Interpenetrating Polymer Networks of Poly(ethyl acrylate) and Poly(styrene-*co*-methyl methacrylate).
II. Physical and Mechanical Behavior

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ABSTRACT: The physical and mechanical properties of poly(ethyl acrylate)–poly(styrene-*co*-methyl methacrylate), PEA–P(S-*co*-MMA), interpenetrating polymer networks (IPN's) have been investigated. Dynamic mechanical spectroscopy measurements *via* Vibron instrumentation show how compatibility increases as MMA-mers replace S-mers in the IPN. Principally, two reasonably sharp glass transitions are replaced by one very broad continuous transition, which may be interpreted as a continuous range of transitions reflecting different local compositions. The extent of molecular mixing increases as the percent MMA increases, but a significant amount of phase separation remains even with the PEA–PMMA IPN's. Application of Bauer's theoretical treatment suggests that both phases exhibit some degree of continuity for most, if not all, of the materials investigated. Stress–strain and tensile data show that the work to break as well as the actual tensile values of the samples steadily increase as the amount of plastic component is increased in the elastomer-rich materials. These IPN's show many features common to the toughened blends and block copolymers. An analysis of the impact properties of IPN's in the light of Bragaw's theory of crack branching in blends confirms the widely found empirical fact that T_g of the rubber component must be at least 60° below test temperature to achieve significant impact improvement.

The synthetic steps employed in the preparation of polymer blends influence their morphology, such as phase domain, size and structure, and extent of molecular mixing. The morphology in turn controls the physical and mechanical behavior of these materials. Thus, there exists a one-to-one relationship between detailed chemical preparative techniques and such behavior as dynamic mechanical spectroscopy (dms) and toughening. In the past few years a considerable body of information has become available which substantiates the synthesis–morphology–property interrelationships. This includes work on mechanical blends,[1] graft copolymers,[2,3] block copolymers,[4,5] and interpenetrating elastomeric networks (IEN's).[6,7] In the first paper of the present series[8] (ref 8 contains a review of the polymer blend literature as well as a summary of IPN studies), the synthesis and morphology of poly(ethyl acrylate)–poly(styrene-*co*-methyl methacrylate) (PEA–P(S-*co*-MMA) interpenetrating polymer networks (IPN's) were presented, principally as observed *via* electron microscopy. The findings included a cellular structure of about 1000-Å diameter and a 100-Å fine structure within the cell walls for incompatible compositions, while only the fine structure remained for semicompatible compositions. The present paper will consider the physical and mechanical properties of the PEA–P(S-*co*-MMA) system, emphasizing dynamic mechanical experiments.

The individual polymers PEA, PMMA, and PS were selected for this study for the following reasons. (1) While PEA and PS are chemically different and known to be incompatible, PEA and PMMA are chemically isomeric and were thought to mix extensively, if not completely. Thus IPN's of PEA with P(S-*co*-MMA) random copolymer compositions would be expected to vary significantly in what is generally termed "polymer compatibility." (2) PS and PMMA have glass temperatures of 100 and 105° so that P(S-*co*-MMA) copolymers would be essentially isoglass, having the same transition temperature, iso-T_g. This latter was expected to simplify the analyses of the resulting physical and mechanical data.

Experimental Section

Synthesis. The syntheses of the materials employed in this investigation have already been described.[8]

Dynamic Mechanical Spectroscopy. The present study employed a direct reading dynamic viscoelastometer, Rheovibron Model DDV-II, manufactured by Toyo Measuring Instruments Co., Ltd., Tokyo. Measurements were conducted at a frequency of 110 Hz from −50 to 175° at a heating rate of 1°/min. Sizes of the specimens used were approximately 0.3 mm × 2.5 mm × 4 cm. Dynamic mechanical data were easily reproduced except for tan δ below −35°.

Previous work on IPN's from this laboratory had employed 3G(10) (three times the shear modulus at ten seconds) as a measure of transition behavior.[9–14] The quantity 3G(10) corresponds roughly to the value of E' taken at 0.1 Hz. Normally, T_g increases at the rate of 6 or 7° per decade of frequency increase.[15] The important point, however, is that measurement of the shear modulus does not directly indicate the magnitudes of the loss quantities.

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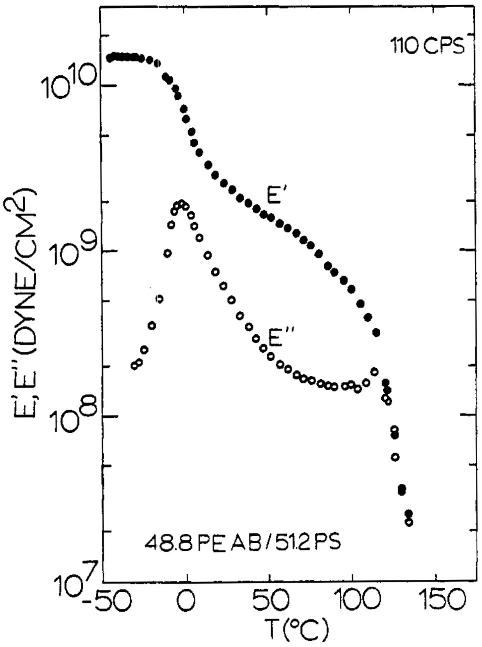

Figure 1. Temperature dependence of *E'* and *E''* of IPN L1. This incompatible material exhibits two distinct glass transitions.

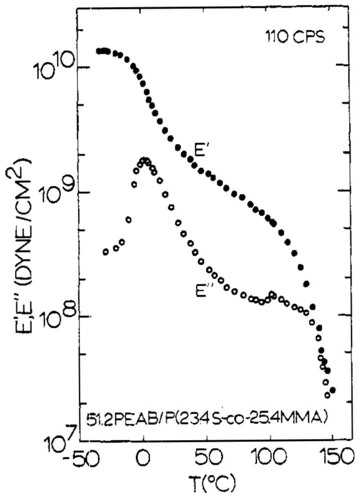

Figure 2. Temperature dependence of *E'* and *E''* of IPN L2. The substitution of half of the S-mers by MMA-mers only slightly changes the mechanical behavior, two distinct transitions still being observable.

Results

Dynamic Mechanical Spectroscopy. The present measurements are designed to complement the morphology studies.[8] While electron microscopy reveals the size, shape, and arrangement of the phases, dms experiments yield insights about the extent of mixing of the two components, at least semiquantitatively.

While simple homopolymers and random copolymers exhibit one glass transition,[9] the phase-separated polymer blends show two such transitions, one for each phase. The total drop in modulus incurred in each transition depends not only upon overall composition, but also upon the relative continuity of the two phases. Shifts and broadening of the transitions are indicative of molecular mixing. Thus, incompatible materials show two relatively sharp transitions, while semicompatible blends show one broad transition.[3]

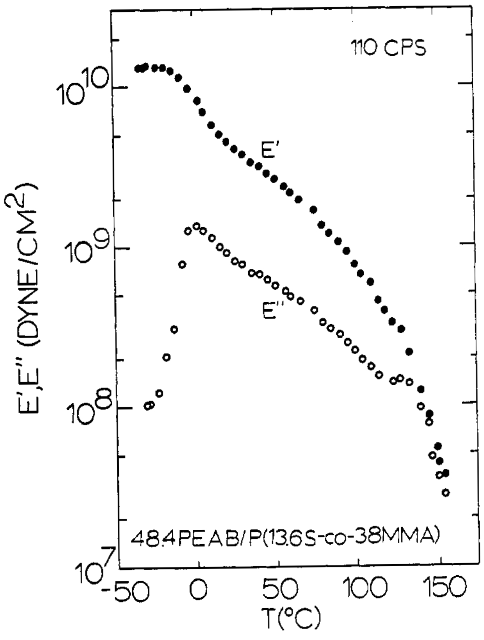

Figure 3. Temperature dependence of *E'* and *E''* of IPN L3. Substitution of further MMA for S-mers results in a much more compatible mixture.

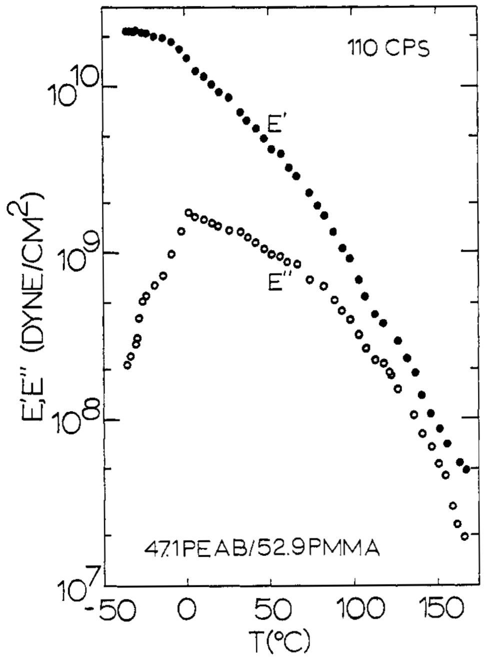

Figure 4. Temperature dependence of *E'* and *E''* of IPN L4. This PEA–PMMA IPN appears to exhibit one broad transition covering over 100°. It may be more exact to say that a series of transitions is taking place at temperatures dependent upon local composition for this semicompatible polymer pair.

Leathery Series. The leathery series comprises the mid-range, 50/50 rubber–plastic materials. Figures 1–4 show *E'* and *E''* as a function of temperature for the 50/50 PEA–P-(S-*co*-MMA) IPN's. These materials were previously designated L1, L2, L3, and L4, depending on the MMA contents. When no MMA-mers are present (50/50 PEA–PS), two well-defined transitions exist, as shown in Figure 1. This behavior is typical of an incompatible system. The PEA transition is about 10° higher than that for the homopolymer elastomer, and the PS transition about 15° lower than that obtained for

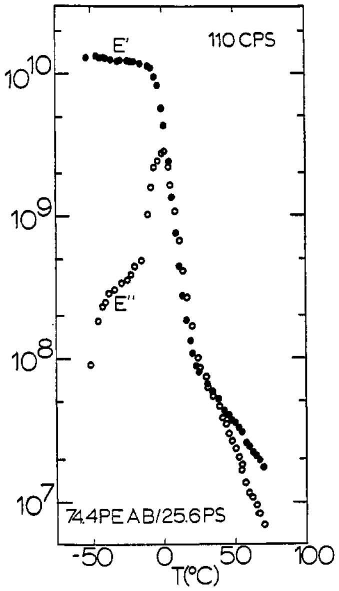

Figure 5. Temperature dependence of E' and E'' of IPN E1.

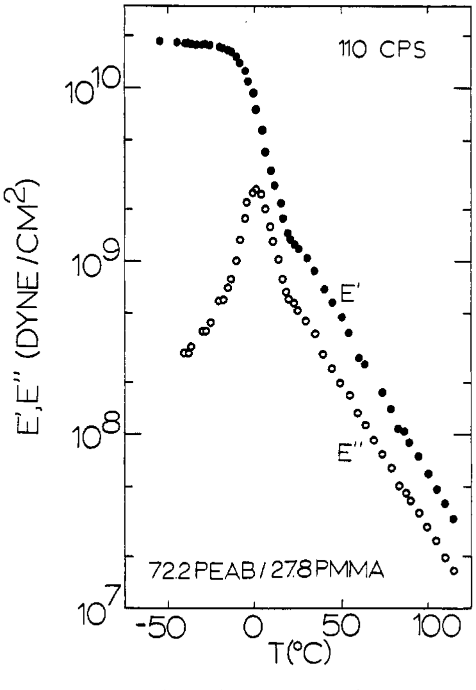

Figure 6. Temperature dependence of E' and E'' of IPN E4.

the homopolymer plastic, each homopolymer containing the same cross-link density as the corresponding IPN component. This inward shift is indicative of the extent of molecular mixing taking place.[16]

As MMA-mers replace S-mers, Figures 2, 3, and 4, the E'' peaks broaden slightly but do not further move inward toward each other, as might be intuitively expected. Instead, the two peaks are gradually supplemented by a broad band of increasing E'' values between the two peaks. It is important to note that the two original peaks do not substantially decline from Figure 1 to Figure 4, but that the area under the central portion of the E'' plot in Figure 4 is substantially higher than in Figure 1. At the same time the E' values have been transformed from two transitions into what

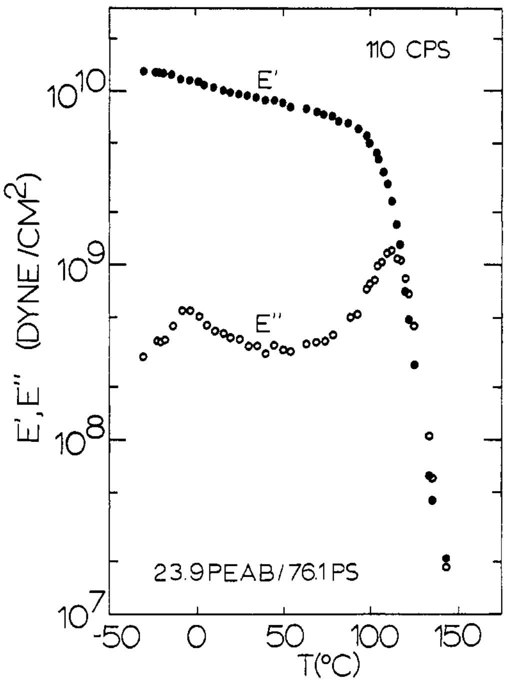

Figure 7. Temperature dependence of E' and E'' of IPN P1. Although E' shows only one transition, the presence of the lower transition is revealed by the E'' maximum near 0°.

appears to be one broad transition covering a temperature span of over 100°.

Elastomeric and Plastic Series. In these materials, either the elastomeric or plastic components comprise the majority phase, at a level of 75%, respectively. For brevity, only the PEA-PS and PEA-PMMA border (limiting) compositions will be presented, since the transformation through the copolymer series is similar to that already shown in Figures 1-4. Figures 5 and 6 show 75/25 PEA-PS and 75/25 PEA-PMMA IPN's of the elastomeric series. The higher glass transition could not be effectively observed because of instrumental limitations. However, the lower transition covers a broader area on the high-temperature side, again probably as a result of increased molecular mixing in the PEA-PMMA IPN. Because of the very rapid drop in E' after the PEA transition, it may be concluded that the elastomer is the more continuous phase.

Quite a different picture is presented in Figures 7 and 8 for 25/75 PEA-PS and 25/75 PEA-PMMA, respectively, of the plastic series. Because of the very small change in E' at the T_g of the PEA component, the plastic phase gives some of the appearances of being continuous, even though the elastomer was synthesized first. As we shall see below, there is reason for assuming that both components are in fact continuous.

Inverse IPN's. In the several materials shown in Figures 1-8, the elastomeric network was synthesized first, and the plastic component monomers were swollen in and polymerized second. When the order of polymerization is reversed, we might expect topological differences to occur, even for truly compatible materials. This is because the chains of the first network will always be strained (swollen) to some extent, and those of the second network will be more nearly at equilibrium. However, these materials also phase separate, the structures grossly resembling black-white inverses,[8] and it is of real interest to see what complications may be incurred in the dynamic mechanical behavior.

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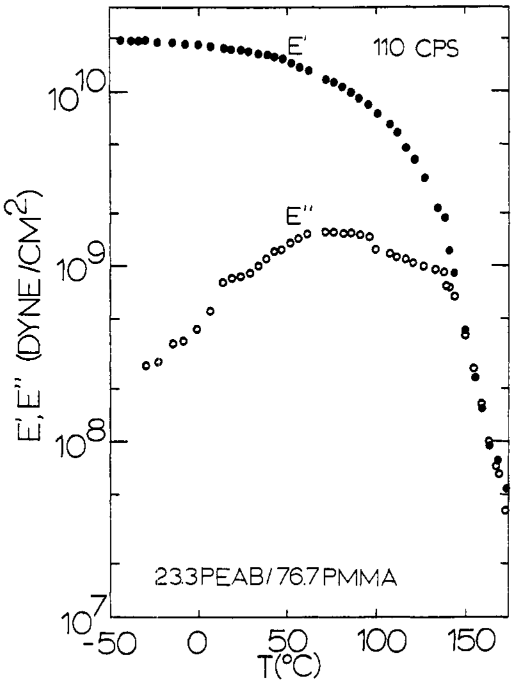

Figure 8. Temperature dependence of E' and E'' of IPN P4. The two loss peaks of Figure 7 have been replaced by one broad loss band covering the full range between the two homopolymer transitions.

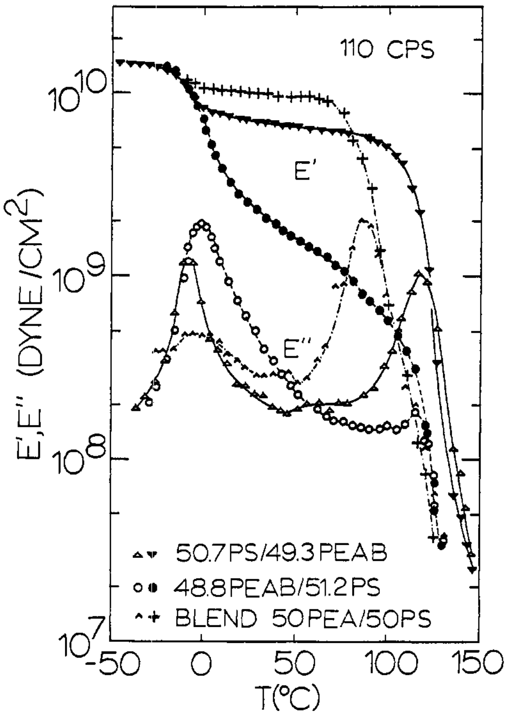

Figure 9. Temperature dependence of E' and E'' of inverse composition I2 is compared with L1 from Figure 1. Also shown is a solution-type blend of the same two polymers. This figure gives striking evidence that the dynamic mechanical properties depend greatly on the exact mode of synthesis.

Figure 9 shows E' and E'' *vs.* T for three different materials: (a) the "inverse" 50/50 PS-PEA preparation, I2; (b) the "normal" 50/50 PEA-PS IPN data from Figure 1, L1; and (c) a blend obtained by simultaneously coprecipitating their dilute solutions. The inverse IPN is seen as being much

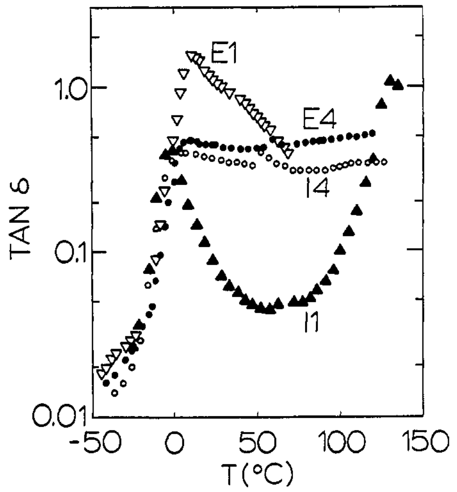

Figure 10. Temperature dependence of tan δ for four IPN's: E1, 74.4 PEAB/25.6 PS; E4, 72.2 PEAB/27.8 PMMA; I1, 24.6 PS/75.4 PEAB; I5, 27.0 PMMA/73.0 PEAB. The individual components of the IPN's were synthesized in the order shown. Sample I5 was not examined in ref 8.

stiffer than the normal, confirming the electron microscope result[8] that PS has a higher degree of continuity in the inverse materials. Surprisingly, the blend has the highest intermediate modulus and the lowest PEA E'' peak. The very high intermediate modulus suggests that its PS forms the "most" continuous phase of the three materials, probably because both phases are un-cross-linked, and by contrast the lower modulus IPN PS phases are continuous but are interpenetrated with elastomer. However, the solution blend PS transition being shifted inward then remains unexplained, except perhaps that the material may have been of a lower molecular weight.

Damping Characteristics of IPN's. It is also instructive to plot the values of tan δ *vs.* temperature, as this quantity is a direct measure of the damping obtained. Figure 10 compares the four normal and inverse elastomeric compositions. The most important observation here is that two samples containing PMMA have tan δ values which are nearly temperature invariant over the range of 0–100°. Sample I1 shows two sharp peaks. Owing to instrumental limitations, only the lower peak was studied with sample E1. Materials containing PMMA rather than PS showed increased damping throughout. The 50/50 PEA-PMMA composition, shown in Figure 4, illustrates this phenomenon.

Phase Continuity Judgments. Plots of storage modulus *vs.* composition at 25°, selected because this temperature is nearly halfway between the two transitions, yield further insight into the question of the relative continuity of the two phases. Employing the theory of Bauer, *et al.*,[17] which is essentially a modification of the earlier mechanical models of Takayanagi[18] we may judge the relative continuity of the two phases. Figures 11 and 12 present storage modulus data as functions of composition for PEAB-PS and PEAB-PMMA IPN's, respectively. Also included are the solution-blended material, a graft copolymer,[19] and data from a mixed latex.[20] The upper solid lines represent a continuous plastic

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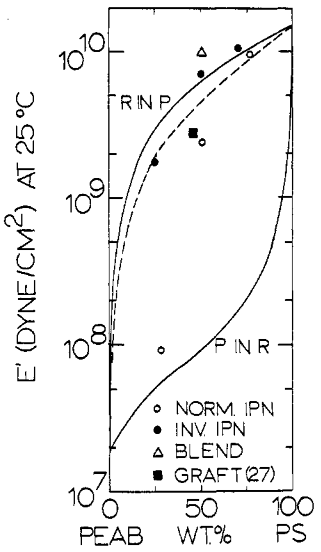

Figure 11. Storage moduli at 25° for PEAB-PS IPN's. R stands for rubber and P stands for plastic. The dotted line indicates the theoretical value of the storage modulus for two continuous phases, based on the Bauer model.

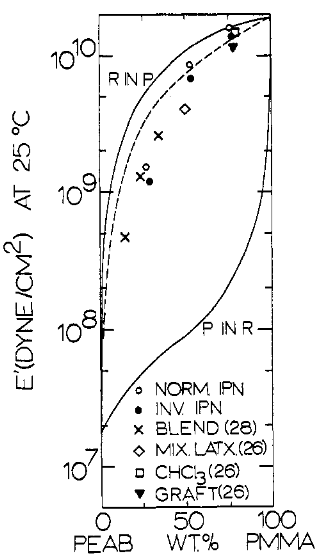

Figure 12. Storage moduli at 25° for PEAB-PMMA IPN's. Within the limits of the Bauer theory, all such blends and IPN's appear to have two continuous phases.

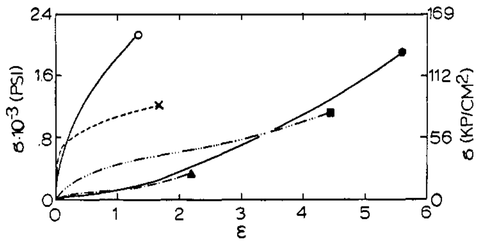

Figure 13. Stress-strain behavior of several elastomeric IPN's: (●) E1, (▲) E2, (■) E3, ×I1, (○) I5. The tensiles and elongations here are comparable to those of the thermoplastic elastomers.

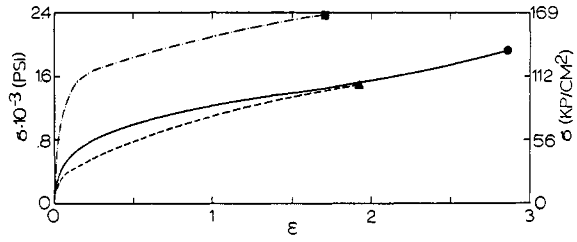

Figure 14. Stress-strain behavior of leathery IPN's: (▲) L1, (●) L2, (■) L4.

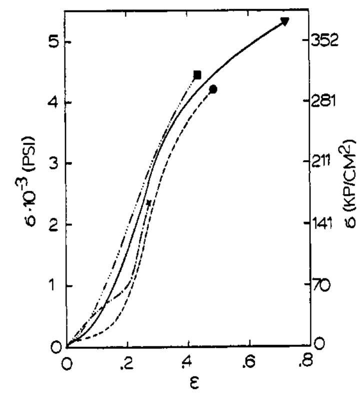

Figure 15. Stress-strain behavior of plastic IPN's: (●) P1, (×) I3, (■) I4, (▼) P4.

phase, while the lower solid lines represent a continuous elastomer phase. The dotted lines indicate the result obtained for two equally continuous phases, all according to theory. Allowing for the relative oversimplification of the mechanical model, the results tend to indicate that both phases do in fact exhibit some degree of continuity, especially the PEA-PMMA compositions. A possible exception is the 75/25 PEAB-PS point in Figure 11, which suggests a continuous elastomeric phase. It should be noted, however, that the theoretical curves were derived for un-cross-linked polyblends.

Stress-Strain Behavior. The stress-strain curves for the elastomeric, the leathery, and the plastic IPN series are given in Figures 13-15. It is observed that the curves for all three IPN series do not exhibit yield points, although yield points may have appeared if materials of still higher plastic content had been employed. Thus the IPN's do not show any cold drawing or "necking," even though this nonuniform elongation is frequently found with toughened plastics.

Elastomeric normal and inverse IPN's are compared in Figure 13. The ultimate elongation, ϵ_{max}, is considerably higher for the normal IPN's than for the inverse ones. The two corresponding inverse IPN's, I1 and I5 (27.0 PMMA/73.0 PEA), show approximately the same ultimate elongation. The difference between samples E1 and I1 is well understood from the morphology of the two IPN's. The polymeric network polymerized first forms the more continuous phase in both cases, *i.e.*, the cell walls are PEA with the normal IPN E1 and PS with the inverse IPN I1. The more continuous rubbery matrix with sample E1 allows much greater deformation than a more continuous plastic matrix. It is, however, not understood at this point why sample E2, the plastic network of which is a random copolymer of S and MMA, is so weak. The dynamic mechanical data showed a considerably lower storage modulus, *E'*, for the normal IPN's as compared to the inverse ones. This difference of approximately one order of magnitude is also reflected in the initial slopes of the stress-strain curves, which are approximately proportional to the storage moduli.

Figure 14 shows the stress-strain curves for the normal leathery IPN's. The higher plastic content emphasizes the influence of the ultimate strain values of the pure plastic homopolymers ($\sigma_{\max}$(PMMA) = 9460 psi; $\sigma_{\max}$(PS) = 6400 psi). The $\sigma_{\max}$ value of sample L2, which contains equal amounts of S- and MMA-mers in the plastic networks, is between the corresponding values of the IPN's L1 and L2. The initial slopes of all three curves are the same, confirming the corresponding dynamic storage moduli of these samples.

The stress–strain behavior of the plastic IPN's is presented in Figure 15. All four IPN's describe almost the same curve, although the tensile strength of the four curves differs somewhat. The morphology as revealed by electron microscopy[8] may explain why all four curves fall in the same range. All electron micrographs show a similar picture: the plastic phase tends to be the more continuous phase for this level of plastic. The similar morphological features resulting from the relatively small amount of PEA causes a similar stress–strain behavior. It is generally observed that the ultimate elongation increases with increasing rubber content, whereas the maximum stress decreases. This behavior is of course expected.

Discussion

In forming polymer blends, the synthesis details control the supermolecular morphology, which in turn controls important physical and mechanical behavioral characteristics. In the previous paper,[8] the electron microscope was employed on osmium tetroxide stained thin sections. A gross cellular structure of about 1000-Å diameter and a fine structure of about 100 Å were observed to coexist in the several materials. The cell size was found to decrease, and the volume fraction of material containing fine structures increased as composition was altered by the substitution of MMA-mers for S-mers in the plastic component.

However, electron microscopy as such does not give any details as to the extent of actual molecular mixing. In the present paper, a study of the loss and storage terms of the modulus complemented the electron microscopy work. The following experimental evidence became apparent. The loss peaks corresponding to the two glass transitions were shifted toward each other to a significant degree in all IPN's studied. Surprisingly, however, the quantitative shift did not depend significantly on MMA-mer substitution. The E'' curve between the two original loss peaks increased in height, resulting in a higher degree of damping than originally evidenced by the two primary peaks. This appears to yield one broad loss peak covering a temperature range of over 100°. A possibly better interpretation is that a broad range of transitions exists, depending on local composition. Together with the electron microscope results,[8] this leads to a strengthening of our previous conclusion[11–13] that extensive but incomplete mixing takes place for PEA–PMMA IPN's, but that PEA–PS IPN's are incompatible.[10]

The value of the storage modulus (E' absolute values) between the transitions was shown to depend on the method of synthesis, as particularly illustrated in Figure 9. Electron microscopy[8] showed that the first component usually exhibits the greater continuity in IPN's. The inverse composition, with the plastic material synthesized first, was considerably stiffer in the region between the transitions, confirming and strengthening this supposition. That the elastomeric material interpenetrates the plastic component in the 50/50 PS–PEA IPN is evidenced by the fact that the "solution-type" blend is still stiffer.

Application of the Bauer-modified Takayanagi theory for un-cross-linked polyblends to the IPN's led to the tentative finding that both phases were continuous with the PEA–PMMA IPN's and related blends, and that possibly both phases could be considered continuous with the PEA–PS IPN's. Unfortunately, the evidence was less clear in the latter case. In an earlier paper on IPN's[10] the theories of Kerner[21,22] and of Hashin and Shtrikman[23] were applied to modulus-composition data. These theories fit in a fair manner in the regions where the modulus changes rather slowly.

Conclusions

The previous paper, part I,[8] on synthesis and morphology and the present paper on physical and mechanical behavior have examined the samples of PEA–P(S-*co*-MMA), together with a few inverse materials. It is instructive at this point to compare the phase structure revealed by the electron microscope with the dms results presented herein. The PEA–PS materials exhibited a cellular structure of about 1000-Å diameter, together with a fine structure. Decreases in cellular dimensions and a corresponding rise to prominence of the fine structure accompanied the replacement of S-mers by MMA-mers, suggesting that phase separation took place later in the second component polymerization, an indication of greater compatibility. The dms results showed a slight inward shift of the transitions for the PEA–PS materials, and a major buildup of multiple transitions accompanied by high damping in the region between the two E'' peaks as MMA-mers replaced S-mers. This result confirms in a semiquantitative manner the conclusion that extensive but incomplete molecular mixing takes place in MMA-rich materials. The inverse IPN's were stiffer than their normal counterparts, confirming the electron microscope result that the network formed first (PS or PMMA for inverse materials) constitutes the more continuous phase. In all of the IPN's considered in these two papers, both networks are probably continuous on a macroscopic scale, and for most of the materials it seems that two continuous phases are also formed.

Acknowledgment. The authors wish to thank the National Science Foundation for support through Grant No. GK-13355.

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