Latex Interpenetrating Polymer Networks Based on Acrylic Polymers. I. Predicted and Observed Compatibilities

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Synopsis

An investigation of the compatibilities of several acrylic latex interpenetrating polymer networks is the subject of this paper. Initially the compatibilities of the various polymer pairs were predicted using the theory of Krause plus some direct measurement of heats of mixing of monomers and of model compounds. The materials were then synthesized using emulsion polymerization, and the extents of mixing of the components were investigated using dynamic mechanical analysis.

INTRODUCTION

An interpenetrating polymer network (IPN) is a unique type of polymer blend consisting of a more or less intimate mixture of two polymer networks.[1-4] IPNs represent a mode of blending two or even more polymers to produce a mixture in which phase separation is not as extensive as it would otherwise be. IPNs exhibit varying degrees of phase separation depending, principally, on the respective compatibilities of the constituent polymers. With highly incompatible polymers, phase separation occurs before the developing crosslinking can hinder it substantially. Although complete compatibility is usually impossible, in cases where the polymers are not so strongly incompatible, very small phases can be achieved. Thus, IPNs with dispersed phase domains ranging from a few microns[5] to a few tens of nanometers[6] and finally to those with no resolvable domain structures[7] have been reported.

IPNs may be synthesized in a variety of ways,[3] and the mode of synthesis is used as a convenient way of subdividing IPNs into various classes. These classes include sequential IPNs[4] simultaneous IPNs,[8] thermoplastic IPNs[9] and latex IPNs.[10] It is with this latter class that this work is concerned.

Latex IPNs are made by conventional emulsion polymerizations, in which one component is polymerized and then the monomer of the second polymer is added, without the addition of any further emulsifier, and is then itself polymerized. The contention is that the second formed polymer polymerizes on the initially formed particles and that at least no substantial amount of pure second polymer particles is formed. There has been much debate[11,12] about the morphologies of emulsion particles formed in this way. In a later paper in this series, it is planned to readdress this problem. Whether the second polymer occurs as a shell on the cores of the first polymer, or whether

the morphology is more complex, with, perhaps, a mixed region or regions, need not concern us for the moment. However, it is unlikely that even a highly compatible pair of polymers synthesized in this way will be totally or even substantially mixed. Nonetheless, the extent of mixing should vary with the degree of compatibility and should be accessible to detection by such sensitive techniques as dynamic mechanical analysis and electron microscopy.

The prediction of the likely compatibilities of the various systems was determined by applying the semiempirical and approximate method of Krause.[13,14] To gather additional evidence for the likely compatibilities, direct measurements by batch calorimetry of the excess heats of mixing of monomers and model compounds were also performed for two of the systems.

In order to predict compatibility behavior using the above empirical method, the values of the solubility parameters δ of the homopolymers are necessary. It is recognized that methods based on solubility parameters are only strictly applicable to nonpolar materials. However, it was thought worthwhile to apply the method to acrylates whose dielectric constants are at least relatively low.[15]

The solubility parameters of the homopolymers may be calculated using

$$\delta = \frac{1}{M} \rho \ \Sigma F_i \tag{1}$$

where ρ is the density of the homopolymer and ΣF_i is the sum of the molar attraction constants for all the chemical groups in the repeat unit. M is the repeat unit molecular weight.

Krause[13,14] presented a method of calculation for predicting the bulk compatibility of polymer pairs. It involves the comparison of the calculated values of χ_{12}, the interaction parameter between the two polymers and $(\chi_{12})_{cr}$, the interaction parameter at the critical point on a phase diagram for that particular binary system. Krause[13,14] stated that if $\chi_{12} > (\chi_{12})_{cr}$, the two polymers should be incompatible at some compositions. The greater the difference between these two values, the smaller will be the range of compositions over which the polymers will be compatible.

The χ_{12} and the $(\chi_{12})_{cr}$ values are calculated from eqs. (2) and (3), respectively:

$$\chi_{12} = \frac{V_r}{RT} (\delta_1 - \delta_2)^2 \tag{2}$$

where V_r is the reference volume which was taken to be the molar volume of the smaller polymer repeat unit. The temperature was taken to be 298 K:

$$(\chi_{12})_{cr} = \frac{1}{2} \left(\frac{1}{n_1^{1/2}} + \frac{1}{n_2^{1/2}} \right)^2 \tag{3}$$

where n_1 and n_2 are the respective degrees of polymerization.

TABLE I
Monomers Used in the Synthesis

| Monomer | Abbreviations | | Supplier |
	Monomer	Polymer	
Isobutyl acrylate	iBa	PiBA	Windsor Laboratories Ltd.
Ethyl methacrylate	EMA	PEMA	B. D. H. Chemicals Ltd.
t–Butyl acrylate	tBA	PtBA	B. D. H. Chemicals Ltd.
n–Butyl acrylate	nBA	PnBA	Koch-Light Laboratories Ltd.
Ethyl acrylate	EA	PEA	B. D. H. Chemicals Ltd.
2-Hydroxyethyl methacrylate	HEMA	PHEMA	Aldrich Chemical Co.

In this study the molecular weight of the first component in the polymer system, M_1, was taken to be equal to 100,000 g/mol. The molecular weight of the second component M_2 was varied up to 60,000 g/mol and the corresponding $(\chi_{12})_{cr}$ values were calculated for comparison with χ_{12}. Krause[13,14] states that this scheme can only serve as a guide to polymer–polymer compatibility and that it is no substitute for experimentation.

In addition to these theoretical methods, direct measurements of the excess heats of mixing were determined for two systems using the monomers as model compounds. For only one of these systems the excess heat of mixing of the saturated analogues of the monomers was also measured at several compositions.

EXPERIMENTAL

Materials

The IPNs were synthesized using commercially available monomers (Table I). The monomers were freed from stabilizers by shaking with 10% NaOH solution (3×) and then washed with distilled water until neutral. The monomer was dried for 24 h over fused granular $CaCl_2$ in a refrigerator. Hydroxyethyl methacrylate (HEMA) was used as supplied.

Latex IPN Synthesis

100 mL of deionized and deaerated water were stirred and gently warmed under nitrogen in a 500-mL four-necked reactor. At 40°C, 10 mL of (10% w/v) sodium lauryl sulfate (6.6% by weight of monomer) followed at 50°C by 1.5 mL of (5% w/v) $K_2S_2O_8$ solution were added while constant speed stirring was continued. At 60°C, 15 g of the first monomer containing 0.4% tetramethyleneglycol dimethacrylate (Polysciences) was added dropwise. After the exotherm was complete, the temperature was maintained at 60°C for 30 min and then gradually increased to 90°C and held at that value for 1 h. The emulsion was then allowed to cool to room temperature. At this stage the polymerization of the second network was commenced. The emul-

sion was again heated to 50°C, and 1.5 mL of the $K_2S_2O_8$ solution was added. For the second network polymerization no new soap was added in an attempt to prevent the formation of new particles. At 60°C the second monomer, containing 0.4% of tetramethyleneglycol dimethacrylate and 1 mol % isoprene, was added dropwise. Again, after the exotherm, the temperature was maintained at 60°C for 30 min and then increased to 90°C and maintained there for 1 h. The emulsion was then allowed to cool, and the polymer was precipitated, using acetone and dilute HCl. The polymer was washed repeatedly with deionized water. All the latex IPNs were dried under vacuum for at least 1 week. All the IPNs were prepared with 1:1 by weight composition. The total solids content of the final latices were close to 20% (w/v). The percentage yields were in the range of 85–95%. The latex IPN containing polyhydroxyethyl methacrylate as the second component was more difficult, because of coagulation, to polymerize than the others. This coagulation was prevented to a large extent by controlling both the temperature and especially the rate of stirring of the emulsion.

Sheet Preparation

Sheets were obtained by hot-pressing the polymers.

Physical Techniques

The excess heats of mixing at 298 K were measured by batch calorimetry using a modified version of the Larkin and McGlashan calorimeter.[16] The calculations and the limitations of this method are discussed in Refs. 17 and 18. A Rheovibron dynamic viscoelastometer (Model DDV-II-B) was used (11 Hz) for all the dynamic mechanical measurements. The heating rate was approximately 1°C/min.

RESULTS AND DISCUSSION

For the calculation of the solubility parameters using eq. (1), the required densities were obtained from the literature,[15] except for poly(hydroxyethyl methacrylate), which was experimentally determined. These densities, plus the δ values determined by the Small[19] and the Hoy[20] methods, are reported in Table II. There is very little difference between the two sets of values, and they are reasonably close to the experimentally determined literature

TABLE II
Densities and Solubility Parameters of Homopolymers

Polymer	Density (kg/m³)	δ (Small) [(J/m³)^½ × 10⁻³]	δ (Hoy) [(J/m³)^½ × 10⁻³]	δ (lit.) [(J/m³)^½ × 10⁻³]
PiBA	1050	17.8	17.7	17.7
PnBA	1040	18.0	18.1	17.8
PEA	1120	18.7	18.9	18.8
PEMA	1120	18.3	18.4	18.6
PtBA	1000	16.3	16.3	16.4
PHEMA	1130[a]	—	23.0	25.2

[a] Experimental value.

values. The Hoy δ values were preferred because the Hoy molar attraction constants used in the calculation are a revised version of the values of Small. The solubility parameter of poly(hydroxethyl methacrylate) was determined from swelling experiments. Approximately 1 g samples of sheet which had been crosslinked using 1 mol % tetramethyleneglycol dimethacrylate were immersed for 14 days in a range of solvents. The solubility parameters of the solvents extended from 14.8×10^3 $(J/m^3)^{1/2}$ (n-hexane) to 29.7×10^3 $(J/m^3)^{1/2}$ (methanol). The swelling factor Q was determined:

$$Q = (m - m_0)/m_0 d \qquad (4)$$

where m is the weight of the polymer after swelling and m_0 is its dry weight. d is the density of the swelling agent. A plot of Q vs. swelling agent solubility parameter was drawn, and the maximum in this plot was taken as the solubility parameter of this polymer.

Pazonyi and Dimitrov[21] have suggested an empirical criterion for predicting compatibility in linear polyblends. They proposed that when the difference between the cohesive energy densities, δ^2, of the components is less than 6.69×10^4 J/m^3, a possibility of compatibility exists. From Table III, it can be seen that none of the polymer pairs constituting the IPN systems are predicted to be compatible. Nonetheless, the values vary very considerably even when the PiBA/PHEMA combination (G) is excluded. Systems A, D, and E have low values, while systems B, C, F, and G are much higher.

Krause[13,14] has stated that if $\chi_{12} > (\chi_{12})_{cr}$ for any polymer pair, then that system should be incompatible at some compositions at least. The greater the difference between the two values the smaller will be the range of compositions over which the pair will be compatible.

For systems A–G, the Krause method[13,14] was applied taking the molecular weight of the first component, M_1, in each polymer pair as 100,000 g/mol. The molecular weight of the second component, M_2, was varied and the corresponding $(\chi_{12})_{cr}$ values calculated using eq. (3). Tables IV and V show the results for systems A–D and E–G, respectively. For systems A, D, and E, $(\chi_{12})_{cr} > \chi_{12}$ up to about 4000, 22,000 and 14,000 g/mol, respectively, indicating the possibility of some compatibility, while for systems B, C, F, and G incompatibility is predicted even when the molecular weight of one

TABLE III
Cohesive Energy Density Differences

Code	Composition	$\delta_1^2 - \delta_2^2$ $[(J/m^3) \times 10^{-6}]$
A	PiBa/PEMA	25.2
B	PiBa/PtBA	47.6
C	PnBA/PtBA	61.9
D	PnBA/PEMA	11.0
E	PEA/PEMA	18.7
F	PEA/PtBA	91.5
G	PiBA/PHEMA	215.7

TABLE IV
Interaction Parameters Calculated by Krause Method

Polymer system	M_1	$(\chi_{12})_{cr}$	χ_{12}
PiBA/PEMA	60,000	0.003	
	20,000	0.006	
(A)	5,000	0.017	0.02
	4,000	0.021	
	2,000	0.038	
PiBA/PtBA	60,000	0.003	
	20,000	0.007	
(B)	10,000	0.011	0.104
	1,000	0.077	
	700	0.124	
PnBA/PtBA	60,000	0.003	
	20,000	0.007	
(C)	10,000	0.011	0.157
	1,000	0.077	
	400	0.181	
PnBA/PEMA	60,000	0.003	
	40,000	0.004	
(D)	30,000	0.005	0.006
	22,000	0.006	
	10,000	0.010	

of the components is very low. This method at least separates the seven materials into two distinct groups.

The interaction parameter at the spinodal, $(\chi_{12})_{sp}$, may be calculated[13,14] for particular compositions using

$$(\chi_{12})_{sp} = \frac{1}{2}\left[\frac{1}{n_1(V_1)_{sp}} + \frac{1}{n_2(V_2)_{sp}}\right] \tag{5}$$

where V_1 and V_2 are the volume fractions of polymers 1 and 2, respectively.

TABLE V
Interaction Parameters Calculated by Krause Method

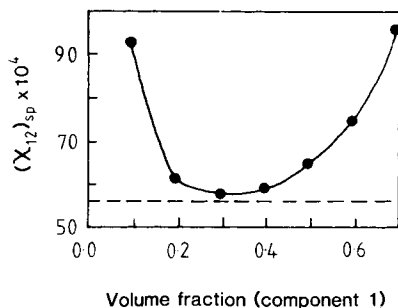| Polymer system	M_1	$(\chi_{12})_{cr}$	χ_{12}
PEA/PEMA	60,000	0.003	
	40,000	0.004	
(E)	20,000	0.006	0.007
	14,000	0.007	
	5,000	0.017	
PEA/PtBA	60,000	0.003	
	20,000	0.006	
(F)	10,000	0.011	0.243
	500	0.145	
PiBA/PHEMA	10,000	0.011	
(G)	5,000	0.019	2.728
	500	0.149	

Volume fraction (component 1)

Fig. 1. $(\chi_{12})_{sp}$ vs. composition curve for system D when the molecular weight of component 1 was taken as 100,000 g/mol and that of component 2 as 22,000 g/mol: (- - -) χ_{12}.

Krause states that if $(\chi_{12})_{sp} > \chi_{12}$, the system will be compatible at that composition. In Figures 1 and 2 plots of $(\chi_{12})_{sp}$ vs. composition for systems D and E, respectively, are shown for the indicated molecular weights. Both curves lie above the calculated χ_{12} values, predicting complete compatibility over the entire composition range.

The methods of Pazonyi and Dimitrov[21] and of Krause[13,14] have grouped the seven blends into two classes with D, E, and possibly A belonging to a group which is likely to be compatible for at least some molecular weights and at some compositions. The other four systems are indicated by both approaches to be much more incompatible. Direct measurements of excess heats of mixing, H_E, of model compounds have been used[22] to predict likely compatibilities between polymer pairs. For systems E and F, which have been predicated to be compatible and incompatible, respectively, excess heats of mixing of the pairs of monomers were determined (see Fig. 3). Both E and F show positive heats of mixing, but the values for F in the midcomposition range are more than twice those of E. The unsaturation of the monomers means that they are, of course, not ideal models for the polymer repeat units. To investigate the effect of unsaturation, the H_E values obtained for the F system using the monomer pair was compared with that obtained for the saturated analogues, ethyl propionate and t-butyl propionate. This comparison is shown in Figure 4. There is clearly a difference between the two model systems, but this is, at least for system F, relatively minor. Further comparisons between saturated models and monomer pairs are being made.

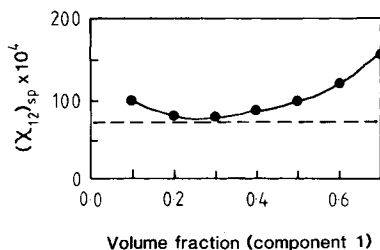For the latex IPNs, the first network was formed; then the second mon-

Volume fraction (component 1)

Fig. 2. $(\chi_{12})_{sp}$ vs. composition curve for system E when the molecular weight of component 1 was taken as 100,000 g/mol and that of component 2 as 13,000 g/mol: (- - -) χ_{12}.
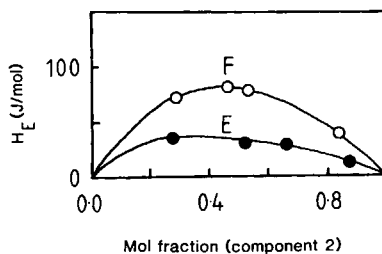
Fig. 3. H_E vs. composition curves for the monomer pairs constituting systems E and F.

omer, plus crosslinker, was added, and the synthesis of the second polymer commenced immediately. Even with a pair of highly compatible polymers, such a mode of synthesis (blending) is unlikely to produce a compatible blend[12,23] unless the monomer of the second polymer can diffuse fully into the seed latex particle before the second polymerization commences. There are differing views[12,23–25] on how rapidly such an equilibrium is achieved. For both systems E and F swelling experiments lasting up to 240 h have been performed. It was observed for both these systems that the time of swelling was an important factor in the control of the particle morphology. This aspect will be presented in a future paper in this series.

Using dynamic mechanical analysis, it is possible to determine from tan δ–, E'–, and E''–temperature plots whether or not any mixing has occurred. Evidence for mixing[26] can come from any or all of the following observations: (1) The inward shifting of the glass transition temperatures T_g, of the components, with, ultimately, their merger to yield a single transition. (2) An increase in the width of the glass transitions which is usually measured at half-peak height or a high value of tan δ in the intertransition region are also indicative of mixing.

Figures 5–8 show the tan δ–, E'–, and E''–temperature plots for all seven latex IPNs.

First, it is clear that for all materials there are two glass transitions, indicating that complete mixing has not occurred in any case. Also, all the IPNs show a very low tan δ maximum value for the lower temperature glass transition. This indicates that the other component, which is still glassy at the T_g of the first component, is present as a continuous phase.
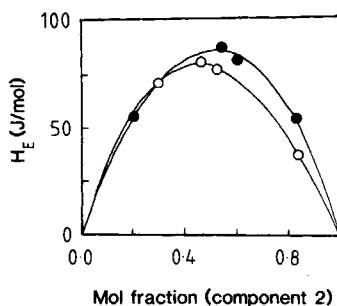

Fig. 4. H_E vs. composition curves for the monomer pair constituting system F(○) and for the saturated analogues of that monomer pair (●).
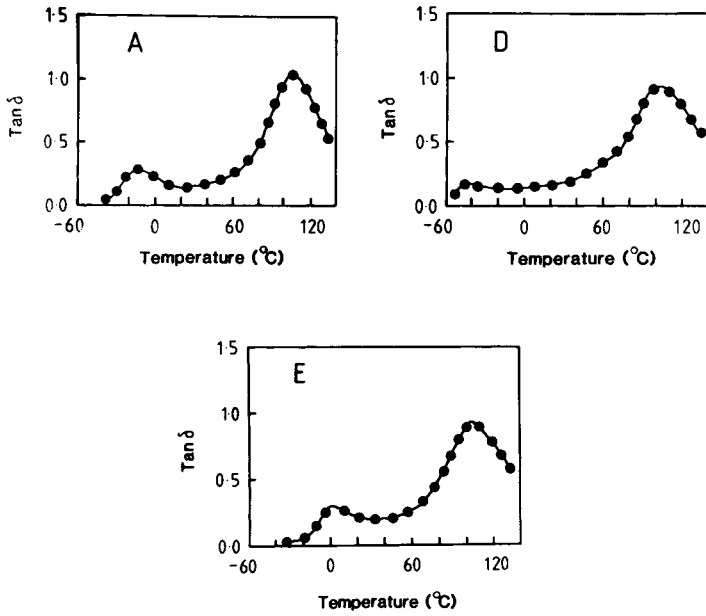
Fig. 5.   Tan δ–temperature curves for latex IPN systems A, D, and E. Frequency was 11 Hz.

A number of observations can, however, be made from Figures 5 and 6, which consign the seven materials to two distinct categories. The marked increase in the half-peak widths of the higher temperature transition for systems A, D, E, and G compared to those of materials B, C, and F indicates
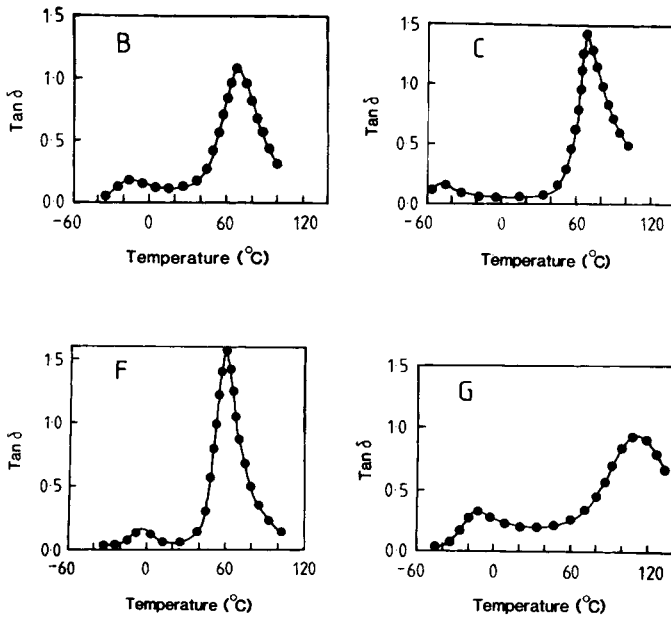

Fig. 6.   Tan δ–temperature curves for latex IPN systems B, C, F, and G. Frequency was 11 Hz.
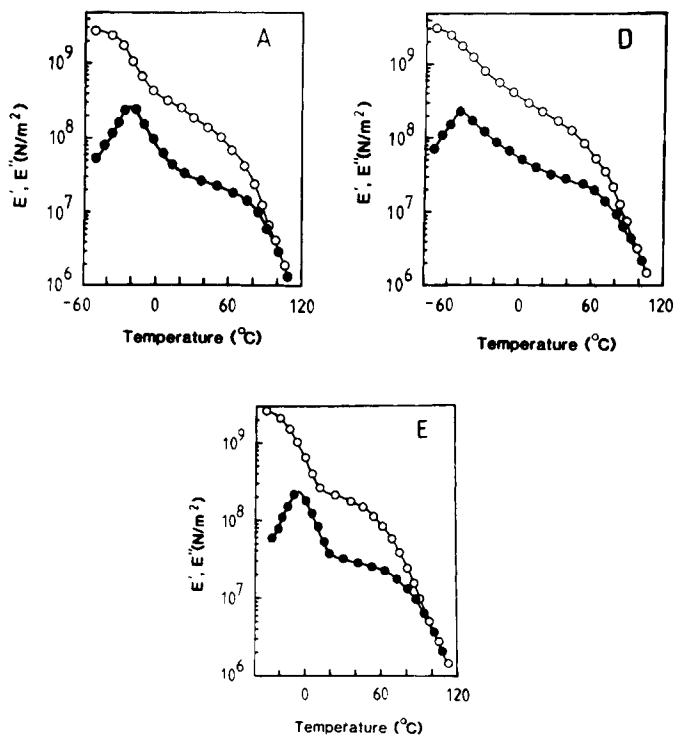
Fig. 7. E' (◯) and E'' (●) –temperature plots for latex IPN systems A, D, and E. Frequency was 11 Hz.

some significant amounts of mixing in the former group. As far as shifts in the temperature of the glass transitions of the components are concerned, there is relatively little inward shifting except in the cases of D and E. When mixing becomes extensive, such inward shifting would be expected.

Another very useful qualitative index of extent of mixing is the magnitude of tan δ in the region between the two glass transitions. If mixing occurs and there is, therefore, an overlap of the relaxation time distributions of the component materials, these inter-transition values of tan δ should be larger than for the case where no mixing occurs. Again, on this basis, materials A, D, E, and G have quite high values, while B, C, and F have typically low values found for polymers in regions where no transition is occurring.

On considering the E'– and E''–temperature curves (Figs. 7 and 8), the single most striking difference is that for the systems (A, D, E, and G) already deduced to show some mixing of the constituted polymers, the higher temperature transitions are present as shoulders rather than, as in the cases of systems B, C, and F, as fully resolved peaks. This, again, is very good evidence of some mixing in the former group of systems. The E'– temperature plots are less useful, generally, than the tan δ– and the E''– temperature plots in yielding information on compatibility, but it is relatively clear that the higher temperature transition for the A, D, E, and G group is distinctly broader than for B, C, and F. This is most marked in the case of system D.
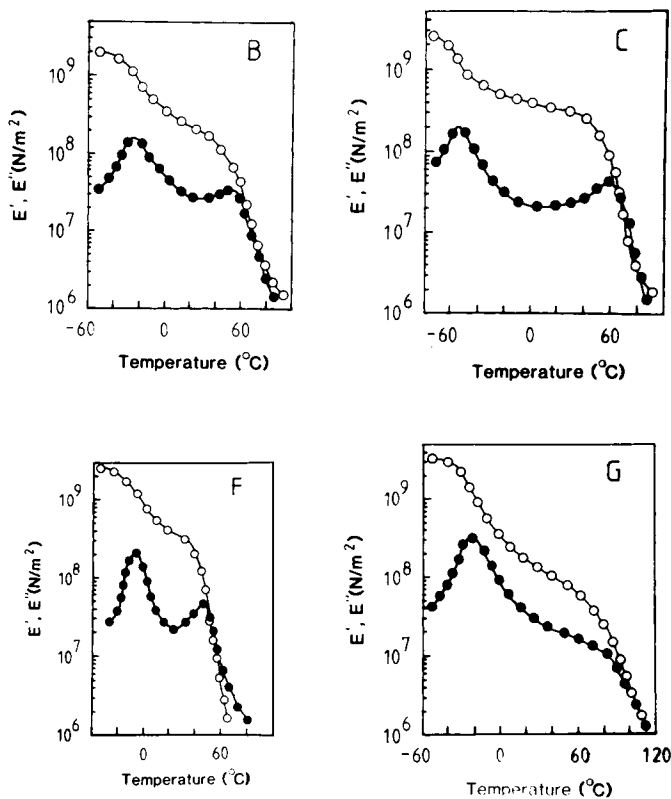
Fig. 8. E' (○) and E'' (●) –temperature plots for latex IPN systems B, C, F, and G. Frequency was 11 Hz.

The results from the dynamic mechanical analysis agree with the solubility parameter based predictions of Krause[13,14] that systems A, D, and E are more likely to exhibit some compatibility than are systems B, C, and F. Thus, at least for these acrylate blends, this essentially semiempirical prediction method is found to be valid. However, for system G, where the difference between the solubility parameters of poly(isobutyl acrylate) and poly(hydroxyethyl methacrylate) is 5.3×10^3 $(J/m^3)^{1/2}$ and, consequently, complete incompatibility would have been expected, it is evident that this material shows the same order of mixing as materials A, D, and E. This must result from a specific interaction between the two component polymers. The most likely interaction would be hydrogen bonding, involving the hydroxyl groups of the poly(hydroxyethyl methacrylate) and the carbonyl groups of the poly(isobutyl acrylate). This system should be investigated further with linear polymers blended from solutions or in the melt.

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