

Semi- and Fully Interpenetrating Polymer Networks Based on Polyurethane–Polyacrylate Systems.

II. Polyurethane–Poly(methyl Acrylate) Semi-1- Interpenetrating Polymer Networks

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Synopsis

A series of semi-1-IPNs based on polyurethane networks and poly(methyl acrylate) were prepared, and their properties and morphologies investigated. All the materials showed substantial phase separation, but the phase sizes were orders of magnitude smaller than those observed for blends of the same linear polymers. The effects of the isocyanate/hydroxyl ratio used in the preparation of the polyurethane, of the molecular weight of the linear polymethyl acrylate component, of the overall composition, and of the molecular weight between crosslinks in the polyurethane networks were investigated. Stress–relaxation experiments were conducted over a range of temperatures and master curves were produced for both components of the semi-1-IPNs and for a semi-1-IPN containing 40 wt% polyurethane. It was found that both the components obeyed a WLF type of equation, but that the semi-1-IPN only showed this type of behavior over a limited temperature range. Several reinforcement theories were applied to experimental dynamic storage modulus data. The closest fit was given by the Davies equation and by the logarithmic rule of mixing. By changing the exponent in the Davies equation to 1/10, a close fit was found. Application of a modified Takayanagi model indicated that these semi-1-IPNs showed some dual phase continuity when the poly(methyl acrylate) composition was relatively high.

INTRODUCTION

An interpenetrating polymer network (IPN) consists of two networks, one of which at least has been synthesized and/or crosslinked in the presence of the other. IPNs have been the subject of a number of reviews.^{1–4} If only one of the two polymers is crosslinked, the product is termed a semi-IPN. For a given system, two semi-IPNs must be distinguished. When the first synthesized material, polymer 1, is crosslinked, a semi-IPN of the first kind results and is referred to as a semi-1-IPN. If polymer 1 is linear and polymer 2 crosslinked, the product is a semi-IPN of the second kind—a semi-2-IPN.

Several studies of semi-IPNs have been reported. Klempner et al.⁵ have investigated the properties and morphologies of semi-1 and semi-2-IPNs of a polyurethane–polyacrylate system. Kim et al.⁶ and Allen et al.^{7–11} have reported detailed studies of polyurethane–poly(methyl methacrylate) semi-IPNs. A study of the morphology of SBR–polystyrene semi-IPNs has also been reported.¹²

In this paper various aspects of the morphologies and properties of semi-1-IPNs formed from a polyurethane¹³ based on a commercial prepolymer, Adiprene L-100, and poly(methyl acrylate) are discussed.

EXPERIMENTAL

Preparation of Materials

The syntheses of the polyurethane networks have been described¹³ previously. In brief, two polyurethanes are involved. The first, system 1, is based on Adiprene L-100, butane-1,4-diol, and trimethylol propane, while system 2 is prepared from toluene diisocyanate, poly(propylene glycol) and trimethylol propane.

To prepare the semi-IPNs, all the reactants were dissolved in the required amount of destabilised methyl acrylate. Dibutyl tin dilaurate (2 wt%) was added as polyurethane promoter. The solutions were degassed and poured into molds¹³ and maintained at 20°C for 24 h to allow the polyurethane formation to occur. The temperature was then raised to 60°C for 18 h followed by a further 6 h at 90°C to achieve the poly(methyl acrylate) polymerization which was initiated with AIBN (0.2% w/w).

The polyurethane homopolymer networks were prepared as in the first stage and the inhibited methyl acrylate was removed slowly under vacuum. The poly(methyl acrylate) homopolymer was also prepared in the same type of mold under the conditions described above.

The blends were prepared by solvent casting tetrahydrofuran solutions (3% w/v) of poly(methyl acrylate) and a linear polyurethane synthesized using Adiprene L-100 and butane-1,4-diol using the same conditions as for the first stage of the semi-IPN preparation.

All materials were placed under vacuum at 20°C for at least 10 days prior to use.

Techniques

The dynamic mechanical data were obtained using a Rheovibron dynamic viscoelastometer (Model DDV-II-B) at a heating rate of approximately 10°C/min. Both the stress-strain and the stress-relaxation data were obtained with a Howden tensometer. In the former case, the strain rate was 2.5 cm/min and in the latter the experimental strain was set at a strain rate of 38 cm/min. The strain in both cases was defined as change in length over the original length.

The swelling experiment, which was conducted to determine \bar{M}_c , the average molecular weight between crosslinks, has already been described.¹³

The longitudinal sonic velocities V_L were determined¹⁴ with a Morgan Pulse Propagation Meter (Model PPM-5R).

Densities, at 23°C, were measured using a Davenport density gradient column.

RESULTS AND DISCUSSION

Solvent cast blends containing 20, 40, and 60 wt% linear polyurethane ($\bar{M}_n = 16,000$ g/mol) and poly(methyl acrylate) ($\bar{M}_n = 150,000$ g/mol) showed gross incompatibility as expected from solubility parameter δ considerations. The polyurethane has an experimentally determined¹³ value of 19.2×10^3 (J/m³)^{1/2} and the poly(methyl acrylate) a value of 20.7×10^3 (J/m³)^{1/2}.¹⁵ Using the Krause method¹⁶ and these values to calculate interaction parameters, it was found that

TABLE I
Variation of Dynamic Mechanical Properties (20°C; 11 Hz) with NCO:OH Ratio

NCO:OH	E' (MN/m ²)	E'' (MN/m ²)	$\tan \delta$
1.1	38.1	22.8	0.60
1.3	31.5	19.8	0.63
1.5	26.2	17.5	0.67

the polymer-polymer interaction parameter was 0.012 and the interaction parameter at the critical point was 0.006, indicating incompatibility over at least part of the composition range.

Semi-1-IPNs containing 40 wt% polyurethane, but with the polyurethane having a range of NCO:OH ratios, were prepared. Table I presents the dynamic mechanical results, and Figure 1 shows the stress-strain behavior of these semi-1-IPNs. From Table I and Figure 1 it is clear that there is a decrease in the dynamic storage modulus E' and the initial modulus of the materials with increasing NCO:OH ratio caused by the increasing looseness of the polyurethane network as the NCO:OH ratio increases. The dynamic loss modulus E'' also falls, but less rapidly, causing a slight rise in $\tan \delta$.

Allen et al. have reported⁷ NMR studies on polyurethane-poly(methyl methacrylate) semi-IPNs with varying NCO:OH ratios. The polyurethanes with low NCO:OH ratios showed a lot of polyether and extended polyether fragments, indicating that the network had loose ends. They argued that these fragments plasticized the semi-IPNs, causing a reduction in modulus. The same phenomenon may occur at high ratios. Swelling experiments¹³ confirmed that \bar{M}_c varied with NCO:OH ratio (see Table II). The lowest \bar{M}_c was obtained at a ratio of 1.1. In all subsequent materials this ratio was used.

The dynamic mechanical results for semi-1-IPNs containing 40 wt% polyurethane, but prepared using different concentrations of AIBN, are shown in Table III. E' decreases with increasing initiator concentration, indicating that the molecular weight of the linear poly(methyl acrylate) component is playing a role. Equivalent bulk-polymerized poly(methyl acrylate) samples had the molecular weights and polydispersities shown in Table IV. The molecular weights of the poly(methyl acrylate) polymerized in the presence of polyurethane may not equal those of the bulk-polymerized samples, but the trend is probably the same despite the likelihood of some transfer to polyurethane resulting in grafting.

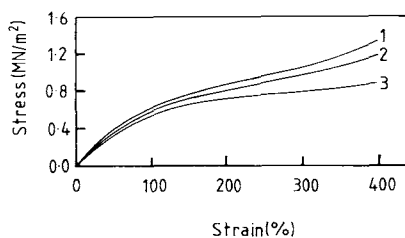


Fig. 1. Stress-strain curves at 20°C for semi-1 polyurethane-poly(methyl acrylate) IPNs containing 40 wt% polyurethane: (1) NCO:OH 1.1; (2) NCO:OH 1.3; (3) NCO:OH 1.5.

TABLE II
 Variation of \bar{M}_c with NCO:OH Ratio

NCO:OH	\bar{M}_c (g/mol)
1.0	10,000
1.1	9,700
1.3	10,100
1.5	11,600

 TABLE III
 Effect of Initiator Concentration on Dynamic Mechanical Properties (20°C; 11 Hz) of 40 wt% Polyurethane-Poly(methyl Acrylate) Semi-1-IPNs

AIBN (wt %)	E' (MN/m ²)	E'' (MN/m ²)	$\tan \delta$
0.2	38.1	22.8	0.60
0.4	33.5	20.4	0.61
0.6	29.6	18.3	0.62

To prepare semi-IPNs with different compositions, the polyurethane precursors were initially dissolved in different amounts of methyl acrylate. With decreasing amounts of methyl acrylate, the polyurethanes would have lower \bar{M}_c values,¹³ but, to keep as near as possible constant \bar{M}_c values, a chain extender, butane-1,4-diol, was used. An \bar{M}_c value of approximately 6400 g/mol was chosen.

Figure 2 shows $\tan \delta$ -temperature plots of three semi-1-IPNs of differing composition and of the corresponding homopolymers. The polymethyl acrylate glass transition has been studied by dynamic mechanical analysis by various¹⁶⁻¹⁹ authors. The glass transition temperature T_g was found to be 30°C at 11 Hz and the activation energy of this transition was 234 kJ/mol.

The semi-1-IPNs show the glass transitions of both components, which is typical of incompatible systems. The polyurethane glass transition, at about -20°C, gains in prominence and shifts to slightly higher temperatures as the polyurethane content increases. Compared to the polyurethane homopolymer T_g , all these transitions are shifted to higher temperatures, indicating some segmental mixing of the two components. This shift did not occur in the blends of linear poly(methyl acrylate) with the linear polyurethane. Compared with the poly(methyl acrylate) homopolymer T_g (30°C), the second transitions of the semi-IPNs show no shift, but the half peak width does increase as the polyure-

 TABLE IV
 Molecular Weights and Polydispersities of Bulk Polymerized Poly(methyl Acrylate) Using Different Initiator Concentrations

AIBN (wt %)	$\bar{M}_n \times 10^{-5}$ (g/mol)	$\bar{M}_w \times 10^{-5}$ (g/mol)	\bar{M}_w/\bar{M}_n
0.2	1.51	8.11	5.40
0.4	1.00	4.21	4.21
0.6	0.52	1.30	2.28

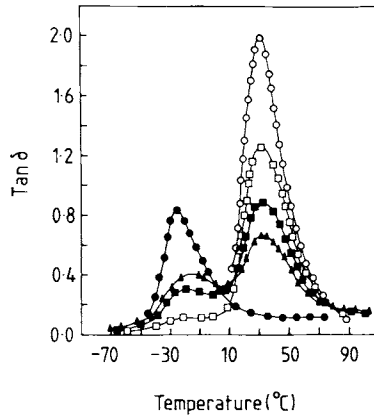


Fig. 2. $\text{Tan } \delta$ -temperature plots (11 Hz) of the polyurethane network (\bullet), poly(methyl acrylate) (\circ), and the semi-1-IPNs containing 20 (\square), 40 (\blacksquare), and 60 (\blacktriangle) wt% polyurethane.

thane content increases, which, again, may be taken as evidence of some mixing of the components.

The E' -temperature plots presented in Figure 3 show a slight shift to higher temperatures and a broadening of the lower temperature transition as the poly(methyl acrylate) content is increased. The position of the higher temperature transition is much less affected. E'' -temperature plots (Fig. 4) again show the shift to higher temperatures of the transition corresponding to the polyurethane-rich phase, indicating some mixing. The second transition is not shifted and remains as a distinct peak, as opposed to becoming a mere shoulder, which is often the case with partly miscible systems.

Figure 5 shows the stress-strain curves, up to 400% strain, for the three semi-1-IPNs and the corresponding homopolymers. They all show rubbery behavior. For the semi-1-IPNs, as the amount of poly(methyl acrylate) increases, the initial modulus also increases, but at strains greater than about 190% the order is reversed. Also, the stresses at 300% strain (see Table V) for the semi-IPNs containing 40% and 60% polyurethane, respectively, are in excess of that of the

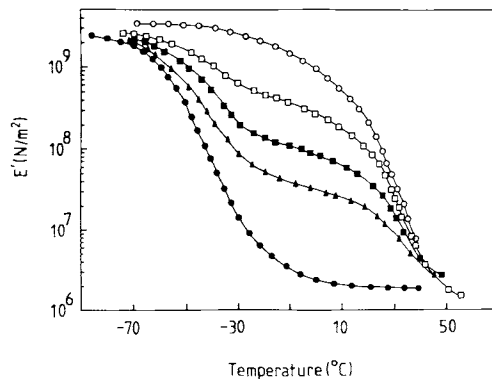


Fig. 3. E' -temperature plots (11 Hz) of the polyurethane network (\bullet), poly(methyl acrylate) (\circ), and the semi-1-IPNs containing 20 (\square), 40 (\blacksquare), and 60 (\blacktriangle) wt% polyurethane.

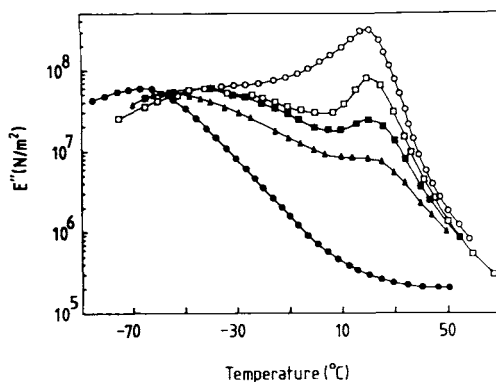


Fig. 4. E'' -temperature plots (11 Hz) of the polyurethane network (●), poly(methyl acrylate) (○), and the semi-1-IPNs containing 20 (□), 40 (■), and 60 (▲) wt% polyurethane.

poly(methyl acrylate) network itself. This enhanced reinforcement may occur as a result of more grafting as the polyurethane content increases. A plot of initial modulus versus composition shows two linear regions of distinctly different slope which intersect at around 25–30% polyurethane content, implying that, at polyurethane compositions lower than this, the poly(methyl acrylate) component constitutes a continuous phase.

Further evidence about the phase continuity of the components may be obtained by measuring the longitudinal sonic velocity as a function of composition. From Figure 6, it is clear that V_L and composition are linearly related for polyurethane contents of at least 20%, indicating²⁰ that the poly(methyl acrylate) component is present as a discrete phase in that range of composition. Kim et al.⁶ studied the density–composition behavior of polyurethane–poly(methyl methacrylate) IPNs and semi-1-IPNs. They found values larger than predicted by simple additivity for the IPNs, but not for the semi-1-IPNs. They claimed⁶ the increase in density was caused by extensive mixing of the components and that a decrease in density arose when a much coarser morphology existed. For

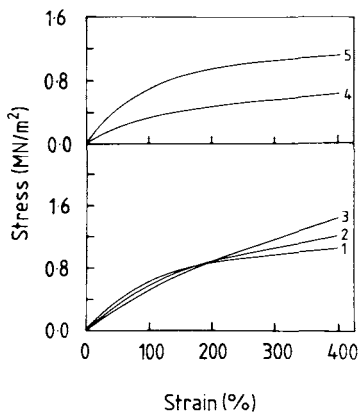


Fig. 5. Stress-strain curves at 20°C for the polyurethane network (4), poly(methyl acrylate) (5) and the semi-1-IPNs containing 20 (1), 40 (2), and 60 (3) wt% polyurethane.

TABLE V
 Stress-Strain Data at 20°C

Polyurethane (wt %)	Stress at 100% strain (MN/m ²)	Stress at 300% strain (MN/m ²)
0	0.72	1.06
20	0.68	1.00
40	0.60	1.10
60	0.54	1.20
100	0.33	0.57

the polyurethane-poly(methyl acrylate) semi-1-IPNs in this study, density values slightly less than additive were recorded (see Fig. 7).

The stress-relaxation of a semi-1-IPN containing 40 wt% polyurethane and of the corresponding homopolymers were measured at 100% strain over the temperature range 20–70°C. Reduced relaxation modulus, $E_r(t)_{red}$, master curves at 20°C (Fig. 8) were constructed and the WLF constants^{21,22} for each material were determined²³ and reported in Table VI. Both the polyurethane and poly(methyl acrylate) obey a WLF type equation very well, but the semi-1-IPN deviates slightly from this type of behavior above 40°C. Sperling and Thomas²⁴ have studied the stress-relaxation of poly(ethyl acrylate)-poly(methyl methacrylate) IPNs over a wide temperature range. The WLF equation was found to fit reasonably well.

\bar{M}_c is an important factor in controlling the morphology and properties of semi-IPNs. Donatelli et al. have reported²⁵ on the effect of crosslink density in IPNs and semi-IPNs on morphology and mechanical behavior concluding that, in general, increasing the crosslink density of the first formed polymer network produces finer phase domains.

To study the effect of \bar{M}_c on properties, some system 2 semi-1-IPNs were prepared by altering the diol-to-triol ratio. The three samples all contained 20 wt% polyurethane with an NCO:OH ratio of 1.1. The \bar{M}_c values were 6900, 3800, and 1700 g/mol. Although only one composition, near one end of the range, was chosen for investigation, it was believed that any trends observed would be typical of any composition.

The stress-strain data shown in Figure 9 illustrates how much \bar{M}_c influences behavior as the material becomes significantly stiffer as \bar{M}_c decreases. This is especially evident at high strains, illustrating that at a composition of 20% polyurethane this network component is still continuous.

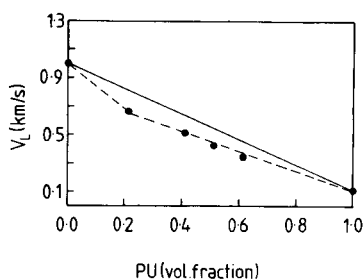


Fig. 6. V_L -composition plot (20°C) of polyurethane-poly(methyl acrylate) semi-1-IPNs.

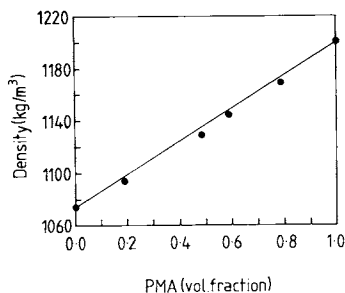


Fig. 7. Density-composition plot (23°C) of polyurethane-poly(methyl acrylate) semi-1-IPNs.

Figures 10-12 show $\tan \delta$, $\log E'$, and $\log E''$ vs. temperature plots, respectively, for the homopolymers and the three semi-1-IPNs. The polyurethane presented is the one with an \bar{M}_c value of 3800 g/mol. The polyurethane network and poly(methyl acrylate) glass transitions occur at -23°C and 28°C , respectively, with the polyurethane showing relatively high damping in the rubbery region. For the three IPNs there are two transitions clearly apparent in both the E' and E'' vs. temperature plots, indicating the phase separated nature of these materials. The lower temperature transition, which is not particularly clear in the $\tan \delta$ -temperature plot (Fig. 10), is the result of a polyurethane-rich phase. The evidence for some mixing with poly(methyl acrylate) component is that for all three IPNs the transition is shifted to higher temperatures, and this shift increases as the \bar{M}_c value decreases. This is particularly clear in Figure 11. However, the higher temperature transition is not shifted with respect to the pure poly(methyl acrylate) transition. Also, the peak widths at half-height remain constant. This can be interpreted in terms of the transition arising from a pure poly(methyl acrylate) phase.

Many theories²⁶ have been developed to relate the modulus of a multiphase system to its composition. Most assume that the adhesion between the phases is perfect and that the dispersed phase is uniformly distributed within the matrix.

Smallwood²⁷ and Guth²⁸ suggested the following relation for the reinforcement of rubber by carbon black:

$$G = G_1(1 + 2.5V_2 + 14.1V_2^2) \quad (1)$$

G and G_1 are the shear moduli of the system and matrix, respectively. V_2 is the

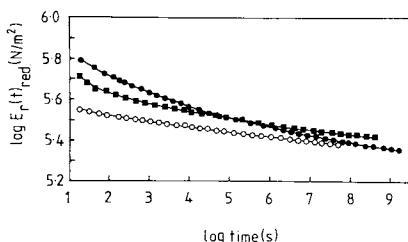


Fig. 8. $\log E_r(t)_{\text{red}}$ -log time plots (20°C) for a polyurethane-poly(methyl acrylate) semi-1-IPN containing 40 wt% polyurethane (■) and for the polyurethane network (O) and the poly(methyl acrylate) (●) homopolymers.

TABLE VI
WLF Constants^a for the Semi-1-IPN and the Homopolymers

Material	C_1	C_2
Polyurethane	16	202
Semi-1-IPN	13.5	124
Poly(methyl acrylate)	12.7	87

^a See Refs. 21-23.

volume fraction of the filler. For two components, Kerner²⁹ derived eq. (2) for shear modulus:

$$\frac{G}{G_1} = \frac{(1 - V_2)G_1 + (\alpha + V_2)G_2}{(1 + \alpha V_2)G_1 + \alpha(1 - V_2)G_2} \quad (2)$$

G_2 is the elastic shear modulus of the inclusions. α is a function of ν_1 , the matrix Poisson ratio:

$$\alpha = 2(4 - 5\nu_1)/(7 - 5\nu_1) \quad (3)$$

Kerner's theory also requires that the inclusion particles be spherical in the mean.

The model proposed by Budiansky³⁰ is based on isolated spherical inclusions set in an infinite matrix which is also a composite material. For two-phase systems, this equation is expressed below:

$$\frac{V_1}{1 + \epsilon(G_1/G - 1)} + \frac{V_2}{1 + \epsilon(G_2/G - 1)} = 1, \quad (4)$$

$$\epsilon = \frac{2(4 - 5\nu)}{15(1 - \nu)}, \quad (5)$$

ν is the Poisson's ratio of the composite and V_1 and V_2 are the volume fractions of the components.

Davies^{31,32} has proposed the following relation:

$$G^{1/5} = V_1 G_1^{1/5} + V_2 G_2^{1/5} \quad (6)$$

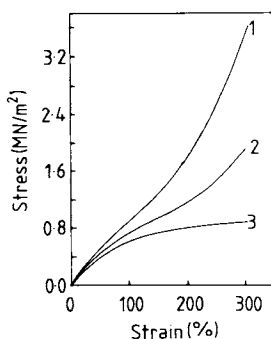


Fig. 9. Stress-strain curves at 20°C for system 2 semi-1-IPNs containing 20 wt% polyurethane and with polyurethane \bar{M}_c values of 1700 (1), 3800 (2), and 6900 (3) g/mol, respectively.

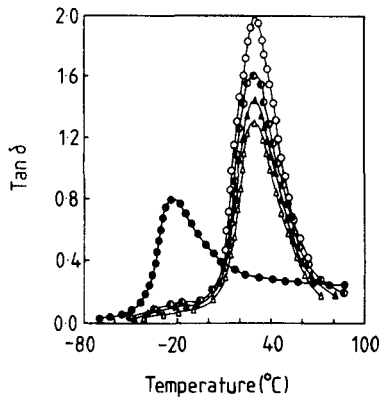


Fig. 10. $\tan \delta$ -temperature plots (11 Hz) of the polyurethane network (\bullet) with an \bar{M}_c value of 3800 g/mol, poly(methyl acrylate) (\circ), and of system 2 semi-1-IPNs containing 20 wt% polyurethane and with polyurethane \bar{M}_c values of 1700 (Δ), 3800 (\blacktriangle), and 6900 (\bullet) g/mol, respectively.

It has been suggested that the Davies equation is best suited to morphologies which have continuity of both phases.

Figure 13 shows experimental E' data against volume fraction for three system 1 poly(methyl acrylate)-polyurethane semi-1-IPNs and for the homopolymers. The solid lines are the modulus-composition behavior, according to the indicated theories. Conversion from shear modulus to tensile modulus E was performed using the following classical relation:

$$E = 2G(1 + \nu) \quad (7)$$

The Poisson's ratio of the polyurethane and poly(methyl acrylate) homopolymers were calculated using the Rao function.³³⁻³⁷ The Poisson's ratio of the semi-IPNs were calculated using the following equation³⁸:

$$\nu = V_1\nu_1 + V_2\nu_2 \quad (8)$$

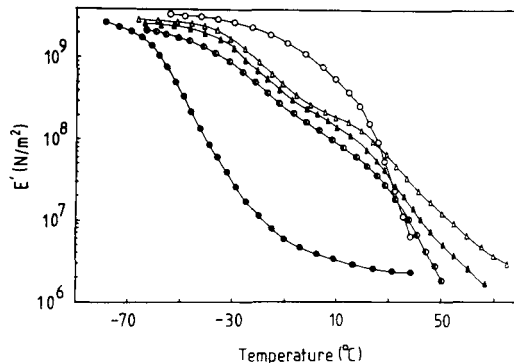


Fig. 11. E' -temperature plots (11 Hz) of the polyurethane network (\bullet) with an \bar{M}_c value of 3800 g/mol, poly(methyl acrylate) (\circ), and of system 2 semi-1-IPNs containing 20 wt% polyurethane and with polyurethane \bar{M}_c values of 1700 (Δ), 3800 (\blacktriangle), and 6900 (\bullet) g/mol, respectively.

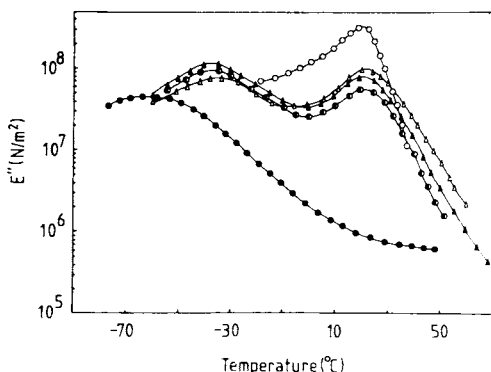


Fig. 12. E'' -temperature plots (11 Hz) of the polyurethane network (●) with an \bar{M}_c value of 3800 g/mol, poly(methyl acrylate) (○), and of system 2 semi-1-IPNs containing 20 wt% polyurethane and with polyurethane \bar{M}_c values of 1700 (Δ), 3800 (▲), and 6900 (◐) g/mol, respectively.

Only the Davies equation and the logarithmic rule of mixing²⁶ come close to fitting the observed data.

To obtain further information about the morphology of these semi-IPNs, theories relating the modulus to the degree of mixing were applied. A general mixing equation which often successfully predicts certain properties of composites with two continuous phases has been presented³⁹ by Nielsen:

$$P^n = P_1^n V_1 + P_2^n V_2, \quad -1 < n < 1 \quad (9)$$

P is a property such as elastic modulus or thermal conductivity. n is some function of the morphology of the system and possibly the property being measured. When $n = 1$, the ordinary rule of mixtures results. The inverse rule of mixtures results when $n = -1$. The logarithmic rule of mixtures^{26,40} is obtained when $n = 0$. This is presented below:

$$\log E = V_1 \log E_1 + V_2 \log E_2 \quad (10)$$

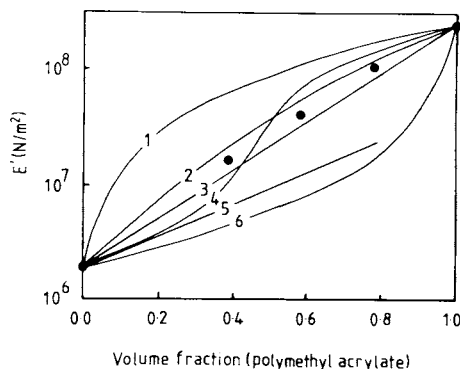


Fig. 13. E' -composition plots for the upper (1) and lower (6) bounds of the Kerner equation, the Davies equation (2), the logarithmic rule of mixing (3), the Budiansky equation (4), and the Guth-Smallwood equation (5). The experimental data for system 1 semi-1-IPNs are shown by the symbol (●).

It has been known for some time⁴¹ that the elastic modulus of many block copolymers and polyblends follows, quite accurately, the logarithmic rule of mixtures which is based⁴⁰ on partial continuity of both phases.

Takayanagi⁴² has developed models for predicting the moduli of both crystalline polymers and polyblends. Prevorsek and Butler⁴³ have applied the Takayanagi models to the morphology of a composite, but their success was limited when compared with other theories of composites.^{29,43-45} The Takayanagi models should apply only to composites which have only one continuous phase. The Takayanagi models can be modified³⁹ to make them applicable to composites with two continuous phases. The modified Takayanagi model is shown in Figure 14. The equations applicable to this model are as follows:

$$P = P_A V_{A\parallel} + P_B V_{B\parallel} + \frac{P_A P_B (V_{A\perp} + V_{B\perp})}{P_A V_{B\perp} + P_B V_{A\perp}} \quad (11)$$

$$V_A + V_B = 1, \quad V_{A\parallel} + V_{A\perp} = V_A, \quad V_{B\parallel} + V_{B\perp} = V_B \quad (12)$$

$$V_{A\parallel} = \alpha, \quad V_{A\perp} = \delta\gamma \quad (13)$$

$$V_{B\parallel} = \beta, \quad V_{B\perp} = \Delta\gamma \quad (14)$$

$V_{A\parallel}$ and $V_{B\parallel}$ are the volume fractions of materials A and B, which behave as continuous phases. $V_{A\perp}$ and $V_{B\perp}$ are the volume fractions which behave as dispersed phases. The morphology is related to the connectivity of the phases, C_A and C_B , by

$$C_A = V_{A\parallel}/V_A = \alpha/V_A \quad (15)$$

$$C_B = V_{B\parallel}/V_B = \beta/V_B \quad (16)$$

Nielsen³⁹ derived eq. (17) and used it to show how $V_{B\parallel}$ varied as V_B was changed:

$$V_{B\parallel} = \frac{(P_B^n V_B + P^n V_A)^{1/n}}{P_B} - \frac{P_A}{P_B} V_{A\parallel} - \frac{P_A (V_{A\perp} + V_{B\perp})}{P_A V_{B\perp} + P_B V_{A\perp}} \quad (17)$$

The following general conclusions³⁹ have been made. If P_B/P_A is much greater than 10, the effect of morphology as given by $V_{A\parallel}/V_A$ is unimportant. For values of P_B/P_A less than 10, the effect of morphology becomes considerably more

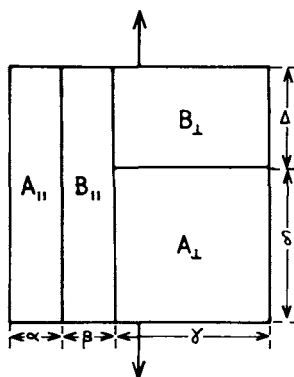


Fig. 14. Modified Takayanagi model. See Ref. 39.

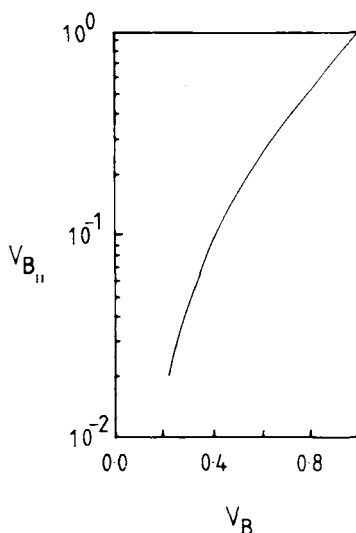


Fig. 15. Log $V_{B||}$ -composition plot calculated from eq. (17).

emphasized, and the part played by $V_{B||}$ becomes much less significant. At intermediate and large values of V_B and at large values of P_B/P_A , $V_{B||}/V_B$ becomes relatively independent of P_B/P_A for any given value of n in excess of zero. As $V_{B||}$, for a given composition, depends largely on n , the greatest effect of changing the phase B morphology appears to manifest itself as a change in the value of n . Nielsen³⁹ further comments that n lies between 0 and 0.33 in nearly all cases.

Figure 13 shows the experimental values of dynamic storage modulus of the polyurethane-poly(methyl acrylate) semi-1-IPNs against volume fraction of poly(methyl acrylate). Line 3 is for the logarithmic rule of mixing and line 2 is for the Davies theory, i.e., $n = 0.20$. It was found that when $n = 0.1$, eq. (9) fits the experimental data. Using this value of n and assuming the connectivity of the polyurethane, $V_{A||}/V_A$, to be 0.5, the volume fraction of the poly(methyl acrylate) hard phase which behaves as if it were continuous, $V_{B||}$, was determined using eq. (17).

Figure 15 shows $V_{B||}$ plotted against concentration of poly(methyl acrylate). Polyurethane is component A and poly(methyl acrylate) component B. As expected, $V_{B||}$ approaches unity as V_B tends to 1. $V_{B||}$ also tends to very low values very rapidly as V_B decreases, indicating that the poly(methyl acrylate) component is present mostly as a discrete phase at low concentrations. When V_B is 0.5, only about 17% of component B behaves as if it were continuous.

Thus, the indication is that in these semi-1-IPNs there is some dual phase continuity when the poly(methyl acrylate) composition is relatively high.

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Received February 15, 1983

Accepted May 31, 1983