Epoxy Resin–Poly(ethyl methacrylate) Interpenetrating Polymer Networks: Morphology, Mechanical, and Thermal Properties

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ABSTRACT: Full (interpenetrating networks (IPNs)) and semi-IPNs of the epoxy resin and poly(ethyl methacrylate)(PEMA) were prepared by the sequential mode of synthesis. These were characterized with respect to their mechanical properties, namely, tensile strength, elongation at break, modulus, and toughness. Thermal properties were studied by differential scanning calorimetry and thermogravimetry. The morphological features were studied through scanning electron microscopy (SEM) and polarized light microscopy. The effects of variation of the blend ratios on the above-mentioned properties were examined. There was a gradual decrease of modulus and tensile strength with consequent increases in elongation at break and toughness for both types of IPNs with increases in PEMA content. The weight retentions in the thermal decomposition of both the semi-IPNs and full IPNs were higher than the epoxy homopolymer. This enhancement was presumably related to the presence of the unzipped ethyl methacrylate monomer, which acted as radical scavengers in the epoxy degradation. An inward shift and lowering (with respect to pure epoxy) of the T_g of the IPNs was observed. The polarized light microscopy exhibits bimodal distribution of particle sizes. The fractography as studied by SEM shows change in fracture mechanics from shear yielding to crazing with increasing PEMA content. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci **67:** 1051–1059, 1998

Key words: interpenetrating polymer networks; morphology; mechanical; thermal; SEM

INTRODUCTION

Polymer blends encompass many different kinds of materials containing two or more polymer components and most exhibit phase separation to a greater or lesser degree. Interpenetrating polymer networks (IPNs) are a new class of polymer blends in network form, in which the possibility of phase separation has been reduced remarkably by arresting the morphologies of the participating components. Here, one polymer is synthesized or crosslinked in the immediate presence of the other.[1–5] When both networks are crosslinked, the morphology is fixed and well defined, and the associated properties do not vary much. IPN properties depend largely on the sequence of formation of two networks. In the sequential technique, the continuous network dictates the properties; while a simultaneous process results in a material with the smallest degree of phase separation and, hence, the highest degree of interpenetration.[6]

Thermoset epoxies are relatively brittle materials. Various toughening agents are added to epoxies to reduce the brittleness. The present study
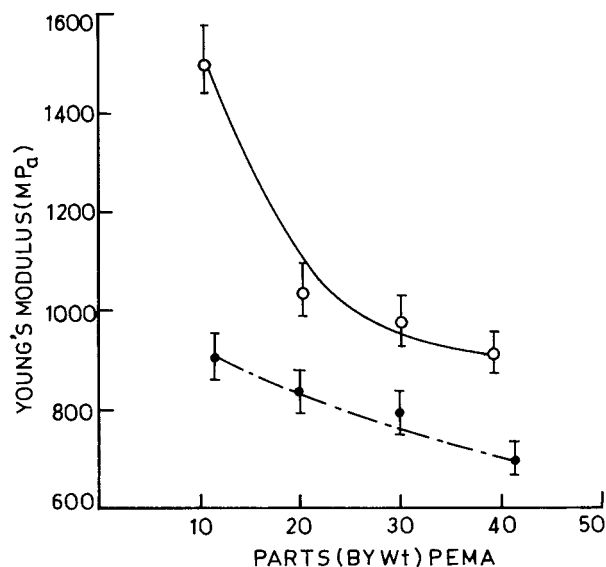
Figure 1 Variation of modulus of epoxy–PEMA semi-IPNs and full IPNs with variation of blend ratio (w/w): (○——○) semiIPN; (○—·—·—○) full IPN; (△) epoxy (pure).

aims at improving the properties of the epoxy resin by blending poly(ethyl methacrylate) (PEMA) by IPN technique. The rubber-reinforcing influence of PEMA on the continuous glassy matrix of epoxy has been studied as a function of PEMA content.

EXPERIMENTAL PROCEDURES

Materials

The diepoxy monomer, diglycidyl ether of bisphenol A (DGEBA from M/s. Ciba Geigy (Araldite GY-250)) was used without further purification. Ethyl methacrylate (EMA) (FLUKA) was purified by washing first with 2% aqueous NaOH solution and then by repeated washing with distilled water and dried over fused $CaCl_2$. Benzoyl peroxide (Bz_2O_2) (B.D.H., India) was purified by repeated crystallization from chloroform. Hy-830 and Hy-850, the two formulated aromatic polyamine adducts from M/s. Ciba Geigy, were used in combination as a crosslinker for the epoxy resin. Both these are epoxy adducts of aromatic polyamine based on diamino diphenyl methane. Hy-850 is an accelerated version of the adduct. A 1 : 1 combination of Hy-830 and Hy-850 gave an optimum gel time. Ethylene glycol dimethacrylate

(EGDM) was used as comonomer and crosslinker for PEMA.

IPN Synthesis

A weighed amount of purified EMA was taken in a three-necked round-bottomed flask and thoroughly mixed with 2% by weight (based on EMA) of benzoyl peroxide. The epoxy precursor, i.e., DGEBA, was then accurately weighed into the flask, and the contents were stirred to give a homogeneous mixture in the desired blend ratio of the components. The mixture was then purged with dry nitrogen and heated in a water bath at a temperature of (60 ± 2)°C for an hour. The flask was then allowed to cool to the room temperature. The epoxy crosslinker was added to the mixture in the flask and shaken thoroughly. When the formation of bubbles ceased, the viscous mass was poured into a glass mold prepared by clipping together two glass plates separated by a Teflon gasket in between, the thickness of which controls the thickness of the sample sheet formed. It was initially kept at room temperature for about 18 h and then heated at 120°C for two hours, followed by further heating at 140°C for one hour. This ensures complete crosslinking and polymerization. Thus, the semiIPNs were produced.

In order to prepare a full IPN the comonomer–crosslinker of PEMA, namely, EGDM, was added to monomer–initiator solution and mixed uniformly before the addition of diepoxy monomer.
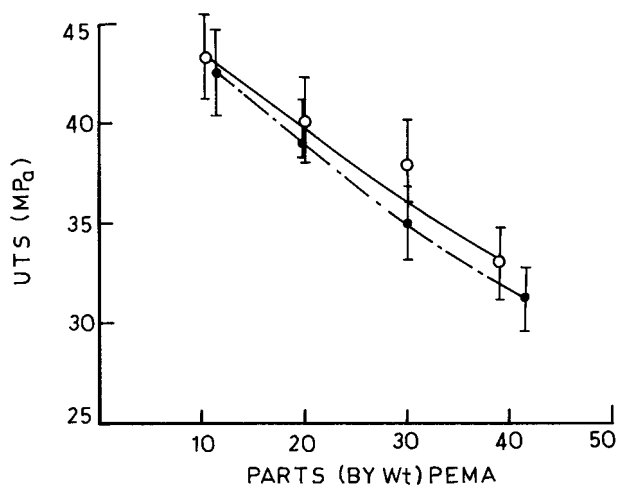

Figure 2 Variation of UTS of epoxy–PEMA semi-IPNs and full IPNs with changes in blend ratios (w/w): (○——○) semiIPN; (○—·—·—○) full IPN; (△) epoxy (pure).
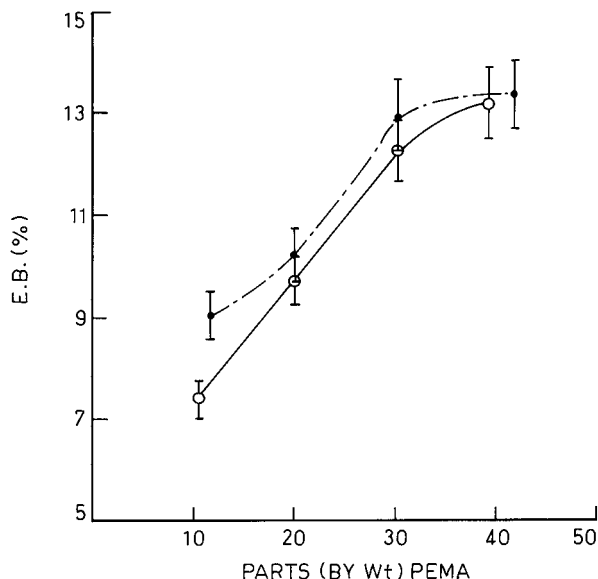
Figure 3 Variation of EB of epoxy–PEMA semiIPNs and full IPNs with changes in blend ratios (w/w): (○———○) semiIPN; (○ — · — · — ○) full IPN; (△) epoxy (pure).

In all cases, the concentration of EGDM was kept constant at 1.6% by weight based on monomer. All other operations were identical to those followed for semiIPNs.

MEASUREMENTS

Tensile Properties

An Instron universal testing machine (model 4204) was used for measuring the tensile properties like tensile strength, percent elongation at break (EB %), and toughness. ASTM D638 method was followed. A crosshead speed of 5 mm/min was maintained. All testings were conducted under ambient conditions in an environmentally controlled room. The samples for tensile measurements were cut in a dumbell shape of 4 mm in width, 50 mm in span, and 1 mm thickness. The overall width of the samples at the two ends of the dumbell was 9 mm. Toughness of the IPN samples was determined from the area under load versus elongation plot. The standard dumbell specimens were visually inspected before measurements and were found to be free from pores or nicks. The data reported are averages of at least six measurements, and typical scattering range of the results was ±5%.

Thermal Properties

Thermogravimetric analysis (TGA) thermograms were obtained on a Du-Pont thermogravimetric analyzer under nitrogen atmosphere at a heating rate of 10°C min. The samples ranging between 8 and 12 mg in weight were placed in platinum sample pans under a continuous nitrogen flow of 1.5 cu ft h. A Du-pont 9000 instrument was used for the differential scanning calorimetry (DSC) studies. DSC scans were taken at the heating rate of 10°C min under a continuous flow of nitrogen.

Morphology

Phase morphology was examined in a Phillips PSEM-500 scanning electron microscope and also by a polarizing microscope, model Leitz.Laborlux 12 POLs at lower magnifications. For scanning electron microscopy (SEM) studies, the fractured surfaces of the samples undergoing failure in tensile testing were used. For polarizing light micrographs, thin discs of undeformed samples were used.

RESULTS AND DISCUSSION

Mechanical Behavior

The mechanical properties of both semi-IPNs (where only epoxy is crosslinked) and full IPNs (where both epoxy and PEMA are crosslinked) have been studied as a function of blend ratios of epoxy and PEMA. The mode of changes in modulus and ultimate tensile strength of the semi-IPNs
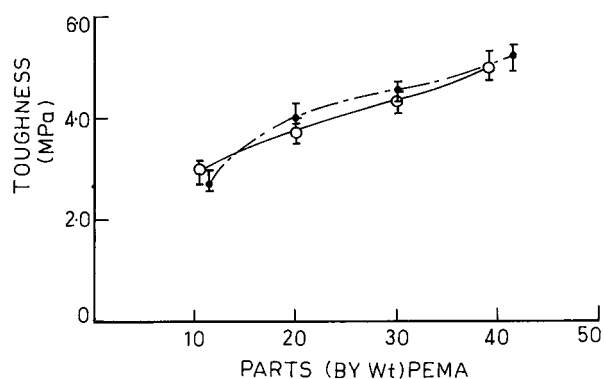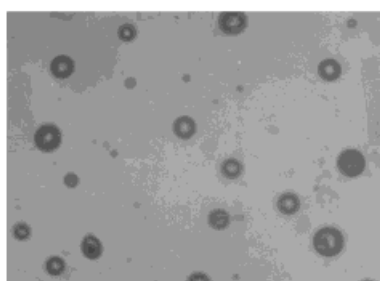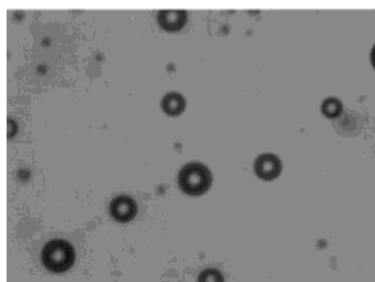

Figure 4 Variation of toughness of epoxy–PEMA semiIPNs and full IPNs with variation in blend ratios: (○———○) semiIPN; (○ — · — · — ○) full IPN; (△) epoxy (pure).
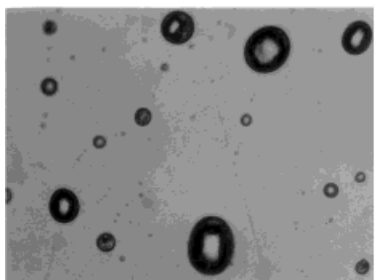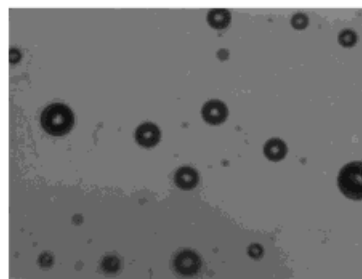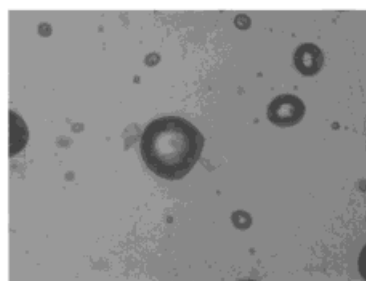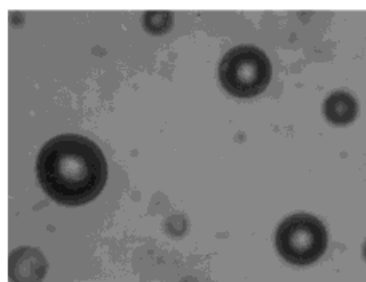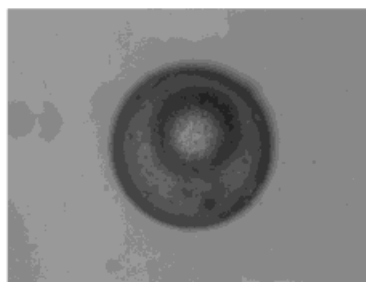
POLARIZING LIGHT MICROGRAPHS

1S

1F

2S

2F

3S

3F

4F

Figure 5   Polarizing light micrographs of epoxy–PEMA sequential IPNs (200×); sets of micrographs 1S–3S refer to 89.63 : 10.37, 79.9 : 20.1, and 69.77 : 30.23 semiIPNs, respectively. Sets of micrographs 1F–4F refer to 88.44 : 11.56, 79.97 : 20.03, 70.07 : 29.93, and 58.53 : 41.47 full IPNs, respectively.
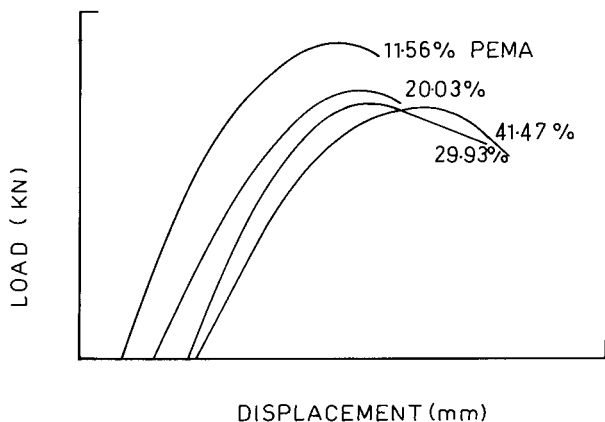
Figure 6 Load versus displacement curves for different compositions of epoxy–PEMA full IPN system. No units have been given, as the scales differ in each curve.

Figure 8 Variation of density of epoxy–PEMA semi-IPNs and full IPNs with variation in blend ratios (w/w): (○———○) semi-IPN; (○—·—·—○) full IPN; (------) calculated from the additivity principle.

and full IPNs have been compared in Figures 1 and 2. The influence of crosslinking of the dispersed network into the subsequently crosslinked matrix network of epoxy is quite evident from the figures. In both the cases of semi-IPNs and full IPNs, there is a reduction in Young's modulus and ultimate tensile strength (UTS) with increase in PEMA content. This decreasing trend may be attributed to the following probable reasons: (1) plasticizing influences of the dispersed PEMA domain; (2) reducing the possibility of complete curing of the epoxy matrix by shielding the reactive sites of epoxy by the dispersed PEMA moieties; (3) increasing the number of stress concentrators and, thus, gradually decreasing the effective cross-sectional area that bears the load.[7]

It is quite interesting to note that the semi-IPNs of epoxy–PEMA system have higher moduli
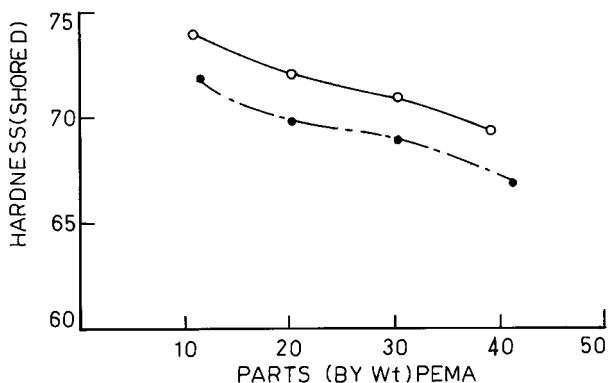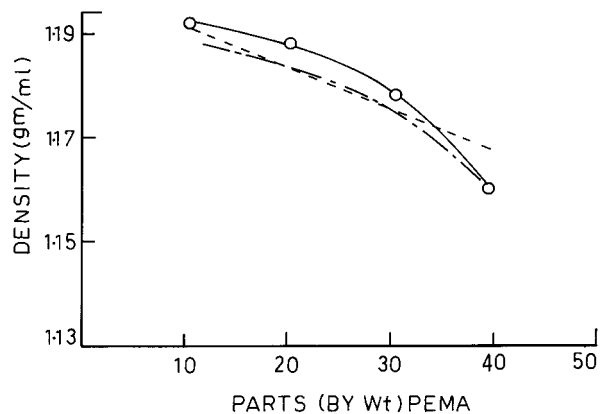
and UTS than the full IPNs. This can possibly be explained by the fact that the PEMA moieties have much higher free volume, and there is ample scope of threading or interpenetration by the linear chains of PEMA; while in the case of full IPNs, the cross links within the PEMA chains make them more compact, reduce the mobility of the chains, and thus lower the statistical probability of threading or interpenetration, thus precluding the reinforcing effect of interpenetration.[8] It is thus interesting to note that the influence of molecular threading outweighs the effect of homo-

Figure 7 Variation of hardness with changes in blend ratios (w/w) of epoxy–PEMA IPN systems: (○———○) semiIPN; (○—·—·—○) full IPN.
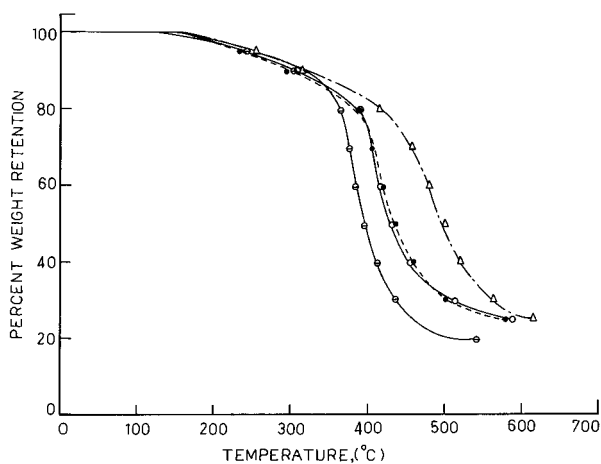

Figure 9 TGA thermograms for epoxy, semiIPN, and full IPN systems of epoxy–PEMA. (○———○) semiIPN; epoxy–PEMA: 79.9 : 20.1 (w/w). (— — — —) semiIPN; epoxy–PEMA: 60.62 : 39.38 (w/w). (○------○) full IPN; epoxy–PEMA: 79.97 : 20.03 (w/w). (⊖——⊖——⊖) epoxy.
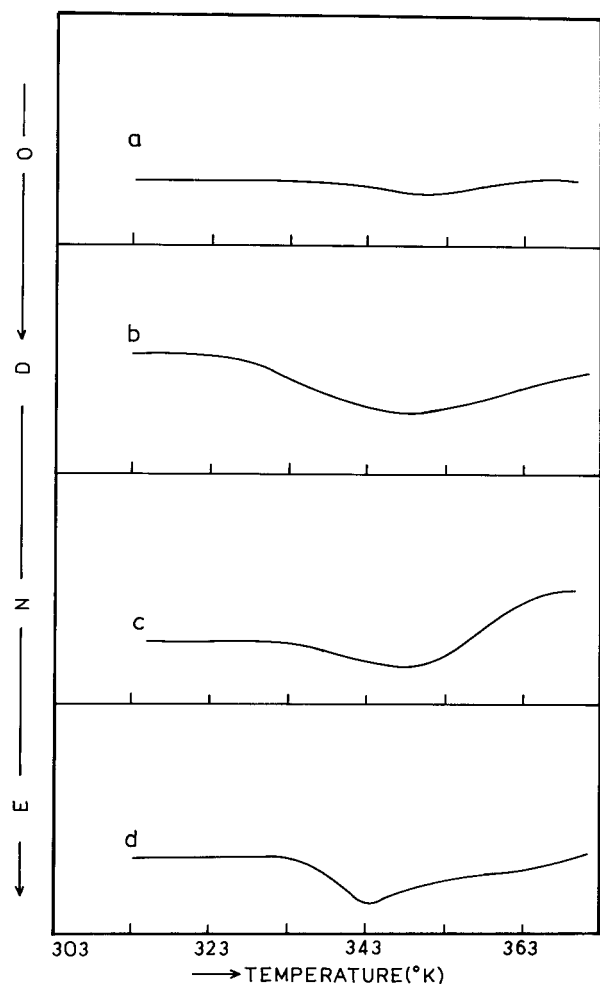
Figure 10   DSC curves for the semiIPNs and full IPNs of the epoxy–PEMA system: (a) semiIPN (79.9 : 20.1, epoxy/PEMA); (b) semiIPN (69.77 : 30.23; epoxy/PEMA); (c) full IPN (79.97 : 20.03 : epoxy/PEMA); (d) full IPN (70.07 : 29.93 : epoxy/PEMA).

polymer crosslinking so far as the mechanical properties are concerned.[9] Figures 3 and 4 show the trend of changes in the EB % at break and toughness as a function of PEMA content. As expected, these two mechanical parameters exhibit an increasing trend with a progressive increase in PEMA content. The plasticizing effect imparted by the PEMA domains, along with an increase in the path length for the crack propagation due to the presence of a multitude of stress concentrators (PEMA moieties), can be accounted for the observed increase in the EB %. Consequently, the energy expended in traversing a greater path will be much higher compared to pure epoxy. Thus, the toughness may be expected to increase with increasing proportions of PEMA.[7,10]

The semi-IPNs by virtue of their relatively higher extent of interpenetration due to the reason discussed earlier undergo less deformation than the full ones and hence have comparatively lower EB % and toughness than the full IPNs. The initial sharp rise in EB % observed during the early stages of PEMA incorporation is not observed during the later stages; this is possibly attributed to the change in state from the dissolved PEMA domains present initially to the phase-separated PEMA domains formed at higher doses of PEMA, as its sizes increase with the increase in PEMA content, as shown by polarized light micrographs (Fig. 5). The degree of improvement in terms of EB % and toughness depend initially on the sizes of the dispersed phase.[11–13] Figure 6 shows the load versus displacement curves for some of the representative samples of epoxy– PEMA full IPNs. The increase in ductility and consequent increase in toughness with increasing PEMA content is apparent. Besides the development of an yield point, the curves display a tendency of necking as the PEMA content gradually increases. Thus, the change in fracture mechanics from a brittle nature to a ductile one exhibiting increasing plastic deformation can be understood from the curves. The hardness versus composition curve (Fig. 7) shows a decreasing trend for both semi-IPNs and full IPNs. In conformity to our earlier observations, the hardness of semi-IPNs lies above those for full IPNs of identical composition.

Density

The observed density values are found to lie above the theoretically calculated average densities predicted by the law of mixtures. This type of densification, possibly due to partial mixing or interpenetration of chains of glassy and rubbery components participating in an IPN formation, has been confirmed by Kewei et al.,[14] which was further supported by Shibayama et al.[15] and Kim et al.[16] The densities of the semiIPNs are somewhat higher than the full ones, a phenomenon that corroborates our earlier observation (see Fig. 8).

Thermal Properties

TGA Studies

The thermogravimetric curves for the semi and full IPNs are compared in Fig. 9. In all the cases, an enhancement in weight retention compared to

SCANNING ELECTRON MICROGRAPHS
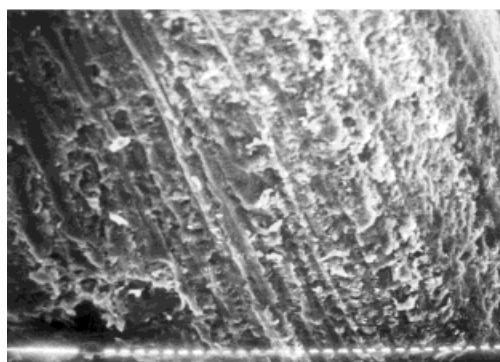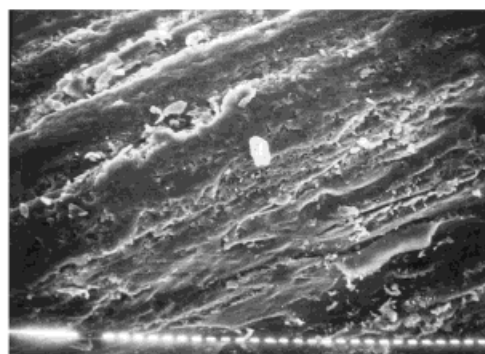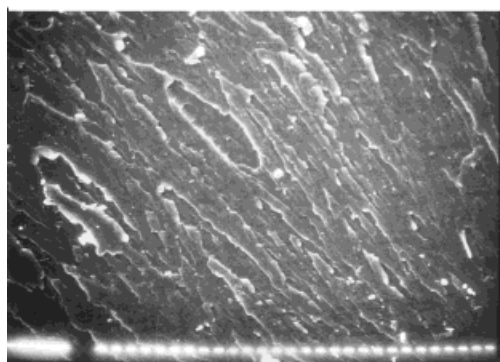
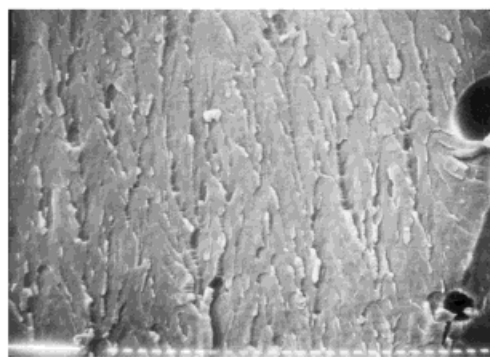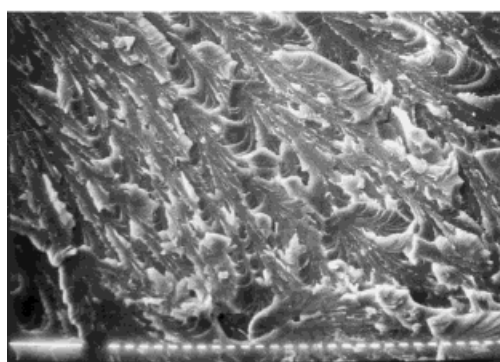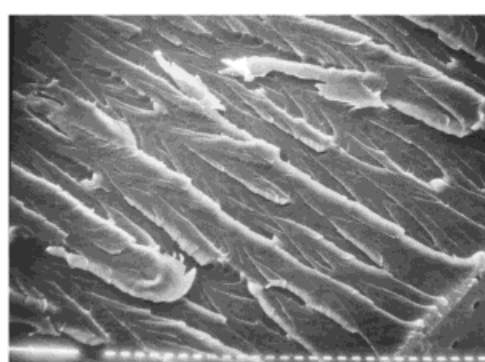**Figure 11** Scanning electron micrographs of epoxy–PEMA sequential IPNs (200×): 1S–3S refer to 89.63 : 10.37, 79.9 : 20.1, and 69.77 : 30.23 semiIPNs, respectively; 1F–3F refer to 88.44 : 11.56, 79.97 : 20.03, and 70.07 : 29.93 full IPNs, respectively.

that of pure epoxy homopolymer was observed. The semi and full IPNs of nearly identical composition exhibit little differences in their degradation pattern; thus, it may be presumed that in the present IPN systems the covalent crosslinks may have little influence on the degradation mechanism. It may also possibly be assumed that the effect of interpenetration on the course of degradation is almost negligible. Thus, the nearly identical behavior of the semi-IPNs and full IPNs may be attributed to the fact that the resistance to degradation (if any) offered by covalent crosslinks, present to a greater extent in the case of full IPNs, is almost counterbalanced by the comparatively higher extent of interpenetration effect observed in case of semi-IPN.

However, the composition of an IPN plays a dominant role in determining the course of degradation and wt % loss, particularly when the degradation products of one polymer have the possibility of any interactions with that of the second polymer, thus blocking the polymerization of the second polymer. In the present system, PEMA yields 100% monomer by an unzipping process like other methacrylates.[17] The relatively higher thermal stability of the semiIPNs containing higher doses of PEMA may possibly be attributed to the higher EMA; monomer concentrations that can scavenge the macroradicals; or pyrolytic products of epoxy, which usually catalyze the degradation process to a higher extent than those with lower proportions of PEMA.

DSC Studies

Two DSC tracings of each of semi and full IPNs of epoxy–PEMA system are shown in Figure 10. The plasticizing influence of the dispersed PEMA phase within the continuous matrix of epoxy is understood well in both cases of semi and full IPNs. The extent of lowering of glass transition temperatures, irrespective of the semi-IPNs and full IPNs, appears to be much higher than that predicted either by weight-average formula ($T_G = W_1 T_{G_1} + W_2 T_{G_2}$) or by the Fox equation ($1/T_G = W_1/T_{G_1} + W_2/T_{G_2}$),[18] where T_{G_1}, and T_{G_2} are the glass transition temperatures of components 1 and 2, respectively, and W_1 and W_2 are their weight fractions. The higher extent of inward shifting of the glass transition temperatures may be attributed not only to the plasticizing effect of PEMA but also to the reduction in crosslinking density through the assumed blocking of the reactive sites

of epoxy. The full IPNs exhibit marginally higher T_G values than the semi-IPNs, and thus possibly indicate that the crosslinking of the PEMA phase had very little influence on glass transition phenomenon; or, conversely, the comparatively higher extent of interpenetration in case of semi-IPNs causes the chain movement to be sluggish enough to raise the T_G values very close to those for full IPNs. With the increase in PEMA content in both the cases of semi-IPNs full IPNs, the T_G value was reduced as expected because PEMA is characterized by a lower glass transition temperature. Another point of importance to be mentioned is the broadening of the glass transition temperature. The transitions, though spanning over a wide temperature range in all the cases, appear to be comparatively sharper in the case of full IPNs over the semi-IPNs, as expected. The broadening of the glass transitions indicates some phase mixing in all cases.

Morphology

Polarizing Light Microscopy

The micrographs of both semi-IPNs and full IPNs are exhibited in Figure 5 as an increasing function of PEMA content. In both cases, we find a bimodal distribution of particle sizes. In these micrographs, the circular dark phase is of PEMA; and the lighter phase represents that of the glassy epoxy, which constitutes the matrix. Essentially, almost spherical PEMA domains are dispersed in the glassy matrix; and the sizes of these spherical domains gradually increase with increase in PEMA content, irrespective of the semi-IPNs and full IPNs. The dispersed phase of PEMA contains varying proportions of epoxy occluded almost centrally within the domains. This is very often observed in the case of rubber modified epoxies and is sometimes explained by second-phase separation inside the rubber-rich dispersed particles. In our present study, the comparatively lesser rigid and hard PEMA is considered to behave as a rubbery modifier to epoxy, and this has been manifested in various mechanical properties studied. Furthermore, it appears that the growth of the domains occurs from outside to inside. From the mode of synthesis, it appears that the cellular domains of PEMA were first nucleated, containing growing chains of PEMA, EMA monomer, and epoxy. The amount of macroradicals and monomer entrapped within the nucleus of course depends

on the concentration of EMA in various compositions of the IPNs. Subsequent heating led to the formation of polymer, which got deposited on the wall itself.

Finally, it is interesting to note that, contrary to the usual observation of full IPNs having relatively smaller and compact domains over the semi-IPNs, the semi-IPNs have smaller and compact domains in our present study. This may possibly be attributed to the mode of synthesis. In the present system, the PEMA domains are formed first in the presence of epoxy precursor. The linear and softer domains as obtained in semi-IPNs are subjected to a compressive force exerted by shrinkage during the cure of epoxy resin at the later stages, when the monomers entrapped within the domains undergo polymerization simultaneously. In the case of full IPNs, however, the already cross-linked relatively harder domains are much more resistant to such squeezing forces exerted by the cured epoxy resin and thus have bigger sizes than the semi-IPNs.[19]

Scanning Electron Microscopy

The scanning electron micrographs of both semi-IPNs and full IPNs for three different compositions of each are shown in Figure 11. The change in fracture mechanics from a predominantly shear yielding to crazing with increasing concentration of PEMA can be easily distinguished. The increased plastic deformation due to leathery PEMA can be easily envisaged. The regular geometric features obtained on the fractured surfaces are quite interesting. The exact shapes of these features depend on the ratio of the velocities of propagation of the primary to secondary cracks. When these are equal, a parabola is formed; whereas if the primary crack propagates faster, then the newly formed crack will be enclosed, and an eclipse is formed.[20] Sometimes, the parabolic features interact and overlap and produce complex geometrical patterns. The macroscopically rough surface observed at higher PEMA concentration and considerable crack branching is indicative of rapid crack propagation. The full IPNs,

however, exhibit some debonded particles and some debonded regions, while the semi-IPNs do not.

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