

Mechanical and Dynamic Mechanical Studies of Epoxy/VAc-EHA/HMMM IPN–Jute Composite Systems

Chandan Datta, Diya Basu, Abhishek Roy, Amarnath Banerjee

Department of Polymer Science & Technology, 92 A.P.C. Road, University of Calcutta, Calcutta 700 009, India

Received 21 October 2002; accepted 9 May 2003

ABSTRACT: Epoxy [50:50 mixture of Di-Glycidyl Ether of Bis-Phenol A (DGEBA) and Epoxidized Novolac (EPN)] was solution blended with Vinyl Acetate-2-Ethylhexylacrylate (VAc-EHA) resin in aqueous medium, in varying weight fractions, with Hexamethoxymethylmelamine (HMMM) as a crosslinker and data was compared with a control. The present work was aimed to optimize the tensile strength, dynamic mechanical strength, impact strength, and toughness by preparing a blend followed by jute composites of a semi- and full interpenetrating network (IPN). In control

experiments epoxy alone was crosslinked (semi-IPN), whereas the DGEBA-EPN and VAc-EHA/HMMM were crosslinked separately (full-IPN), using jute as the substrate for making composites. Composites of full-IPN systems of epoxy/VAc-EHA system had higher moduli and UTS than the semi-IPN systems. Dynamic mechanical study showed that full-IPN systems have higher T_g values than semi-IPN systems. The impact strength increases with increasing proportions of VAc-EHA copolymer. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 958–963, 2004

INTRODUCTION

The chemical, mechanical, and viscoelastic properties of the fiber–matrix interphase dominate the ultimate performance characteristics of fiber-reinforced polymeric composites. These three fundamental properties are certainly related to one another. The importance and popularity of fiber-filled (natural or synthetic) epoxy composites are due to their unusually high strength and stiffness for a given weight of material. In recent years, greater emphasis has been rendered in the development of fiber-filled epoxy composites based on natural fibers with a view to replace glass fibers either solely or in part for various applications. The scope for using jute fiber in place of traditional glass fibers stems from the lower specific gravity and workable specific modulus of the jute fiber (1.45 and 19 GPa, respectively). Moreover, the much lower cost and renewable nature make it an attractive fiber for use as a reinforcing material in the fiber-filled composites. Again the nonabrasive nature of the jute fiber permits higher fiber loading in the composite without the fear of extensive damage to compounding and molding equipment that occurs when much harder glass fiber is used.

Interpenetrating polymer networks (IPNs) are a new class of polymer blends in network form, in

which the possibility of phase separation has been remarkably reduced by arresting the morphologies of the participating components. Based on crosslinking type, the IPNs are classified under two headings—semi-IPN and full-IPN. In semi-IPN, one of the polymers is in crosslinked form and the other is in linear form, while in full-IPN both networks are crosslinked, the morphology fixed and well defined.^{1–5}

The present study aims in improving the properties of water borne EPN–jute fiber composites. This was accomplished by designing a waterborne 50:50 DGEBA to EPN blend as the resin part along with two modified amine hardeners. One was an adduct of DGEBA with liquid eutectic mixture of *m*-phenylene diamine (MPDA) and diamino diphenylsulphone (DPDS) (H1) in emulsified form, and the other was cyanoethylated DETA (H2) system. The reduced viscosity so characteristic of any emulsion, practically zero VOC, and better wettability of fibers make our selection of a water-borne epoxide matrix system valuable. The resin was blended with Vinyl acetate-2-Ethyl-hexyl-acrylate copolymer (VAc-EHA) and a full-IPN system was designed by using Hexamethoxymethylmelamine (HMMM) as the crosslinker. Both the systems were taken as matrices for developing jute fiber-reinforced composites, and its mechanical and dynamic mechanical properties were studied.

Correspondence to: N. Banerjee.

Contract grant sponsor: C.S.I.R grants (to C.D., SRF, and D.B., SRA).

Materials used

Two types of epoxy resins were employed one was an unmodified liquid diglycidyl ether of bisphenol A (Ciba Speciality Chemicals, India, Araldite GY 250)

with a furnished value of equivalent weight per epoxide group of 185–192. The other was an epoxidised novolac resin synthesised in our laboratory. Phenol and 37% w/w Formalin both from E. Merck, India, for novolac preparation were used as received. Epichlorohydrin was used for epoxidation of novolac and purchased from S.D. Fine Chem, India. Diethylenetriamine, MPDA, and DPDS was used in the preparation of modified hardeners for the epoxy resins, and acrylonitril were also purchased from S.D Fine chemicals India. VAc-EHA copolymer in emulsion form was obtained from Macromoles, India. Hexa-methoxymethyl-melamine (HMMMM) was prepared in the laboratory using standard procedure. The nonionic surfactant, Triton X-100, was purchased from Aldrich (Milwaukee, WI). Jute fiber was obtained from Jute Fabric from Fort Gloster, India.

Mechanical properties

Tensile properties

An Instron universal-testing machine (model 4304) was used for measuring the tensile properties like tensile strength, modulus, and toughness. ASTM D638 method was followed. A crosshead speed of 5 mm/min was maintained. All testing were conducted under ambient conditions in an environmentally controlled room. The samples for tensile measurements were cut in a dumbbell shape of 50 mm in span, 4 mm in width, and 1.7 mm in thickness. The overall width of the samples at the two ends of the dumbbell was 9 mm. The standard 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 $\pm 5\%$.

Impact properties

Izod impact strength was determined using ASTM D256. The unnotched samples for measurements were cut to $70 \times 10 \times 3$ -mm dimensions. In all cases, 12 specimens were tested and average values were reported.

Dynamic mechanical properties

A DuPont dynamic mechanical analyzer (Model 983) was employed for dynamic evaluation of the FRP test pieces using a fixed frequency (1 Hz) over a temperature range of 30–200°C (303–473 K) in an atmosphere of N₂.

Morphology

Phase morphology was examined in a Phillips PSEM-500 scanning electron microscope. For scanning elec-

tron microscope (SEM) studies, the solvent etched surfaces and the fractured surfaces of the samples undergoing failure in tensile testing were used.

EXPERIMENTAL AND RESULTS

The individual polymers were first separately diluted with distilled water, and stirred well to maintain a solid content of 50% by weight for convenience. Then a weighed amount of EPN and DGBEA (50 : 50) was taken in a three-necked, round-bottomed flask. VAc-EHA copolymer was then accurately weighed and introduced into the flask. The mixed hardener (H1 : H2 = 5 : 1) of epoxy are added at this mixture to 25% by weight. The contents of the flask were then stirred well to give a homogeneous mixture. When the formation of bubbles ceased, the viscous mass was applied on both sides of jute fabric by a hand layup technique. Four layers of green laminates were squeezed between two Mylar films using pressure of a hand roller so as to minimize voids and to avoid accumulation of excess matrix resin as far as possible. The hand-pressed laminates free from excess resin were allowed to cure. It was then initially kept at room temperature for about 24 h, and then heated at 80°C for 4 h, followed by further heating at 150°C and finally postcured in an oven at 80°C for 6 h. The volume fraction of fiber was maintained at 30% in all cases. The samples of semi-IPNs thus obtained are referred to as S-5, S-10, S-15, S-20, where S denotes semi- and 5, 10, 15, 20 denotes percentages of VAc-EHA in the IPNs.

To get full-IPN, a crosslinker for the acrylic copolymer, namely HMMMM, was added to the mixture at the final stage. In all cases the concentration of HMMMM was kept constant at 20% by weight based on VAc-EHA copolymer. All other steps were identical to those followed for semi-IPNs. The samples of full-IPNs are referred to as F-5, F-10, F-15, and F-20, where F denotes full and 5, 10, 15, and 20 denotes percentages of VAc-EHA in the IPNs.

Mechanical behavior

Figures 1 and 2 show the stress versus strain % curves for some of the representative samples of IPNs of Epoxy/VAc-EHA. By virtue of higher extent of interpenetration.

As discussed earlier, strain percent of semi-IPNs are higher than the full-IPNs. The curve displays the tendency of necking as the VAc-EHA copolymer content gradually increases. Thus, the change in fracture mechanics from a brittle nature to a ductile one is due to an increase in plastic deformation as understood from Figure 2.

The mechanical properties of both semi-IPNs (where only epoxy was crosslinked) and full-IPNs (where both

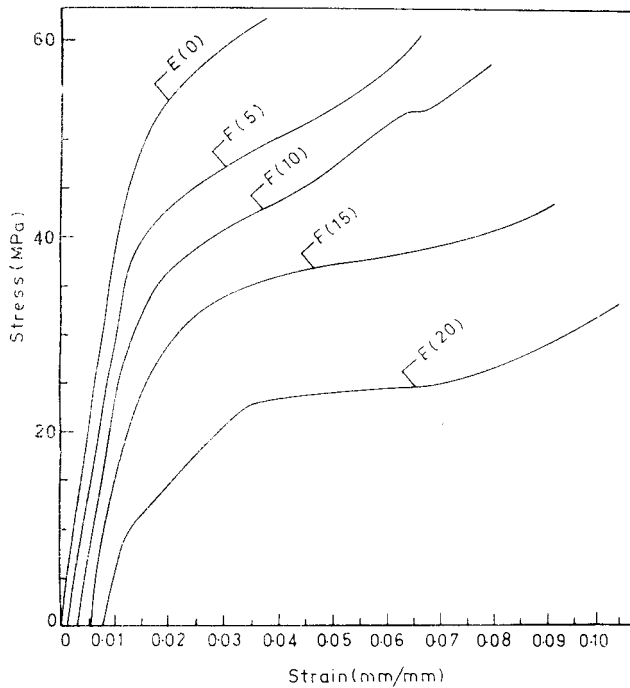


Figure 1 Variation of stress vs strain % of full-IPN systems.

epoxy and VAc-EHA were crosslinked) had been studied as a function of blend ratios of epoxy and VAc-EHA. The mode of changes in ultimate tensile strength and modulus of the semi-IPNs and full-IPNs had been compared in Figures 3 and 4. The influence of crosslinking of

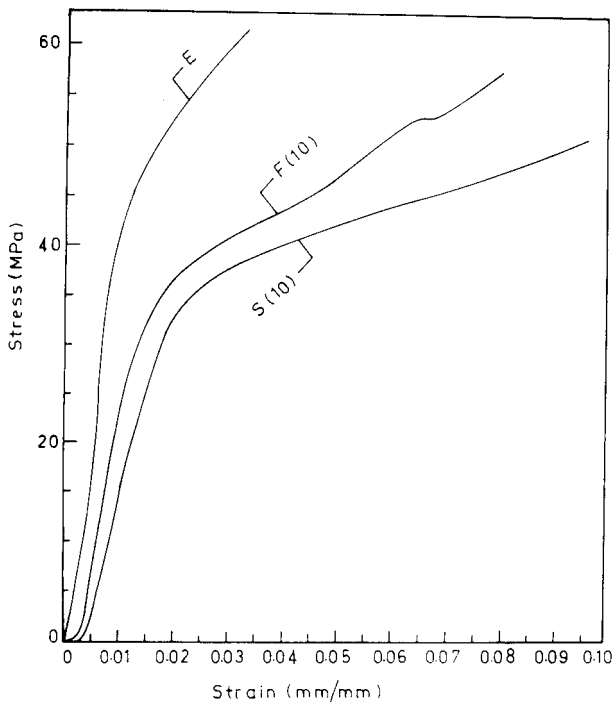


Figure 2 Variation of stress vs strain % of epoxy, full-IPN and semi-IPN systems.

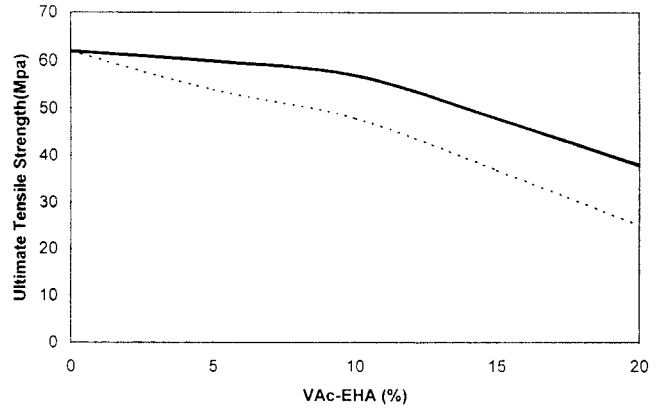


Figure 3 Variation of ultimate tensile strength vs % VAc-EHA of IPN systems. (...) Semi-IPN; (—) full-IPN.

the dispersed network into the subsequently crosslinked matrix network of epoxies was quite evident from the figures. In both the cases of semi-IPNs and full-IPNs, there was a reduction in Young's modulus and ultimate tensile strength (UTS) with increase in VAc-EHA content. This decreasing trend might be attributed to the following probable reasons: (1) reducing the possibility of complete curing sites of epoxies matrix by shielding the reactive sites of epoxies by the dispersed VAc-EHA matrix; (2) another important reason might be the plasticizing influences of the dispersed VAc-EHA domain.

It was observed that the full-IPNs of the Epoxy/VAc-EHA system had higher moduli and the UTS than the semi-IPNs. This could be possibly explained by the fact that the VAc-EHA moieties have much higher free volume, and there was an ample scope of interpenetration by linear chains of the VAc-EHA copolymer; hence, in the case of the full-IPNs, the crosslinks within the chains make them more compact.

Impact properties

Figure 5 shows the impact strength vs VAc-EHA % of full-IPN and semi-IPN systems. The degree of im-

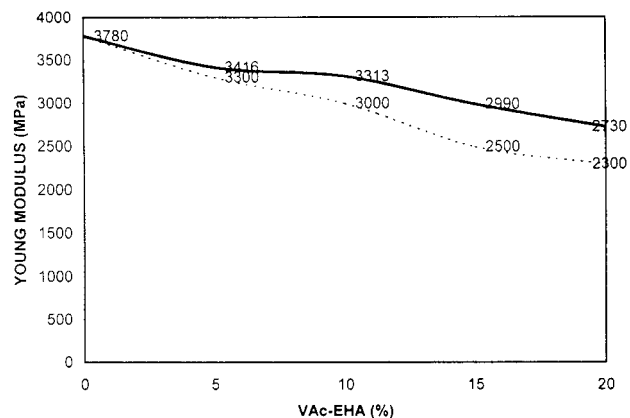


Figure 4 Variation of Young's modulus vs % VAc-EHA of IPN systems. (...) Semi-IPN ; (—) full-IPN.

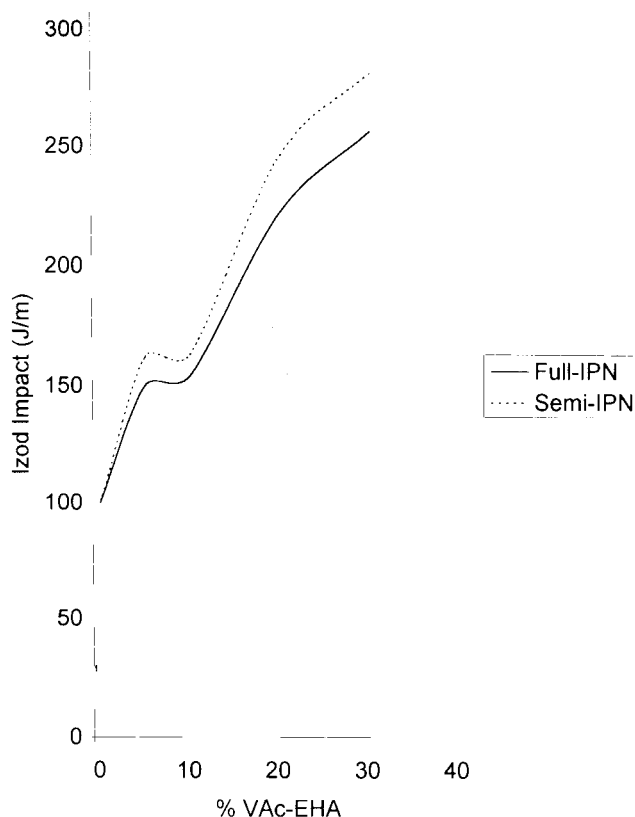


Figure 5 Variation of impact strength vs VAc-EHA % of IPN systems.

provement in terms of strain % and impact strength depends on the sizes of the dispersed phase. Thus, the impact strength may be expected to increase with increasing proportions of the VAc-EHA copolymer. The lack of impact modification from the acrylate at 10% level for both systems as evident from the Izod Impact results also points to a similar conclusion as obtained from DMA. This is due to acrylate resin at the 10% level, actively taking part in the crosslinking of the epoxide resin.

Addition of VAc initially causes crosslinking of epoxy groups present in the blend, and at 10% addition all the epoxy groups are probably crosslinked, decreasing the impact. This is reflected in the curve (Fig. 5) as a shoulder. Further addition of VAc-EHA acts as the impact modifier, not as the crosslinker of epoxy group, which is rarely available.

However, at a higher dosage level, the strength properties of our systems decreased; manifested by a lower strength and modulus and higher impact strength (Figs. 2–5). This can be explained by the dilution of the much harder epoxide systems by a softer acrylate modifier. Similarly, at this dosage level the acrylate retained its expected role as an impact modifier for our water-borne epoxide systems, manifested by an improved value for impact strength.

Dynamical mechanical analysis

The importance of the dynamic storage modulus in many structural applications is well known. A clear understanding of the storage modulus–temperature curve obtained during a dynamic mechanical test provides valuable insight into the stiffness of a material as a function of temperature.

Storage modulus

The importance of the dynamic storage modulus in many structural applications is well known. A clear understanding of the storage modulus–temperature curve obtained during a dynamic mechanical test provides valuable insight into the stiffness of a material as a function of temperature. Figure 6(a) shows the storage modulus–temperature curves of epoxy, semi-IPN systems, and full-IPN systems, respectively. The storage modulus value decreases gradually with increase in VAc-EHA content in both systems. This is due to the relative low modulus of the VAc-EHA resin. Full-IPN systems have higher E' than semi-IPN systems at the same VAc-EHA content. This is due to the increase in effective crosslinking density in the full-IPN systems compare to that of semi-IPN systems.

The storage modulus went for a sharp fall at around 80°C for all the systems (glass transition) before the subsequent plateauing. The appearance of relatively constant moduli (plateaus) at higher temperatures indicated that stable crosslinked networks existed in all the systems.

Loss modulus

Figure 6(b) shows the loss modulus (E'')–temperature curves of epoxy, semi-IPN, and full-IPN systems. If the applied mechanical energy (work) is not stored elastically, it must be lost, converted to heat through molecular friction, that is, viscous dissipation within the material. The T_g value decreases gradually with an increase in VAc-EHA content in both systems. The T_g value of 10% at the VAc-EHA level of both the systems is expected to be slightly higher, which may be due to the 10% level, the reason that 10% acrylate resin actively takes part in the crosslinking of the epoxide resin. The full-IPN systems have higher T_g values than semi-IPN systems (Table I). This is due to the fact that crosslinking efficiency and the extent of interpenetrating network formation in the epoxy/VAc-EHA/HMMM blend increases with an increase in VAc-EHA/HMMM percent.^{11–13}

Tan δ

Figure 6(c) shows the tan δ vs temperature curves of epoxy, semi-IPN, and full-IPN systems. Tan δ is a damping term that can be related to the impact resistance of a

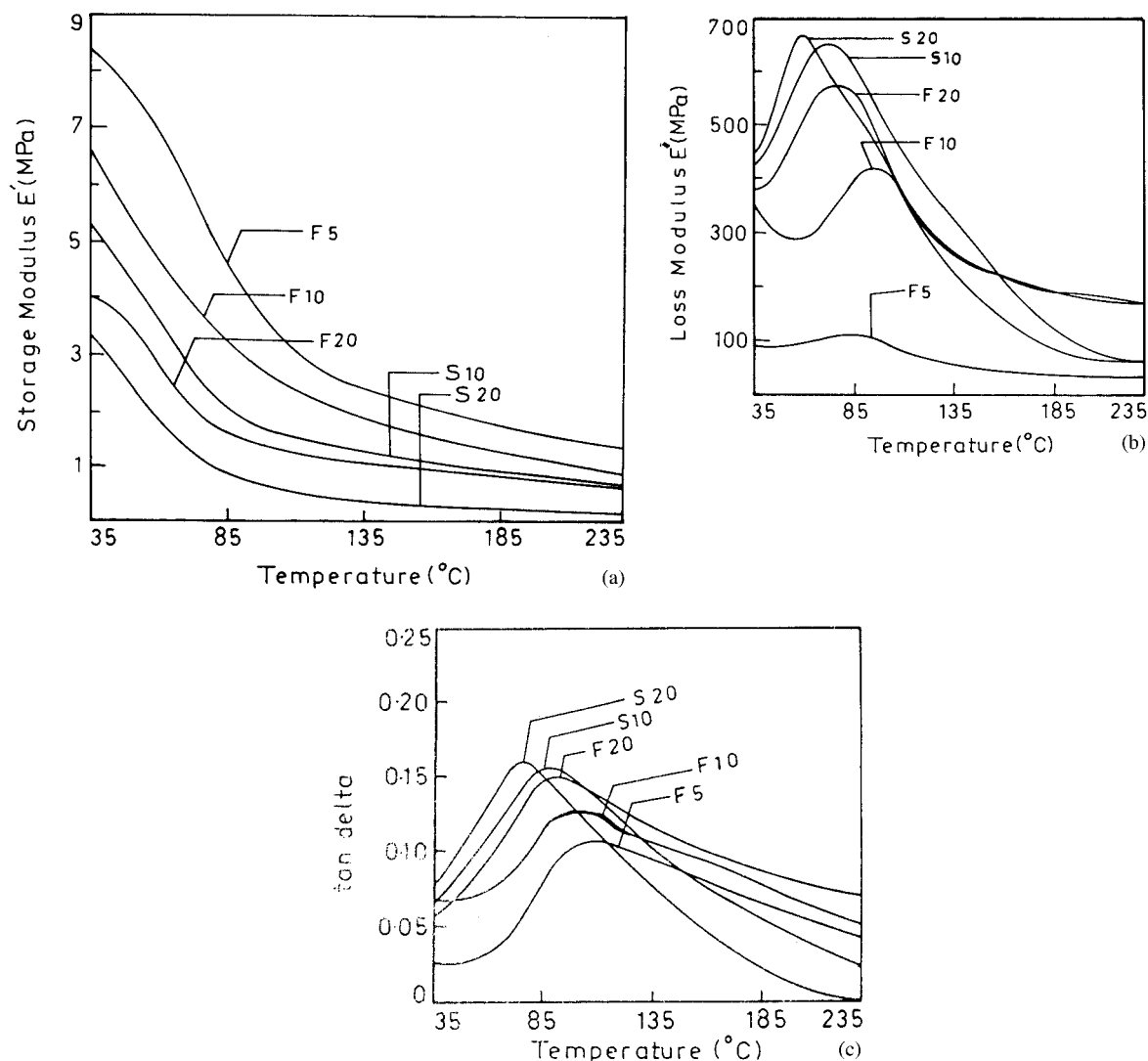


Figure 6 (a) Variation of storage modulus with temperature of full-IPN and semi-IPN systems. (b) Variation of loss modulus with temperature of full-IPN and semi-IPN systems. (c) Variation of $\tan \delta$ with temperature of full-IPN and semi-IPN systems.

material. The higher the peak $\tan \delta$ value, the greater the degree of molecular mobility. On comparing the temperature corresponding to maximum $\tan \delta$ peak values of Figure 6(c), full-IPN systems have higher values compared to semi-IPN systems at the same VAc-EHA content. This decreasing trend of semi-IPN systems might be attributed to the following probable reasons: (a) reducing the possibility of complete curing sites of the epoxy matrix by shielding the reactive sites of epoxy by the

dispersed VAc-EHA matrix; (b) another important reasons might be the plasticizing influences of the dispersed VAc-EHA domain.

Again, the $\tan \delta_{\max}$ value of the full-IPN systems are lower than the semi-IPN systems. This lowering of $\tan \delta_{\max}$ is due to the restricted chain mobility arising out of the higher crosslinked density obtained from the epoxy and VAc-EHA/HMMM. Thus, additional crosslinking restricted the segmental motion of the polymer chains, thereby reducing the energy that was dissipated during the glass-rubber transition.

TABLE I

Sample designation	Temp. at E'_{\max} ($^{\circ}\text{C}$)	Temp. at $\tan \delta_{\max}$ ($^{\circ}\text{C}$)	$\tan \delta_{\max}$
F5	88	95	0.11
F10	102	110	0.125
F20	77	85	0.15
S10	75	81	0.155
S20	67	75	0.156

Scanning electron microscopy

The scanning electron micrographs of both semi-IPNs and full-IPNs for different compositions of each are shown in Figure 7. The change in fracture mechanics from a predominantly shear yielding to crazing with increasing concentration of VAc-EHA can be easily

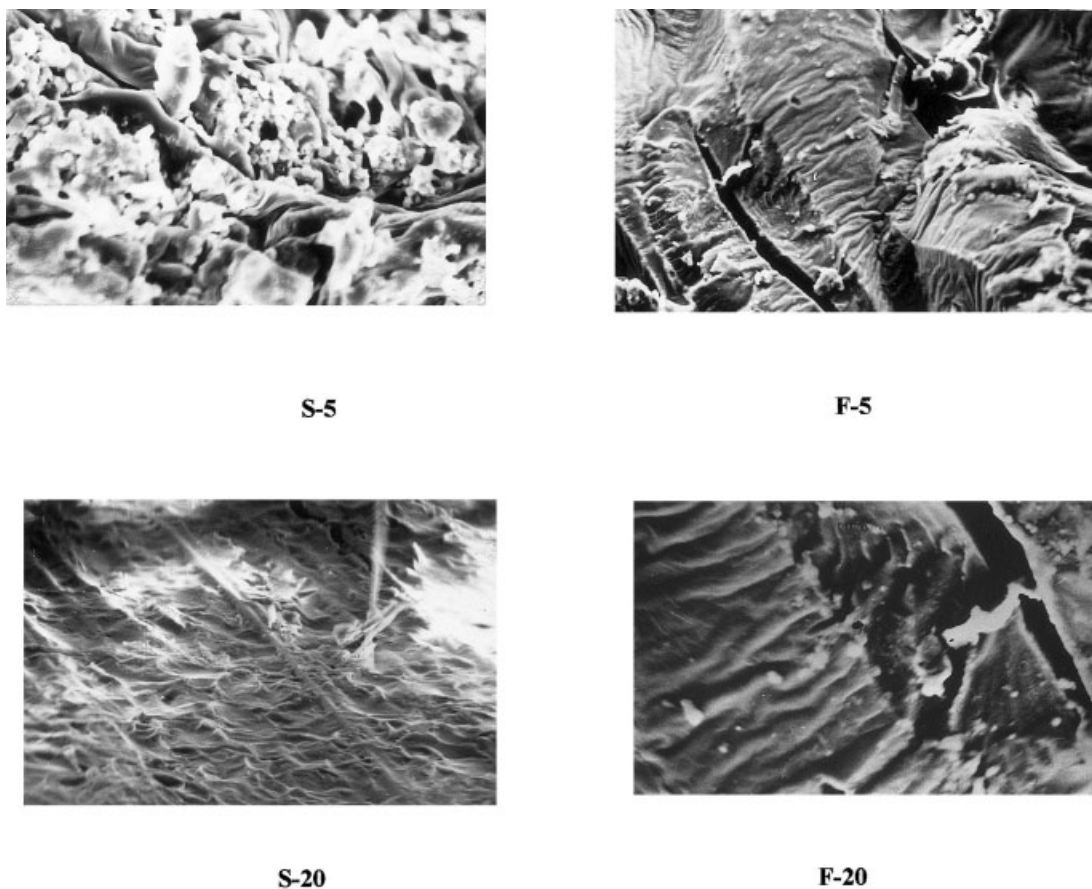


Figure 7 Scanning electron micrograph of the IPN systems of magnification ($\times 400$).

distinguished. The increased plastic deformation due to leathery VAc-EHA copolymer 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 the secondary cracks. When these are equal, a parabola is formed. But if the primary crack propagates faster, then the newly formed crack will be enclosed, and a new eclipse is formed.^{14,15}

Sometimes, the parabolic features interact and overlap and produce complex geometrical patterns. Macroscopically rough surface is observed at higher VAc-EHA 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.

CONCLUSION

1. Full-IPNs of the epoxy/VAc-EHA system had higher moduli and UTS than the semi-IPNs.
2. Dynamic mechanical study showed that full-IPN systems have higher T_g values than semi-IPN systems.

3. The impact strength increases with increasing proportions of VAc-EHA copolymer.

References

1. Lee, H.; Nevilli, K. Handbook of Epoxy Resins; McGraw-Hill: New York, 1967.
2. Potter, W. G. Epoxide Resins; Iliffe Books: London, 1960.
3. May, C. A., Ed. Epoxy Resins: Chemistry and Technology; Marcel Dekker: New York, 1988, 2nd ed.
4. Ravve, A. Principles of Polymer Chemistry; Kluwer Academic/Plenum: New York, 1998, 2nd ed.
5. Allen, F. J.; Hunter, W. M. J Appl Chem 1957, 7, 86; Sperling, L. H. Recent Advances in Polymer Blends, Grafts and Blocks; Plenum Press: New York, 1974, p. 404.
6. Othmer, K. Encyclop Chem Technol 1988, 2, 290.
7. Jensen, R. E.; Johnson, C. E.; Ward, T. C. J Polym Sci Part B Polym Phys 2000, 38, 2351.
8. Galgoci, E. C.; Komar, P. C. J Coats Technol 1999, 71, 891.
9. Mukhopadhyay, S.; Basu, D.; Banerjee, A. N.; Mitra, B. C. J Appl Polym Sci 1997, 63, 985.
10. Li, F.; Larock, R. C. J Appl Polym Sci 2000, 78, 2721.
11. Datta, C.; Basu, D.; Banerjee, A. N. J Appl Polym Sci 2002, 86.
12. Datta, C.; Basu, D.; Roy, A.; Banerjee, A. N. J Appl Polym Sci, communicated.
13. Datta, C.; Basu, D.; Banerjee, A. N. J Appl Polym Sci 2002, 85, 2800.
14. Narisawa, I.; Murayama, T.; Ogawa, H. Polymer 1982, 23, 291.
15. Sepe, M. P. Adv Mater Process 1992, 4, 32.