

## **Glass-Rubber Transition Behavior and Compatibility of Polymer Pairs: Poly(ethyl Acrylate) and Poly(methyl Methacrylate)**

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### **Synopsis**

A series of interpenetrating polymer networks were prepared containing PMMA and PEA as their two components. Corresponding telomer mixtures and random copolymers were also prepared for comparison purposes. The glass-rubber transition studies were made via shear modulus and dilatometric measurements. The results indicate one very broad transition for the IPN's rather than two transitions expected for incompatible polymer pairs. An interpretation based on the compatibility or near-compatibility of the PEA/PMMA pair is offered.

### **INTRODUCTION**

Most polymer-polymer mixtures exhibit mutual insolubility, known technically as incompatibility.<sup>1</sup> However, in those few cases where the heat of mixing is near zero or negative, the slight entropy gain obtained on mixing may allow mutual compatibility or partial compatibility. The heat of mixing of poly(ethyl acrylate) (PEA) and poly(methyl methacrylate) (PMMA), which are isomeric, is known to be approximately zero.<sup>1</sup> Further, at least one composition, 79/21 PEA/PMMA, was shown by Hughes and Brown<sup>2</sup> to have a single very broad glass-rubber transition and may exhibit partial compatibility.<sup>1</sup> This paper will explore the glass transition behavior and compatibility of the system PEA/PMMA over the complete composition range and compare the results obtained to those using random copolymers.

### **EXPERIMENTAL PROCEDURES AND RESULTS**

#### **Sample Preparation**

Two methods of synthesis were employed in this work:

- (1) A series of interpenetrating polymer networks (IPN)<sup>3,4</sup> were prepared by swelling techniques previously described.<sup>3</sup> In brief, a solution of ethyl acrylate monomer, containing tetraethylene glycol dimethacrylate

(TEGDM) for crosslinking and benzoin for activation was polymerized photochemically for 24 hrs. The recipe for the PEA and PMMA (below) was 100 ml monomer, 2 ml TEGDM, and 0.3 g benzoin. For a polymer above its glass transition temperature, a soft but stable elastomer is formed.<sup>5</sup> After vacuum drying to remove traces of remaining monomer, controlled quantities of methyl methacrylate plus TEGDM and benzoin were swelled in, followed by a second photopolymerization and vacuum drying. In each case clear, transparent materials were obtained. The center portion of the final sheet was employed to assure sample uniformity. These samples contain a small number of graft polymerization-type bonds, but this number is smaller than the individual network crosslink densities.<sup>6</sup>

(2) The counterpart random copolymer systems employed were prepared in a normal, single-stage photopolymerization. For these samples, the desired quantities of the two monomers were mixed with TEGDM and benzoin as above and were photochemically polymerized.

Telomers of PEA and PMMA were also prepared photochemically. In this case, 10% by volume of 1-dodecanethiol was employed as a chain transfer agent<sup>7</sup> and TEGDM was omitted. Intrinsic viscosities<sup>8-10</sup> showed number-average molecular weights of approximately 6,200 and 6,400 for PEA and PMMA, respectively. All mixtures of the two components yielded one clear homogeneous phase after heating to 135°C with stirring for 4 hr.

### Glass-Rubber Transition Behavior

Three times the shear modulus at 10 sec,  $3G(10)$ , was obtained on several IPN's as a function of temperature from  $-50^{\circ}\text{C}$  to  $+150^{\circ}\text{C}$ , employing a modified Gehman torsional instrument.<sup>3</sup> The homopolymers and random copolymers were also studied for comparison. The results for the IPN's and homopolymers are shown in Figure 1, where  $\log 3G(10)$  is plotted versus temperature.<sup>11</sup> In all cases, only one transition was observed, this being unusually broad for the midrange compositions.<sup>3,11</sup>

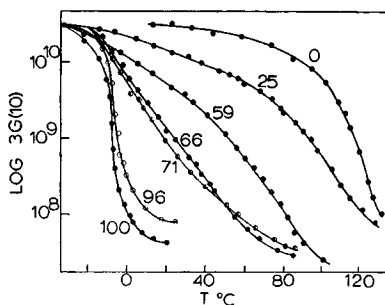


Fig. 1. Log modulus vs. temperature for PEA/PMMA IPN's. Numerical values indicate wt-% PEA. All compositions were found to exhibit only one transition region.

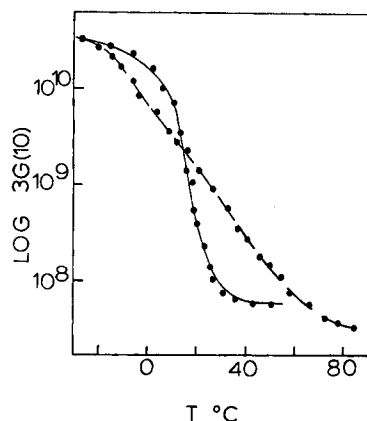


Fig. 2. The modulus of an IPN containing 66% PEA (broken line), is compared to a random copolymer containing 63% PEA (full line). Both preparations have approximately the same crosslink density. Note transition width difference.

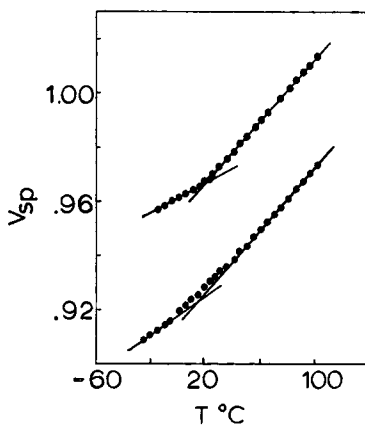


Fig. 3. Comparison of transition widths via dilatometry. Lower curve: IPN containing 57% PEA, 43% PMMA, by weight. Upper curve: random copolymer containing 53.5% EA and 46.5% MMA, by weight. Upper curve displaced vertically by  $+0.03 \text{ cm}^3/\text{g}$  to separate data.

The observation of a single broad transition of ca.  $80^\circ\text{--}100^\circ\text{C}$  wide may be compared to the value of ca.  $20^\circ\text{C}$  obtained for the counterpart random copolymers, as shown in Figure 2. In this example, an IPN and a random copolymer of nearly identical overall monomer compositions are compared. It should be noted that while the two glass transition temperatures ( $T_g$ ) are nearly the same as measured at  $3G(10) = 1 \times 10^{10} \text{ dynes/cm}^2$ , the difference in transition width is very significant.

The telomer solutions were systematically heated and cooled in test tubes at the rate of  $1^\circ\text{C}/\text{min}$ , after an initial heating of several hours at  $135^\circ\text{C}$ . The point where a glass rod could just be made to penetrate the material

under hand pressure, the softening temperature, is closely related to  $T_g$  and was assumed to equal  $T_g$  for the purposes of this paper. These values are shown for a range of compositions in Figure 3. The corresponding values of  $3G(10) = 1 \times 10^{10}$  dynes/cm<sup>2</sup> for the IPN's and random copolymers are also illustrated, as well as the dilatometrically obtained  $T_g$  results. The three sets of  $T_g$  values are seen to correspond approximately over the entire composition range. It is of some interest that these  $T_g$ 's obey the semiempirical equation developed for random copolymers<sup>13</sup>

$$T_g = W_1 T_{g1} + W_2 T_{g2} + KW_1 W_2 \quad (1)$$

where  $W_1$  and  $W_2$  are the weight fractions of materials having  $T_{g1} = 253^\circ\text{K}$  and  $T_{g2} = 373^\circ\text{K}$ , and  $K$  is an empirical constant having the value of approximately  $-80$  in the present case.

### Dilatometry

A dilatometer, similar to that described by Bekkedahl<sup>14</sup> was employed, using mercury as the confining fluid. Stem corrections, as well as expansion coefficients of the glass and mercury, were accounted for. The heating rate was approximately  $1^\circ\text{C}/\text{min}$ .

The results for an IPN are compared to those obtained from a random copolymer in Figure 3. As previously observed with the mechanical data, the IPN transition is seen to be unusually broad.

An important point involves the volume coefficients of expansion,  $\beta$  and  $\beta_g$ , above and below  $T_g$ , and their difference,  $\Delta\beta$ . At temperatures far from  $T_g$ , the IPN's may be expected to behave more nearly like the corresponding random copolymers. The experimental results are summarized in Table I and compared to literature values for pure PEA and pure

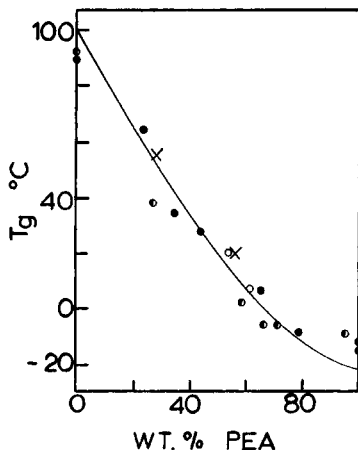


Fig. 4. Glass-rubber transition values or  $3G(10) = 1 \times 10^{10}$  dynes/cm<sup>2</sup> values vs. overall composition: (●) telomer mixtures; (⊙) IPN's; (○) random copolymers; (×) IPN dilatometry data.

TABLE I  
Dilatometric Results for IPN's

Sample	$T_g, ^\circ\text{C}$	$B_g, \frac{\text{cm}^3}{\text{g } ^\circ\text{C}} \times 10^4$	$B_r, \frac{\text{cm}^3}{\text{g } ^\circ\text{C}} \times 10^4$	$\Delta\beta, \frac{\text{cm}^3}{\text{g } ^\circ\text{C}} \times 10^4$
100% PMMA <sup>12</sup>	105	1.95	5.0	3.05
27.6% PEA	54	1.67	5.32	3.65
57% PEA	21	2.65	5.52	2.87
100% PEA <sup>12</sup>	-22	2.8	6.1	3.3
Random, 53.5% EA, 46.5% MMA	19	2.47	5.65	3.18

PMMA.<sup>12</sup> The present results are essentially in line with the literature, suggesting that a sufficient temperature range was covered to clear the broad IPN transition.

### CONCLUSIONS

The experimental findings of interest include: (1) all mixtures of PEA and PMMA produced clear, transparent materials; (2) both modulus and dilatometric studies indicate one broad transition rather than two distinct transitions.<sup>3,11</sup>

There are several possible interpretations of these findings. First, if two phases actually exist in this system, their transitions might be smeared due to hydrostatic tension or pressure caused by unequal expansion coefficients.<sup>15</sup> This might cause the two transitions to be run together. Second, the broad temperature range in the IPN transition could be attributed to a near-continuum of series connected phase compositions in the material, each phase composition making its specific contribution to the shear modulus.<sup>16</sup> Third, the system PEA/PMMA may be forming one stable phase at accessible temperatures. The breadth of the transition may then be due to an extension the second possibility down to the molecular level, where random concentration fluctuations might be important. Experiments are in progress to further clarify the phase relationships in this system.

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