

Blends Containing Polymers of Epichlorohydrin and Ethylene Oxide. II. Polyacrylates

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Synopsis

The phase behavior of blends of various polyacrylate homopolymers and two commercial ethyl acrylate (EA) and *n*-butyl acrylate (nBA) copolymers with polyepichlorohydrin (PECH), poly(ethylene oxide) (PEO), and a copolymer of epichlorohydrin and ethylene oxide [P(ECH/EO)] was examined using differential scanning calorimetry and optical indications of phase separation on heating, i.e., lower critical solution temperature (LCST) behavior. Poly(methyl acrylate) (PMA) was shown to be miscible with PECH, PEO, and P(ECH/EO) while only PECH was found to be miscible with the higher polyacrylates: poly(ethyl acrylate), EA copolymer, poly(*n*-propyl acrylate), and nBA copolymer. However, even PECH was found to be only partially miscible with poly(*n*-butyl acrylate). In general, glass transitions observed by DSC for blends were not as broad as those found in corresponding polymethacrylate blends. 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 polyacrylates decreases with increasing size of the alkyl group. The commercial copolymers seem to interact more exothermically with PECH than the corresponding homopolymers. The interaction with PMA is apparently larger for PECH than for PEO or for P(ECH/EO). Interactions for the latter two are about the same. The apparently exothermic interactions between ECH and EO units are not sufficiently strong to preclude miscibility of P(ECH/EO) with PMA. As for the polymethacrylates, it is clear that the chlorine moiety of PECH is needed for miscibility with higher polyacrylates.

INTRODUCTION

Based on recent publications,¹⁻⁴ it seems that halogenated polymers often form miscible blends with many different polymethacrylates but fewer polyacrylates. For example, a vinylidene chloride/vinyl chloride copolymer was found to be miscible with a large number of polymethacrylates but two phase systems were obtained when it was blended with either poly(methyl acrylate) or poly(ethyl acrylate).³

Part I of this study⁵ showed that polyepichlorohydrin (PECH) is miscible with poly(methyl methacrylate) (PMMA), poly(ethyl methacrylate) (PEMA), poly(*n*-propyl methacrylate) (PnPMA), and poly(*n*-butyl methacrylate) (PnBMA) and that both chlorine and ether units are involved in the miscibility behavior observed. It is the purpose of this second part to examine how the replacement of the α -methyl group in polymethacrylates by an α -hydrogen to give corresponding polyacrylates affects the miscibility behavior with PECH. To study the importance of the ether group in the PECH backbone on the miscibility behavior, the polyacrylates have also been blended with an epichlorohydrin/ethylene oxide copolymer [P(ECH/EO)]

and poly(ethylene oxide) (PEO). The influence of the size of the pendant alkyl group on the miscibility behavior has also been investigated using homopolymer polyacrylates, prepared in the laboratory, with methyl, ethyl, *n*-propyl, and *n*-butyl groups. Two copolymers based primarily on ethyl acrylate and *n*-butyl acrylate are available as commercial rubbers. They have some unidentified comonomer included in their structures for posterior crosslinking, and they have been included in this work to learn what effect this slight change in polymer structure has on miscibility behavior. Sorption and transport of small molecule probes in blends of PMA and PECH are reported in the literature.^{6,7} To our knowledge, none of the other systems have been studied previously.

Independent of the obvious academic interest in understanding miscibility behavior in terms of molecular structure, blends of polyepichlorohydrin and polyacrylic rubbers are commercially of great importance. They show some valuable combinations of properties such as an excellent balance of high and low temperature properties and lower cost compared to simple polyacrylic rubber compounds.⁸

MATERIALS AND PROCEDURES

The polymers used in this study are described in Table I. PECH, P(ECH/EO), and PEO are the same materials used in Part I of this series. The polyacrylates were obtained from different sources and are all rubbery materials at room temperature. The poly(methyl acrylate) used to blend with PECH and PEO was supplied by Celanese, while the poly(methyl acrylate) used to blend with P(ECH/EO) was supplied by Polysciences, Inc. The PMA from these two sources have the same T_g and density but no molecular weight information is available for PMA from Polysciences. As already mentioned, poly(ethyl acrylate) and poly(*n*-butyl acrylate) were available as homopolymers and with some comonomer included in their molecular structures. The latter are commercial products from B. F. Goodrich Co. marketed under the designations HYCAR 4051EP and HYCAR 4043. These polyacrylic rubbers are copolymers consisting primarily of monomeric acid esters and a lesser amount of chlorine type reactive cure monomer. Monomers of this type can be generically represented as⁹



HYCAR 4051EP has an ethyl acrylate content greater than 95% and the reactive cure site comprises the remainder of the polymer. HYCAR 4043 is based primarily on *n*-butyl acrylate and also contains a chlorine type reactive cure monomer but no detailed information was available from the supplier, B. F. Goodrich, about the relative content of *n*-butyl acrylate. Based on glass transition temperature values, one suspects, however, that it is much less than 95%. We will refer to these rubbers, in this study, as EA copolymer and nBA copolymer, as shown in Table I.

Blends of the polyacrylates and acrylic rubbers with PECH were prepared by casting from toluene solutions containing about 5–10% of polymer by weight. The solvent was slowly evaporated at room temperature until the

TABLE I
 Polymers Used in This Study

Abbreviation	Polymer	Structure	Density (g/cm ³)	Molecular wt Information	T_g (°C) ^a	Source (Designation)
PECH	Polyepichlorohydrin	$\left[\begin{array}{c} \text{CH} - \text{CH}_2 - \text{O} \rightarrow \\ \\ \text{CH}_2 \\ \\ \text{Cl} \end{array} \right]_n$	1.367 ^a	$\begin{aligned} \bar{M}_n &= 2.83 \times 10^5 \\ \bar{M}_w &= 5.55 \times 10^5 \end{aligned}$	-23	B.F. Goodrich Co. (Hydrin 100)
P(ECH/EO)	Poly(epichlorohydrin/ ethylene oxide) (approx. equimolar)	$\left[\begin{array}{c} \text{CH} - \text{CH}_2 - \text{O} \rightarrow_x \dots \left[\text{CH}_2 - \text{CH}_2 - \text{O} \right]_y \\ \\ \text{CH}_2 \\ \\ \text{Cl} \end{array} \right]_{x+y}$	1.279 ^a	$\begin{aligned} \bar{M}_n &= 2.45 \times 10^5 \\ \bar{M}_w &= 5.13 \times 10^5 \end{aligned}$	-41	B.F. Goodrich Co. (Hydrin 200)
PEO	Poly(ethylene oxide)	$\left[\text{CH}_2 - \text{CH}_2 - \text{O} \right]_n$	1.219 ^b	$M_w = 300,000^d$	-76	Aldrich Chemical Co. Inc.
PMA	Poly(methyl acrylate)	$\left[\begin{array}{c} \text{CH}_2 - \text{CH} \rightarrow \\ \\ \text{C} - \text{O} - \text{CH}_3 \\ \\ \text{O} \end{array} \right]_n$	1.211 ^a	$\bar{M}_w = 576,000^e$	+17.8	Cellanese Chemi- cal Co.
PEA	Poly(ethyl acrylate)	$\left[\begin{array}{c} \text{CH}_2 - \text{CH} \rightarrow \\ \\ \text{C} - \text{O} - \text{C}_2\text{H}_5 \\ \\ \text{O} \end{array} \right]_n$	1.211	—	+18.0	Polysciences Inc. (25% solids in toluene)
			1.121 ^a	$M_w = 137,000^a$	-16.1	Celanese Chemi- cal Co.

(Continued)

TABLE I
 (Continued from previous page)

Abbreviation	Polymer	Structure	Density (g/cm ³)	Molecular wt Information	T_g (°C) ^a	Source (Designation)
EA copolymer	Copolymer of primary ethyl acrylate and a chlorine containing monomer to permit curing.		1.154 ^a	—	-10.8	B.F. Goodrich Co. (Hycar 4051EF)
PnPa	Poly(<i>n</i> -propyl acrylate)	$\left[\text{CH}_2 - \underset{\begin{array}{c} \\ \text{C} - \text{O} - \text{C}_3\text{H}_7 \\ \\ \text{O} \end{array}}{\text{CH}} \right]$	1.081 ^a	—	-35	Polysciences Inc. (25% in toluene)
PnBA	Poly(<i>n</i> -butyl acrylate)	$\left[\text{CH}_2 - \underset{\begin{array}{c} \\ \text{C} - \text{O} - \text{C}_4\text{H}_9 \\ \\ \text{O} \end{array}}{\text{CH}} \right]$	1.00/1.09 ^f	—	-53	Polysciences Inc. (20% in toluene)
nBA copolymer	Copolymer of primarily <i>n</i> -butyl acrylate and a chlorine containing monomer to permit curing.		---	---	-39.3	B.F. Goodrich Co. (Hycar 4043)

^a Determined experimentally in this study.^b Ref. 16.^c Ref. 17.^d Aldrich catalog.^e Ref. 18.^f Ref. 19.

films looked dry, and then they were placed in a vacuum oven at 110°C to remove any residual solvent.

Methylene chloride was used instead of toluene to cast blends of P(ECH/EO) with PMA, PEA, and EA copolymers. For these blends the vacuum oven was set at 80°C.

Since no good solvent was found for dissolving the nBA copolymer, blends of PECH and P(ECH/EO) with this rubber were made in a Brabender Plasticorder with the temperature set at 170°C. The rubbers were cut into small pieces and charged to the Brabender using a low rotation speed. This procedure lasted about 13 min. When all the polymer had been charged to the Brabender, the rotation speed was increased to 30 rpm and the two rubbers were mixed for about 7 additional minutes at 170°C.

Poly(ethylene oxide) was blended with PMA by casting from methylene chloride using the procedure mentioned above. To remove residual solvent, the blends were placed in a vacuum oven at 80°C.

A Perkin-Elmer Differential Scanning Calorimeter was used to measure glass transitions at a heating rate of 20°C/min. The blends were first heated to about 127°C and subsequently quenched at 320°C/min to -63°C. The glass transitions were recorded in a second heat using the same heating rate.

Melting point depression analysis was performed with PEO/PMA blends which was the only system containing a crystalline polymer. A series of experiments using cyclic heating and cooling at 10°C/min were done with this blend to find the interaction energy density B from the melting point depression.

Visual observations for blend phase separation on heating or lower critical solution (LCST) behavior were done on a hot plate at a heating rate between 5 and 10°C/min using the procedure previously described.¹⁰

Density measurements were made at 30°C in a gradient density column for all the miscible blends, using the procedure described in Part I of this series.⁵

RESULTS FOR POLYEPICHLOROHYDRIN BLENDS

The glass transition versus composition relations are presented in Figures 1-6 for PECH blends with PMA, PEA, EA copolymer, PnPA, PnBA, and nBA copolymer. Except for PECH/PnBA all the blends show a single glass transition, at a temperature intermediate to those of the pure polymers, which changes regularly as the composition is varied. Based on this, these blends are judged as miscible.

The blend of PECH with PnBA shows a single glass transition at low PECH concentrations, but as the PECH concentration increases there are two glass transitions. One occurs at the same temperature as the T_g of PECH and the other occurs at a temperature higher than the T_g of PnBA (Fig. 5). These findings suggest that two phases exist for large concentrations of PECH in the blend. One is pure PECH, and the other contains both polymers but is rich in PnBA. A blend containing about 40% PnBA was prepared using methylene chloride instead of toluene to cast the film. The same result was observed. Interestingly enough, if the equivalent commercial acrylic nBA copolymer is blended with PECH, a completely miscible system is obtained (Fig. 6).

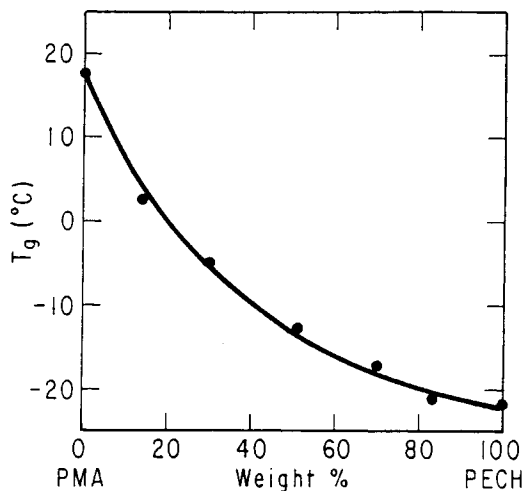


Fig. 1. Glass Transitions for PMA-PECH blends determined by DSC using the onset method of determining T_g from thermograms.

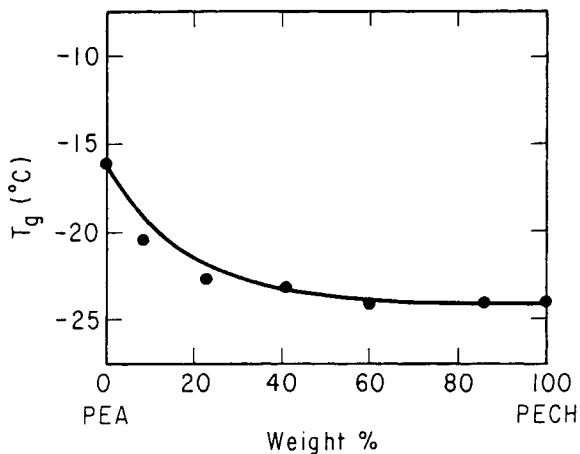


Fig. 2. Glass transitions for PEA-PECH blends determined as in Figure 1.

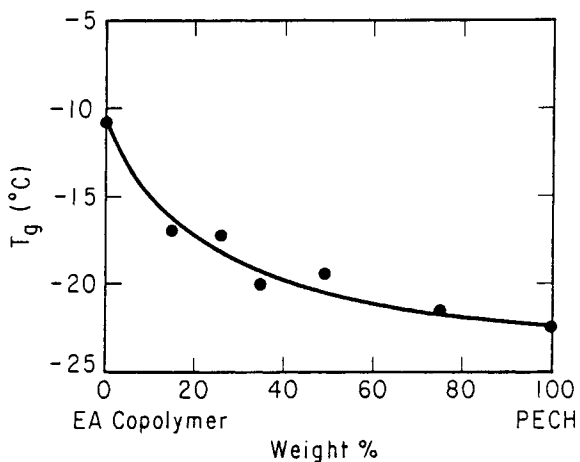


Fig. 3. Glass transitions for EA copolymer-PECH blends determined as in Figure 1.

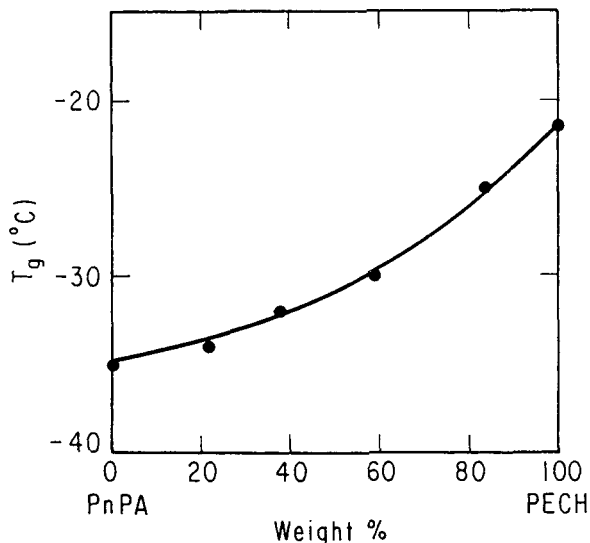


Fig. 4. Glass transitions for PnPA-PECH blends determined as in Figure 1.

Blends of PECH with the polymethacrylates exhibit very broad glass transitions relative to the pure polymers. The broadening is at a maximum for blends containing 70% PMMA and 78% PEMA. Based on the normalized transition breadth (Fig. 7) it was observed that in general polyacrylates show a smaller transition breadth than the corresponding polymethacrylates. The normalized transition breadth is defined as the ratio of the transition breadth for the blend, determined as the difference between the onset and completion temperatures of the transitions, and the difference in glass transitions for the pure polymers, ΔT_g , plus the transition breadth of the polymer with the higher T_g .⁵ Due to the fact that ΔT_g for these systems

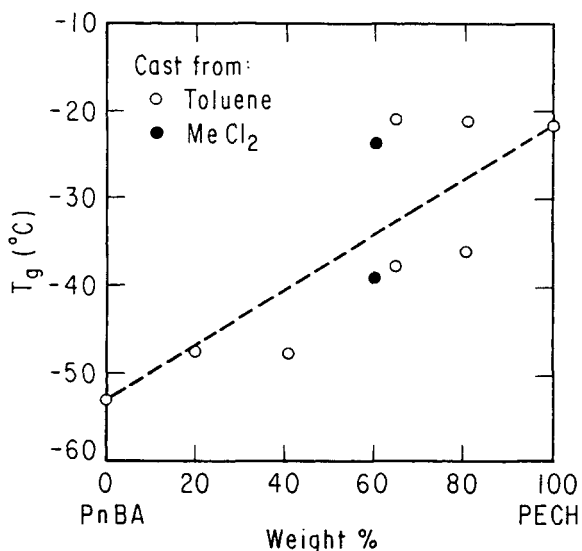


Fig. 5. Glass transitions for PnBA-PECH blends determined as in Figure 1.

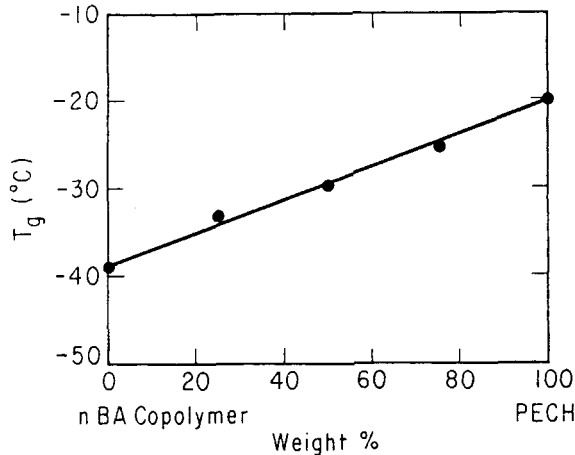


Fig. 6. Glass transitions for nBA copolymer-PECH blends determined as in Figure 1.

is small, the normalized transition breadth for the pure polymers, defined as described above, is greatly increased. In these cases when the pure polymers show extremely different normalized transition breadth, it seems more appropriate to compare the maximum normalized transition breadth for the blends relative to the normalized transition breadth for the pure polymers. A detailed discussion about the meaning of the transition breadth was given earlier.⁵

These blends were examined visually as described earlier¹⁰ for the existence of LCST behavior. Blends of PECH with the homopolymer polyacrylates were clear at room temperature with the exception of those containing PnBA which were slightly cloudy. When heated, a cloud point was observed in every case as shown in Figure 8. The cloud points occur at the highest temperature for PMA and the lowest for PnPA. This suggests

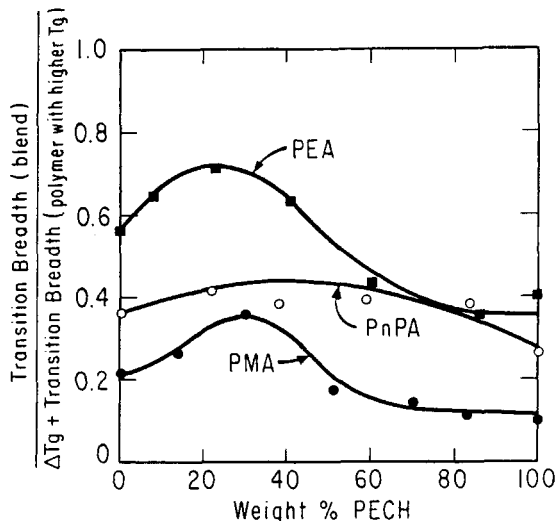


Fig. 7. Transition breadths for polyacrylates blends with PECH normalized by the difference in component T_g 's plus the breadth of the polymer with higher T_g .

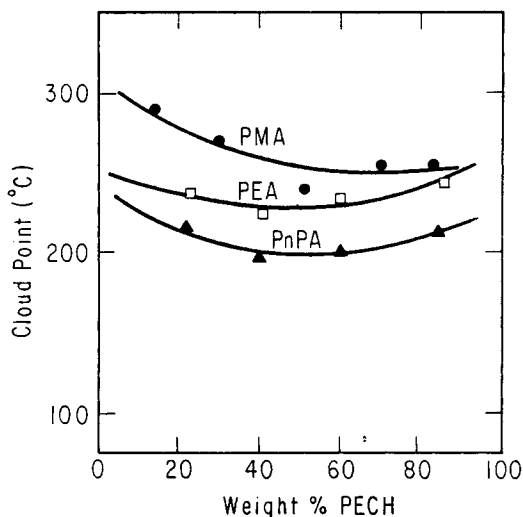


Fig. 8. Cloud points for blends of PMA, PEA, and PnPA with PECH.

that the strength of the interactions causing miscibility decreases as the size of the alkyl pendant group increases.

It should be noted here that the T_g of PECH and the T_g of PEA are only 5°C apart, and so one could question if the single T_g observed for these blends has a real meaning or is the result of a superposition of the glass transitions for the pure polymers. The additional observations concerning the clarity of the blends at room temperature and the occurrence of a cloud point on heating suggest that the single T_g is real and PECH is miscible with PEA.

Blends of PECH with the commercial acrylic rubbers had a slight initial cloudiness, due to the cloudiness of the EA copolymer and nBA copolymer themselves. However, distinct cloud points could be observed for blends of PECH with the EA copolymer which occurred at a slightly higher temperature than observed for blends of PECH with the PEA homopolymer (Fig. 9), suggesting stronger interactions in the former case than in the latter. The normalized transition breadth was found to be slightly larger for PEA than for EA copolymer blend with PECH (Fig. 10), which is in good accordance with the observed LCST behavior, i.e., the system that phase separates at higher temperatures is the one that shows sharper transitions. No cloud point could be observed for blends of PECH with the nBA copolymer due to the severe initial cloudiness of the blends. However, the normalized transition breadth for this system is slightly larger than for PECH/EA copolymer blend, as seen in Figure 11, suggesting a weakness of the interactions in the blend containing nBA copolymer.

Density measurements were performed for all the miscible blends at 30°C. Since the blends and the pure polymers are all in the rubbery state at this temperature, the complications that arise in many other systems due to thermal history differences is¹¹ minimized here because the systems are in, or at least closer to, an equilibrium state. Specific volumes versus composition are presented in Figures 12–16. In general, the excess volume of

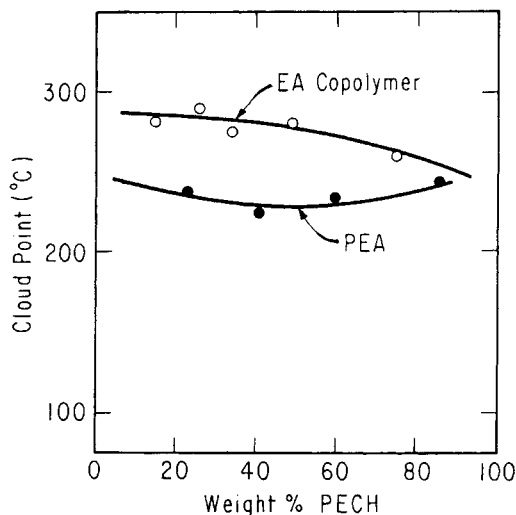


Fig. 9. Cloud points for blends of PEA and EA copolymer with PECH.

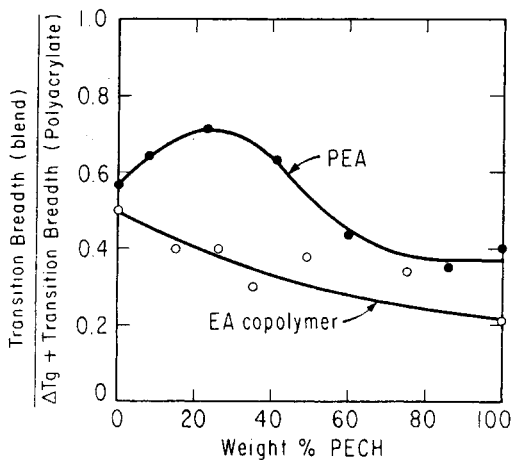


Fig. 10. Transition breadths for PEA-PECH and EA copolymer-PECH blends normalized as described in Figure 7.

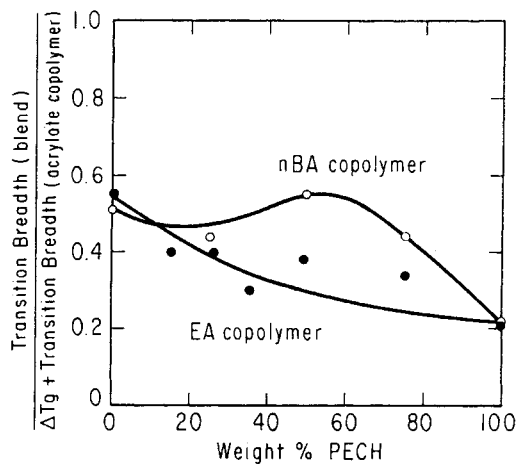


Fig. 11. Transition breadths for EA copolymer and nBA copolymer blends with PECH, normalized as described in Figure 7.

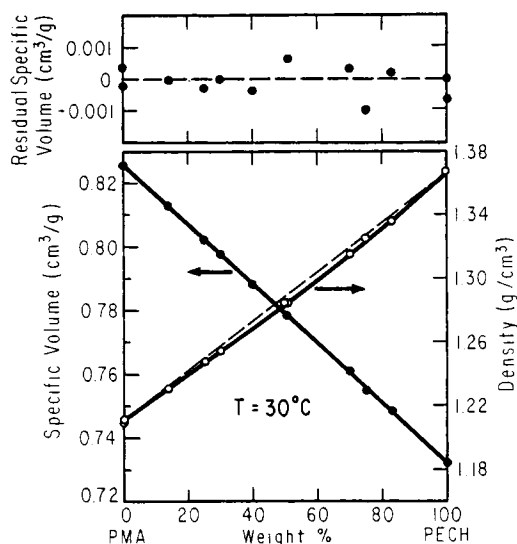


Fig. 12. Specific volumes for PECH-PMA blends at 30°C.

mixing is small and does not exceed the magnitude of experimental uncertainty, $\pm 8 \times 10^{-4} \text{ cm}^3\text{g}^{-1}$. With the exception of blends of PECH and the EA copolymer, the observed values follow the rule of volume additivity shown as the dotted line.

PECH/EA copolymer blends do not follow the additivity rule as may be seen in Figure 14. Rather, large negative excess volumes of mixing are observed for PECH-rich blends while large positive excess volumes of mixing are observed for lower PECH concentrations. No explanation for this observation is known at the present time.

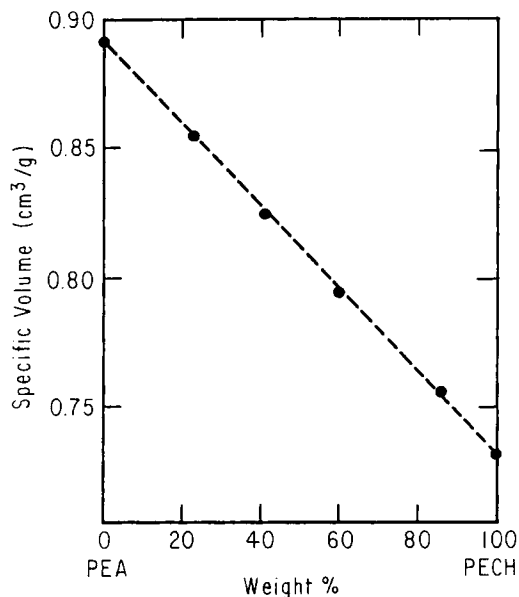


Fig. 13. Specific volumes for PECH-PEA blends at 30°C.

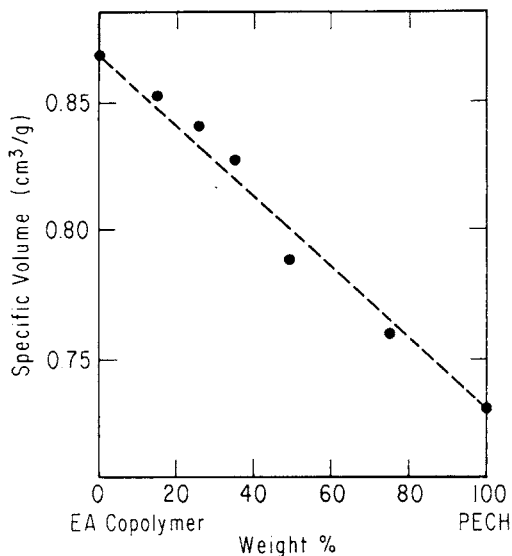


Fig. 14. Specific volumes for PECH-EA copolymer blends at 30°C.

RESULTS FOR POLY(EPOCHLOROHYDRIN/ETHYLENE OXIDE) BLENDS

The number of polyacrylates that are miscible with P(ECH/EO) is considerably less than observed with PECH. Actually, only the first member of the polyacrylate series, PMA, was found to be miscible with P(ECH/EO). Figure 17 shows the glass transition vs. composition relation for this system.

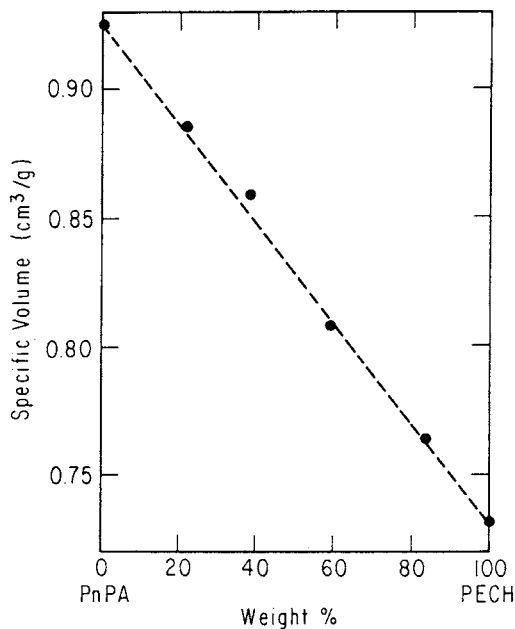


Fig. 15. Specific volumes for PECH/PnPA blends at 30°C.

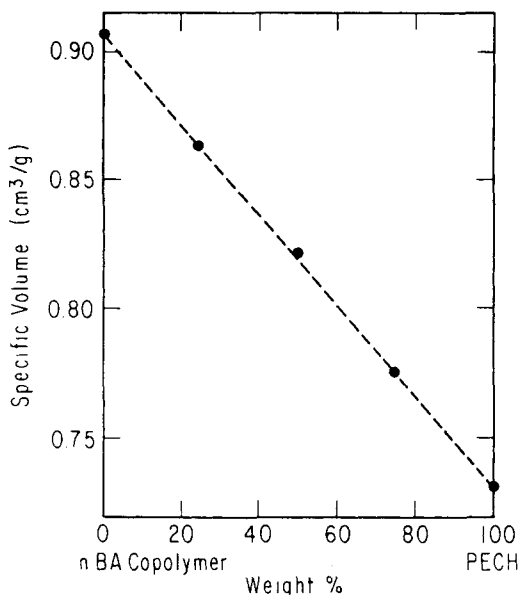


Fig. 16. Specific volumes for PECH/nBA copolymer blends at 30°C.

For each composition, two temperatures are indicated referring to the onset and the end of the DSC transition as explained in Part I of this series. The difference between the two temperatures gives a measure of the transition breadth. Even though a single glass transition is observed over the whole composition range (Fig. 18), the transitions are rather broad, except at high concentrations of P(ECH/EO), as can be seen by the shadowed area in Figure 17. The change in heat capacity at T_g , ΔC_p , is shown in Figure 10 as a function of composition. At intermediate compositions, ΔC_p follows a simple additivity rule. However, at the extreme compositions, the observed ΔC_p is lower than the calculated one.

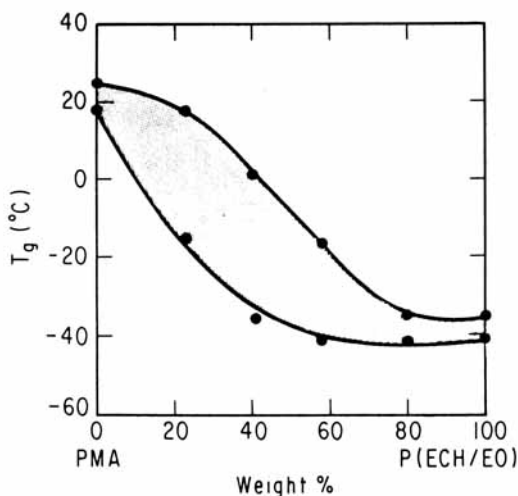


Fig. 17. Glass transitions for P(ECH/EO)/PMA blends from DSC. Upper and lower points indicate the onset and end of the transition.

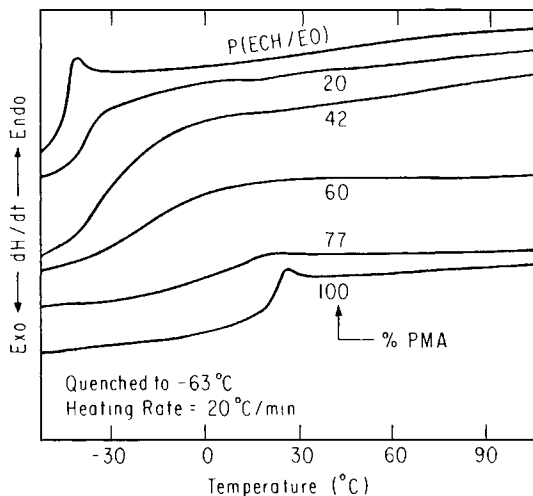


Fig. 18. Thermograms for blends of P(ECH/EO) with PMA.

This blend exhibits phase separation on heating or lower critical solution behavior at considerably lower temperatures than PECH/PMA blends do (Fig. 20). The broader T_g 's, as seen in Figure 21, and lower cloud points for P(ECH/EO)/PMA compared to PECH/PMA blends suggest that the interactions are weaker in the former than in the latter.

Figures 22 and 23 show the glass transition temperatures as a function of composition for blends of PEA and EA copolymer with P(ECH/EO) respectively. Two T_g 's are seen in both cases. One corresponds to the T_g of P(ECH/EO), and the other one is slightly displaced to lower temperatures. This suggests the existence of two phases, one consisting of pure P(ECH/EO) and the other one containing both P(ECH/EO) and PEA or EA copolymer but richer in the polyacrylate component. In this case, no significant changes were observed when the EA copolymer was used instead of PEA. The degree of interaction is so low that incorporation of the comonomer in the backbone does not improve miscibility.

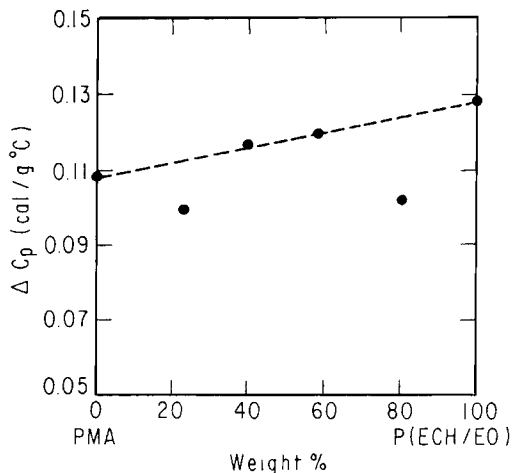


Fig. 19. Change in heat capacity at T_g for P(ECH/EO)-PMA blends.

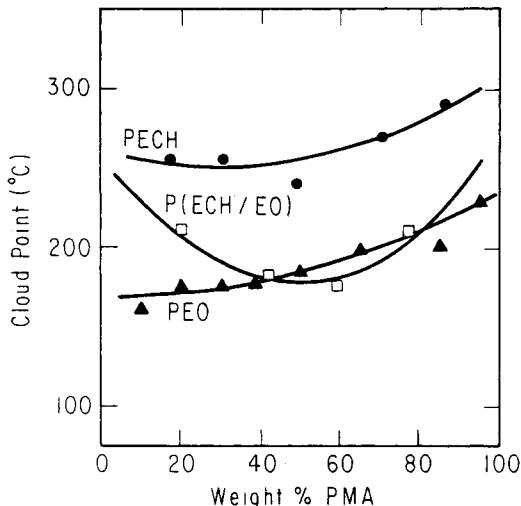


Fig. 20. Cloud points for blends of PECH, P(ECH/EO), and PEO with PMA.

The observed specific volumes for the miscible blend (Fig. 24) follow the volume additivity rule very closely, indicating a very small excess volume of mixing. This complementary result reinforces the previous conclusions deduced from the breadth of the glass transitions, and the temperatures at which phase separation were observed. P(ECH/EO) is miscible with PMA, but the interactions must be very weak.

RESULTS FOR POLY(ETHYLENE OXIDE) BLENDS

Poly(ethylene oxide) with \bar{M}_w of 300,000 was blended with PMA and the glass transition temperature vs. composition relation is shown in Figure 25. A single glass transition is observed over the whole range of compositions, at temperatures located between the glass transitions of the pure polymers, which changes regularly as the composition is varied. The thermograms for this blend are presented in Figure 26. Clear, amorphous films

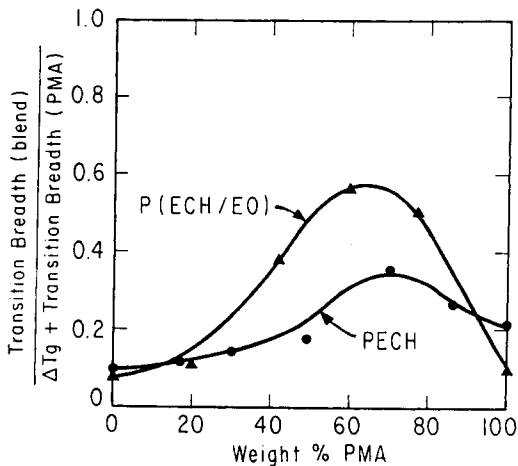


Fig. 21. Transition breadths for P(ECH/EO) and PECH blends with PMA, normalized as described in Figure 7.

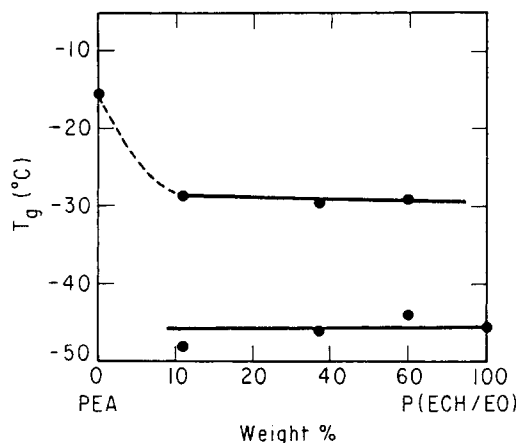


Fig. 22. Glass transitions for PEA/P(ECH/EO) blends determined as in Figure 1.

were obtained for blends containing up to 15% PEO. Above 35% PEO, the blends became progressively cloudier due to PEO crystallinity. When the amount of PEO was 50% or more, the blends were heated above the melting point for 5 min and then quenched to -133°C using liquid N_2 . Using this procedure, the PEO crystallinity was reduced but not removed completely. On subsequent heating, crystallization often occurs at a temperature where the glass transition should be located which makes it somewhat difficult to ascertain a value for the T_g .

The cloud point curve for this system is shown in Figure 20 together with the cloud points for PECH/PMA and P(ECH/EO)/PMA blends. This curve occurs at a lower temperature than for PECH/PMA blends and at about the same temperature for P(ECH/EO)/PMA blends. This suggests that the strongest interactions occur between PECH and PMA.

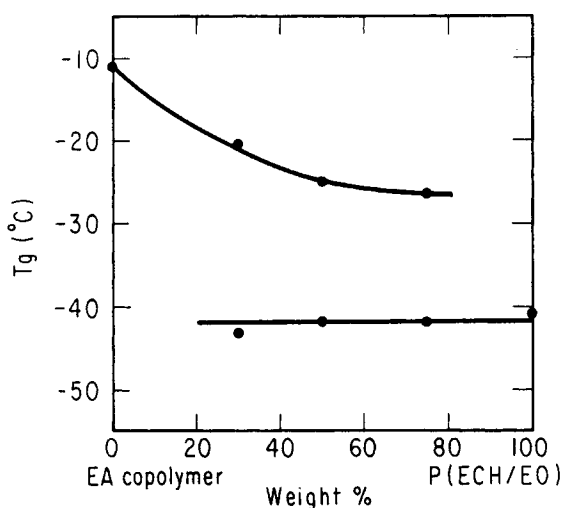


Fig. 23. Glass transitions for EA copolymer/P(ECH/EO) blends determined as in Figure 1.

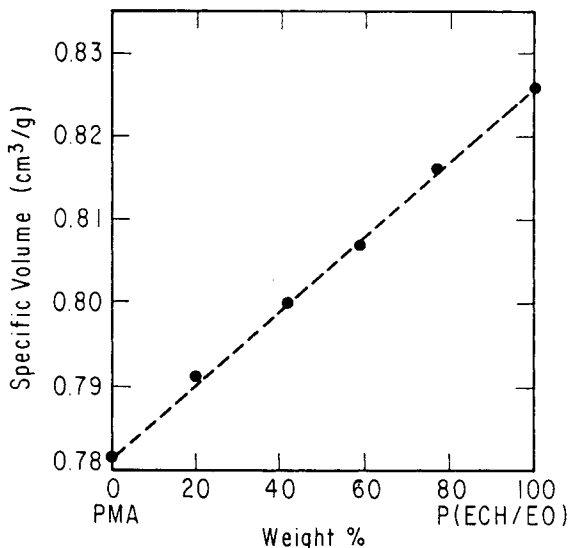


Fig. 24. Specific volumes for P(ECH/EO)/PMA blends at 30°C.

Poly(ethylene oxide) is a crystalline polymer; therefore, one can obtain information about the interaction parameter in blends by melting point depression analysis. Using the simple equation based on the Flory-Huggins theory, developed by Nishi and Wang,¹² and using the same procedure as in Part I of this series,⁵ the interaction energy density B was found to be -1.27 cal/cm^3 . To minimize the effects due to different thermal histories a cyclic heating-cooling procedure, as described in Experimental, was used.

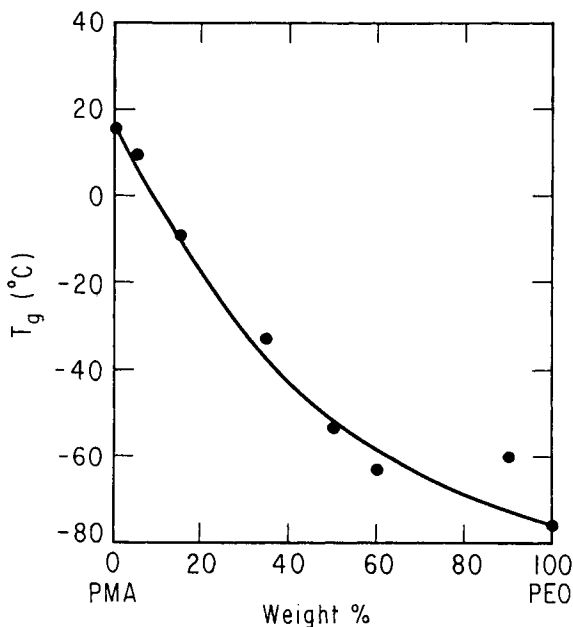


Fig. 25. Glass transitions for PMA-PEO blends, determined as in Figure 1.

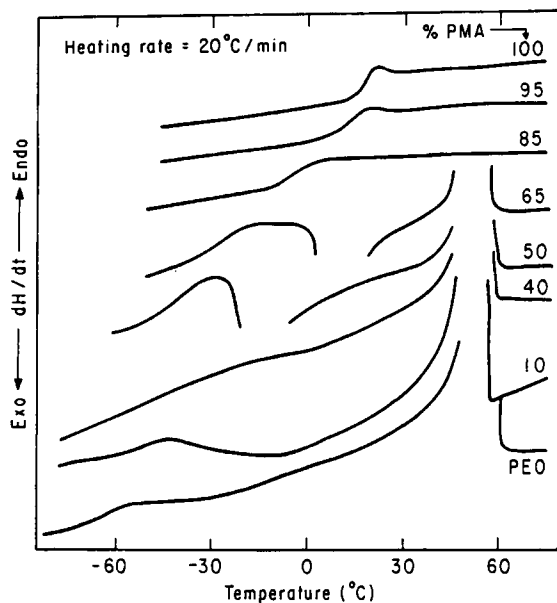


Fig. 26. Thermograms for blends of PEO with PMA.

A blend of poly(ethylene oxide) and poly(ethyl acrylate), containing 20% PEO, was also cast from a solution of methylene chloride. The as-cast film was cloudy but became more clear on heating after the PEO melted but was never completely clear. A single T_g was observed by DSC at the same temperature as that for pure PEA. Although the blend contained only 20% by weight of PEO, the crystallinity was high and could not be reduced by quenching the molten sample to -63°C as was possible for a PEO/PMA blend of similar composition. These observations suggest that PEO is immiscible with PEA; however, further experiments are needed to completely understand the phase behavior of this system.

SUMMARY

Table II summarizes the phase behavior observed for blends of polyacrylates with the polymers of epichlorohydrin and ethylene oxide which have been the subject of this series of papers.⁵ With regard to the homopolymer acrylates, these observations are quite similar to those reported earlier⁵ for the corresponding series of polymethacrylates. The main difference is that PnBMA is completely miscible with PECH while PnBA is only partially so. Two commercial acrylic rubbers, based primarily on either ethyl acrylate or *n*-butyl acrylate but containing small amounts of a chlorine type reactive cure monomer, have been included in this study for comparison with the corresponding homopolymers. PECH is miscible with both the homopolymers and the copolymer of ethyl acrylate. On the other hand, PECH is only partially miscible with the homopolymer of *n*-butyl acrylate but appears to be completely miscible with its copolymer.

Since all of the polymers employed in this study are amorphous, except for poly(ethylene oxide), it has not been possible to gain quantitative information about the interactions between the various blend pairs using the

TABLE II
Summary of Phase Behavior Observations^a

	PECH	P(ECH/EO)	PEO
PMA	Miscible	Miscible	Miscible
PEA	Miscible	Partially miscible	Tentatively not miscible
EA copolymer	Miscible	Partially miscible	n.t.
PnPA	Miscible	n.t.	n.t.
PnBA	Partially miscible	n.t.	n.t.
nBA copolymer	Miscible	Similar T_g 's	n.t.

^a n.t. = not tested.

simple and convenient melting point depression approach.¹³ Further, experimental determination of mixture specific volumes did not yield any useful information about the relative strengths of interactions within this set of systems. However, the fact that a nearly zero excess volume of mixing was obtained in most all cases suggests that these interactions are relatively weak. This conclusion is in agreement with observations on the sorption and transport of small molecule probes in blends of PMA and PECH.^{6,7} All of these miscible blends do show phase separation on heating, and the temperatures at which this happens can then be a useful but qualitative indicator of the relative strengths of the various interactions if it is assumed that molecular weight and free volume type effects are of lesser importance. Some conclusions, based on cloud point curves, about the effects of molecular structure on the interactions responsible for miscibility are noted below.

Evidently there is some type of specific interaction involving the pendant ester groups of the polyacrylates (and also polymethacrylates as seen previously⁵) and the ether oxygen in poly(ethylene oxide) or the chlorine plus nearby hydrogens and the ether oxygen in polyepichlorohydrin. As mentioned previously,⁵ the interaction involving the chlorine unit is easier to understand than the interaction involving the ether oxygen. As in the case of the polymethacrylates,⁵ increasing the size of the alkyl pendant group reduces the net interaction of the polyacrylates with PECH as seen by the lowering of the temperatures at which phase separation occurs on heating shown in Figure 8. Only poly(methyl acrylate) is miscible with poly(ethylene oxide) or the epichlorohydrin/ethylene oxide copolymer in complete analogy with observations for the polymethacrylates. Evidently, the increased dispersive interactions that result from larger alkyl pendant group size outweighs whatever specific interaction is involved to yield a net interaction which becomes unfavorable for miscibility at a certain alkyl group size. It is interesting that PECH blends can accommodate a much broader range of alkyl group sizes and retain miscibility than can PEO or the P(ECH/EO) copolymer.

The cloud point curve shown in Figure 20 suggests that PMA interacts more exothermically with PECH than with either PEO or P(ECH/EO). The latter two seem to have rather comparable interactions with PMA which is somewhat different from earlier observations with PMMA. One could apply the binary interaction model for copolymer systems¹⁴ as described previously for blends of PMMA with these same polymers.⁵ Since quantitative information is not available for all of the various binary interaction

parameters, it is difficult to conclude much from this approach except to say that the apparently exothermic interactions between ECH and EO units in the copolymer chain¹⁵ are not sufficiently strong to preclude miscibility of this copolymer with PMA. A thorough discussion of this point was made earlier⁵ for the analogous case for blends with PMMA and is not repeated here.

The phase behavior of the commercial copolymers in blends with PECH is of both fundamental and practical importance. Unfortunately, information about the identity and the amount of the comonomer incorporated into these materials for the purpose of allowing them to be vulcanized is not available. The presence of this monomer seems to assist miscibility with PECH since the homopolymer of *n*-butyl acrylate forms only partially miscible blends with PECH, whereas the corresponding commercial copolymer, HYCAR 4043, is completely miscible with PECH based on glass transition behavior. Although both the homopolymer and the copolymer, HYCAR 4051EP, of ethyl acrylate are completely miscible with PECH, the cloud points shown in Figure 9 suggest that the copolymer interacts more favorably with PECH than does the homopolymer in good accord with the comparison for the *n*-butyl acrylate based polymers. A comparison between normalized transition breadth is also in agreement with the previous observations.

It is of interest to examine the available evidence relating to the differences in interaction of PMMA and of PMA in the various blends described in this and the previous paper. Based on the temperatures at which phase separation occurs on heating we may conclude the following: The interactions of PECH with PMMA and PMA seem to be quite similar; the interactions of the copolymer P(ECH/EO) seem more favorable with PMA than with PMMA; and PEO interacts more favorably with PMMA than with PMA. The latter is supported by a quantitative comparison of interaction parameters deduced from melting point depression analysis: for PMMA $B = -2.8 \text{ cal/cm}^3$ while for PMA $B = -1.27 \text{ cal/cm}^3$.

Based on normalized transition breadths, the broadening of the glass transition was found to be smaller in the polyacrylates blends with PECH than in those containing polymethacrylates. The connection between this observation and strength of interactions in both series is not easy to understand at this point.

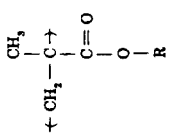
No comparison is made here between the glass transition broadening observed for polyacrylate and polymethacrylate blends with P(ECH/EO) due to the difficulties previously found⁵ in defining unambiguously the transition breadth for the blend of P(ECH/EO) with PMMA.

It would be desirable to compare the phase behavior for blends containing other halogenated polymers and polymethacrylates or polyacrylates with those investigated in this study. Table III summarizes the phase behavior for these blends. For comparison purposes, we divide these halogenated polymers into two groups. In the first group constituted by poly(vinyl chloride) and vinylidene chloride/vinyl chloride copolymer, the polymethacrylates are more miscible than the polyacrylates. Another characteristic of these systems is that the strength of the interactions shows a maximum for an intermediate size of the alkyl pendant groups. In the second group,

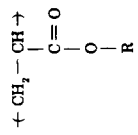
TABLE III
Summary of Phase Behavior for Blends Containing Halogenated Polymers and Polymethacrylates or Polyacrylates

R	Poly(vinyl chloride)		Vinylidene chloride/vinyl chloride copolymer		Poly(vinylidene fluoride)		Polyepichlorohydrin		Epichlorohydrin/ethylene oxide copolymer	
	Poly-methacrylate ^a	Poly-b acrylate ^b	Poly-methacrylate ^a	Poly-b acrylate ^b	Poly-methacrylate ^a	Poly-b acrylate ^b	Poly-methacrylate ^a	Poly-b acrylate ^a	Poly-methacrylate ^a	Poly-b acrylate ^b
-CH ₃ CH ₃ -CH ₂ CH ₃	Miscible ^d Miscible ^d	Immiscible ^e Miscible ^e	Miscible ^f Miscible ^f	Immiscible ^f Immiscible ^f	Miscible ^g Miscible ^g	Miscible ^g Miscible ^g	Miscible ^h Miscible ^h	Miscible ^h Miscible ^h	Miscible ^h Immiscible ^h	Poly-b acrylate ^b Miscible ^h Partially miscible ^h
-CH ₂ CH ₂ CH ₃ -CH ₂ CH ₂ CH ₂ CH ₃	Miscible ^d Miscible ^d	Miscible ^d Miscible ^d	Miscible ^f n.t.	Immiscible ^f n.t.	n.t. n.t.	n.t. n.t.	Miscible ^h Miscible ^h	Miscible ^h Partially miscible ^h	n.t. n.t.	n.t. n.t.

a



b



n.t. = not treated.
d Ref. 2.
e Ref. 1.
f Ref. 3.
g Ref. 4.
h This study.

constituted by PECH, P(ECH/EO), and poly(vinylidene fluoride), the experimental results suggest that the strength of the interactions decreases as the size of the alkyl pendant group increases. On the other hand, for PECH and P(ECH/EO) the miscibility with the polymethacrylates is approximately the same as with the polyacrylates. For P(ECH/EO), the polyacrylates are slightly favored while for PECH the polymethacrylates are slightly favored. At this point it is not possible to conclude anything about poly(vinylidene fluoride) since only two members of these series were tested.

As a conclusion one can say that it is not an easy task to establish trends for the phase behavior within this group of systems.

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