

Blends Containing Polymers of Epichlorohydrin and Ethylene Oxide. Part I: Polymethacrylates

A. C. FERNANDES, J. W. BARLOW, and D. R. PAUL,
*Department of Chemical Engineering and Center for Polymer Research,
University of Texas, Austin, Texas 78712*

Synopsis

The phase behavior of blends of various polymethacrylates with poly(epichlorohydrin) (PECH); poly(ethylene oxide) (PEO); and a copolymer of epichlorohydrin and ethylene oxide [P(ECH/EO)], was examined using differential scanning calorimetry (DSC), dynamic mechanical properties, and optical indications of phase separation on heating, namely lower critical solution temperature (LCST) behavior. Poly(methyl methacrylate) (PMMA), was shown to be miscible with PECH, PEO, and P(ECH/EO), while only PECH was found miscible with the higher polymethacrylates: poly(ethyl methacrylate), poly(*n*-propyl methacrylate), poly(*n*-butyl methacrylate), and poly(cyclohexyl methacrylate). However, even PECH was found to be only partially miscible with poly(isopropyl methacrylate). In many cases, unusually broad glass transitions were observed by DSC for blends which are believed to be the result of equilibrium composition fluctuations. All mixtures showed LCST behavior and based on this and excess volume measurements, to the extent possible, qualitative conclusions were made concerning the relative strength of the interactions among the various blend pairs. For PECH, it appears that the interaction with polymethacrylates decreases with increasing size of the alkyl pendant group, with poly(cyclohexyl methacrylate) being a possible exception. The interaction with PMMA is apparently about the same for PECH and PEO, but somewhat less for P(ECH/EO). The latter is consistent with an intrachain attraction of ECH and EO believed to exist. The reasons for similar interactions of PEO and PECH with PMMA are not understood; however, it is clear that the chlorine moiety of PECH is needed for miscibility with higher polymethacrylates.

INTRODUCTION

In an earlier paper,¹ we reported that poly(epichlorohydrin) (PECH), is miscible with a series of linear aliphatic polyesters¹ which is consistent with the reported miscibility of other halogen-containing polymers with those containing carbonyl structures.¹⁻⁷ For example, chlorine-containing polymers such as poly(vinyl chloride) (PVC), and vinylidene chloride/vinyl chloride copolymers are found to be miscible with various polyesters and acrylic polymers. The reason for miscibility in these systems is suggested to be related to interactions involving the halogen group on one component and the carbonyl group on the other. This interaction is generally believed responsible for the exothermic heats of mixing observed, indirectly, from thermodynamic studies of melting-point depression of blends containing a crystallizable component,¹⁴ or from studies of solvent sorption behavior.⁷ For example, the miscibility of PVC with a wide range of polymethacrylates and polyacrylates² is widely believed to involve hydrogen bonding between the α -hydrogen of PVC,⁷ although there is mounting evidence that the interaction may be more complex.⁴

Based on the above, we have extended our investigation of PECH homopolymer and copolymers to include mixtures with various polymethacrylates and polyacrylates. This paper reports our results for blends with the polymethacrylates and a subsequent paper will deal with the polyacrylate series.

During the course of this work, Anderson and Rodriguez⁶ reported on the compatibility of PECH and a commercial copolymer of epichlorohydrin and ethylene oxide, P(ECH/EO), with PMMA. They concluded that blends of PECH/PMMA and P(ECH/EO)/PMMA were miscible based on the clarity of the films and the observation of a single glass transition over the whole composition range. The published differential scanning calorimetry (DSC) thermograms show a single, but broad, glass transition for both systems.

The interpretation of PECH phase behavior with polyacrylates and polymethacrylates is potentially complicated by the fact that PECH contains both chloride and ether functionality in its molecular structure. Thus, one purpose of this work is to examine the relative importance of the ether and chlorine units on the miscibility with polymethacrylates in addition to the influence of the size of the alkyl pendant group to the polymethacrylates.

Since we are interested in comparing PECH and P(ECH/EO) miscibility with the polymethacrylates, the recent reports⁸⁻¹¹ on the miscibility of poly(ethylene oxide) (PEO) and PMMA are of fundamental importance. Thus, for purposes of comparison, we have included blends of PEO with PMMA using a PEO sample with $\bar{M}_w = 3 \times 10^5$ which is somewhat higher than employed in the studies previously mentioned.⁸⁻¹¹ Some preliminary results will be presented concerning the miscibility of PEO and PEMA.

A variety of techniques, including DSC, mechanical spectroscopy, density measurements, and optical appearance, have been employed where appropriate to determine blend phase behavior.

MATERIALS AND EXPERIMENTAL PROCEDURES

The poly(epichlorohydrin) and poly(epichlorohydrin-co-ethylene oxide) (approximately equimolar in ethylene oxide and epichlorohydrin) are commercial products of the B.F. Goodrich Company sold under the tradenames of Hydrin 100 and Hydrin 200, respectively. Both materials are rubbery at room temperature and neither crystallizes. The poly(ethylene oxide) was from Aldrich Chemical, Inc. and had a relatively high molecular weight. The polymethacrylates were obtained from a variety of sources, and they are all amorphous glassy materials at room temperature. Descriptions and acronyms for all materials are given in Table I (preceding References).

Typically, blend films were prepared from solutions containing 5 to 10% wt polymer in an appropriate common solvent. Toluene was used as the solvent for preparing PECH/polymethacrylate blends, although tetrahydrofuran was also used to prepare PECH blends with PnPMA, PnBMA, and PCHMA in order to investigate potential solvent influence on the observed phase behavior. Methylene chloride was found to be more suitable for preparing solutions containing either P(ECH/EO) or PEO and the polymethacrylates, probably as a result of this solvent's ability to interact strongly, through hydrogen bond formation, with the ether oxygen. Films were pre-

pared by pouring the solutions into disposable aluminum pans, which were then covered with perforated aluminum foil and placed in a hood at room temperature for several days until the majority of solvent evaporated and the films appeared "dry." The remaining solvent was then removed from PECH-containing films by placing the pans in a vacuum oven at 110°C for three days. This temperature was found not to be high enough to completely remove the solvent from blends with a high content of PMMA. So an additional three days of drying in an air oven at 130°C was used to remove toluene from the PECH/PMMA cast films. Cast films containing PEO or P(ECH/EO) were prepared in a similar manner and dried in vacuo for three days at 80°C. An additional three days in vacuo at 100°C were required to completely dry PEO/PMMA-containing films.

To explore the potential influence of preparation process on the resulting phase behavior, P(ECH/EO)/PMMA blends, containing 40 and 60% by weight PMMA were prepared by melt mixing the ingredients in a Brabender Plasticorder at 190°C. The mixing blades were set at a speed of 10 rpm for the 7 minutes required to add and flux the polymers. The speed was then increased to 30 rpm and the polymers were allowed to mix for about 5 additional minutes. Films were obtained by compression molding the melt in a Carver press set at 190°C, followed by slow cooling to room temperature.

A Perkin-Elmer DSC-2 and a Rheovibron equipped with computerized data stations were used to measure transition behavior. Glass transition temperatures (T_g) were measured with the DSC-2 using a 20°C/min heating rate after conditioning the samples by heating them to 177°C (except where noted), holding for 5 mins, followed by quenching to -63°C or -133°C. The Rheovibron was operated at 110 Hz and heating rates of about 2°C/min, from -130°C to 150°C.

The blends were examined for lower critical solution temperature (LCST) behavior by heating on a hot plate following a procedure described previously¹² using heating rates between 5 and 10°C/min.

The densities were measured at 30°C in a density gradient column using aqueous solutions of calcium nitrate. Several columns with different density ranges were used. At least three measurements per sample were made, and the average is reported.

RESULTS FOR POLY(EPICHLOROHYDRIN) BLENDS

Poly(methyl Methacrylate) and Poly(ethyl Methacrylate)

Blends of PECH with PMMA and with PEMA were optically transparent at room temperature. DSC thermograms for both systems exhibit single, composition-dependent T_g s which are plotted versus composition in Figures 1 and 2. However, there was considerable broadening of these transitions at intermediate compositions for both systems with maxima at about 30% PMMA and 20% PEMA as seen in Figure 3, together with other systems to be discussed later. The transition breadth used here is the difference between the onset and completion temperatures of the transition defined by the intersections of the base lines above and below T_g with the best straight line which can be drawn tangent to the thermogram in the transition region.

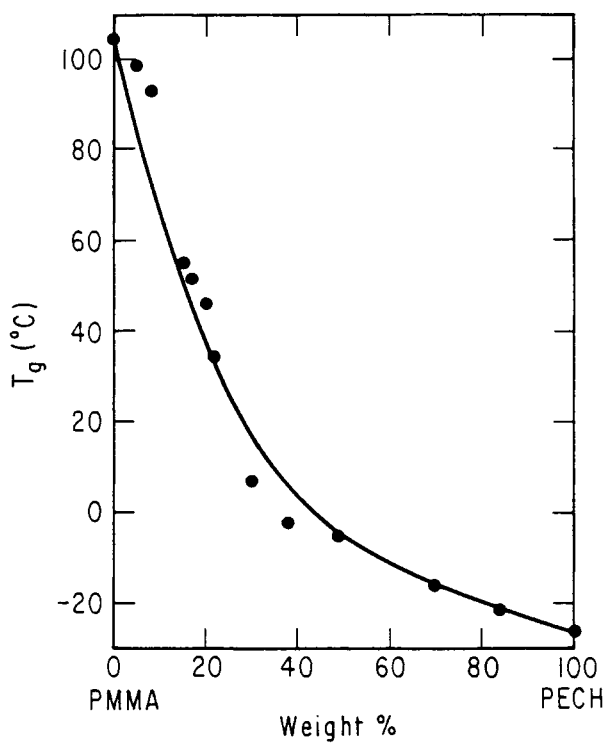


Fig. 1. Glass transitions for PMMA-PECH blends determined by DSC using the onset method of determining T_g from thermograms.

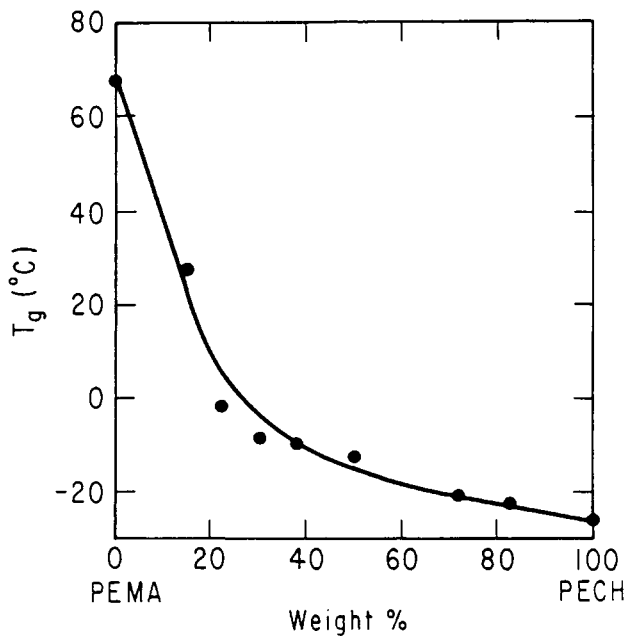


Fig. 2. Transitions for PEMA-PECH blends determined as in Fig. 1.

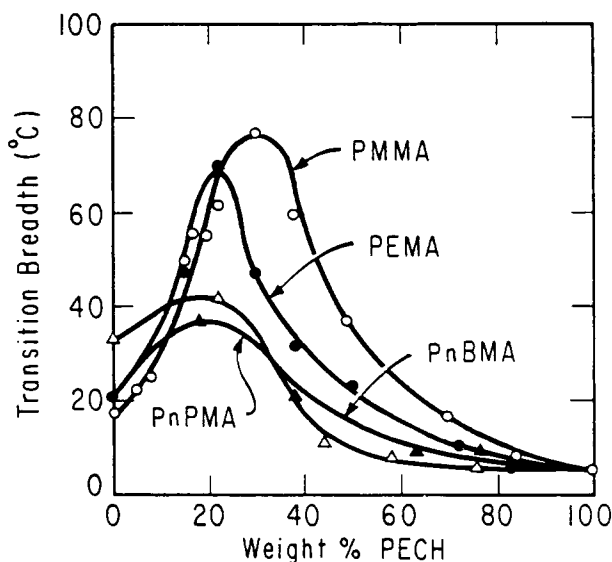


Fig. 3. Breadth of glass transitions from DSC for PECH blends with various polymethacrylates.

For comparison purposes, Rheovibron results for the PECH/PMMA and PECH/PEMA systems are presented in Figures 4–7. The elastic portion of the complex modulus, E' , is seen to decrease smoothly from a plateau value as the temperature is raised through the transition temperature. The onset of this decrease varies with blend composition in the expected way. No phase heterogeneity, which usually shows up as multiple plateaus in the E' versus temperature plot, is apparent in either Figure 4 or Figure 6. $\tan \delta$, shown for PECH/PMMA blends in Figure 5 and for PECH/PEMA blends in Figure 7, shows the expected peaks at the mechanical transition temperature with no evidence of transition peaks at lower temperatures. The peaks at intermediate blend compositions for both systems shift smoothly with composition and show a broadening consistent with the transition measurements obtained by DSC. Figures 8 and 9 present the transition temperatures taken from the E'' peak maximum as a function of composition. At any composition the mechanical transition temperature at 110 Hz is typically 15 to 20°C higher than the transition temperature measured from changes in heat capacity for both blend systems as expected.

In our opinion, the observed T_g broadening is not the result of microheterogeneity, if this latter term implies thermodynamic phase segregation, but stems from composition fluctuations which are possible at equilibrium for miscible mixtures.¹³ These composition fluctuations for mixtures are in excess of the normal thermal fluctuations in density observed for pure components¹⁴ and are frozen-in as the mixture is cooled. On heating, molecular motions become active and the range of temperature over which this happens reflects the degree of frozen-in fluctuations. However, it is rather easy to understand that the magnitude of fluctuations increases as the affinity of

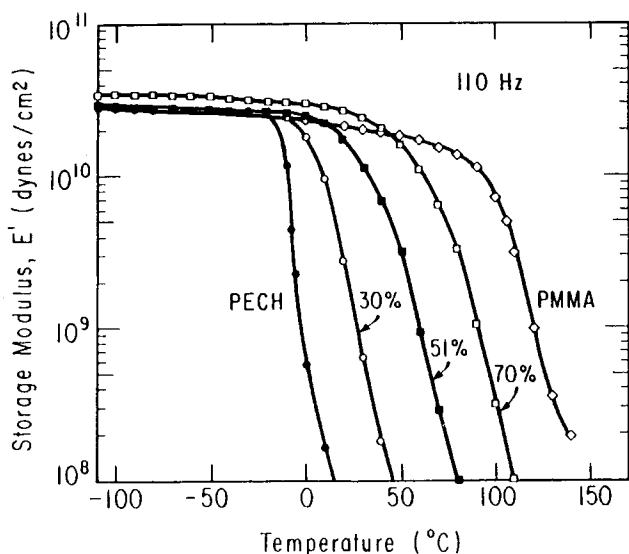


Fig. 4. Storage modulus versus temperature for PMMA-PECH blends.

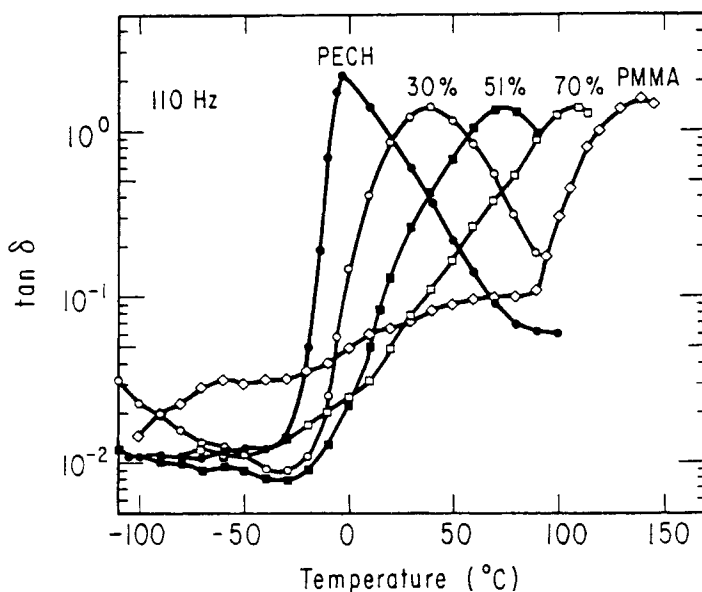


Fig. 5. $\tan \delta$ versus temperature for PMMA-PECH blends.

the components comprising the mixture for each other decreases. At the extreme limit of phase instability, these fluctuations become macroscopic.

Since none of the blend components are crystallizable, it is not possible to obtain a measure of the heat of mixing of these components by the melting-point depression method.¹⁵ It has been suggested for other amorphous miscible blend systems that the volume change on mixing generally follows the heat of mixing in magnitude and sign.¹⁶⁻²⁰ Consequently, blend-specific

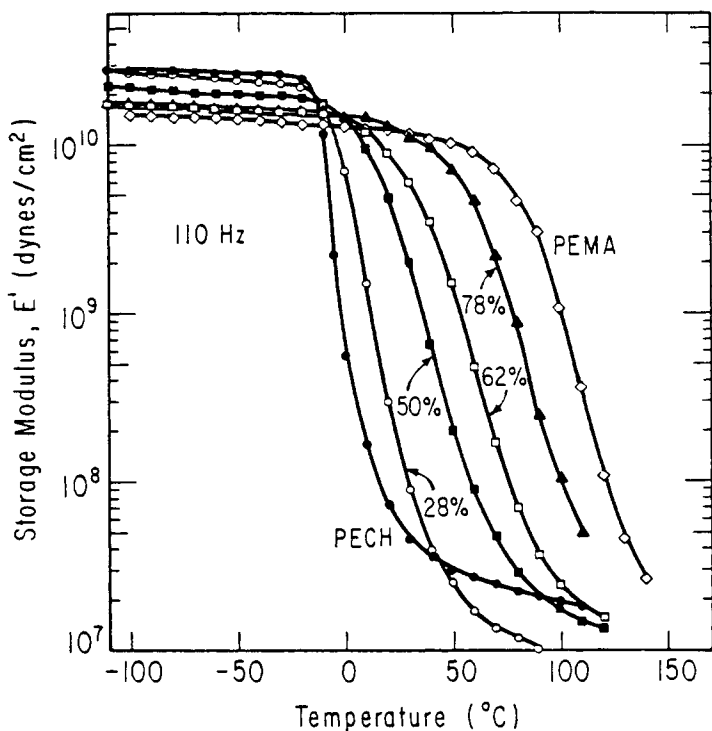


Fig. 6. Storage modulus versus temperature for PEMA-PECH blends.

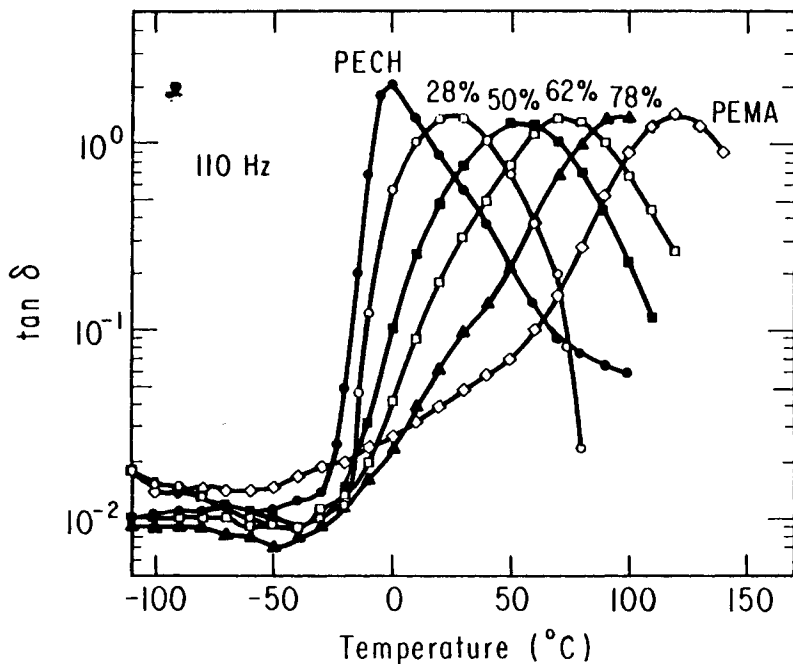


Fig. 7. Tan δ versus temperature for PEMA-PECH blends.

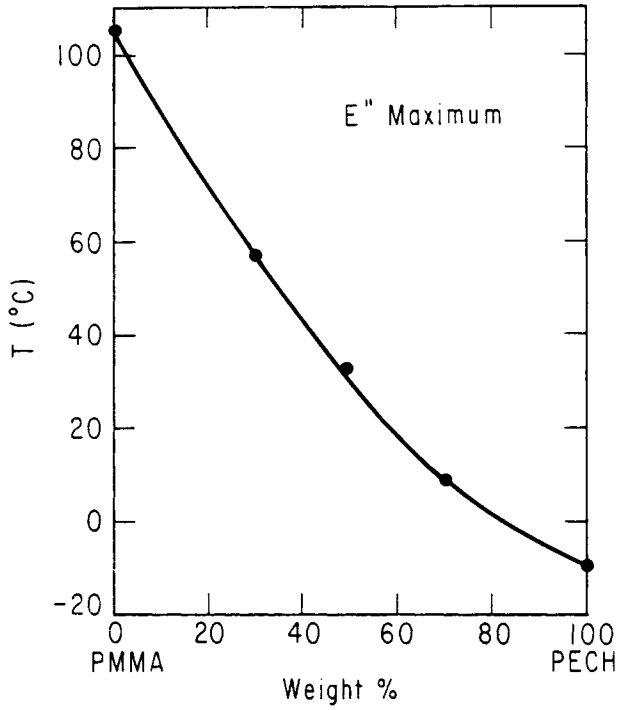


Fig. 8. Temperatures at which loss modulus shows maxima for PMMA-PECH blends.

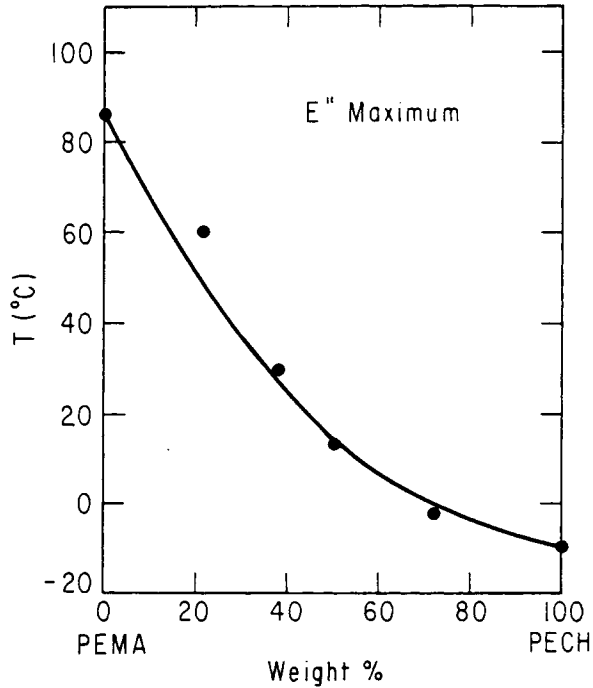


Fig. 9. Temperatures at which loss modulus shows maxima for PEMA-PECH blends.

volume measurements were made at 30°C in an attempt to learn whether PMMA or PEMA interacts more strongly with PECH. These data are shown in Figures 10 and 11 for PMMA/PECH and PEMA/PECH, respectively. As indicated there, some blend compositions are in the glassy state at 30°C while others are in the rubbery state. To properly interpret the specific volume data, it is necessary that the blend and its components be compared in the same state.^{17,21} Most of the blend compositions are in the rubbery state at 30°C. Consequently, the PMMA and PEMA end points corresponding to the "equilibrium" liquid state were established by extrapolating literature-specific volume data from the rubbery state to the observation temperature as indicated by the construction shown in Figure 12 for PMMA.²² A similar construction was used to establish the equilibrium liquid-specific volume of PEMA²³ at 30°C, and these end points are shown as open circles in Figures 10 and 11. It is apparent from these figures that rubbery state-specific volumes of the PMMA/PECH blends are smaller than the tie line values, whereas those of the PEMA/PECH blends are larger. The volume change on mixing or the excess specific volume, V^E , were computed from the definition

$$V^E = V - w_1V_1 - w_2V_2 \quad (1)$$

where V is the specific volume of the blend, V_i the specific volume of pure component i , and w_i the weight fraction of i in the blend. The excess volumes of PEMA/PECH blends in the rubbery state at 30°C are positive while those of PMMA/PECH blends in the rubbery state are negative, as shown in Figure 13. This observation implies that the interaction between PMMA and PECH

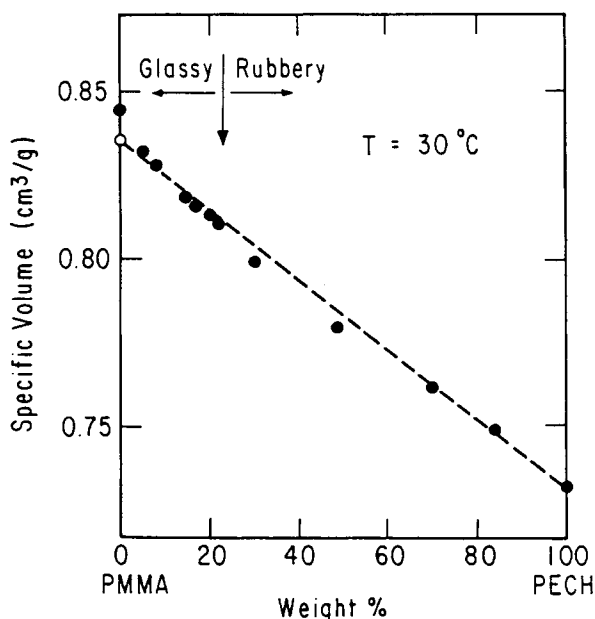


Fig. 10. Specific volumes for PMMA-PECH blends at 30°C (solid points). Open circle is estimated equilibrium liquid value for PMMA obtained by extrapolation shown in Fig. 12.

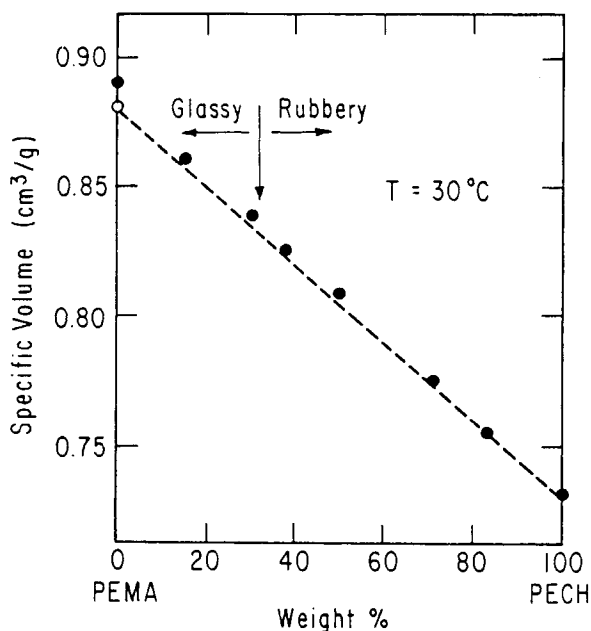


Fig. 11. Specific volume for PEMA-PECH blends at 30°C (solid points). Open point has same meaning as in Fig. 10.

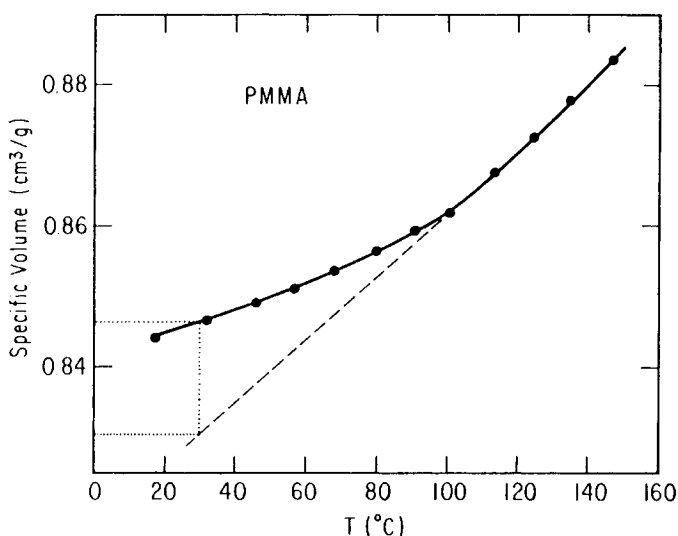


Fig. 12. Specific volume versus temperature for PMMA (22) showing method of estimating equilibrium liquid value by extrapolation.

is more exothermic than that between PEMA and PECH, but one could question whether the positive excess volume of mixing in the case of the miscible PECH/PEMA blend is real or not. Inaccuracy in the extrapolated specific volume of PEMA²³ may be a factor.

Previous investigations²¹ have repeatedly shown that blends are miscible because of exothermic interactions between the blend components. One ex-

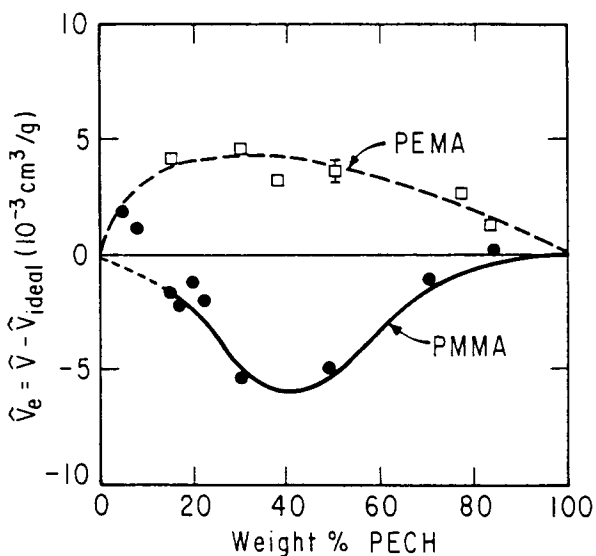


Fig. 13. Excess volume for blends of PECH with PMMA and PEMA computed from data in Figs. 10 and 11 using open circles as values for pure polymethacrylates.

pects a negative excess volume of mixing as a natural consequence of an exothermic heat of mixing; however, such a relation is not assured by any thermodynamic principles. To our knowledge one case has been reported where a positive excess volume was observed²⁴ for a miscible polymer blend.

Miscible blend systems often show phase separation on heating^{21,25} or lower critical solution temperatures (LCST) and it is generally accepted that this phenomenon is related to the strength of interactions between the binary components. That is, the more exothermic the interaction between two polymers, the higher the temperature at which phase separation occurs. The simplest argument for understanding this is based on the general observation that for liquid mixtures the heat of mixing approaches zero or the athermal ideal as the temperature is increased. Since polymer mixtures require an exothermic heat of mixing to be miscible, demixing can be expected to occur as the melt is raised to a temperature level where intermolecular interactions are overcome by thermally driven Brownian motions. By this argument, miscible systems with strong interactions will require higher temperatures to phase separate than systems which interact less strongly. More sophisticated arguments involving equation of state effects²⁵ and excess heat capacity effects²⁶ have also been advanced to explain LCST behavior. It suffices to note here that the observed phase-separation temperature or cloud point of a binary polymer mixture is found to vary with blend composition, component molecular weights, polydispersities,²⁷ and interaction strengths.²¹ However, it should be possible to qualitatively rank the interactions between PECH/PMMA and PECH/PEMA by examining the temperature at which they phase separate. These data are shown in Figure 14 together with other PECH-containing systems to be discussed later. It is seen that the cloud-point temperatures for the PMMA-containing system are about 50°C higher than for the system containing PEMA, a result that is qualitatively in agreement with the excess volume results.

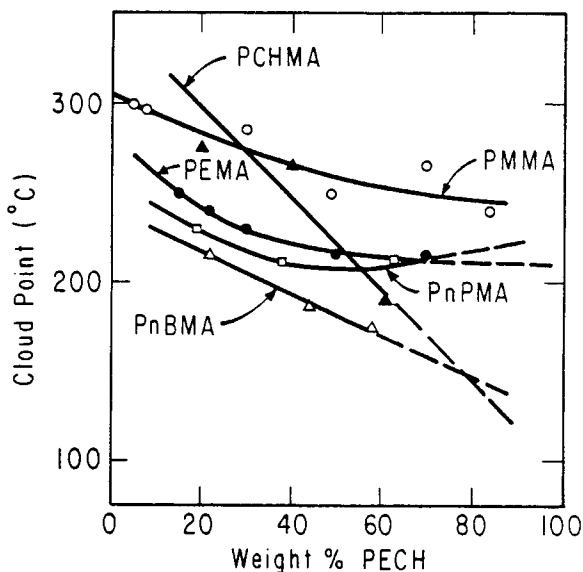


Fig. 14. Cloud points for blends of PECH with various polymethacrylates.

Several qualifying remarks must be made concerning these cloud-point measurements. Due to the similarity of the refractive indices of PECH and PMMA or PEMA, it was quite difficult to assess accurately the temperature of phase separation using the simple technique of visual observation. For each blend composition several samples were tested and the temperatures presented in Figure 14 are averages. The dashed line indicates cases where it was not possible to discern a reliable cloud point. Since the experiments were performed at a finite heating rate the equilibrium cloud points may be somewhat lower than those shown. Great care must be taken when doing cloud-point measurements not to confuse light scattering caused by decomposition. PMMA, for example, is known to sequentially depolymerize to monomer at relatively low temperatures and to undergo random chain scission at higher temperatures.²⁸ These decomposition reactions will lead to bubble formation in the blend and light scattering which could be mistaken at the early stages of decomposition for phase separation. The observed cloud points for PECH/PMMA were detected at a temperature above the first stage of depolymerization, therefore the observed LCST in blends with a high content in PMMA may have been slightly affected by this. The existence of phase separation could not be rechecked in the DSC, due to this fact.

To summarize, both PMMA/PECH and PEMA/PECH blends appear to be miscible by the usual single T_g criterion. Measurements of densities and cloud points provide consistent, albeit qualitative, evidence for claiming that PMMA interacts more strongly with PECH than does PEMA.

One possible structural reason for this difference could be that the increased side chain length sterically interferes with the interaction between the PECH unit and the ester carbonyl or simply increases the hydrocarbon content of the polymethacrylate causing increased repulsion. To explore these possibilities, blends of PECH and other polymethacrylates with larger

hydrocarbon pendant groups, PnPMA, PnBMA, and PCHMA, were prepared and tested. The results for these systems are summarized below.

**Poly (*n*-propyl Methacrylate), Poly(*n*-butyl Methacrylate), and
Poly(cyclohexyl Methacrylate)**

In contrast to blends with PMMA and PEMA, blends of PECH with polymethacrylates having larger pendant groups form slightly cloudy films when cast from toluene. DSC measurements on toluene-cast films show two T_g s when the PECH level is less than 15% by weight in blends with PnPMA, 30% in blends with PnBMA, or 50% in blends with PCHMA. At higher PECH concentrations only one T_g is detected, but this value does not vary with blend composition in the usual way. Rather, it remains quite close to the T_g of PECH. The lack of a second T_g at these higher PECH concentrations may be the result of extreme T_g broadening caused by a gradation in PECH concentrations throughout the sample²⁹ or, in the limit of very high PECH levels, by the general difficulty associated with detecting the T_g of a minor component. At any rate, one would conclude that toluene-cast films are, at best, partially miscible. When these same materials are cast from tetrahydrofuran (THF), however, the films obtained are transparent and completely homogeneous throughout the composition range. Only one T_g is observed at each blend composition, and the T_g varies monotonically with composition in the usual way, indicating that films prepared from THF are miscible at all compositions.

This difference in phase behavior points out the importance of solvent choice when preparing blends by the solution casting method. The apparent partial miscibility shown by the toluene-cast samples is probably the result of more limited solubility of these higher hydrocarbon content polymethacrylates in toluene relative to that in THF. Such limited solubility could result in the premature precipitation of the polymethacrylate during the film-drying process causing the presence of two T_g s at the higher polymethacrylate levels in the blends. We believe that the results obtained from THF-cast blends represent the true equilibrium behavior of these systems since no phase separation, like that noted for the toluene-cast blends, occurred during repeated heating in the DSC to temperatures below which LCST behavior occurs. Figures 15 and 16 show the observed T_g versus composition from DSC thermograms for PECH/PnPMA and PECH/PnBMA blends cast from THF. For each composition two different temperatures are indicated. The lower is the temperature at the onset of transition and the upper one is the temperature at the end of transition. These temperatures were determined as previously described. The distance between these two temperatures gives a measure of the transition breadth for the blends and may be compared to that observed for the pure polymers. As is the case with PMMA- and PEMA-containing blends, the transitions are quite broad and the breadth of the transition again appears to peak near 20% by weight of PECH, however, the peak magnitudes are much reduced as seen in Figure 3, relative to those for PMMA- and PEMA-containing blends.

The cloud points shown in Figure 14 suggest that polymethacrylates interact with PECH in the order PMMA > PEMA > PnPMA > PnBMA.

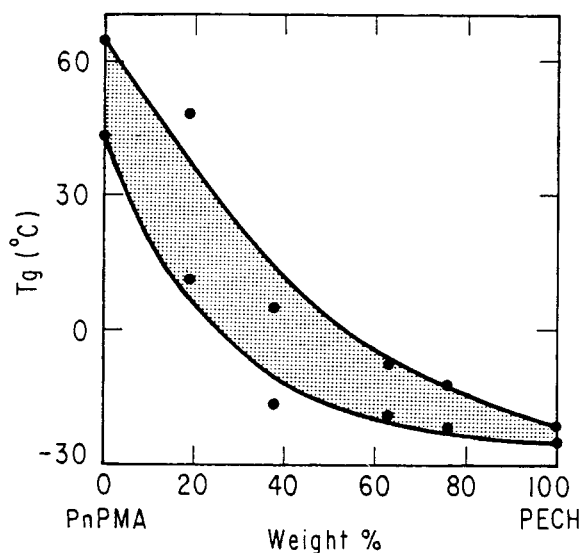


Fig. 15. Glass transitions for PECH-PnPMA blends from DSC. Lower points indicate onset temperature and upper points correspond to completion temperatures as discussed in text.

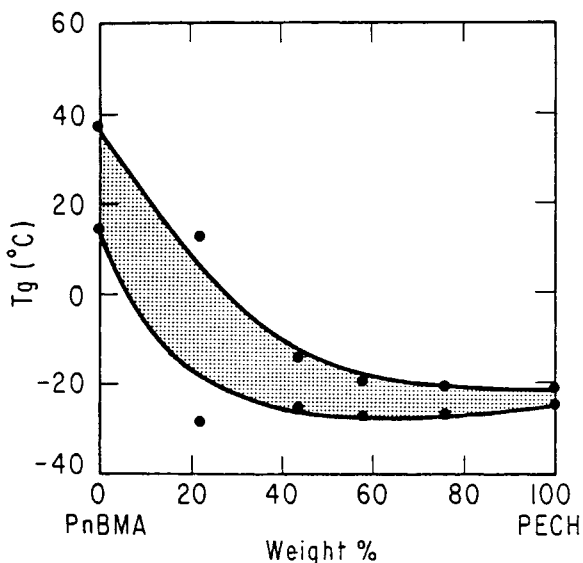


Fig. 16. Glass transitions for PECH-PnBMA blends from DSC. Upper and lower points have meaning described in Fig. 15.

At first sight, broader glass transitions for PMMA blends seems inconsistent with the suggestions that PMMA interacts more exothermically with PECH than other polymethacrylates do, based on cloud-point and volumetric observations, and that the glass transition broadening stems from composition fluctuations. As stated earlier, weaker interactions are expected to permit larger equilibrium fluctuations in composition. However, for a given

composition variation, the variation in mixture T_g will be larger the greater the difference in T_g of the two components comprising a given mixture. In the present systems, the difference in T_g for the polymethacrylates and that of PECH stands in the following order: PMMA > PEMA > PnPMA > PnBMA. Consequently, to compare the proposed extent of actual composition fluctuations or the presumed level of interaction, the observed T_g breadth must be normalized for the difference in T_g 's of the components. One way is to merely divide the measured transition breadth of the blend by the difference in glass transitions of the components, ΔT_g , as shown on the left side of Figure 17. However, since the two T_g 's are defined as the onset temperatures, this ignores the finite breadth of the transition of the higher T_g component, the polymethacrylates, which may contribute to the breadth of the blend transition. As a result, this ratio could be greater than unity as in fact is seen for PnBMA. This can be circumvented by adding to ΔT_g the breadth of the polymethacrylate transition and using this sum for the normalization as shown on the right side of Figure 17. On this basis, the extent of T_g broadening seems more consistent with the observations noted earlier, suggesting that the interactions with PECH become less favorable as the size of the polymethacrylate pendant group becomes larger.

Glass transition temperatures versus composition for PECH/PCHMA blends are shown in Figure 18. Blends cast from THF show a single T_g . The transition breadths for this system are considerably smaller than for any of the previous systems. The maximum transition breadth is about 32°C at 41% PECH even though ΔT_g for this system is practically the same as for PECH and PMMA. The particular shape of the cloud-point curve is extremely asymmetric (Fig. 14), which makes it difficult to rank the interactions of this system with those for the other polymethacrylates. At present we cannot offer an explanation for this apparently anomalous behavior for PCHMA blends.

The ranking stated above for polymethacrylates containing linear aliphatic chains suggests that increasing the length of the side chain has an

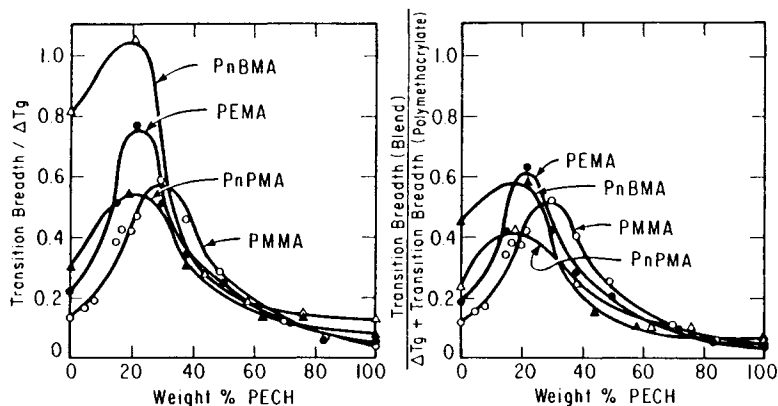


Fig. 17. Transition breadths shown in Fig. 3 normalized by the difference in T_g 's for polymethacrylates and PECH (left) and by the difference in component T_g 's plus the breadth of the pure polymethacrylate transition (right).

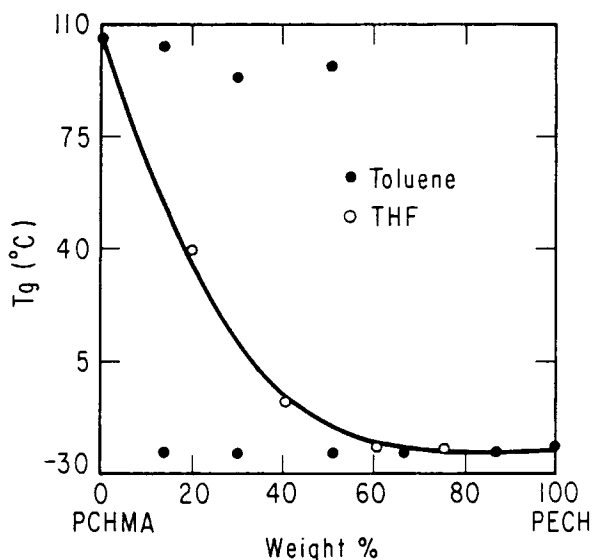


Fig. 18. Glass transitions for PECH/PCHMA blends from DSC: cast from toluene (solid points) and cast from THF (open points).

adverse effect on miscibility with PECH. It is interesting to note, that for all members of the polymethacrylate series, the glass transition versus composition curve shows a corresponding trend. There is a rapid decrease in T_g at low PECH concentrations, then T_g remains almost constant and close to that of pure PECH when the amount of polymethacrylate in the blend decreases. The constancy of the blend glass transition at high PECH concentrations is more noticeable as the size of the pendant group in the polymethacrylate increases. If the glass transition is taken as the end or as the midpoint of the transition a more regular T_g versus composition curve is obtained.

As a further check to be sure that these blends are indeed miscible, the existence of LCST behavior was confirmed by a DSC technique. PECH/PnBMA and PECH/PCHMA containing about 60% of PECH were heated to a temperature above the observed cloud point. The samples were annealed at this temperature for various periods of time and then quenched and scanned again. It was observed that the initially single T_g splits into two T_g s whose positions change with annealing time. The longer the annealing time, the further apart are the two T_g s.

Poly(isopropyl Methacrylate)

One way to demonstrate the potential effect of geometric interference mentioned earlier is to examine blends of PECH with polymethacrylates which contain bulky hydrocarbon esters, such as those derived from isopropyl or isobutyl alcohols. The effect is demonstrated in Figure 19 where the T_g s for PiPMA/PECH blends, determined by DSC, are shown. While PnBMA/PECH blends appear to be miscible, PiPMA/PECH blends show optical cloudiness and two T_g s which are characteristics of an immiscible or, at best,

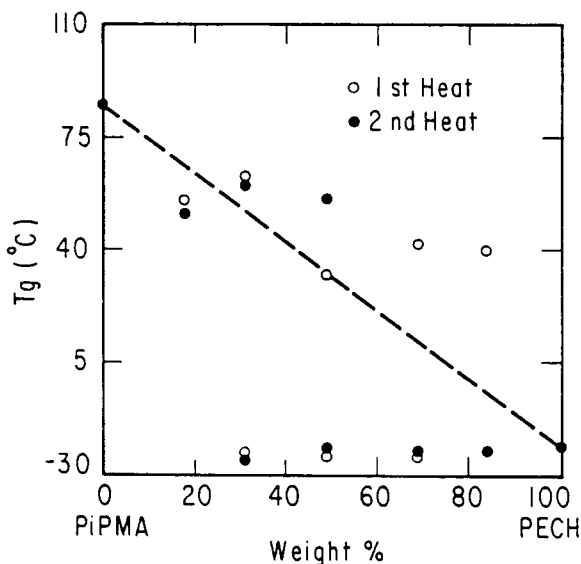


Fig. 19. Glass transitions for PECH/PiPMA blends from DSC. The open points show the T_g s observed in the first heat. The solid points show the T_g s observed in the second heat after quenching to -63°C .

partially miscible mixture. The lower T_g is essentially that of PECH while the upper transition is lower than that of pure PiPMA and relatively insensitive to blend composition. Apparently a small amount of PECH is soluble in PiPMA which lowers its T_g to about 50°C . Continued addition of PECH beyond the solubility limit (somewhere below 20% PECH) has no further effect except to create within the material a pure PECH phase. It is interesting to note that the PiPMA-rich phase, which is detectable over the entire composition range when the films are first heated, becomes very difficult to detect at high PECH levels in the blend after annealing at 177°C for 5 min followed by a rapid quench to -63°C . The reason for this behavior is not well understood.

RESULTS FOR POLY(EPICHLOROHYDRIN/ETHYLENE OXIDE) BLENDS

Poly(epichlorohydrin/ethylene oxide), P(ECH/EO), was blended with PMMA using methylene chloride as the solvent. The resulting films had a slight cloudiness at room temperature that increased with P(ECH/EO) content due to the cloudy nature of pure P(ECH/EO). When these films were tested by DSC, a single glass transition was observed at a temperature intermediate to the glass transitions of the pure polymers, as shown in Figure 20. For each composition, two different temperatures are indicated having the same meaning as for PECH/PnPMA and PECH/PnBMA described earlier. The transitions are quite broad, but not as broad as the transitions observed for PECH/PMMA, in spite of the larger ΔT_g between these two polymers. A maximum transition breadth of 64°C was observed in a blend containing about 40% of P(ECH/EO), compared to a maximum of 77°C in a blend con-

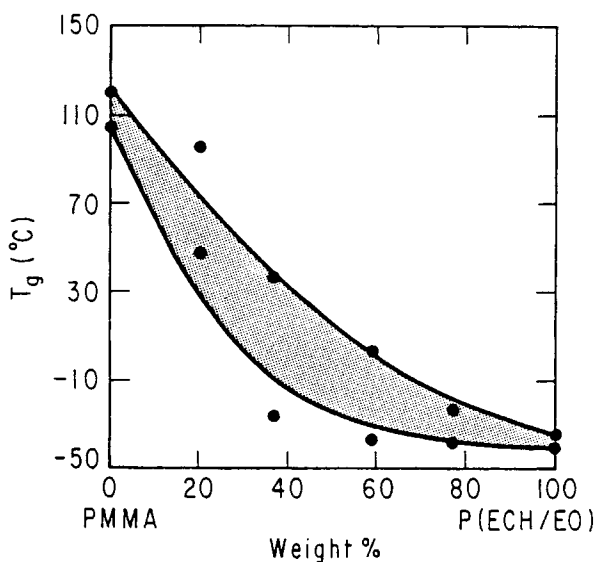


Fig. 20. Glass transitions for P(ECH/EO)-PMMA blends from DSC. Upper and lower points indicate the onset and end of the transition.

taining 30% of PECH. It should be noted here that the number of blend compositions tested for P(ECH/EO)/PMMA was smaller than for PECH/PMMA.

These blends were also tested in the Rheovibron with the results shown in Figures 21 and 22. Both the loss modulus E'' and $\tan \delta$ show a single peak located between the peaks obtained for the pure polymers. The temperatures at which the maximum in loss modulus occurred are shown in

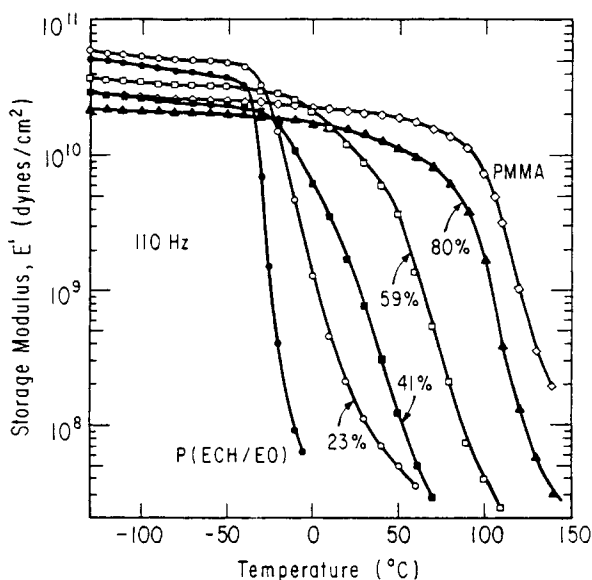


Fig. 21. Storage modulus versus temperature for P(ECH/EO)-PMMA blends.

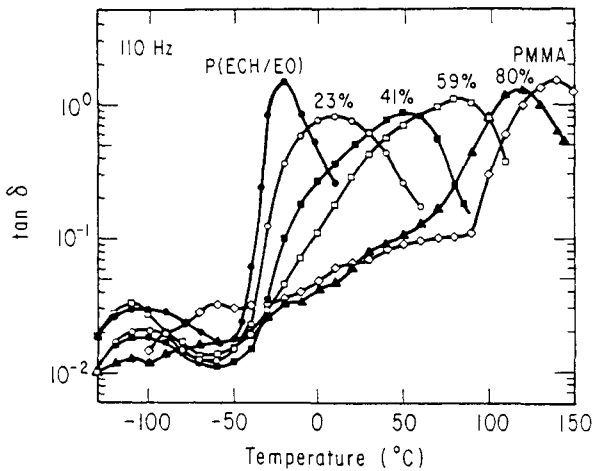


Fig. 22. $\tan \delta$ versus temperature for P(ECH/EO)-PMMA blends.

Figure 23 as a function of composition. As observed by DSC, broad peaks are obtained except at low concentrations of PMMA. The broadest peak is observed when the PMMA content is around 60%. This broadening is also apparent by the gradual way the storage modulus E' varies with temperature. At other compositions, E' changes more sharply with temperature in the transition region. These trends were the same for samples mechanically blended in the Brabender where solvent effects are not present. When DSC results for PECH/PMMA and P(ECH/EO)/PMMA blends are compared, the maximum transition breadth is observed for PECH/PMMA, but the Rheovibron measurements suggest a much broader transition for P(ECH/EO)PMMA. This is especially apparent when one compares the storage modulus of these two blends in Figure 21 and Figure 4.

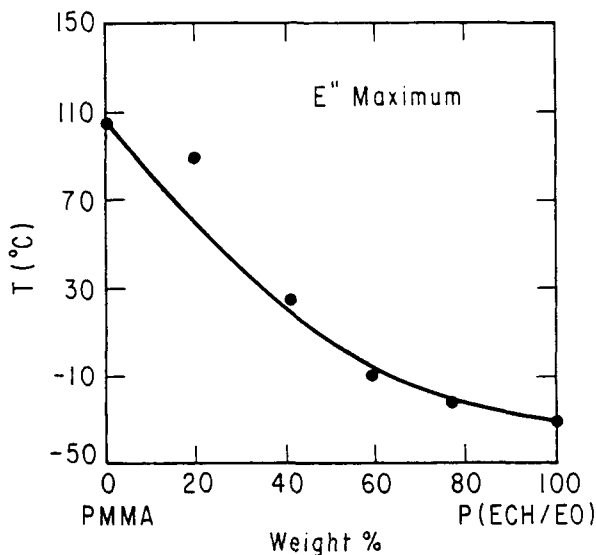


Fig. 23. Temperatures at which loss modulus shows maxima for P(ECH/EO)-PMMA blends.

In spite of the slight initial cloudiness of these blends, the detection of cloud points on heating was quite unambiguous. As shown in Figure 24, phase separation occurred at temperature considerably lower than those observed for PECH/PMMA blends.

Density measurements were also performed with this blend to find the excess volume. It is known that P(ECH/EO) absorbs considerable water³⁰ due to the ether groups in the molecule. The weight gain observed when P(ECH/EO), PMMA and its blends were immersed in water for 43 hours is shown in Figure 25. Since aqueous calcium nitrate solutions were used in

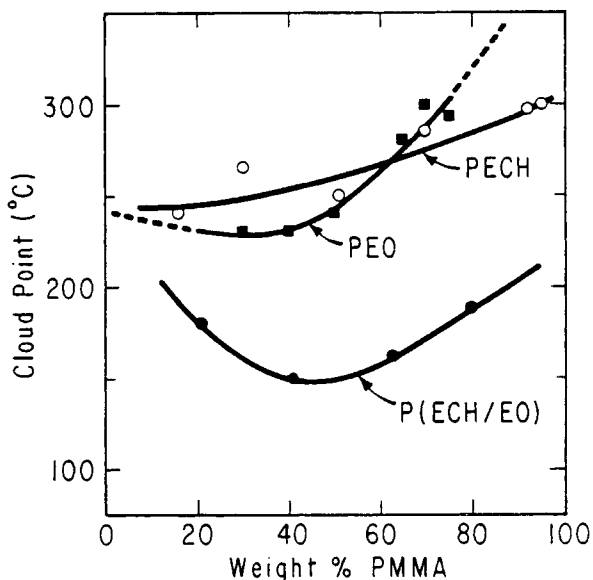


Fig. 24. Cloud points for blends of PMMA with PECH, P(ECH/EO) and PEO.

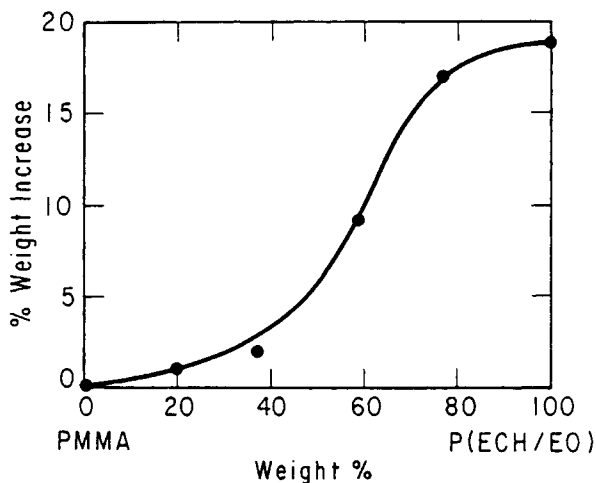


Fig. 25. Weight gain versus composition for P(ECH/EO)-PMMA blends immersed in water for 43 hours.

the density gradient column, extra care had to be taken in performing these measurements. The samples were weighed before they were placed in the column where they were left for only 12 hours, the time needed to reach the equilibrium position, and were weighed again immediately after they were taken out of the column. No significant change in weight was observed during this period of time. Surprisingly the excess volume observed for this blend shown in Figure 26 is about as large as that observed for PECH/PMMA. The specific volume of pure PMMA used in the calculations is the estimated equilibrium value, obtained by extrapolation shown in Figure 12.

Based on the dynamic mechanical results and cloud point measurements, one may conclude that PMMA exhibits stronger interactions with PECH than with P(ECH/EO). The similar changes in volume on mixing for these two systems may be due to geometrical packing considerations. That is, even though PECH interacts more exothermically with PMMA, P(ECH/EO) does not have as many pendant groups as PECH which may favor better packing between the molecules in the blends.

The next higher member in the polymethacrylates series, PEMA, was found to be immiscible with P(ECH/EO), based on glass transition behavior as shown in Figure 27.

RESULTS FOR POLY(ETHYLENE OXIDE) BLENDS

The films obtained from solution-casting blends of PMMA and poly(ethylene oxide) (PEO), from methylene chloride were transparent up to 25% of PEO. Above 30% of PEO, the cast films became gradually more cloudy due to the crystallinity of poly(ethylene oxide).

Thermograms for blends containing 25% PEO or less showed a distinct and single composition-dependent glass transition (see Fig. 28) that changes with composition in the manner expected for a miscible system. For blends containing 30% or more PEO, no glass transition could be detected owing to PEO crystallinity. Attempts to reduce this crystallinity by quenching

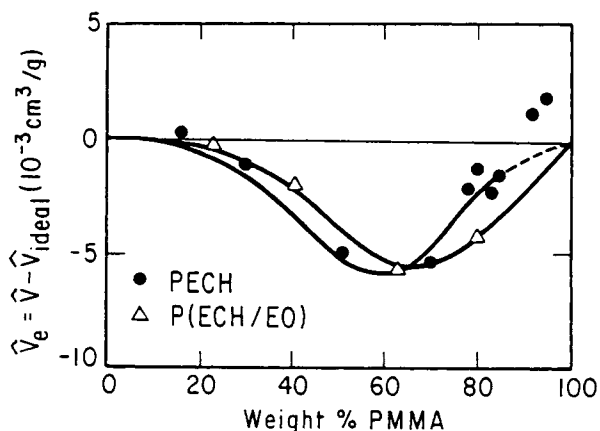


Fig. 26. Excess volume for blends of PMMA with PECH and P(ECH/EO) computed as in Fig. 13.

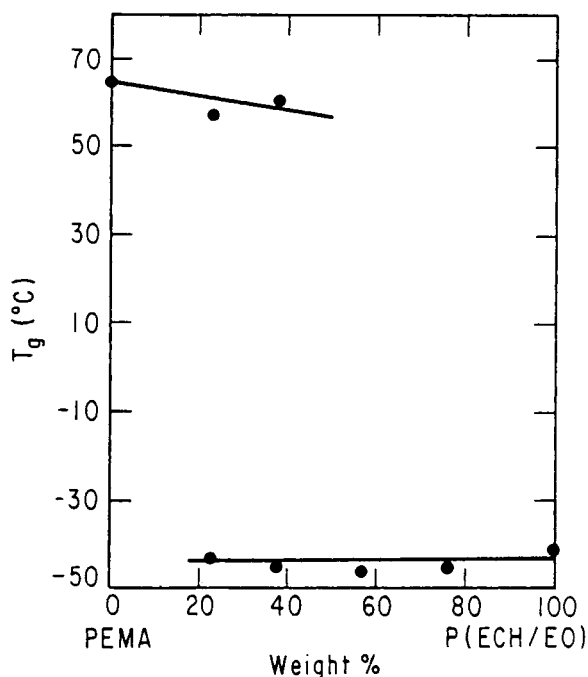


Fig. 27. Glass transitions for P(ECH/EO)-PEMA blends from DSC.

molten specimens by liquid nitrogen cooling in the DSC did not improve on this situation.

Considering the large difference in T_g s for PMMA and PEO, the breadth of the glass transitions is not as large as that seen for PMMA blends with PECH or with P(ECH/EO). For example, the broadening observed in blends containing 25% PMMA is 45°C for PEO/PMMA, compared with 74°C for PECH/PMMA or 48°C for P(ECH/EO).

PEO/PMMA blends were examined for phase separation on heating using the technique mentioned earlier. Very distinct cloud points were observed for blends in the midcomposition range with the results shown in Figure 24. No cloud point could be detected for blends rich in PMMA prior to temperatures where severe decomposition occurs. PEO-rich blends become somewhat clearer above the melting point, but were never completely clear owing to the cloudy nature of pure PEO melts (apparently due to impurities in this polymer). This fact made it very difficult to determine whether these blends showed any phase separation on heating or not. For comparison purposes, the cloud points observed for blends of PMMA with PECH and with P(ECH/EO) are also shown in Figure 24. Blends with P(ECH/EO) phase separate at significantly lower temperatures than do blends with PEO or with PECH, which for these purposes exhibit separation at about the same temperatures.

Since PEO is a crystalline polymer one can find the interaction parameter, B , using melting-point depression analysis. To minimize morphological effects due to different crystal thicknesses, care was taken in the way the melting points were measured. The blends were all subjected to the same

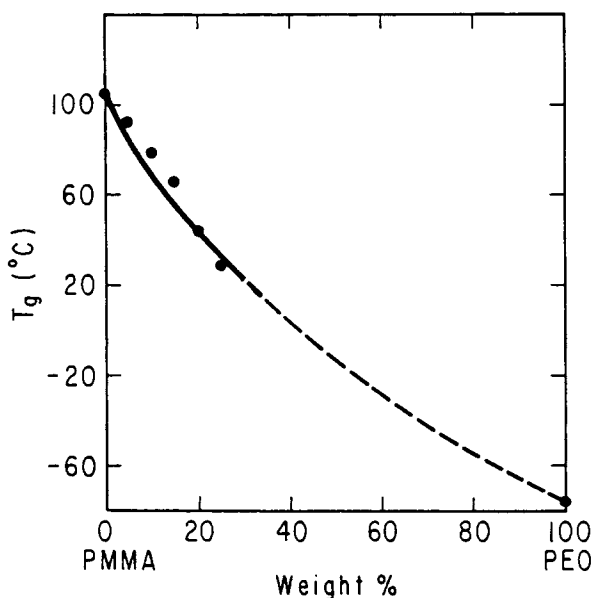


Fig. 28. Glass transitions for PEO-PMMA from DSC. The dashed line represents the expected behavior of T_g versus composition, for the blends where the T_g could not be detected.

thermal history. Using a heating rate of $10^\circ\text{C}/\text{min}$, the samples were heated to 127°C where they were held for 15 min. Then they were quenched to -63°C at a cooling rate of $320^\circ\text{C}/\text{min}$. The blends were left at this temperature for 30 min and the melting temperature was recorded in a subsequent heating at $10^\circ\text{C}/\text{min}$.

The Nishi and Wang equation¹⁵ was used to find the interaction parameter:

$$\left[1 - \frac{T_m}{T_m^\circ} \right] = - \frac{BV_{2u}}{\Delta H_{2u}} \cdot \phi_1^2 \quad (2)$$

where T_m° is the melting temperature of the pure crystalline polymer, T_m is the melting temperature in the mixture, ϕ_1 is the volume fraction of the amorphous polymer, V_{2u} and ΔH_{2u} are the volume and the heat of fusion per mole of repeat units of the crystalline polymer, respectively, and B is the binary interaction energy density. From the slope of the line, T_m versus ϕ_1^2 , B was found to be $-2.8 \text{ cal}/\text{cm}^3$ using $V_{2u} = 38.9 \text{ cm}^3/\text{mole}$ ³¹ and $\Delta H_{2u} = 2100 \text{ cal}/\text{mole}$.³¹ This agrees quite well with the value of $-2.85 \text{ cal}/\text{cm}^3$ found by Martuscelli et al.⁹

Since PEO/PMMA blends are crystalline over a large range of compositions and PEO is water soluble, no density measurements were made.

Poly(ethylene oxide) was solution blended with PEMA using methylene chloride. A blend containing 30% PEO and 70% PEMA was cloudy up to the decomposition temperature but DSC results were not conclusive since no glass transitions could be detected due to the crystallinity of PEO. The amount of PEO crystallinity in this blend was larger than that of a PEO/

PMMA blend with the same composition. From these preliminary experiments, we tentatively conclude that PEO and PEMA are not miscible; however, further work clearly is needed to be certain of this.

DISCUSSION

Of all the polymethacrylates considered only PMMA is miscible with the three polymers, PECH, P(ECH/EO), and PEO. It is of interest to compare the interactions of the latter three with PMMA and to understand, if possible, the reasons for this. Since PEO is the only crystallizable one of the three, it is the only one for which a quantitative estimate of the interaction with PMMA could be obtained. We have commented on the volume change on mixing and the broadening of the glass transition for each of the three pairs; however, based on the complexities of interpreting these quantities, it is not possible to use these data to unambiguously assign an order of the strength of the interactions with PMMA for these three polymers. We feel somewhat more secure in qualitatively drawing such conclusions from the cloud-point data in Figure 24. Since all three binaries are miscible, then at a given temperature below the lower critical solution temperatures, we know that the interaction parameters, B , applicable for the three binaries are all negative. Since blends based on either PECH or PEO show phase separation at about the same temperatures (see Fig. 24), the B values for their blends with PMMA must be of similar magnitude; whereas, the magnitude of B for blends of PMMA with P(ECH/EO) must be somewhat smaller owing to the substantially lower temperatures at which these mixtures phase separate on heating.

The argument that a net exothermic heat of mixing between two polymers can only be achieved by the existence of some specific interaction has often been used in the recent literature. Dissimilarity instead of similarity between two polymers seems to favor miscibility, i.e., most of the known miscible blends consist of polymers having electron-acceptor groups and polymers having electron-donor groups.

Although the above reasoning is rather simplistic, some conclusions are apparent. The existence of a specific interaction as a necessary condition to achieve miscibility between two polymers presents only a partial explanation of our experimental results. Particularly it is not readily apparent how one explains why PEO is miscible with PMMA or the rank of interactions between PECH, P(ECH/EO), and PEO.

It is possible to rationalize some of these observations using the recently published³² binary interaction model for mixing random copolymers of monomers 1 and 2 with a polymer comprised of monomer 3. This model gives the following expression for the overall blend interaction parameter

$$B = B_{13}\phi'_1 + B_{23}\phi'_2 - B_{12}\phi'_1\phi'_2 \quad (3)$$

in terms of interaction parameters for the three binary homopolymer mixtures, B_{ij} , and copolymer composition ϕ'_1 or ϕ'_2 , where $\phi'_1 + \phi'_2 = 1$.

Figure 29 illustrates the predictions of this model for the case where all three B_{ij} values are positive (left) and for the case where all three values

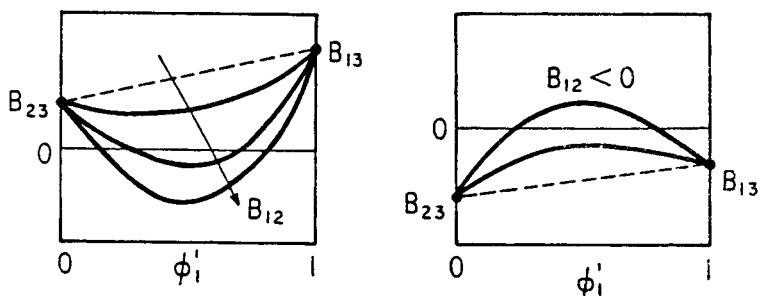
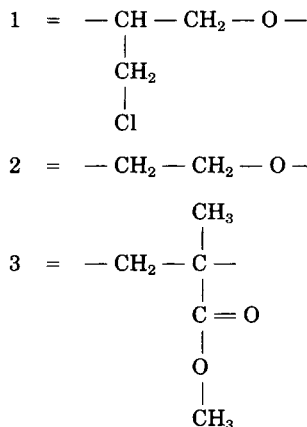


Fig. 29. Predictions of interaction energy density for blends of copolymer (1 + 2) with homopolymer (3) given by Eq. (3) when all $B_{ij} > 0$ (left) and when all $B_{ij} < 0$ (right).

are negative (right). For the present case, we make the following assignments



From the observations summarized above, we may state that $B_{13} \cong B_{23} < 0$. Preliminary experiments in our laboratory³³ indicate that PEO and PECH also form a miscible pair so we can tentatively say that $B_{12} < 0$. Thus, these systems fulfill the conditions of the right-hand part of Figure 29 in that all B_{ij} are negative. Based on this one might expect that the interaction of P(ECH/EO) with PMMA should be less favorable for miscibility than those for PMMA with PECH or PEO which are judged to be about the same. This is, in fact, what we conclude from Figure 24.

As shown in Figure 29, when all B_{ij} are positive, random copolymers of 1 and 2 may exhibit a window of miscibility with polymer 3 over a certain range of copolymer compositions. Likewise, when all B_{ij} are negative, these copolymers may exhibit a window of immiscibility with 3 for a certain range of copolymer compositions. These windows exist when the B_{ij} stand in the following relationship to each other

$$|B_{12}| > (\sqrt{|B_{13}|} + \sqrt{|B_{23}|})^2 \quad (4)$$

Windows of miscibility, when all $B_{ij} > 0$, are well known. This system is the first to our knowledge where all $B_{ij} < 0$, and apparently the relative magnitudes of the various B_{ij} are not such that a window of immiscibility is observed.

SUMMARY

Table II summarizes the phase behavior of various polymethacrylates with poly(epichlorohydrin), with poly(ethylene oxide), and with a commercially available random copolymer of epichlorohydrin and ethylene oxide. Each blend system classified as fully miscible did exhibit phase separation on heating, or LCST behavior, at relatively high temperatures. Most of these miscible blends had rather broad glass transitions, as observed by DSC, compared to those of the pure components. This T_g broadening has been discussed in terms of equilibrium composition fluctuations which become frozen into the glassy state on cooling and influence the range of temperatures over which molecular motions become active on subsequent heating. The magnitude of such fluctuations become larger as the interactions causing miscibility are weaker. At a critical level of interaction, the fluctuations grow to macroscopic dimensions; however, in the present systems such phase separation occurs at temperatures well above the glass transition region. To assess the relative magnitude of composition fluctuations from thermal data, it was found necessary to consider the difference in glass transitions of the components comprising the blends and the breadth of these pure component transitions (Table II precedes the References).

Density data for selected blends were determined and analyzed to learn about volume changes which occur on mixing. This analysis, however, is complicated by the fact that the polymethacrylates are glassy at room temperature while PECH and its copolymers are elastomeric. To provide a consistent reference state in the calculation of excess volume, the specific volumes of the polymethacrylates were extrapolated linearly from the melt state to give a hypothetical equilibrium liquid value. Based on this, volume changes on mixing were negative in all cases except for the PEMA/PECH system which showed a volume increase.

Since poly(ethylene oxide) was the only crystallizable component, it was not possible to obtain quantitative information about interaction parameters for the other blends. While T_g broadening and volume changes on mixing presumably are influenced by the strength of the interactions present, we believe the relative order of interaction strengths can best be assessed from the temperatures at which phase separation occur on heating for the various blends. Based on this, we conclude that the interactions between PMMA-PECH and PMMA-PEO are roughly the same; whereas, the interaction between PMMA-P(ECH/EO) is somewhat less which has been rationalized based on the apparent intramolecular attraction between epichlorohydrin and ethylene oxide residues which is believed to exist.^{32,33} The interaction between PECH and polymethacrylates seems to decrease as the size of the pendant group gets larger or more bulky; however, poly(cyclohexyl methacrylate) seems to be something of an exception to this.

Blends of polymethacrylates with poly(vinylidene fluoride),³ a styrene/acrylonitrile copolymer,³⁴ and an α -methyl styrene/acrylonitrile copoly-

mer³⁵ also show tendencies for decreasing interaction as the alkyl pendant group gets larger. However, blends with poly(vinyl chloride)^{2,5} and a vinylidene chloride/vinyl chloride copolymer⁴ show strongest interactions for alkyl groups of intermediate size. While poly(ethylene oxide) appears to interact as strongly with PMMA as poly(epichlorohydrin) does, it is evident from Table II that having the chlorine groups present apparently is necessary for forming miscible blends with the higher polymethacrylates.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, to the Army Research Office and to the Instituto Superior Tecnico, Universidade Tecnica de Lisboa, Portugal for their support of this research.

TABLE I
Polymers Used in this Study

Abbreviation	Polymer	Structure	Density (g/cm ³)	Molecular Weight Information	T _g (°C)	Source
PECH	Polyepichlorohydrin ^a	H +C - CH ₂ - O + CH ₂ Cl	1.367 ^a	$\bar{M}_n = 2.83 \times 10^5$ $\bar{M}_w = 5.55 \times 10^5$ ^d	-23	B.F. Goodrich Co. Hydrin 100
PECH EO	Polyepichlorohydrin ethylene oxide ^a (approx. equimolar)	H +C - CH ₂ - O + CH ₂ - CH ₂ - O + CH ₂ Cl	1.279 ^a	$\bar{M}_n = 2.45 \times 10^5$ $\bar{M}_w = 5.13 \times 10^5$ ^d	-41	B.F. Goodrich Co. Hydrin 200
PEO	Polyethylene oxide ^a	+CH ₂ - CH ₂ - O +	1.219 ^c	$\bar{M}_n = 300,000$ ^c	-76	Aldrich Chemical Co., Inc.
PMMA	Poly(methyl methacrylate)	CH ₃ +CH ₂ - C + C - O - CH ₃ O	1.184 ^a	$\bar{M}_n = 130,000$ $\bar{M}_w = 52,900$	+105	Rohm & Haas Plexiglass V811
PEMA	Poly(ethyl methacrylate)	CH ₃ +CH ₂ - C + C - O - C ₂ H ₅ O	1.122 ^a	$\bar{M}_n = 438,000$	-66	DuPont, Elvacite 2042
PnPMA	Poly(n-propyl methacrylate)	CH ₃ +CH ₂ - C + C - O - C ₃ H ₇ O	1.06 ^b	$[\eta] = 2.0$ dl/g ^b	+44	Polysciences, Inc.
PiPMA	Poly(isopropyl methacrylate)	CH ₃ +CH ₂ - C + C - O - $\begin{array}{c} \text{CH}_3 \\ \\ \text{CH} \\ \\ \text{CH}_3 \end{array}$ O	1.03 ^b	$[\eta] = 2.3$ dl/g ^b	-86	Polysciences, Inc.
PnBMA	Poly(n-butyl methacrylate)	CH ₃ +CH ₂ - C + C - O - C ₄ H ₉ O	-	High M_n	+29	Scientific Polymer Products, Inc., Cat #111A
PCHMA	Polycyclohexyl methacrylate	CH ₃ +CH ₂ - C + C - O - $\begin{array}{c} \text{S} \\ \diagup \quad \diagdown \\ \text{---} \end{array}$ O	1.10 ^b	$\bar{M}_n = 492,000$	+106	Rohm & Haas

^aDetermined experimentally in this study

^bRef. 14

^cK. Remadna, MSC thesis

^dRef. 16

^eAldrich Catalog

TABLE II
 Summary of Phase Behavior Observations

	PECH	P(ECH/EO)	PEO
PMMA	miscible	miscible	miscible
PEMA	miscible	immiscible	tentatively not miscible
PnPMA	miscible	n.t.	n.t.
PnBMA	miscible	n.t.	n.t.
PiPMA	partially miscible	n.t.	n.t.
PCHMA	miscible	n.t.	n.t.

n.t. -- not tested.

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