer diffusion[100,105] and forward recoil spectrometry (FRES)[106]. A slight variation on the above techniques is to prepare an initially phase-separated mixture and monitor the ensuing dissolution. Light, neutron, and x-ray scattering[107–109], as well as fluorescence spectroscopy[110] can be utilized in this regard.

Of course measurement of the self-diffusion constant in a polymer blend can be used to assess the magnitude of X [Equation (11)] in miscible systems. Some of the above described methods have in fact been utilized for precisely this purpose. Other measures of bulk diffusion, which however do not rely on an initial gradient, include NMR techniques[111–115], photon correlation spectroscopy[116,117], and forced Rayleigh scattering[118–120].

B. GLASS-TRANSITION CHARACTERISTICS

The most popular method of adducing the degree of homogeneity in polymer blends is by measurement of the temperature of transitions from rubbery to
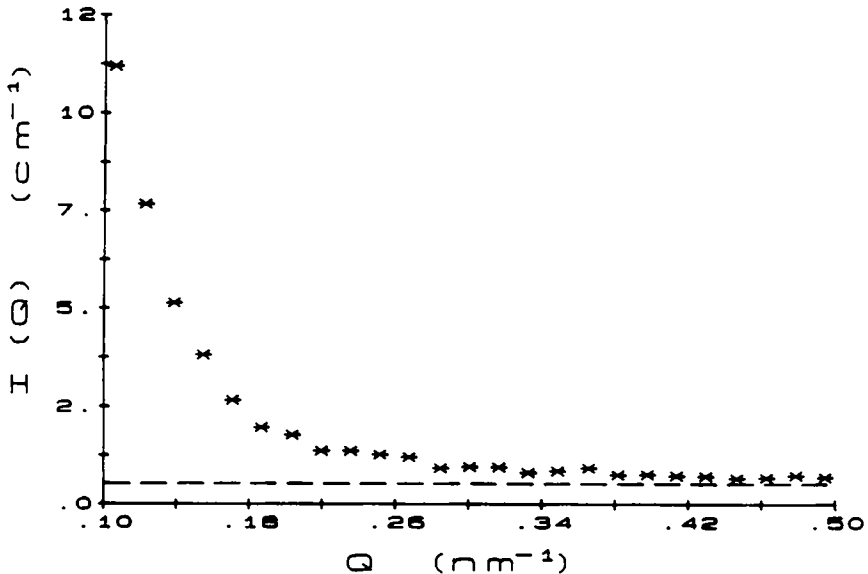
FIG. 5.—Small-angle neutron differential scattering cross section (•••) *versus* the reduced scattering angle measured from a sample consisting of sheets of IR (N_w = 23 000) and deuteriated 1,2-BR (N_w = 3200) which were in contact for 162 h at 52°C. The scattering contrast significantly exceeds the incoherent background scattering (- - -) determined from measurements on the individual polymers, evidencing the thermodynamic miscibility of these species[23].

glassy behavior. This can be accomplished with a variety of methods, including calorimetry and dynamic mechanical measurements, as well as less common techniques such as dilatometry, nuclear magnetic resonance, dielectric response, and radio thermal luminescence. The observation of distinct transitions corresponding to the respective components of the blend indicates the existence of a multiphase structure. The appearance of a single transition, while consistent with phase homogeneity, is not unambiguous evidence of thermodynamic miscibility. If the respective T_gs are close (*ca.* 10°C), they may appear as a single, broad transition. Dynamic mechanical characterization of glass transitions has an advantage in this regard. The appearance of a single transition in mechanical testing must be independent of the deformation frequency if the morphology is in fact homogeneous. For example, a single glass transition was observed in heterogeneous blends of IR and 1,4-BR at 110 Hz, while at a lower test frequency, both transitions were in evidence[121]. This likely indicates a different dependence of the free volume of the components on temperature (or a different activation energy for relaxation), which in itself signifies a phase separated morphology.

Glass transition behavior actually provides only an indication of the structure of a blend, rather than directly reflecting the thermodynamics. When the domain size is sufficiently small, the thermal or mechanical response may be no longer sensitive to the details of the heterogeneous structure. For example, when the domains of a blend of NR with *cis*-polypentenamer were 5 to 10 nm in diameter,

dynamic mechanical measurements revealed only a single glass transition, intermediate in temperature to that of the pure components[122]. There is also evidence suggesting that when the interfacial energy for a pair of polymers is small [e.g., NR and 1,4-BR[123] or BR and styrene–butadiene copolymer (SBR)[124- 126]], a broad or interconnected interface region, developed perhaps upon vulcanization, can cause disappearance of the expected distinct glass transitions. The influence of the interface can also cause a shift in the temperature of the individual glass transitions in a multiphase blend from the values for the pure components[89,127]. There have been many studies of the effect of the composition of a miscible blend on its glass-transition temperature[128–131].

When a component is present at low concentration, the greater sensitivity of mechanical measurements can be advantageous, since the observed quantity is a change in the loss tangent rather than a deviation in the rate of change of a measured quantity such as the heat capacity.

C. ELECTRON MICROSCOPY

The most straightforward method of examining the structure of multiphase polymeric systems is direct observation in the electron microscope. The principle difficulty is ensuring that sufficient contrast exists when the electron density of the rubber components are similar. Particularly when a difference in unsaturation exists, staining techniques (e.g., with OsO_4 or RuO_4) have long been successfully employed. Of particular interest for elastomer blends is the ebonite method[132], in which the preferential reaction of one of the rubber phases with sulfur and zinc effects a large increase in its electron density. Another method takes advantage of any differential capacity for swelling in a particular solvent in order to obtain phase contrast[133]. The blend sample is immersed in the solvent, stretched, and subsequently observed in the electron microscope after evaporation of the solvent. The phase which was more swollen will have become more thinned out by stretching. To avoid the distortion in zone sizes and shapes encountered with differential swelling, advantage can be taken of differences in susceptibilities to pyrolysis of the rubbers in a blend[134]. Differential pyrolysis selectively removes one of the rubbers, causing its domains to become more transmissive in the electron microscope. Several approaches have been described for obtaining electron micrographs of the transient structure that may arise in multicomponent rubbers as a result of deformation[135].

Recent advances in digital image analysis have facilitated rapidly obtaining particle size data from micrographs[136,137]. With resolution limits as low as a few tenths of a nm[138], in principle, the electron microscope can be used to probe blends of the finest dispersion[139]. In practice, the problem of contrast and the need to obtain thin sections (with the concomitant potential for artifacts in the observed structure) limit the extent of usefulness.

D. X-RAY AND LIGHT SCATTERING

The irradiation of matter usually gives rise to scattering of a portion of the incident intensity, where both the energy and propagation vector of the scattered waves may differ from that of the incident radiation. The angular dependence

of the elastic scattering provides morphological information. Elastic light, x-ray, and neutron scattering all result from heterogeneities in the structure of the irradiated material. In a homogeneous system, thermal fluctuations in density and composition are responsible for the scattering. In multiphase polymer blends, the angle dependence of the scattering reflects the size and spatial distribution of the phases, and so it can be usefully applied to the study of the morphology of rubber blends. There is an extensive literature devoted to methods of analyzing scattering data from multiphase systems (see, for example, References 140 and 141).

The application of light scattering to solid-state polymer blends is not as popular as its use in the characterization of dilute polymer solutions, due to difficulties in the former with multiple scattering and sample transparency. In the area of elastomer blends, much of the light scattering work has focussed on block copolymers[142,143]. Phase separation in blends is sometimes judged from the appearance of enhanced light scattering (cloud point). When an initially homogeneous blend is taken past the spinodal curve on the phase diagram, strong segregation effects are operative; nevertheless, high sample transmittance can result from small domain sizes (relative to the wave length of light) in a heterogeneous blend. Of course, the components must have a sufficiently different refractive index for observable scattering.

The application of x-ray scattering to polymer blends is well established, and often complements light scattering results. This is particularly true in two-phase systems in which the particle sizes extend over a broad range. In Figure 6 is displayed the particle size distribution determined from small-angle x-ray measurements from a blend of 1,4-BR with polychloroprene (CR), along with results obtained from analysis of electron micrographs[69]. Although there are limitations associated with extracting particle size distributions both from micrographs and from scattering curves, it can be seen that the different techniques are in reasonable agreement.

A method purporting to distinguish between homopolymer blends and the corresponding copolymers from the angle and breadth of the amorphous halo in the wide-angle diffraction pattern has been described[144].

In addition to measurement of static structure factors, dynamic light scattering can be utilized to probe concentration fluctuations in blends[145]. A previously mentioned example is the application of photon correlation spectroscopy to the study of diffusion in polymer mixtures[116,117].

E. SMALL-ANGLE NEUTRON SCATTERING

The principal application of SANS to polymer blends has been the determination of the interaction parameter. In a scattering experiment, the measured quantity (the intensity as a function of scattering angle) represents the Fourier transform of the correlation function describing concentration fluctuations in the mixture. The magnitude of these equilibrium fluctuations is governed by the contact energies for the species. Using the random phase approximation to calculate the correlations of concentration fluctuations, the scattering intensity for a miscible two component system can be obtained as[7]
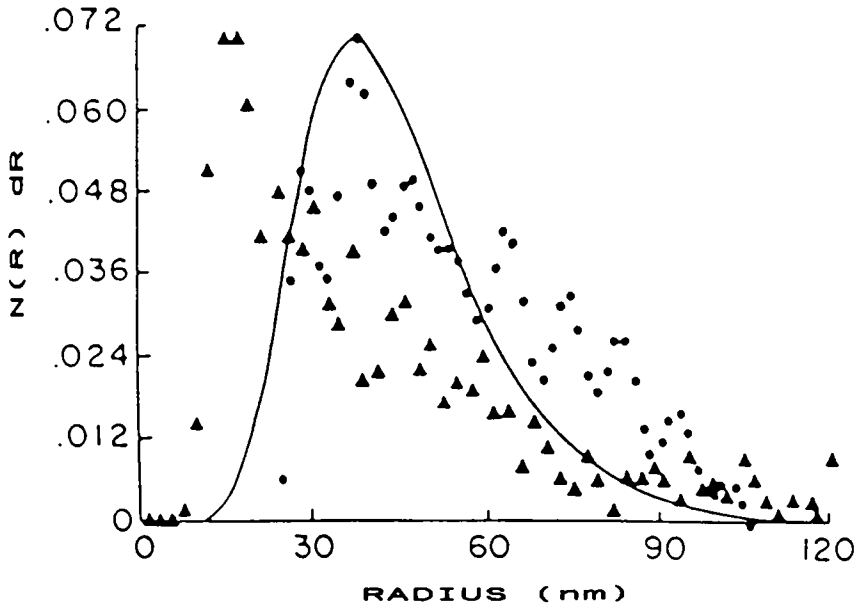
FIG. 6.—BR particle size distribution in an extensively mixed CR blend as inferred from analysis of electron micrographs (▲ ▲ ▲), Fourier inversion of small-angle x-ray scattering data (● ● ●), and the log normal distribution function giving the best fit to the experimental x-ray scattering curves (—)[69].

$$I(q)^{-1} = (N_i \phi_i g_i)^{-1} + (N_j \phi_j g_j)^{-1} - 2X, \qquad (14)$$

where q is the reduced scattering angle (momentum transfer) and g refers to the scattering function for the chain molecule. At low angles, the latter depends only on the radius of gyration of the chain. A value for the interaction parameter can be obtained by using X as an adjustable parameter and fitting Equation (14) to the experimental data. This expression is valid for the scattering of light and x rays, as well as neutrons. The advantage of the latter is that advantage can be taken of the dependence of SANS contrast on isotopic composition. The replacement of protons with deuterons in one of the components will enhance the scattering intensities but has a smaller thermodynamic effect than, for example, the use of electron dense substituents in order to improve the x-ray scattering intensities. As the stability of the blend is reduced there is an increase in scattering intensity, leading to a "cloud point" upon phase separation.

Aside from block-copolymer studies (where the microphase separation can be identified from the development of maxima in the scattering curve due to the regular supermolecular structure[146]) and measurements of the interaction parameter in isotope mixtures[44,147,148], the application of SANS to blends of rubbers has been very limited to date. Some preliminary SANS work on IR blended with deuteriated 1,2-BR has been reported[23]. Also SANS was used to measure the increase in coil size of high-molecular-weight polydimethylsiloxane (PDMS) when blended with lower-molecular-weight PDMS[149].

The resolution of the SANS technique limits its utility for the study of phase separated blends, in which the domains may be too large. The flow-induced coalescence of BR domains dispersed in a CR matrix was measured from the loss of neutron scattering intensity when initially isotopically pure BR particles coalesced to form particles containing both isotopes of the BR[69].

F. FLUORESCENCE

Fluorescence techniques provide a sensitive probe of polymer morphology. If the two components of a blend are labeled with donor and acceptor fluorophores respectively, nonradiative energy transfer is possible. The efficiency of this energy transfer is strongly dependent on the distance between the fluorophores; phase separation will suppress the interaction. Measurement of the relative intensity of the donor and acceptor fluorescence intensity can therefore reveal the spatial proximity of the blend components[150-152]. A somewhat related technique relies on the quenching of a labeled species by the second component of a blend to reduce the fluorescence intensity when the morphology is homogeneous[153-155]. Upon phase separation the quenching is reduced, effecting an increased intensity.

Excimer fluorescence also has found application in the study of polymer blends containing aromatic polymer constituents[156-159]. The intensity of the excimer fluorescence can increase upon phase separation due to the resulting increased local concentration of phenyl-bearing constituents.

G. NUCLEAR MAGNETIC RESONANCE

There are a number of NMR methods for probing the structure of polymer blends. The segmental mobility associated with the rubbery state will broaden NMR linewidths. If the components of a blend have different glass-transition temperatures, proton NMR can be utilized to assess the phase structure of a blend by taking advantage of the rapid decrease of proton–proton coupling with nuclear separation[160-162]. At a temperature intermediate between the glass-transition temperatures of the components, observation of only a single broad linewidth is evidence of spatial homogeneity on a scale of about one nanometer.

Similar ^{13}C NMR experiments can be conducted, but additional insights into the molecular motions in miscible blends can be obtained. If two polymers are segmentally mixed in accordance with their thermodynamic miscibility, their chain segments will experience the same free volume and the same local fluctuations in free volume. Accordingly, it is expected that the onset of mobility will transpire at the same temperature for both components of a miscible blend. In miscible blends of IR and 1,2-BR, however, it has been shown that spatial homogeneity on a segmental level is not accompanied by equivalent temperatures for the onset of segmental mobility of the components[163]. The differing local free-volume requirements for liquid-like motion in 1,2-BR and in IR give rise to linewidth broadening, associated with the onset of this mobility, at different temperatures for the two components.

Several methods are suitable for blends containing polymers of equivalent glass-transition temperatures. Proton magic angle spinning NMR can be applied to blends in which most of the protons on one of the components have been

replaced with deuterium[164]. The residual protons on the deuteriated component will experience strong dipolar interactions with other protons only if the components are intimately mixed. Another technique also requiring a deuteriated component, but capable of providing more information, is crosspolarization magic angle spinning ^{13}C NMR[165-168]. The transfer of spin polarization from protons to the ^{13}C atoms of the deuteriated component can only transpire if these carbons are in spatial proximity to the protons, which requires mixing on a nanometer level. Interactions between very closely lying chains in a miscible blend can also be studied using two-dimensional nuclear Overhauser spectroscopy[169-172].

NMR imaging of solids is an increasingly popular technique which may have applications to polymer blends. Recently it has been used to characterize the phase sizes with a spatial resolution of less than 50 μm in immiscible mixtures containing polybutadiene[173]. Approaches to analyzing sequence distributions from ^{13}C measurements on polymer mixtures have also been described[174].

H. SOLUTION BEHAVIOR

Since the slow diffusion of polymers in the solid state makes achieving equilibrium difficult, the behavior of polymer mixtures in solution has often been studied in an effort to assess miscibility. Solution blending facilitates the attainment of equilibrium in so far as it enhances molecular mobility; however, miscibility between polymers in solution does not parallel their thermodynamic compatibility in the absence of solvent. At sufficient dilution, any polymer pair will form a homogenous solution in a common solvent. Phase separation of a polymer pair in a common solvent is sometimes taken as an indication of their immiscibility, although when a sufficiently large difference in the respective polymer–solvent interaction parameters exists, phase separation can occur in solutions of miscible polymers[39]. It is even more common, and unsurprising, to find instances of miscible solutions involving polymer pairs that, in the absence of solvent, exist as a phase separated blend. As an example, blends of BR and polypentenamer form a miscible solution in toluene, while electron micrographs clearly indicate heterogeneity in films cast from this solution[122].

An assessment of the magnitude of the interchange enthalpy for a blend without specific interactions can be made from the solubility parameters of the components, although the solubility parameter data available in the literature are usually too imprecise for reliable quantitation. According to classical lattice theory, the interchange enthalpy contribution to the free energy is related to the solubility parameters as[6,17]

$$X = (V/RT)(\delta_i - \delta_j)^2. \qquad (15)$$

This equation ignores any differences in liquid structure between the components (Section II, B, 1). Equation-of-state effects, for example, likely underlie reports that solubility parameter data do not correlate with the degree of compatibility of blends of NR, BR, and SBR[175] (see Section V, 5, 1). Various methods are available to measure the polymer–solvent interaction parameter[176]. When the forces between the chain segments are not just van der Waals interactions, the solubility parameter approach obviously becomes less useful.

Another means for obtaining polymer–polymer interaction parameters from polymer–solvent interactions is the use of gas–liquid chromatography[177]. Retention volumes of gas-phase components on solid phases comprised of the polymeric materials of interest (the respective pure components and their mixtures) provide an indirect measure of X. A related method is the determination of X from the uptake of vapor by the polymer blend[178].

V. MISCIBLE ELASTOMER MIXTURES

If only high-molecular-weight polymers are considered, the instances of miscible rubber blends are very rare. While a few examples of miscible blends of a rubber and plastic are known (for example, polyvinylchloride with, respectively, nitrile rubber[15,16] or epoxidized natural rubber[179]), reviewed below are cases of miscible blends of two elastomers.

A. EXAMPLES

1. *Polyisoprene–polybutadiene blends.*—Polybutadiene and 1,4-polyisoprene are polymers having only a very slight polarity (from their carbon–carbon double bonds) and are without capacity for chemical reaction with one another. It is expected that miscible mixtures of the two will consist of simple van der Waals fluids, as has in fact been confirmed by infrared analysis[24,180]. A further expectation is that miscible blends will be limited to only components of low molecular weight, and, moreover, will exhibit UCST.

As discussed in Section II, A, the interaction parameter for van der Waals mixtures must be positive and, for miscibility to be realized, have a magnitude less than the spinodal value determined by the molecular weights of the components. The interaction parameter measured for blends of IR with polybutadiene of various microstructure are listed in Table I[181]. These results were obtained from determination of the miscible compositions with the lowest critical interaction parameter [as calculated from Equation (6)] and from the immiscible blends with the highest X_{cr}. It is observed that as the concentration of 1,2 units in the BR increases, there is a large increase in miscibility with IR. At high levels of 1,2 units, phase separation can not be induced even at extremely high molecular weights, indicating a remarkable degree of miscibility given the absence of specific interactions[23,24,99]. Blends of 1,4-polyisoprene with 1,2-polybutadiene are unusual, not only because of this miscibility, but because it is a unique instance of miscibility between chemically distinct, high-molecular-weight homopolymers without specific interaction between the components. The miscibility suggests a near equivalence in polarizability between the respective chain units of the 1,2-polybutadiene and the 1,4-polyisoprene, along with a close similarity in liquid structure. At higher 1,4 content, a larger mixing endotherm restricts miscibility to low-molecular-weight components.

Based on the solubility parameters for the polymers, it is clear that the exchange enthalpy between IR and BR becomes more endothermic (reduced miscibility) as the concentration of 1,4-units in the latter increases[182]. There will also be a contribution to the free energy of mixing from any differences in the liquid structure of the two components. Displayed in Figure 7 is the density

TABLE I

MISCIBILITY IN MIXTURES OF IR WITH BR COPOLYMERS[180,181]

1,4 units in BR	X^a	N^b	$\Delta\alpha$, deg^{-1} ^{c}
92%	2.4×10^{-3}	830	8.7×10^{-4}
74%	1.7×10^{-3}	1200	6.7×10^{-4}
59%	0.7×10^{-3}	2900	5.7×10^{-4}
3%	$<1.7 \times 10^{-4}$ ^{d}	$>10\ 000^d$	1×10^{-5}

^{a} Experimentally determined for blends containing the critical concentration of components.

^{b} Highest degree of polymerization for miscibility with equal concentrations of components of equivalent molecular weights.

^{c} The difference in the room temperature thermal expansion coefficients of IR and the indicated BR.

^{d} Phase separation was not observed in this system at the highest available molecular weights.

measured for IR blended with 1,4-BR and 1,2-BR respectively[99,181,182]. While the volumes of the latter mixtures are simply additive in the volume of the components, 1,4-BR/IR blends exhibit a negative excess volume, indicating large liquid structural differences between these components.

Although absence of an excess volume upon mixing does not imply nonadditivity of the enthalpy and noncombinatory entropy, any such equation-of-
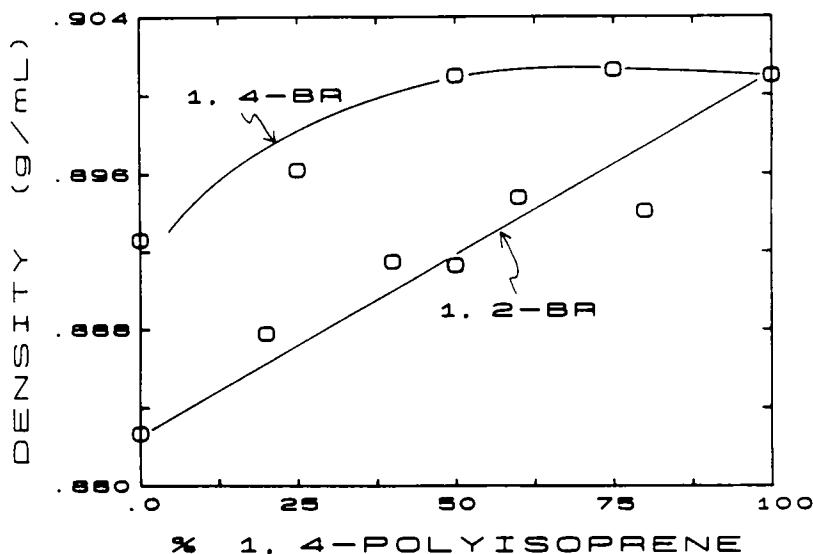

FIG. 7.—The density measured at room temperature for IR mixed with 86% 1,2-BR and 92% 1,4-BR. The latter blends exhibit deviation from additivity indicative of a mismatch in the liquid structure of the pure components[182].

state contributions to the free energy must be vanishingly small in blends of 1,2-BR with IR in order that miscibility be observed at high component molecular weights. Significant differences in liquid structure are made apparent by comparison of the thermal expansion coefficients of the components. The difference in the thermal expansion coefficients of IR and polybutadiene is greatly diminished as the vinyl content of the latter increases (Table I). The mismatch in liquid structure between IR and BR of high 1,4 content are responsible at least in part for the reduction in miscibility of IR with 1,4-BR[181,182].

As described in Section II, B, 1, a further consequence of significant equation-of-state effects is the potential for lower critical solution temperatures. It is expected that when the temperature of a miscible blend of BR and IR is reduced, phase segregation will eventually transpire, since the driving force for miscibility is the combinatory entropy. Such upper critical solution temperatures, however, have not been observed, evidently lying below the glass-transition temperatures of the mixtures[23,24,99]. Contrarily, as illustrated in Figures 8 and 9, phase separation of miscible mixtures of IR with BR of high 1,4 content can be induced by increases in temperature[181,182]. When the BR microstructure is less than 15% 1,4, no phase separation in blends with IR has ever been observed[23,24,99]. The absence of an LCST is consistent with increased similarity in the expansivities of the components at higher 1,2 microstructure.

Blends of syndiotactic 1,2-BR with IR have been found to be phase separated at molecular weights for which the corresponding atactic 1,2-BR blend with IR
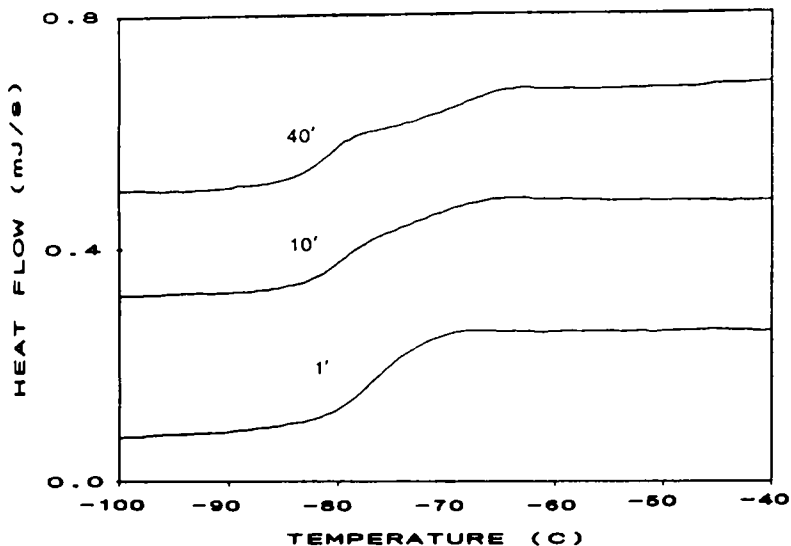

FIG. 8.—The glass-transition behavior of blends of IR (N = 4500) with 59% 1,4-BR (N = 1700) at the critical concentration of the components [Equation (5)]. The samples were heated from 30°C to 50°C and held at the latter for the indicated time period, followed by quenching to −125°C. The displayed curves, corresponding to measurements made in the ensuing reheating, reflect the increasing extent of phase separation transpiring just above the LCST[182].

FIG. 9.—The glass-transition behavior of blends of IR (N = 1940) with 92% 1,4-PBD (N = 440) at the critical concentration of the components [Equation (5)]. The samples were heated from 30°C to 75°C and held at the latter for the indicated time period, followed by quenching to −125°C. The displayed curves, corresponding to measurements made in the ensuing reheating, reflect the increasing extent of phase separation transpiring just above the LCST[181].
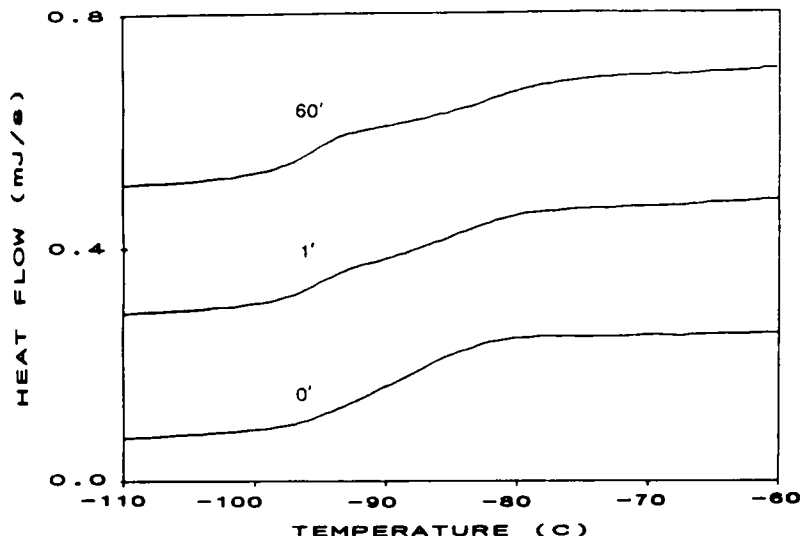
would be miscible[23,24]. This demonstrates that the enthalpy of mixing in IR blends depends significantly on the tacticity of the BR. The polarizability transverse to the chain backbone of 1,2-BR is dependent on orientation with respect to the pendent vinyl group.

2. *Epoxidized polyisoprene and chlorinated polyethylene.*—When 25 mole% of the chain units of polyisoprene are epoxidized (to form a random copolymer of 2,3-epoxy-2-methylbutane with the original 2-methyl-2-butene[183]), blends with chlorinated polyethylene (25% by weight chlorine) were found to be miscible[184]. The origin of the miscibility is reported to be specific interactions involving the oxirane ring with the chlorine. At higher levels of epoxidation (50 mole%), phase separated blends were obtained unless the chlorine content of the polyethylene was increased. These particular miscibility results are actually only valid for components of the molecular weights employed in this study, so that the specific levels of epoxidation and chlorine necessary for miscibility are also molecular-weight dependent.

3. *Copolymer mixtures.*—Some unsurprising examples of rubber blends reported to be miscible include SBR copolymers of different styrene level[185], nitrile rubbers (NBR) of different acrylonitrile content[186], and SBR and BR[124,125,187]. It is expected that a copolymer would in some cases be miscible with another copolymer of only slightly different composition. More interestingly, blends of a copolymer with a chemically distinct homopolymers are sometimes found to be miscible, even when the corresponding homopolymer blends are all immiscible. Although there are no specific interactions in these cases, a net mixing exotherm

can exist due to dilution of the more unfavorable unlike contacts within the copolymer upon blending with a homopolymer or a second copolymer[188-190].

The seemingly contradictory findings regarding the homogeneity of some rubber blends containing copolymers[191,192] can likely be attributed to differences in microstructure and molecular weight of the various materials employed. Assessments concerning the miscibility of various rubbers[193] are of no import when the effect of the molecular weight and concentration are ignored. Particularly for van der Waals mixtures, the role of molecular weight is of central importance with regard to the phase structure of polymer mixtures (Section II, A).

4. *Isotope mixtures.*—The contribution to X from isotopic substitution usually represents an unwanted complication in attempts to use small-angle neutron scattering to measure the mixing energy of a blend containing a deuteriated component. The molar volume isotope effect can be directly measured in binary isotope blends however, and can provide a means to probe the thermodynamics of nearly ideal polymer mixtures.

In large polyatomic molecules, this molar volume isotope effect primarily reflects differences in the vibrational motions arising from their dependence on mass and mass distribution[194-196]. The effect is dominated by the C–H symmetric stretching mode, the anharmonicity of which results in a slightly greater bond length for C–H bonds than for C–D bonds. Mixing of the isotopes causes an increase in molar volume of the deuteriated species and a corresponding contraction of the hydrogenous component. The free energy change resulting from the mixing of isotopes can be considered as consisting of a contribution from the compression or dilation of each species to its volume in the mixture, and from the ensuing mixing at constant volume of the two components[197,198]. For large molecules, the latter contribution is negligible relative to the excess free energy arising from the molar-volume change; therefore, the isotope effect in polymer mixtures is essentially the free-energy change associated with altering the molar volume of the pure components to that which they have in the blend.

Isotope blends comprised of rubbers are most useful, since an equilibrium morphology is most readily attained. The isotope effect has been investigated in polymer blends containing 1,4-BR[147,199] and 1,2-BR[44,148].

<div align="center">B. PROPERTIES</div>

Although the incidence of miscibility in high polymers is not high, it does confer the potential advantages of a reduced dependence of the morphology on mixing conditions, along with a minimal propensity for subsequent changes in morphology. The effect of miscibility on properties, and in particular, the benefits of a homogeneous morphology, are not, however, particularly significant beyond the alteration of the glass-transition temperature.

1. *Rheology and mechanical properties.*—The absence of interfaces in a miscible blend can yield, in principle, greater mechanical integrity than expected in a multiphase structure. When the components of a miscible rubber blend chemically react (*i.e.*, specific interactions) or have a mismatched liquid structure, a negative excess volume results. This densification may provide an improvement of mechanical properties due to the greater number of chain per cross-sectional area. Specific interactions can also directly enhance properties

by the resultingly higher cohesive energy density. Such improvements have been reported for miscible polymer blends in the glassy state[200].

In regular mixtures (described in Section II), densification, and the attendant synergistic properties, are absent. The nature of the deformation and flow of a blend in general provides little indication of the existence of miscibility. Although the viscosity and modulus of block copolymers markedly decrease in magnitude at the upper critical solution temperature due to dissolution of the ordered supramolecular structure associated with the phase separated morphology[201,202], there is no corresponding discontinuity in the mechanical properties of homopolymer blends in the vicinity of a critical solution temperature. The fundamental rheological quantities most significantly modified by changes in composition of a miscible blend are the monomeric friction coefficient and the terminal relaxation time[180]. The dependence of the local friction coefficient on composition will usually be dominated by any composition dependence of the glass-transition temperature. The magnitude of the friction coefficient will also directly influence the terminal relaxation time. This relaxation time also has a strong dependence on molecular weight, which will impart an additional composition dependence if the components differ in molecular weights. The weight-average molecular weight of a blend is simply the weight average of the corresponding quantities for the pure components.

Since nearly athermal mixing will always be accompanied by negligible alterations in the configuration of the polymer chains, the density of entanglements (which reflect the uncrossability of chain contours) should vary in regular mixtures between the entanglement concentrations found in the pure components. In blends of IR and 1,2-BR, for example, the entanglement density was found to exhibit a monotonic variation over the entire composition range[180]. Even in blends with specific interactions, moreover, interaction parameters of substantial magnitude (e.g., greater than 10^{-2} in absolute magnitude) have been observed to have negligible effect on chain dimensions[203]. The effect of the interaction energy on the spatial distribution of chain segments[45-48] can evidently influence the topological interactions[204,205]. Effort has been expended in trying to predict the concentration of entanglements in miscible blends[204-206]. The difficulty is that even in a pure material the entanglement density has an obscure relationship to molecular features of the chains. Various semiempirical correlations of rubbery plateau moduli with molecular characteristics have appeared[207-211]. These attempts neglect details of the chain structure and have had limited success. As long as the particular molecular factors responsible for the entanglement concentrations in polymeric liquids are incompletely understood, predictions of plateau moduli in miscible blends can have only limited success.

One empirical approach to the prediction of blend properties is the use of simple mixing rules[212,213],

$$\eta_{ij}^n = \phi_i \eta_i^n + \phi_j \eta_j^n, \tag{16}$$

based on series ($n = 1$) and parallel ($n = -1$) representations of blend properties in terms of the component properties. A variation is to take the exponent of Equation (16) to equal zero and employ the "logarithmic rule of mixtures,"

$$\eta_{ij} = \eta_i^{\phi_i} \eta_j^{\phi_j}. \tag{17}$$

The viscosities calculated according to Equation (17) for a series of miscible blends of IR with 1,2-BR are displayed in Figure 10, along with experimentally measured viscosities[24,180]. Although the experimental results can be roughly approximated by taking the exponent n to be a fitting parameter, such empirical "mixing rules" are without merit for the prediction or detailed accounting of properties.

The series model can be extended to second order,

$$\eta_{ij} = \phi_i \eta_i + \phi_j \eta_j + x_{ij} \phi_i \phi_j. \tag{18}$$

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.*, $x_{ij} > 0$) can be a criterion for polymer miscibility[200]. In fact, however, Equation (18) has been shown to be completely incapable of describing the viscosity results of miscible rubber blends[180].

Since a flow field is capable of altering the configuration of polymer chains, it can, in principle, influence the phase morphology through changes in the nature of the segment interactions. The uncoiling of a macromolecule would presumably increase the number of unlike contacts. Flow-induced phase separation of polymers from solution is known to occur due to orientational crystallization[214,215]. This can also be brought about without crystallization due to the unfavorable contact energies promoted by chain uncoiling, as well as the relaxation provided the chain molecules by their precipitation from the flowing
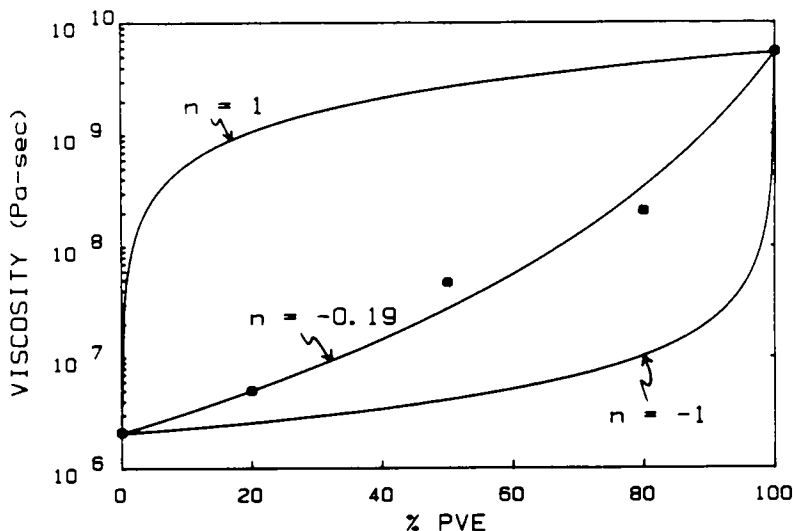

FIG. 10.—Newtonian viscosity (*i.e.*, measured in the limit of zero dynamic shear rate) for 1,2-BR/ IR mixtures. The solid curves represent the upper ($n = 1$) and lower ($n = -1$) bounds predicted by Equation (16), along with the calculated viscosity using a "best-fit" value of $n = -0.19$ respectively. Equation (17) would correspond to linear interpolation between the viscosities of the pure components[24,180].

solution[216]. Strain-induced phase separation in a graft copolymer was inferred from the resulting physical properties of the rubber[217], but direct probes of the morphology indicated that homogeneity was probably maintained during orientation[135]. If specific interactions can transpire between the components of a mixture, then an increase in the incidence of unlike contacts could promote miscibility. Experiments possibly demonstrating this effect have been reported[218].

2. *Crystallization.*—The intimate mixing associated with miscible rubber blends does not preclude formation of a crystalline phase when a crystallizable component is present. The primary effect of miscible blending is changes in the rate of crystallization[219,220]. Correlations claimed between the heat of fusion of a crystallizing component in a blend and the extent of phase homogeneity probably reflect such alterations in crystallization rate[221].

The melting behavior of a polymer can be affected by its presence in a miscible blend. The thermodynamic stability conferred upon the liquid state by formation of a miscible blend reduces the relative stability of the crystalline state and thus will lower the equilibrium melting point. By assuming equilibrium crystallization, the melting point depression can be related to the Flory interaction parameter[222,223]. For purely dispersive interactions between components, the largest change in melting temperature corresponds to ideal (athermal) mixing. The resulting suppression of the melting point, however, will be immeasurably small for polymers.

A series of IR/1,2-BR mixtures was isothermally crystallized for varying duration[99]. The measured melting temperatures, tabulated in Table II, were found to be equivalent within the precision of the data. These results are consistent with an interaction parameter of negligible magnitude in these blends. The pure IR attained about a 30% extent of crystallinity based on the measured heat of fusion. In blends the IR was significantly less crystalline, even after 37 days at $-9°C$. Any difference in IR crystallinity, however, between samples with 10% and 25% 1,2-BR was less than the precision in the measurement of the heat of fusion. For samples with greater than 25% 1,2-BR, interestingly no melting endotherms were detected, even though the instrumental sensitivity was more than sufficient if the reduction in crystallinity of the IR was simply proportional to the concentration of 1,2-BR.

TABLE II

CRYSTALLIZATION RESULTS FOR IR/1,2-BR BLENDS[97]

% IR	T_{melt}, °C	ΔH^a	Crystallinity[b]
100	4.6 ± 0.5	19. ± 1	29%
90	4.8 ± 1.2	11. ± 4	18%
75	4.3 ± 2.3	11. ± 3	17%
60	—	0	0%

[a] Joules per gram of IR after 37 days at $-9°C$.
[b] Based on a perfect heat of fusion of 64.0 J/g.

VI. HETEROGENEOUS RUBBER BLENDS

Although the great majority of elastomer blends are heterogeneous, the components may be referred to as compatible if some technically advantageous combination or compromise of properties can be realized from the blend. In fact, as described in this section, the ability to alter the morphology provides greater potential for performance benefits than can be realized with miscible polymer blends.

A. DISTRIBUTION OF COMPOUNDING INGREDIENTS

An important consideration in obtaining acceptable vulcanizate properties in a rubber blend is the development of a satisfactory network structure in each of the phases. During mixing, curatives more often make first contact with the lower viscosity phase, since it tends to occupy the outer regions of the flowing rubber mass (see Section VI, B, 1). This is consistent with reports that initially the curatives locate within the continuous phase[224], since the lower viscosity component tends to become the continuous phase. Generally, the details of the mixing scheme will affect the initial distribution of curatives. Since the levels of sulfur and accelerators typically employed in rubbers are below their solubility limits, curative migration can occur[225-228]. Due to the higher solubility of sulfur in unsaturated elastomers and the greater affinity of many accelerators for more polar rubbers[225,229-231], significant differences in crosslink density of the phases of rubber blends can result. In addition, if the rate of vulcanization varies considerably between the elastomers of the blend, depletion of the curatives in the faster curing component can cause curative migration and further the cure imbalance[2,232]. Obviously the problems encountered with curative imbalance are particularly significant when the components of a blend are more dissimilar.

Preblending of curatives into the respective elastomers at optimal concentrations prior to blending of the rubbers can improve the blend crosslink distribution[224], although usual practice is to incorporate the curative last in order to avoid prevulcanization (scorch) problems. Alterations in blend physical properties can sometimes be realized from the use of very short, high-temperature cure cycles[232]; however, the initial distribution of curatives obtained during the mixing stage becomes more critical. Cure imbalances can be overcome by the chemical modification of accelerators so that the respective solubilities in the components of a rubber blend will be more nearly equal[233-235] and by the direct attachment of curatives to the polymer chain[236-238].

Crosslinking by ionizing radiation can avoid complications with curative distribution, although uniform crosslink densities will not necessarily be achieved. Generally the extent of radiation crosslinking in a given component will not be significantly affected by the nature of the other component, at least for blends of the typical hydrocarbon rubbers. In principle, however, the penetrating power and crosslinking efficiency of the radiation can be influenced by the electron density and atomic numbers of the blend constituents[239].

The state of cure of the phases in a blend can be analyzed from changes in the magnitude of the damping peaks[240] and from freezing-point-depression measurements on swollen networks[241].

Along with the desirability of having a balanced crosslink density in the rubber phases, there also exists the requirement that, for mechanical integrity, the phases must be chemically bound to one another. The extent of interfacial crosslinks is sensitive to both the rate of vulcanization, as well as the specific cure systems employed[242-244]. When a monomeric component soluble in both polymers is present in a blend, the interface may be richer in this component than are the bulk phases. This results from the dilution in energetically unfavorable interactions between dissimilar polymer chains at the interface by virtue of the presence of the third component[246]. In principle, this effect could promote accumulation of curative at the interface.

A somewhat analogous method of promoting interfacial connectivity is by incorporation into the blend of a block or graft copolymer containing segments identical to, or at least miscible with, each of the rubber phases[246,247]. Provided the block lengths are sufficiently long relative to the corresponding homopolymer molecular weights, the copolymer additive will preferentially locate at the interface in a configuration whereby it is intimately mingled with each phase[248,249]. Because of their greater ability to favorably configure themselves, block copolymers are superior to grafts in this regard. The use of such a polymeric compatibilizer for ethylene–propylene–diene rubber (EPDM) blended with SBR has been described[250]. The main practical drawback to utilization of the approach in general is the added cost of the block copolymer.

The distribution of fillers and various processing aids in a multicomponent rubber stock can also be nonuniform, with a resulting influence on properties. Extensive investigations in this area have demonstrated the preferential uptake of carbon black by certain rubbers, with unsaturated polymers exhibiting the greatest affinity for carbon black[251].

During mechanical mixing of carbon black with unsaturated elastomers, sufficient interaction, primarily chemisorption, occurs to prevent any subsequent transfer of the black. If the method of mixing is less vigorous (*e.g.*, solution blending) or involves rubbers of higher saturation, transfer of the carbon black to phases with which it is more compatible can occur. The nonuniform distribution of carbon black can influence various properties such as, for example, the processing behavior. In a study in which both components had a high affinity for carbon black, it was found that blends viscosities were independent of the distribution of carbon black within the blend[252]. This distribution did, however, alter the elastic properties. Similarly it was determined that die swell, to some extent, could be correlated with the location of the carbon black in a rubber blend[253].

The oils, resins, and other compounding ingredients used in a rubber formulation can also, of course, have differing affinities for the phases of a blend. Both their nonuniform distribution, as well as postmixing migration, have been observed[2,254-256].

B. PROPERTIES

The performance of a heterogeneous rubber blend will represent a compromise of the components' properties provided the distribution of components

and of the compounding ingredients is uniform. The potential for the absence of such uniformity actually underlies much of the attraction of polymer blending.

1. *Rheology.*—Blending of rubbers is often utilized to obtain a better processing material. This improvement may consist of lowering the stock viscosity, or producing a material that is less prone to fracture or crumbling when subjected to flow. The elastic behavior, and the related phenomena of die swell and shrinkage, can also be altered by blending. Qualitatively, the expectation is that the processing behavior of the blend will be intermediate between that of the components. In fact, however, polymer blends can often display anomalous rheological properties. The viscosity of a blend may exhibit minima or maxima as a function of the composition. Very complex dependencies on composition have been observed (Figure 11)[257].

The morphology of a blend can rearrange in order to better accommodate the applied stresses. This principle of minimum energy dissipation[258] underlies the often encountered sheath/core configuration. Since in the vicinity of a wall of the containing vessel the velocity gradients tend to be highest, while at the core of a flowing polymeric material (through a die, on a roll mill, etc.) there is often plug flow, the lower viscosity component will tend to accumulate toward the surface of the polymer mass[85]. The result is a blend viscosity which can, in the limit, be as low as that of the lower viscosity component. Incorporation of only a few percent of EPDM to a fluoroelastomer[259] or of PDMS to an SBR[85] was found to significantly reduce steady state viscosities. This can be attributed to the lower viscosity, lubricious component taking up residence at the interface, giving rise to a lubricating layer and perhaps some interfacial slippage.

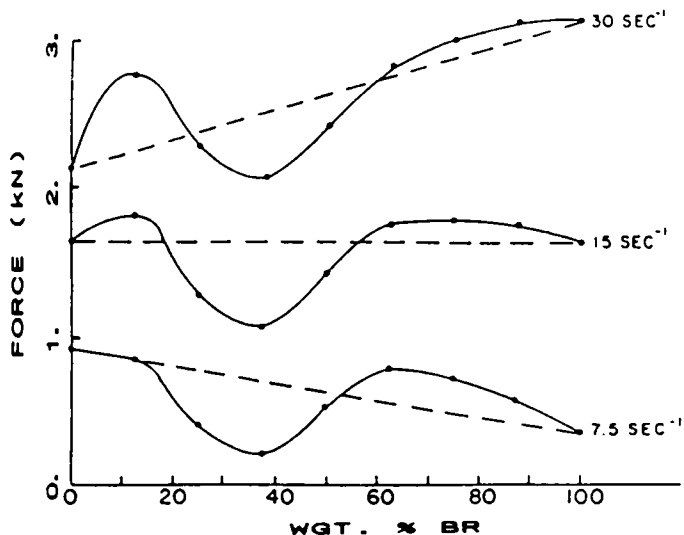The additional energy dissipated into dispersed particles when the contin-

FIG. 11.—Capillary die extrusion force (which, neglecting end effects, is proportional to the shear stress) at different nominal shear rates measured as a function of BR content in blends with NR[257].

uous phase is sheared is reported to contribute to an elevation in the resistance to flow[260]. Contrarily, it has also been suggested that the internal circulation occurring in the dispersed particles of a sheared blend may contribute to viscosity minima, the secondary flow giving rise to "drag reduction" [261].

There are available theoretical treatments which attempt to predict the viscosity of blends[262-264], but their utility is not obvious. An additional complication in predicting the rheology of industrially interesting rubber blends is the presence of a third phase of inextensible filler. As discussed above, the filler is often nonuniformly distributed in the various phases.

2. *Modulus.*—The obvious factors expected to govern the modulus of an elastomer blend are the individual component moduli and the nature of the blend morphology. In a heterogeneous blend, however, the details of the morphology do not generally exert much influence on the stress–strain response. While the expectation would be for the continuous phase to have more influence, the stress–strain response of EPDM/BR blends, at roughly comparable concentrations of both elastomers at least, was found to be unaffected by change in the BR domains from continuous to discrete[65]. When one component of the blend is present as discrete particles, in blends of NR with either SBR or BR[265] and in EPDM mixtures with BR[266], there was no observed effect of domain size on modulus. Similarly, the stress–optical coefficient has been reported to be insensitive to phase separation, although its magnitude is claimed to be related to the degree of phase interaction[267].

In carbon-black-reinforced elastomer blends, the distribution of filler can profoundly influence the modulus. Displayed in Figure 12 is the dynamic shear modulus measured for an elastomer blend in which the carbon-black distribution
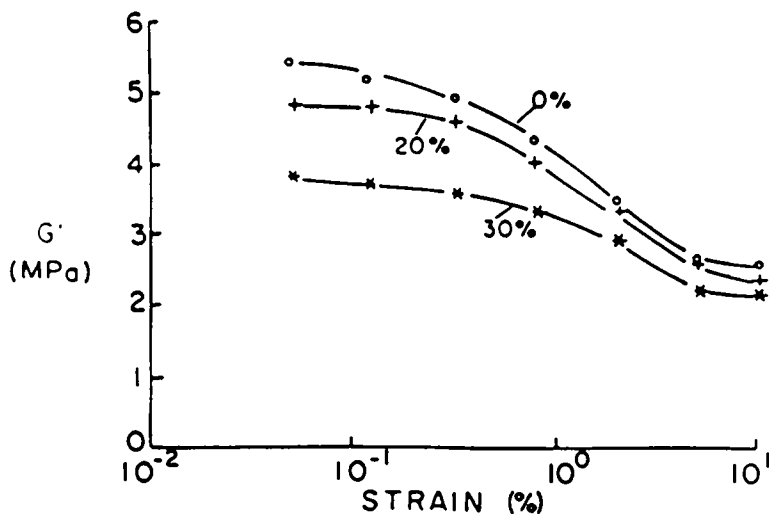
FIG. 12.—Dynamic-shear modulus measured for an SBR with 105 phr carbon black in which the indicated portion of the polymer was added as gum rubber during a second stage after incorporation of the carbon black into the initial rubber[268].

was systematically varied[268]. It can be seen that, particularly at the lower strains where the carbon-black network structure dominates the stiffness properties, an increase in the nonuniformity of this filler distribution results in a lower stock modulus. This indicates that the transfer of a portion of the carbon black from one phase would lower its modulus proportionally more than the increase in modulus of the phase with the higher carbon-black concentration. The effect of carbon-black distribution on modulus is thus related to the nonlinear dependence of rubber modulus on carbon-black loading[269,270].

   3. *Transport properties.*—The transport properties of polymer blends are of interest both for the practical application of blends in air retention, vapor resistance, permeation selectivity, etc., as well as the insight into the morphology of the blend which can be gained from study of the penetration of small molecules into the structure. Measurement of the effect of blend composition on permeability in various rubbers has been described[271]. The passage of vapor through a rubbery material entails dissolution of the gas into the rubber, molecular diffusion, and subsequent evaporation of the gas from the other side of the specimen. The kinetics of this process can usually be described as Fickian, whereby the concentration of the vapor in the rubber is proportional to the external pressure (Henry's Law), and the flux of this gas is proportional to its concentration gradient (Fick's Law). The permeability coefficient, P, is thereby expressed as the product of two proportionality constants, the Henry's Law solubility coefficient and the diffusion constant. The diffusion constant can vary with penetrant concentration, while at higher pressures, the solubility coefficient may become pressure dependent. Heterogeneous blends (for example, rubber-modified polyethylene,[272]) have been reported to possess synergistic permeability behavior, although most exhibit a permeability that is intermediate between those of the components. Attempts to model the transport properties of blends use some formulation of parallel and series models as their basis. If the continuous phase is the more permeable, a parallel configuration represents the limiting behavior, with the dispersed phase effecting a more tortuous path of the penetrant. The series model serves as the limiting case when the dispersed phase exhibits the greater permeability. These extremes can be combined to obtain a more general expression for the permeability in heterogeneous blends[273]. More extended structures, particularly lying in a stacked or lamellar configuration, can lead to reduced permeability due to the more tortuous path that must be taken by penetrants. Models for transport phenomena in such morphologies have been advanced[274].

   In elastomers, conductive or semiconductive electrical properties result from the presence of carbon black. Blending of elastomers with different affinities for black provides an opportunity to control the state of aggregation and connectivity of the carbon black, and thereby influence the electrical conductivity. Displayed in Figure 13 is the electrical conductivity measured for blends of CR with various rubbers[275]. It can be observed that conductivities can be achieved in these blends that exceed those of the pure components. This is due to increased agglomeration of carbon black in these immiscible blends. Carbon black tends to redistribute when mixed into blends, particularly when it has a low affinity for one of the phases. This can result in an accumulation of carbon black at the interface[187] and consequently higher electrical conductivity. Blends of rubbers
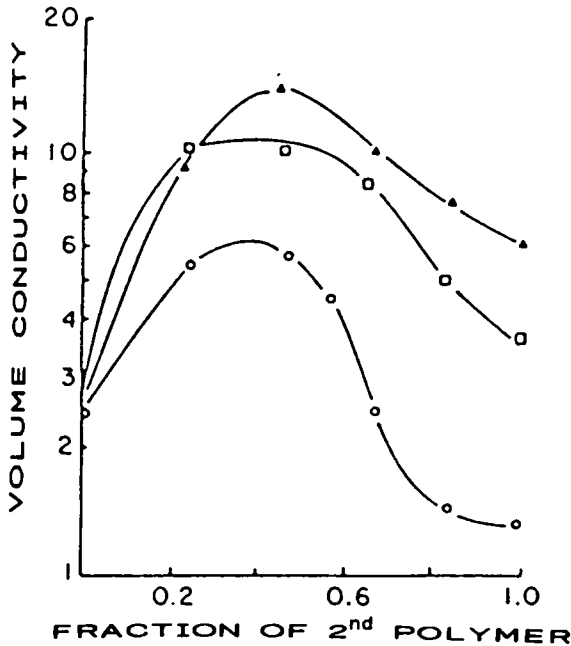
FIG. 13.—Volume conductivity of blends of CR with chlorinated butyl ($\triangle \triangle \triangle$), nitrile ($\square \square \square$), and natural rubber (O O O)[276].

with similar affinity for carbon black (*e.g.*, SBR/NR) do not exhibit this synergism.

4. *Adhesion and tack.*—Acceptable levels of both the (cocure) adhesion and the autoadhesion (or tack) of rubber stocks can often be obtained only through the blending of rubbers. Adhesion is unlike many properties in that it is essentially a surface phenomenon; accordingly, the adhesion and tack performance of a blend reflect only the composition at the surface. This provides for the possibility of obtaining an elevated level of tack or cured adhesion without necessarily requiring the use in a blend of a high concentration of a particular rubber possessed of the desired adhesion properties. Whether this is realized in practice depends upon the method by which the blend is prepared as well as the rheological characteristics of the blend constituents.

The tack of a series of blends of NR with various synthetic rubbers were reported to parallel the NR content[276]. Similarly, blends of NR and SBR exhibited autoadhesion that increased monotonically with NR concentration, with a maximum, however, observed when the NR was 80% of the total polymer[277]. This synergism was attributed to the optimal green strength of such a composition. In general, green strength will affect autoadhesion only when the latter is limited by the energy required for rupture of the bonding. Often the ability of the plied surfaces to fuse together is the controlling variable in tack measurements[98,99]. When BR was blended with a BR containing grafted isopropylazodicarboxylate groups (this latter polymer exhibits very high autoadhesion[278]), high tack in

the blend stocks was only obtained when the copolymer rubber constituted the continuous phase[135]. The behavior described in these examples suggests surface compositions that must at least approximately reflect that of the bulk.

When the components of a blend differ widely in viscosity, the lower viscosity rubber may have become concentrated at the surface during processing in order to minimize viscous energy dissipation (Section VI, B, 1). In Table III are shown the measured tack from blends of NR with SBRs of different viscosity[279]. Greater levels of autoadhesion are obtained when the NR has the lower relative viscosity, since it was then found to be present in higher concentration at the surface of the rubber sheets. A similar demonstration of the influence of relative viscosities on the spatial distribution of components in a blend is seen in the effect on autoadhesion of selective incorporation of carbon black into the components of a blend (Table IV)[279]. By the same principle. nonadhering rubber sheets were obtained by incorporating a few percent of PDMS into NR and SBR stocks, the PDMS evidently taking up residence at the surface[280].

An interesting consequence of nonrandom surface compositions is seen (Table V) in the adhesion of blends composed of NR, SBR, and a terpolymer consisting of styrene, butadiene, and 3 mole% of N-isobutoxymethylacrylamide (IBMA)[279]. When only a small fraction of NR is present in blends with SBR alone, the tack is low. Replacing a portion of the SBR with the IBMA–SBR terpolymer effects a large increase in autoadhesion; nevertheless, blends of SBR and IBMA–SBR without NR have negligible autoadhesion. The IBMA–SBR itself is devoid of tack, yet its presence in SBR/NR blends promotes high autoadhesion. This seeming paradox results from the lack of a correspondence between the surface and bulk compositions. During mixing at elevated temperatures, IBMA–SBR undergoes a condensation reaction leading to coupling of the IBMA moieties. This crosslinking markedly increases the viscosity of the SBR phase, so that during processing, the SBR locates in the core of the test sheets. The NR constitutes most of the surface phase, so that its high autoadhesive capacity is most fully taken advantage of upon incorporation of IBMA–SBR into the blend.

While NR is usually selected to impart autoadhesion to a blend, both because of its superior performance in this regard, as well as its general utility and low cost, other elastomers can be employed for this purpose. For example, in blends with chlorobutyl rubber, it has been reported polychloroprene produces a larger increase in tack than does NR[281].

TABLE III

AUTOADHESON OF BLENDS OF NR WITH SBRs OF DIFFERENT VISCOSITY[279]

SBR	Mooney viscosity[a]	Autoadhesion, J/m^2
Synpol 8107[b]	25	1010
FRS-1502[c]	52	2600
FRS-179[c]	80	4390

[a] ML 1 + 4 (100°C).
[b] Synpol Inc.
[c] Firestone Tire and Rubber Co.

TABLE IV

EFFECT OF FILLER DISTRIBUTION ON AUTOADHESION[279]

Mix cycle[a]:			
initially	at 1 min	at 2 min	Tack, J/m^2
SBR	filler	NR	1120
NR	filler	SBR	250
SBR, NR	filler	—	1010

[a] 30/70 NR/SBR blends with 50 phr HAF carbon black mixed in a Brabender mixer.

An example of the use of blending to improve cocure adhesion is when highly unsaturated rubbers must be bonded to materials of low unsaturation. Good adhesion between blends of IR, BR, and chlorinated butyl rubber and blends of EPDM and butyl rubber was obtained only when the level of chlorinated butyl exceeded 75%[282]. A reduction in the level of chlorinated butyl rubber, and an increase in polyisoprene, on the other hand, gave superior adhesion to SBR. The magnitude of the adhesion in all cases was found to be influenced by the nature of the cure system. The adhesion of epichlorohydrin rubber to unsaturated rubbers was accomplished by blending the epichlorohydrin with 25–50 phr of polychloroprene[281]. There are also prescriptions for improving the metal adhesion of rubbers by blending[283–285]. Although few studies investigate the surface composition, it undoubtedly has a large role in determining the adhesion obtained with rubber blends.

5. *Hysteresis.*—Lower hysteresis may be achieved in a rubber stock by various methods (*e.g.*, reduced carbon-black loading or higher crosslink density) which, however, are accompanied by a sacrifice of other aspects of performance. Blending of elastomers affords a means to achieve lower hysteresis with a better compromise of other properties. The hysteresis of a blend is often found to be lower than the weighted average of the components, particularly in filled systems with a nonuniform carbon-black distribution. The phase with the lower carbon-

TABLE V

AUTOADHESION OF NR/SBR BLENDS CONTAINING IBMA–SBR[279]

Composition, phr			
NR	SBR	IBMA–SBR[a]	Autoadhesion, J/m^2
60	40	—	1400
30	70	—	300
30	40	30	1050
20	40	40	670
—	70	30	0

[a] Emulsion random terpolymer consisting of styrene/butadiene/N-(*iso*-butoxymethyl)acrylamide (23/70/7 by weight).

black loading will have both reduced modulus and hysteresis. Particularly when this softer phase is the continuous phase, a low blend hysteresis may result[134]. The origin of this effect can be seen by introducing a nonuniform distribution of carbon black in a single component stock by delaying addition of a portion of the polymer until after the carbon black has been well dispersed in the initial portion. The hysteresis measured on a series of compounds prepared by this method is displayed in Figure 14, along with the concentration weighted sum of the hysteresis generated in two stocks with the full carbon-black loading and without carbon black, respectively[268]. Most of the hysteresis reduction accompanying a nonuniform distribution of carbon black can be attributed to the nonlinear relationship between hysteresis and carbon-black loading, particularly at very high loadings.

Lower hysteresis in the form of tire treads with reduced rolling resistance has been obtained by the addition of chlorobutyl rubber (which itself is relatively hysteretic) to NR/BR blends[286,287]. By introduction of a nonuniform distribution of the carbon black into these blends, further reductions in rolling loss can be realized[288].

6. *Failure properties.*—Improved failure properties can result from the blending of elastomers, including attainment of a level of performance that exceeds that of either pure component. An important aspect of the structure of a rubber blends is the nature of the interphase bonding. Although even the presence of voids (or a completely unbound dispersed phase) can toughen a material by reducing the stress concentration through blunting of the crack tip,
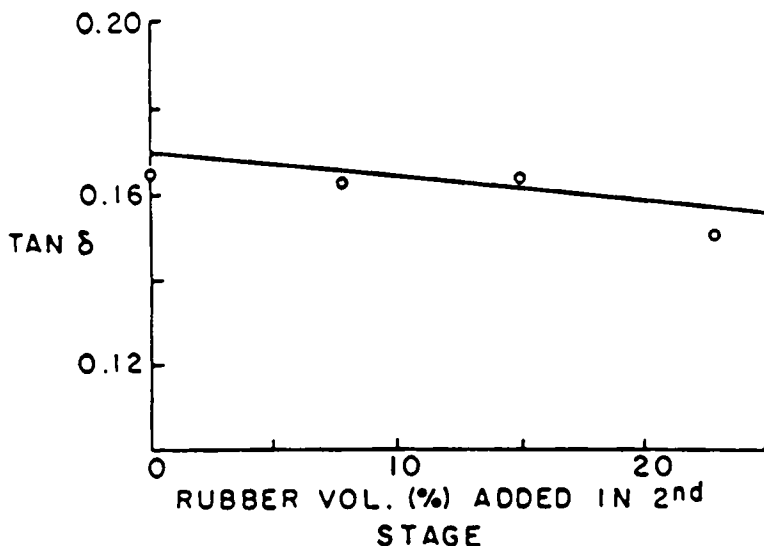

FIG. 14.—The ratio of the dynamic loss and elastic moduli for an SBR with 105 phr carbon black, in which a portion of the rubber was added after the black was mixed into the stock. The agreement between the experimental data (O O O) and the loss tangent calculated from the hysteresis measured independently for the two rubbers (—) suggests minimal transfer of filler[268].

the mechanical integrity of an intercrosslinked morphology will usually lead to superior performance. In blends of SBR and chlorobutyl rubber, for example, a three-fold increase in fatigue life was obtained by the introduction of interphase crosslinking[267]. Similarly, providing for interfacial coupling improved the tensile strength of EPDM/silicone-rubber blends[289]. The relative magnitude of the interfacial bonding compared to the cohesive strength of the rubbers themselves can influence performance. For example, blends of EPDM and BR exhibited greater tear strength than either pure component when the interphase bonding was weak enough to promote deviation in the direction of crack propagation[290]. Strong interfacial bonding, however, resulted in tear resistance intermediate between that of the individual rubbers because the cracks were not deviated but proceeded through the particle. Blends of cis-1,4-BR and syndiotactic 1,2-BR prepared in a proprietary fashion are reputed to have exceptional resistance to tearing and cracking due to interpenetration of the phases[291]. When scrap rubber is blended with another elastomer, it is usually found that tensile strength and fatigue life are poor, primarily due to an absence of interphase crosslinking. When additional carbon black is incorporated into the blend, however, this interfacial adhesion increases along with substantial improvement in ultimate properties[292].

In general, a higher strength continuous phase will give rise to a higher strength blend. For example, when a nonuniform distribution of carbon black is present, greater tear resistance is found for 1,4-BR/NR and SBR/NR blends when the reinforcing filler is deposited principally in the continuous phase[134]. Similar effects on the cut growth resistance of rubber blends have been reported[293]. When cocontinuity exists in NR blends, the expectation is that greater strength will be obtained when the reinforcing filler is present in the other component, since the ability of NR to crystallize upon extension confers a measure of self-reinforcement that is lacking in noncrystallizing rubbers. On the other hand, a disproportionate loading of carbon black in the NR phase in blends with 1,4-BR yielded better properties due to improved carbon-black dispersion[294].

Blending of unsaturated rubbers with, for example, EPDM, is an established method of obtaining resistance to ozone cracking without the use of staining or expensive antiozonants[295,296]. A balanced distribution of filler is reported to provide the greatest level of ozone resistance[297].

VII. SUMMARY

The thermodynamic and kinetic factors governing the morphology of miscible polymer blends have been much investigated. While conceptually straightforward, modern theories of mixtures are more difficult to implement than the simple lattice theories which consider only molecular volumes. Particularly with regard to rubber mixtures, significant performance advantages associated with miscibility remain to be demonstrated. Phase separated blends are more complex; the factors controlling their structure development are difficult both to elucidate and to control. Nevertheless, extensive applications have been found for such blends. Their utilitization will likely continue to burgeon, particularly as more

attention becomes focussed on the details of the spatial distribution of the domains in heterogeneous mixtures.

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