

Epoxy/Poly(methyl methacrylate) Interpenetrating Polymer Networks—Morphology, Mechanical and Thermal Properties

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SYNOPSIS

Full and semi-IPNs were prepared from epoxy and poly methyl methacrylate (PMMA), by the sequential mode of synthesis and were characterized by measurements of ultimate tensile strength (UTS), elongation at break, modulus, and toughness. Aromatic polyamine adducts and ethylene glycol dimethacrylate were used as the crosslinkers for epoxy and comonomer/crosslinker for methyl methacrylate monomer, respectively. Higher UTS and modulus of the semi-IPNs over full IPNs were attributed to the higher probability of interpenetration. The weight retention in the thermal decomposition of the IPNs and semi-IPNs were higher than the epoxy homopolymer. This enhancement was presumably related to the presence of the unzipped methyl methacrylate monomer which acted as radical scavengers in the epoxy degradation. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Since its first synthesis by Millar¹ in 1960, the term interpenetrating polymer networks (IPNs) has been used to describe the combination of crosslinked polymer networks in which at least one polymer is synthesized and/or crosslinked in the immediate presence of the other.²⁻⁶ The multipolymer systems, thus obtained, display a broad range of properties from toughened elastomers to high impact plastics.

Epoxy resins have excellent mechanical, electrical, and adhesive properties. But when cured with stoichiometric amounts of polyfunctional amines, they are rather brittle, being only slightly tougher than inorganic glasses. Various additives are used in epoxy formulations to mitigate this shortcoming. Thermoplastic resins such as PMMA are tougher than the thermosets, having fracture energies of the order of 1 kJ/m². The high fracture toughness of PMMA is not unexpected, because the large free volume available in these amorphous materials al-

lows them to absorb the energies associated with crack growth and propagation.⁷

The present study is aimed at preparing elastomer-plastomer polyblends by the IPN technique and characterizing their mechanical and thermal properties along with some of their morphological features. The point of interest is that an attempt has been made to toughen epoxy, a hard, rigid, and brittle elastomer with PMMA, another hard and relatively tougher elastomer.

EXPERIMENTAL

Materials

Diglycidyl ether of bisphenol A, DGEBA (Araldite Gy 250) from M/s Ciba Geigy was used as received; MMA monomer (Merck, India) was purified by washing with caustic soda solution, distilled water followed by vacuum distillation. Benzoyl peroxide (Bz₂O₂) (B.D.H., India) was used as initiator. Aromatic polyamine adducts from M/s Ciba Geigy was used as crosslinker for epoxy. Ethylene glycol dimethacrylate (EGDM) was used as a comonomer with MMA for crosslinking.

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IPN-Synthesis

A weighed amount of purified MMA was taken in a three-necked, round-bottomed flask and thoroughly mixed with 2% by weight (based on MMA) of benzoyl peroxide. The epoxy precursor, i.e., DGEBA, was then accurately weighed into the flask and the contents stirred to give a homogeneous mixture. The flask was heated in a water bath for 1 h at $60 \pm 2^\circ\text{C}$ with continuous stirring and allowed to cool to room temperature. Weighed amounts (60% by weight of DGEBA) of aromatic polyamine adducts were then added to maintain the stoichiometric proportion required for complete curing. It was again homogeneously mixed with the contents of the flask and allowed to settle for 1–2 min for releasing any gases formed. This, in effect, helps in getting a smooth, uniform, pore-free sheet. The contents of the flask were then poured into a glass mould, closed tightly, and kept for 18 h at ambient temperature.

It was then post cured in an oven at 120°C for 2 h followed by further heating at 140°C for 1 h to complete crosslinking and polymerization. The sheets were finally kept in a vacuum for over 3 days until constant weight was achieved. The samples thus produced were semi-IPNs.

For full IPNs, a similar method was followed except that, before mixing the epoxy precursor with the monomer-initiator mix, the comonomer/crosslinker of MMA, i.e., EGDM, was added to the extent of 1.6% by weight of the monomer (MMA) taken.

MEASUREMENTS

Tensile Properties

Tensile properties such as tensile strength, percent elongation at break (EB%), and toughness were measured using an Instron Universal testing machine (model 4204) at room temperature according to low strain rate tensile testing method as per ASTM D638. A crosshead speed of 5 mm/min was used. All testing was conducted at ambient conditions in an environmentally controlled room. The samples for the tensile measurements were cut in a dumbbell shape of 4 mm in width, 50 mm in span, and 1 mm in thickness. The overall width of the samples at the two ends of the dumbbell was 9 mm. Toughness of the IPN samples was determined from the area under load vs. elongation plot. The standard dumbbell specimens were visually inspected before measurement and were found to be free from nicks or pores. The data reported are averages of at least six measurements, and typical scattering range of

the results was $\pm 5\%$ and has been shown as error bars for each data point.

Thermal Properties

TGA thermograms were obtained on a Du-Pont Thermogravimetric analyzer under nitrogen atmosphere at a heating rate of $10^\circ\text{C}/\text{min}$. The samples ranging between 8 and 12 mg in weight, and were placed in platinum sample pans under a continuous nitrogen flow of 1.5 cubic feet/h. The samples were in the shape of thin discs.

Morphology

Phase morphology of IPN samples was examined by a Phillips scanning electron microscope (PSEM-500). The fracture surfaces of the samples undergoing failure in tensile testing were etched in solvent (acetone) and used as specimens after coating with a thin layer of gold using a high vacuum gold sputterer.

RESULTS AND DISCUSSION

Mechanical Properties

The influence of degree of crosslinking of polymer networks I and II on the properties of the final IPN has been extensively studied.^{8,9} Variations of mechanical properties with respect to change in blend ratio are illustrated in Figures 1 and 2.

In the present plastomer-plastomer IPN system, it is observed that with increase in relatively tougher plastomer, PMMA,⁷ either linear (semi-IPNs) or crosslinked (full IPNs) into the more rigid and brittle matrix of epoxy resulted in an overall decrease in tensile strength and modulus (Fig. 1).

This may be explained by the plasticising influence of the dispersed PMMA particles within the epoxy network. Condensation polymerisation of epoxy resin produces a broad distribution of low molecular weight species.¹⁰ On the contrary, the free radical polymerization of MMA produces PMMA of relatively higher molecular weight. Consequently, the prepolymerized PMMA (which undergoes further polymerization during subsequent operations) are embedded as distinct discrete phases in the epoxy matrix. Thus, a two-phase system emerges, having a multitude of weak sites rather than only a few as found in a single phase polymer. These dispersed phase of PMMA (constituting the weak sites) reduce the effective cross-section that bears the load, causing a reduction in modulus and UTS.¹¹ With increase

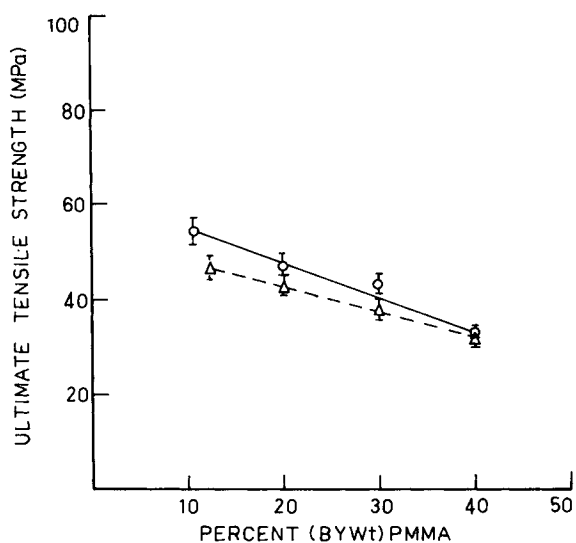
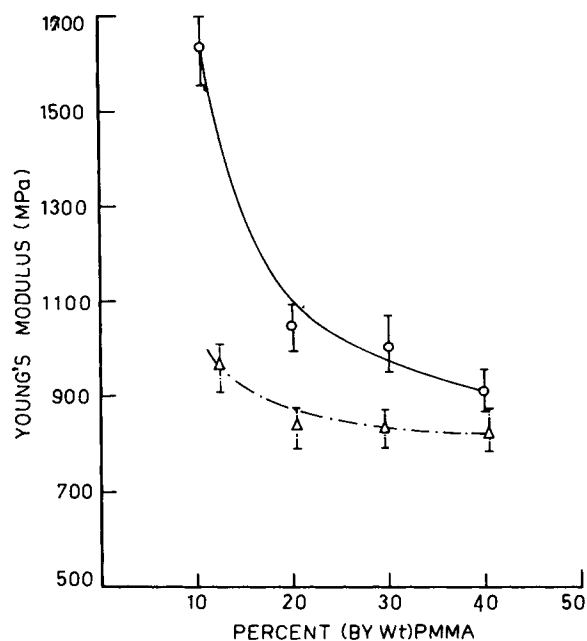


Figure 1 Variation of TS and modulus of epoxy-PMMA semi- and full IPNs with variation of blend ratio (w/w). ○ — ○ semi-IPN, and △ - - - △ full IPN.

in PMMA content from 90 : 10 to 60 : 40, epoxy: PMMA, there is a progressive lowering of modulus and UTS. This can be attributed to either an increase in number or increase in sizes of the dispersed PMMA phase or a combined effect of the two.

Both percent strain at break and toughness increase with increase in PMMA content (Fig. 2). This is in keeping with earlier observations of decreasing modulus and UTS and can be attributed to the same plasticising effect of the dispersed phase. The increasing number of stress concentrators or

weak sites initiate a number of cracks during tensile loading. A crack can rapidly propagate through a single phase polymer and failure occurs expending a small amount of energy. In the presence of many cracks the associated stress fields interfere with one another and instead of extending all the way across the specimen, the propagating crack tips may end roughly opposite one another.¹¹ According to Griffith,¹² the energy of fracture should be proportional to the amount of new surfaces generated by the fracture. Thus, as many cracks are formed during the fracture process, more energy should be absorbed in breaking the material, and this energy is dissipated throughout a larger volume, leading to an increase in EB% and toughness.

Figures 1 and 2 reveal that the semi-IPNs have higher mechanical properties than the corresponding full IPNs, i.e., they have higher modulus and UTS

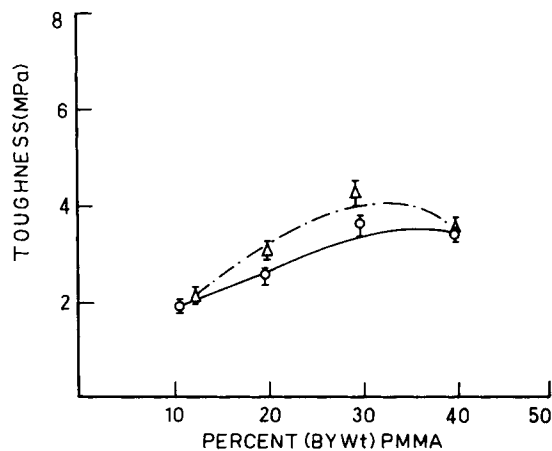
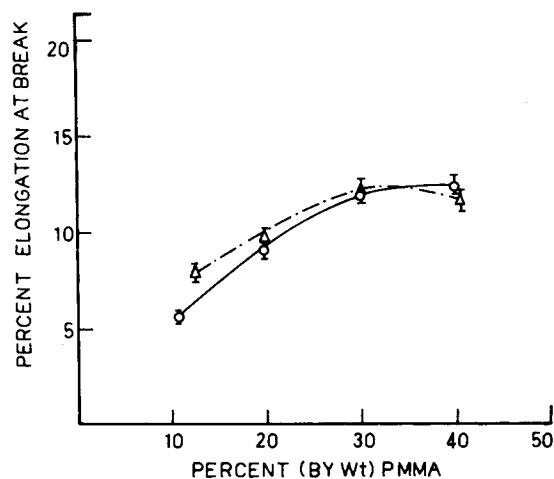


Figure 2 Variation of EB (%) and toughness of epoxy-PMMA semi- and full IPNs, respectively, with changes in blend ratio (w/w); ○ — ○ semi- and △ - - - △ full IPNs.

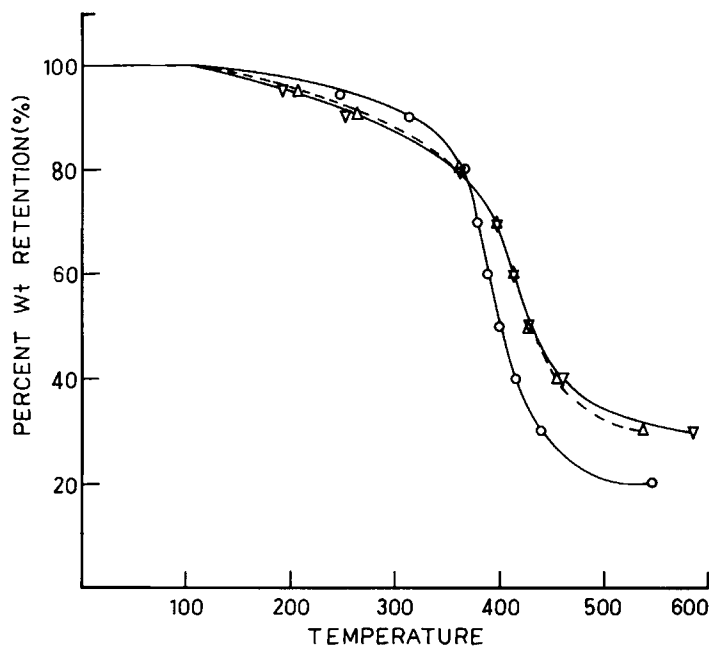


Figure 3 TGA thermograms for epoxy, semi, and full IPN systems of epoxy-PMMA
 ○ — ○ epoxy; △ - - - △ semi-IPN of (79.92/20.08) epoxy-PMMA, and ▽ — ▽ (79.69/20.31) full IPN of epoxy-PMMA.

values than the respective full IPNs. The trends in changes of EB % and toughness also corroborate this observation. This can possibly be explained by the fact that, although rigid and hard, the PMMA moieties have much higher free volume and there is ample scope of threading or interpenetration in semi-IPNs, i.e., where the methacrylate chains are linear. On the contrary, in the case of full-IPNs, the higher degree of crosslinking makes it more compact and lowers the statistical probability of threading or interpenetration, thereby precluding the reinforcing effect of interpenetration. This extent of threading outweighs the effect of homopolymer crosslinking of full IPNs.¹⁴

Thermal Properties

The thermogravimetric analysis (TGA) results are shown in Figure 3. The epoxy-poly(methylmethacrylate) IPNs, both semi- and full, exhibit enhancement of the weight retention compared to the weight retention of pure epoxy. The comparison between the full and semi-IPNs indicate that there is no significant difference in the degradation behavior and that the enhancement is not related to interpenetration. The weight retention enhancement can be explained by the thermal degradation behavior of PMMA. The thermal degradation of PMMA is known to yield almost 100% monomer by the step-

wise unzipping process.¹⁴ One possible explanation is that the unzipped monomers act as radical scavengers for the radicals produced from the degradation of epoxy, thus delaying further reaction of the radicals into the thermodegradative products of epoxy.

Morphology

The primary mode of fracture in a crosslinked thermoset polymer-like epoxy is shear yielding in which the deformation appears to be highly localized in that the tearings originate from separate, randomly distributed points along the crack front. Once crack propagation was initiated, it could not proceed to a perceptible level.^{15,16}

From the SEM micrographs of the tensile fractured surface of the specimens (Fig. 4), it is evident that in both semi- and full IPNs (designated as S and F series, respectively), crack initiation follows the similar shear yielding mechanism involving extensive viscoelastic and plastic deformation, resulting in increased toughness and elongation. In the case of full IPN, the dense, crosslinked PMMA network offers strong, rigid obstacles, surrounding which the material can accumulate damage, resulting in resin-particle debonding and matrix cracking, as evidenced by the appearance of crazing, the extent of which increases with increase in PMMA content.

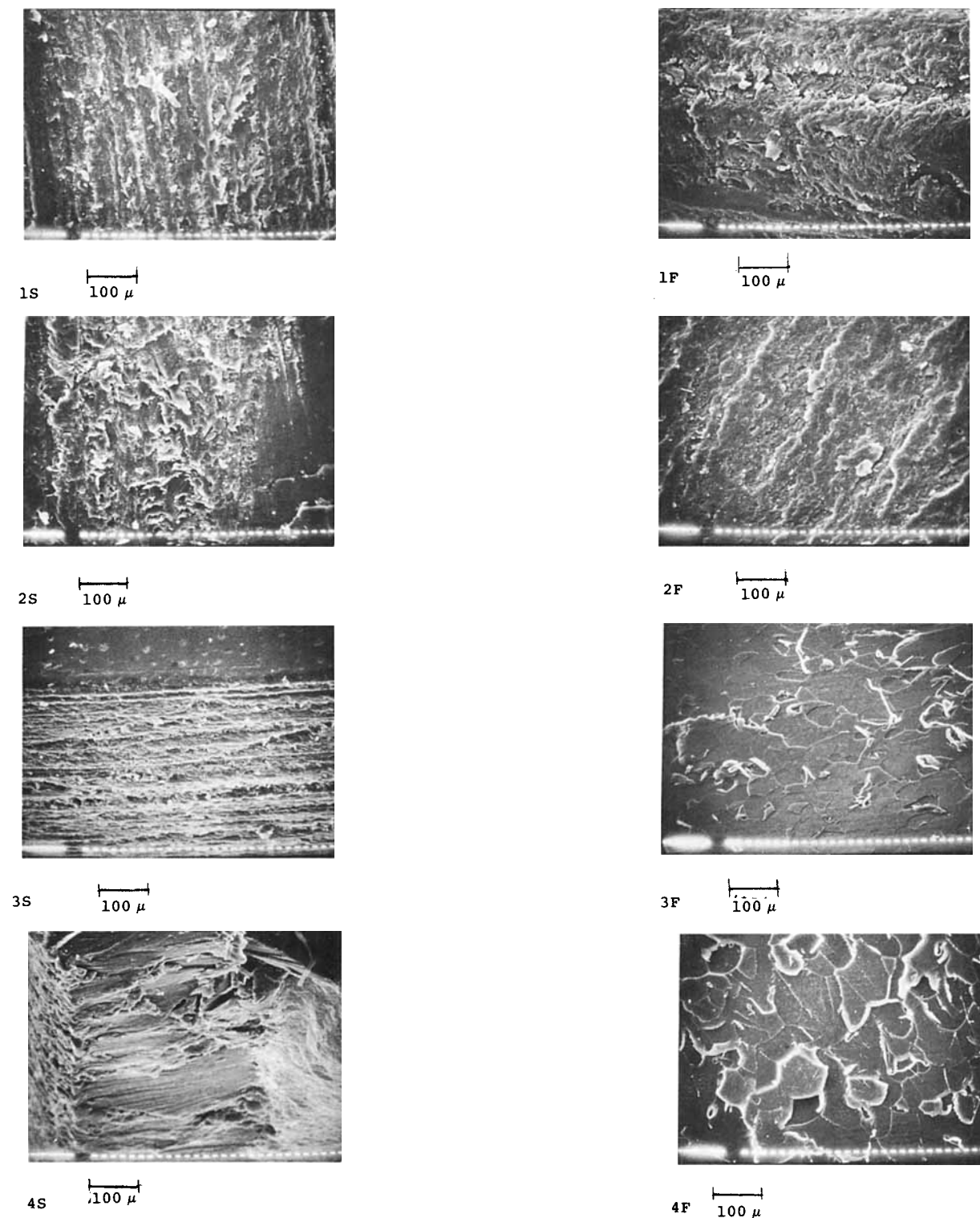


Figure 4 Scanning electron micrographs of epoxy-PMMA sequential IPNs ($200\times$); sets of micrographs 1S/2S/3S/4S refer to (89.29 : 10.71); (79.92 : 20.08); (69.94 : 30.06) and (60.06 : 39.94) semi-IPNs, respectively. 1F/2F/3F/4F refer to (87.58 : 12.42); (79.69 : 20.31); (70.32 : 29.68); (59.48 : 40.52) full IPNs epoxy-PMMA system, respectively.

Once debonding occurs, the debonded particle acts as a stress concentrator and it becomes energetically more favorable for this crack to grow than for debonding events to be generated in greater number.

For semi-IPNs, physical entanglement between the linear PMMA phase and crosslinked epoxy network introduces many more sites of crack arrest and initiation. Thus, the SEM micrographs take the appearance of "swiss cheese" characterized by extensive shear banding.¹⁷ Here, the continuity of crack propagation through considerable crack branching, delocalization of particles, and bridging of microcracks through threading are the characteristic features.

CONCLUSION

It can be concluded that an effective polymer blend (made by the interpenetration technique) based on epoxy and PMMA can be formed, having improved toughness compared to rigid, brittle epoxy homopolymer. From analysis of data presented, both in tabular form and in graphs, it is seen that properties such as UTS and modulus showed higher values for semi-IPNs, i.e., where PMMA remained uncrosslinked. The semi-IPNs were further characterized by lower toughness and elongation than full IPNs. There was enhancement in thermal stability of the IPNs compared to pure epoxy. There was hardly any difference in thermal stabilities of the semi- and full IPNs, indicating that crosslinking and interpenetration had little relation to degradation behavior. Crosslinking of the dispersed PMMA phase caused a distinct change in the phase morphological pattern by precluding threading or interpenetration.

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