

Epoxy–Poly(butyl methacrylate) Interpenetrating Polymer Networks: Morphology and Various Physical, Mechanical, and Thermal Properties

D. CHAKRABARTY* and B. DAS

Department of Plastics & Rubber Technology, Calcutta University, 92, Acharya Prafulla Chandra Road, Calcutta–700 009, India

SYNOPSIS

Semi- and full interpenetrating polymer networks (IPNs) of epoxy resin and poly(butyl methacrylate) (PBMA) were prepared by the sequential mode of synthesis. These were characterized with respect to their mechanical properties, such as ultimate tensile strength, percent elongation at break, and modulus. The densities of these samples were evaluated and compared. Differential scanning calorimetry (DSC) and thermogravimetric analysis were undertaken for thermal characterization of the IPNs. Phase morphology was studied by polarized light microscopy of the undeformed specimens and by scanning electron microscopy of the fractured surfaces of samples undergoing tensile failure. The effects of variations of the blend ratios on the above-mentioned properties were examined. A gradual decrease in modulus and tensile strength was observed for both the semi- and full IPNs with consequent increases in elongation at break and toughness as the proportion of PBMA increased. The densities also followed the same pattern. Semi-IPNs, however, were characterized by higher densities, tensile strengths, and moduli than the corresponding full IPNs. The DSC tracings displayed broadening of transitions, indicating some phase blending. The percent weight retentions in the thermal decomposition of the IPNs and pseudo-IPNs were higher than that observed during the thermal degradation of the epoxy resin homopolymer network. Phase-separated PBMA domains of various sizes were presumed to be responsible for the increased toughness of PBMA-modified epoxy. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Interpenetrating polymer networks (IPNs) are a new class of polymer blends in network form in which at least one component is polymerized and/or cross-linked in the immediate presence of the other.^{1–4} The multipolymer systems thus obtained display a broad range of properties, from toughened elastomers to high-impact plastics. The physical nature of the constituent networks, their relative proportions in the blends, etc., control the ultimate performance of the resulting IPNs.^{5–8}

In the case of IPNs prepared from glassy and rubbery polymer, the rubber reinforcing effect

(when the glassy component is the continuous phase) or the filler reinforcing effect (when the rubbery component is the continuous phase), in addition to the interpenetration effect, plays a key role in determining the various properties. When the two networks are formed simultaneously, the resulting IPNs are associated with the smallest degree of phase separation; whereas in an IPN formed by sequential technique, the ultimate properties are dictated by the continuous network.⁹

The present study involves the synthesis of sequential IPN systems (both semi- and full) from an epoxy resin and poly(butyl methacrylate) (PBMA), and the evaluation of their mechanical, physical, and thermal properties. We have also attempted to find a suitable correlation between the morphologies de-

* To whom correspondence should be addressed.

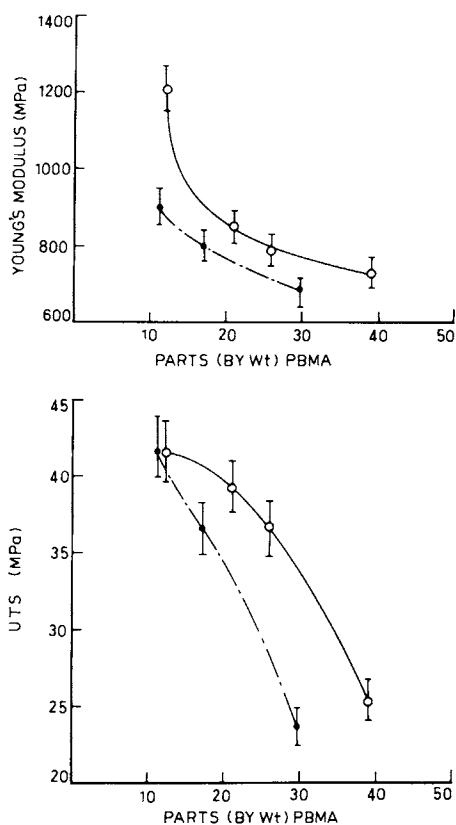


Figure 1 Variation of TS and modulus of epoxy-PBMA semi- and full IPNs with variation of blend ratio (w/w): ○ — ○ Semi-IPN, and ● — · · · — ● full IPN.

veloped in the IPN systems and the various properties.

EXPERIMENTAL

The diepoxy monomer, diglycidyl ether of bisphenol A [DGEBA, from M/s. Ciba Geigy, India (Araldite GY-250)], was used as received. Butyl methacrylate [BMA (FLUKA), West Germany] was purified by washing first with 2% aqueous NaOH solution and then by repeated washing with distilled water, and dried over fused CaCl_2 . The initiator used was benzoyl peroxide (Bz_2O_2) (B.D.H. India). The initiator was purified by repeated crystallization from chloroform. Formulated aromatic polyamine adducts, HY-830 and HY-850 (both from M/s Ciba Geigy) were used in combination as a cross-linker for the epoxy resin. Both are epoxy adducts of an aromatic polyamine based on diaminodiphenyl 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 for crosslinking PBMA.

IPN Synthesis

A weighed amount of inhibitor-free BMA was taken in a three-necked, round-bottomed flask and thoroughly mixed with 2% by weight (based on BMA) of benzoyl peroxide. DGEBA was then accurately weighed into the flask and the contents were stirred to give a homogeneous mixture. The flask was then purged with dry N_2 and heated in a water bath for 1 h at $60 \pm 2^\circ\text{C}$ with continuous stirring. It was then allowed to cool to room temperature. Weighed amounts (60% by weight of DGEBA) of aromatic polyamine adducts mix were then added. It was again homogeneously mixed with the contents of the flask and allowed to settle for 1–2 min to release any gases formed. This, in effect, helps in obtaining a smooth, uniform, pore-free sheet. The contents of the flask were then poured into a glass mold (formed by clipping together two glass plates separated by a Teflon gasket) which was 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 ensure complete crosslinking and polymerization. Finally, the sheets were kept in vacuum for over 3 days until constant weight was achieved. The samples thus produced were semi-IPNs.

In order to prepare a full IPN, the comonomer-crosslinker of BMA, namely EGDM, was added to the monomer-initiator solution and mixed uniformly before the incorporation of the diepoxy monomer. In all cases, the concentration of EGDM was kept constant at 1.6% by weight based on BMA. All other operations were identical to those described for a semi-IPN.

MEASUREMENTS

Tensile Properties

Tensile properties such as tensile strength, modulus, percent elongation at break (EB %), and toughness were measured using an Instron Universal testing machine (model 4204) at room temperature according to the low-strain-rate tensile testing method, as per ASTM D-638. All testings were conducted at ambient conditions in an environmentally controlled room using a crosshead speed of 5 mm per min. The tensile specimens were cut in a dumbbell shape of 4-mm width, 50-mm span, and 1-mm thickness. The area under the load-versus-displacement plot was taken as a measure of the IPN samples' toughness. The data reported are averages of at least six measurements; typical scattering range of the results

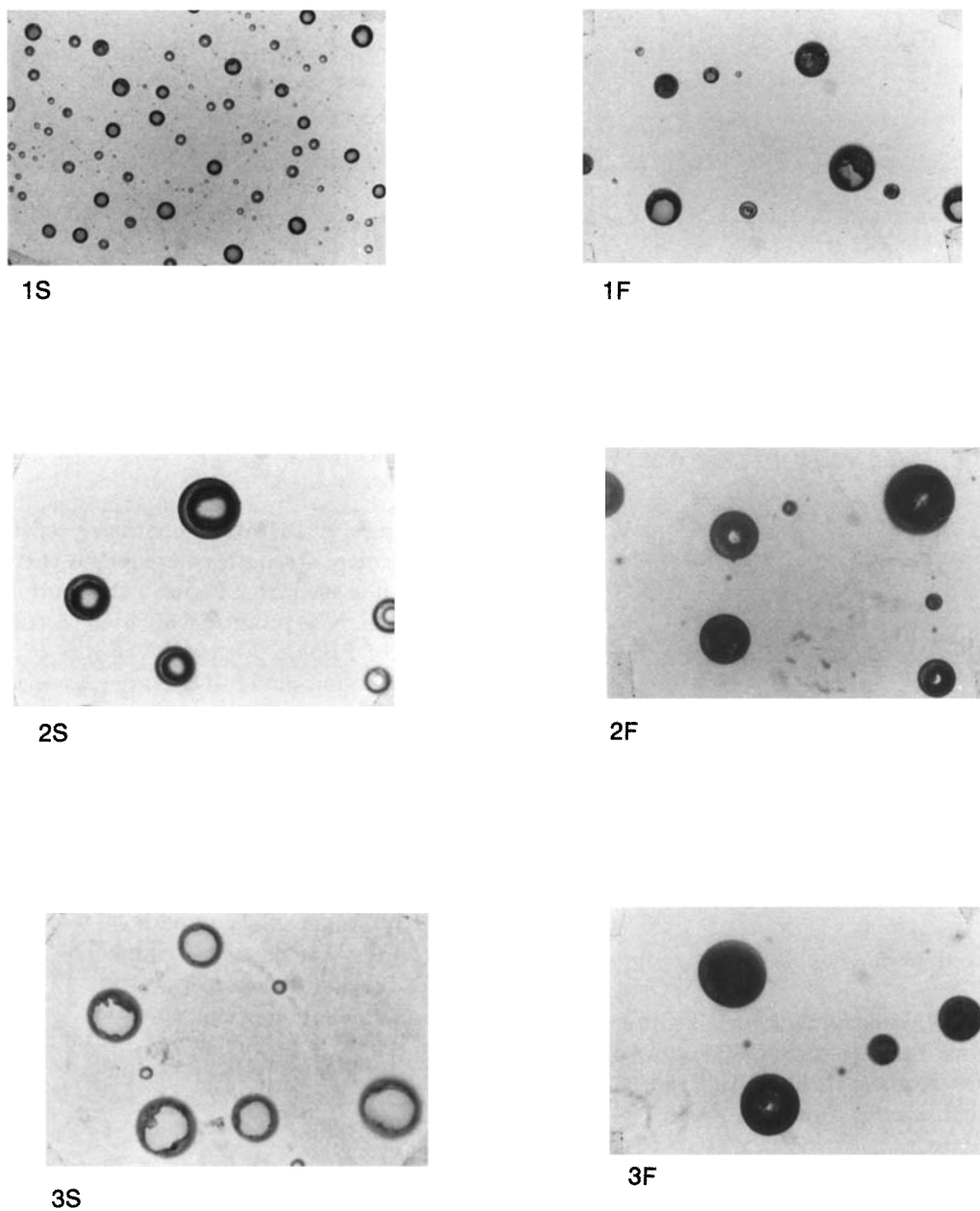


Figure 2 Polarizing light micrographs of epoxy-PBMA sequential IPNs (200 \times). Sets of micrographs 1S/2S/3S refer to 87.95/12.05, 78.96/21.04, and 74.17/25.83 epoxy-PBMA semi-IPNs, respectively, and 1F/2F/3F refer to 88.65/11.35, 82.89/17.11, and 70.48/29.52 full IPNs of epoxy-PBMA system, respectively.

was $\pm 5\%$ and has been shown as an error bar for each data point.

Density

Densities of different samples were measured at room temperature using hydrostatic technique, following ASTM D-792.

Thermal Properties

Thermogravimetric analysis (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, weighing between 8 and 12 mg, were placed in a platinum sample pan

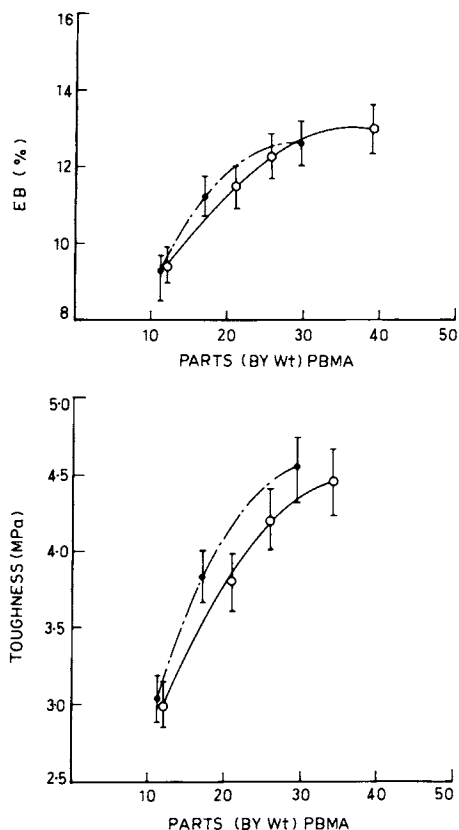


Figure 3 Variation of EB (%) and toughness of epoxy-PBMA semi- and full IPNs, respectively, with changes in blend ratio (w/w): \circ — \circ semi-IPN, and \bullet — \bullet full IPNs.

under a continuous flow of nitrogen at the rate of $1.5 \text{ ft}^3/\text{h}$.

A Du Pont 9000 instrument was used for differential scanning calorimetry (DSC) studies. The DSC tracings were made at the heating rate of $10^\circ\text{C}/\text{min}$ under a continuous flow of nitrogen.

Morphology

A Phillips PSEM-500 scanning electron microscope (SEM) was used for examining the phase morphology of the fractured surfaces of specimens undergoing tensile failure. Surface morphology of the undeformed samples was examined by a polarizing microscope (model Leitz, Laborlux 12 POLs) at lower magnifications.

RESULTS AND DISCUSSION

Mechanical Properties

The effects of the variation of blend ratio on modulus and ultimate tensile strength (UTS) are illustrated

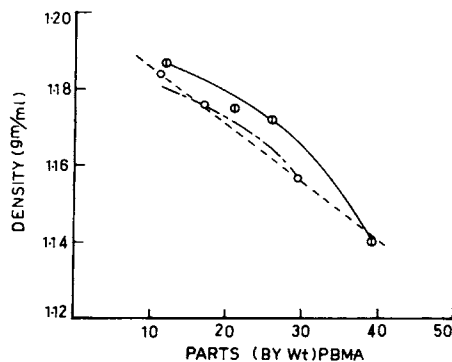


Figure 4 Variation of density of epoxy-PBMA semi- and full IPNs with variation in blend ratio (w/w): \circ — \circ semi-IPN; \circ - - - \circ full IPN; ----- calculated from additivity principle.

in Figure 1. PBMA is characterized by quite low mechanical strength compared to the epoxy resin. Thus it is seen from Figure 1 that both modulus and UTS decrease progressively with increasing proportions of PBMA. Although the rate of modulus fall for both semi- and full IPNs decreases with increase in PBMA content beyond approximately 20% (by weight), the UTS of both semi- and full IPN fall off quite sharply within the entire range of PBMA concentrations studied. It is well known that condensation polymerization of epoxy resin produces a broad distribution of low molecular weight species.¹⁰ On the contrary, the free radical polymerization of *n*-BMA produces elastomeric *p*(*n*-BMA) of relatively higher molecular weight. The kinetic chain length, or the degree of polymerization which is a function of monomer concentration, was initially not

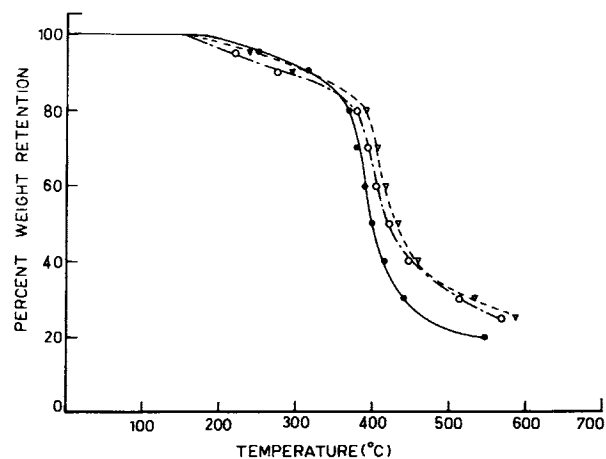


Figure 5 TGA thermograms for epoxy, semi-, and full IPN systems of epoxy-PBMA: \bullet — \bullet epoxy; \circ - - - \circ semi-IPN (78.96/21.04: epoxy-PBMA); Δ - - - Δ full IPN (82.89/17.11: epoxy-PBMA).

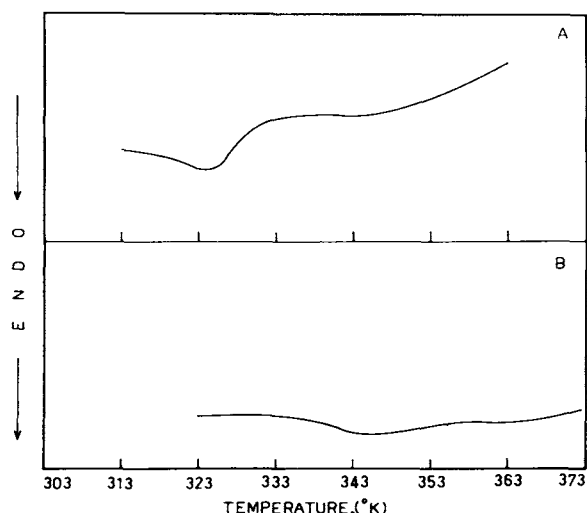


Figure 6 DSC curves for the semi- and full IPNs of epoxy-PBMA system: (A) Semi-IPN (78.96/21.04: epoxy-PBMA); (B) Full IPN (82.89/17.11: epoxy-PBMA).

too great so that the rubbery domains, formed with low concentration of monomer, were solubilized in the epoxy matrix and resulted in sharp fall in modulus. With the onset of phase separation at higher concentrations of PBMA, as is evident from polarizing light micrographs (Fig. 2), the influence on modulus decreases.

The ultimate load that a material can withstand at the point of break is a function of effective cross section of the specimen, and this load-bearing, effective cross-sectional area progressively decreases with increase in PBMA concentration. Furthermore, as the continuous epoxy resin matrix is substituted more and more by the phase-separated rubbery domains at higher doses of PBMA, the UTS undergoes a steep fall.

In conformity with the above observations, both the percent elongation at break and the toughness exhibit increasing trends with increasing PBMA contents (Fig. 3). The increase in EB %, which, of course, almost levels off in cases of both semi- and full IPNs beyond 25–30% of PBMA with increased PBMA content, may possibly be attributed to the capacity of the dispersed elastomeric PBMA domains of undergoing stretching within itself or at the resin-rubber interface. The latter, of course, occurs to a smaller extent at higher PBMA doses because of phase separation. Thus the influence on EB % at higher concentrations of PBMA is not so remarkable.

The improvement in toughness can be attributed initially to the increase in ductility due to the incorporation of relatively elastomeric PBMA when

it remains in the dissolved state, and subsequently to the *in situ* phase separation producing rubber-rich domains at higher concentrations of PBMA. McGarry and coworkers^{11,12} noticed a marked improvement in toughness when a resin-rubber mixture containing a small fraction of the elastomer was allowed to phase-separate into a rubber-rich phase finely dispersed in an epoxy resin-rich matrix. The degree of improvement depended critically on the size of the rubber-rich domains and reached a maximum when the size distribution ranged between 1–5 μm .^{13–15} Manzione and Gillham¹⁶ observed that for optimum toughness the mix should contain a portion of dissolved rubber and a certain volume fraction of phase-separated rubber particles. Thus a two-particle-size distribution of domains at higher PBMA content becomes much more predominant and leads to improved toughness.

It is interesting to note from Figures 1 and 2 that the semi-IPNs have higher mechanical properties than the corresponding full IPNs, i.e., they have higher modulus and UTS values than the respective full IPNs. Correspondingly, the EB % and toughness of the full IPNs are found to be higher than the respective values for semi-IPNs. This can be explained by the fact that the soft, elastomeric PBMA moieties have much higher free volume and, because the observation is being made at a temperature higher than its T_g , there is ample scope for threading or interpenetration with the epoxy resin-rich matrix, particularly in the case of semi-IPNs, where the chains are linear and have greater mobility. On the contrary, in the case of full IPNs, the higher degree of crosslinking restricts the mobility of the PBMA chains and lowers the statistical probability of threading, and thereby precludes the reinforcing effect of interpenetration. The extent of threading thus outweighs the effect of homopolymer crosslinking of full IPNs.¹⁷

Density

Figure 4 shows the trend of changes in density for the semi- and full IPNs of the epoxy resin-PBMA system as a function of blend composition.

The densities of both the semi- and full IPN systems decrease with increasing PBMA content. Since PBMA is less dense than epoxy, it can be assumed that the density of the blend system should decrease as more and more epoxy was substituted. However, the salient feature of the density-versus-composition curve is that the densities of both the semi- and full IPNs lie above the curve calculated on the basis of the additivity principle,¹⁸ which states that

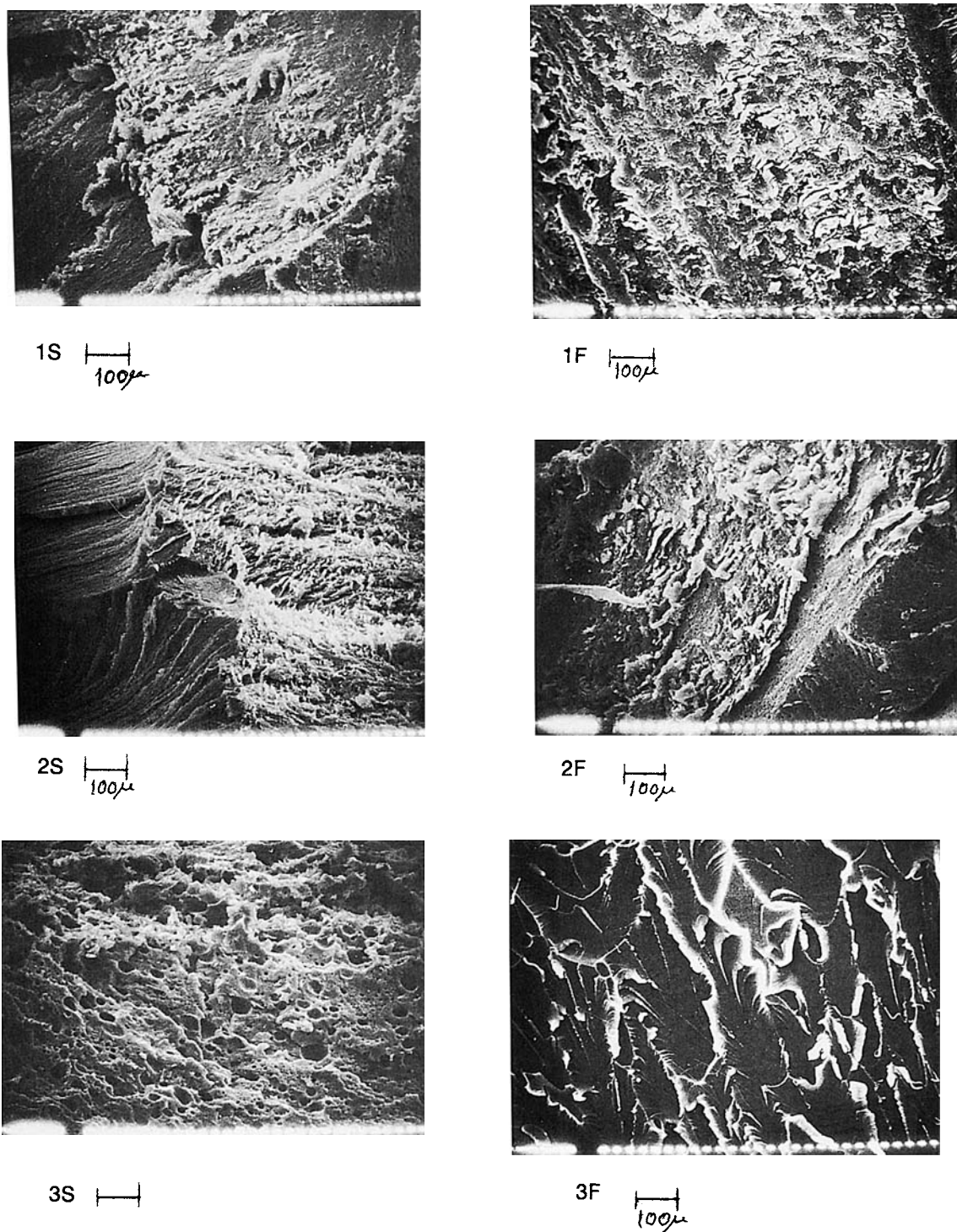


Figure 7 Scanning electron micrographs of epoxy-PBMA sequential IPNs (200 \times): Sets of micrographs 1S/2S/3S refer to 87.95/12.05, 78.96/21.04, and 74.17/25.83 epoxy/PBMA semi-IPNs, respectively, and sets of micrographs 1F/2F/3F refer to 88.65/11.35, 82.89/17.11, and 70.48/29.52 epoxy-PBMA full IPNs, respectively.

$$d = w_1 d_1 + w_2 d_2$$

where, d is the density of the IPN sample, w_1 and w_2 are the weight fractions of the constituents, and d_1 and d_2 are the corresponding densities, respectively. Moreover, the density curve of the semi-IPNs lies above that for full IPNs. The phenomenon may be explained by the possible interpenetration between the constituent networks, which may lead to a higher density than the average density of a physical blend. Furthermore, the extent of interpenetration might be greater in the case of semi-IPNs, for the same reason which led to its higher mechanical properties over full IPNs.

Thermal Properties

Thermogravimetry

Figure 5 compares the TGA curves of the semi- and full IPNs of epoxy-p(*n*-BMA) with that of the pure epoxy homopolymer. The two IPN systems considered here are of nearly identical composition, and both exhibit an enhancement in weight retention. This enhancement can be explained by the degradation behavior of PBMA, which is assumed to yield monomeric BMA and but-1-ene as the major degradation products by the stepwise unzipping process.¹⁹ These unzipped degradative products act as radical scavengers for the radicals produced from the degradation of epoxy which, as proposed by Anderson^{20,21} and Lee,²² also follows a free radical process of degradation and thus delays further reaction of the radicals into the thermodegradative products of epoxy.

DSC Studies

Figure 6 shows the DSC tracings of a semi-IPN of epoxy-p(*n*-BMA) containing 21.04 percent by wt of linear p(*n*-BMA) and a full IPN containing 17.11% (by weight) of crosslinked p(*n*-BMA). The broadening of the glass transition, though narrow, indicates phase mixing. The rubbery PBMA dissolved in the epoxy resin lowers the epoxy T_g remarkably. The transition of the full IPNs is comparatively sharper than that of semi-IPN.

Morphology

Polarizing Light Microscopy

Bimodal distribution of particle sizes is indicated in the polarizing light micrographs (Fig. 2) of both semi- and full IPNs. Although the domains of full

IPNs are bigger than those of the corresponding semi-IPNs of nearly identical composition, the differences in sizes are narrowed with increasing concentrations of p(*n*-BMA). In the present study the methacrylate domains are formed first; thus, in the case of semi-IPNs, the linear elastomeric domains are not capable of withstanding the shrinkage force which is exerted on them during the subsequent epoxy cure. On the contrary, the crosslinked PBMA domain in full IPNs might be expected to resist the subsequent shrinkage force to some extent and is capable of retaining its size and shape. Furthermore, the polymethacrylate domains are characterized by epoxy resin inclusion of varying degrees. However, with increase in PBMA content as the polymethacrylate domains grow in size, the content of occluded epoxy gradually diminishes and the domains appear to be quite compact and dense, particularly in the case of full IPNs.

Scanning Electron Microscopy

The SEM micrographs (Fig. 7) show extensive shear yielding and crack propagation through transparticle fracture, interfacial debonding, or cohesive failure of the matrix, particularly at the higher concentration of PBMA. With increasing PBMA concentrations, crack propagation does not take place around the particles; on the other hand, the interfacial adhesion is such that instead of the particles stretching from the absorption of energy, they debond from the matrix and are pulled out. In the case of full IPNs, crack propagation through crazing is predominant even at higher PBMA concentrations.

REFERENCES

1. H. L. Frisch, K. C. Frisch, and D. Klempner, *Pure Appl. Chem.*, **53**, 1557 (1981).
2. L. H. Sperling, *Polymer Alloys*, Plenum Press, New York, 1977.
3. L. H. Sperling, *Interpenetrating Polymer Networks and Related Materials*, Plenum Press, New York, 1981.
4. D. A. Thomas and L. H. Sperling, *Polymer Blend*, D. R. Paul and S. Newman, Eds., Vol. 2, Academic Press, New York, 1978.
5. K. Frisch, D. Klempner, and S. Migdal, *J. Polym. Sci., Polym. Chem. Ed.*, **12**, 885 (1974).
6. K. Frisch, D. Klempner, and S. Migdal, *Polym. Eng. Sci.*, **14**, 76 (1974).
7. H. L. Frisch and D. Klempner, *Polym. Sci. Technol.*, **11**, 203 (1980).
8. L. H. Sperling, *Polym. Eng. Sci.*, **25**, 517 (1985).
9. D. Klempner, K. Frisch, and H. L. Frisch, *J. Elastoplast.*, **5**, 196 (1973).

10. C. B. Bucknall, *Toughened Plastics*, Applied Science Publishers, Ltd., London, 1977.
11. F. J. McGarry and A. Willner, Research Report R 68-6, School of Engineering, Massachusetts Institute of Technology, 1968.
12. J. N. Sultan and F. J. Macgarry, Research Report R 68-8, School of Engineering, Massachusetts Institute of Technology, 1968.
13. F. J. McGarry, *Proc. R. Soc. Lond.*, **A319**, 59 (1970).
14. J. N. Sultan and F. J. McGarry, *Polym. Eng. Sci.*, **13**, 29 (1973).
15. C. K. Riew, E. H. Rowe, and A. R. Siebert, *Advances in Chemistry Series*, No. 54, R. D. Deanin and A. M. Crygnola, Eds., 1976.
16. L. T. Manzione and J. K. Gillham, Paper presented at the 178th ACS Natl. Meeting, Org. Coat. Plast. Div., Washington D.C., 1979.
17. K. C. Frisch, D. Klemperer, H. L. Frisch, and H. Ghiradella, in *Recent Advances in Polymer Blends, Grafts & Block*, L. H. Sperling, Ed., Plenum, New York, 1974.
18. D. R. Paul, *Polymer Blends*, Vol. 2, D. R. Paul and S. Newman, Eds., Academic Press, Inc., New York, 1978, Chap. 12.
19. S. L. Madorsky, *Thermal Degradation of Organic Polymers*, Interscience, New York, 1964.
20. H. C. Anderson, *Analyt. Chem.*, **32**, 1592 (1960).
21. H. C. Anderson, *Polymer*, **2**, 452 (1961); H. C. Anderson and Z. Koll, **184**, 26 (1962).
22. L. H. Lee, *J. Polym. Sci.*, **3**, 859 (1965).

Received August 6, 1995

Accepted November 23, 1995