Mechanical and Dynamic Mechanical Studies of Resol/Vinyl Acetate-2-Ethylhexylacrylate/ Hexamethoxymethylmelamine Interpenetrating Network Systems

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ABSTRACT: Resol was solution blended with vinyl acetate–2-ethylhexylacrylate (VAc–EHA) resin in aqueous medium, in varying weight fractions, with hexamethoxymethylmelamine (HMMM) as crosslinker, and data was compared with a control. The present work was aimed at getting an optimum combination of tensile strength, dynamic mechanical strength, impact strength, and toughness by synthesis of an interpenetrating network (IPN) of the resins. The control gave a semi-IPN system, in which the resol crosslinked, while the acrylic did not, whereas the blend, where HMMM was the crosslinker, gave a full IPN system. Full IPNs of the resol/VAc–EHA system had higher moduli and ultimate tensile strength than the semi-IPNs. 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 90: 1765–1771, 2003

Key words: interpenetrating network; phenolics; dynamic mechanical analysis; vinyl acetate–2-ethylhexylacrylate; impact strength

INTRODUCTION

Thermoset phenolic resin is one of the earliest synthetic resins to possess excellent fire retardancy, low smoke density, and toxic emission,[1–3] though its application is limited because unmodified phenolic is a brittle material. A lot of research work has been conducted to toughen phenolic resin. The polyester–phenolic copolymer has been synthesized to improve the mechanical properties and heat resistance.[4] The flexural strength improves when phenoxy resin is blended with resol-type phenolic resin.[5] Interpenetrating polymer networks (IPNs) are a new class of polymer blends in the network form, in which the possibility of phase separation has been remarkably reduced by arresting the morphologies of the participating components. On the basis of crosslinking, two kinds IPN are well defined—one is the semi-IPN and another is the full IPN. In the semi-IPN, one of the polymers is in crosslinked form and the other is in linear form; in the full IPN, both networks are crosslinked, the morphology is fixed and well defined.[6,7] The present study aims at improving the properties of the resol by blending vinyl acetate–2-ethylhexyl acrylate copolymer by the IPN technique.

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EXPERIMENTAL

Materials

Resol was prepared by the method cited in the literature.[9,10] The hardener for resol was *p*-toluenesulfuric acid (PTSA), (Merck, Germany) 0982 H from Bakelite AG (Germany). VAc–EHA copolymer was obtained from Macromoles, India. Hexamethoxymethylmelamine (HMMM) was prepared in the laboratory using the standard procedure.[12]

Methods

The individual polymers were first separately diluted with distilled water to maintain a solid content of 50% by weight for convenience, under a well-stirred condition. Then a weighed amount of Resol was placed in a three-necked round-bottom flask and thoroughly mixed with 7% by weight (based on Resol) of PTSA[11] for 20 min.

VAc–EHA copolymer 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. When the formation of the 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 then initially kept at room temperature for about 24 h and then heated at 80°C for 4 h, followed by further heating at 120°C for one hour. Thus, the semi-IPNs were produced.

In order to prepare a full IPN, crosslinker for acrylic copolymer, namely, HMMM, was added to the mixture at final stage. In all cases, the concentration of HMMM was kept constant at 20% by weight based on VAc–EHA copolymer. All other operations were identical to those followed for semi-IPNs.

Tensile properties

An Instron Universal-Testing machine (model 4304) was used for measuring the tensile properties like tensile strength, modulus, and toughness. The 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 into dumbbell shape of 50 mm span, 4 mm width, and 1.7 mm 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 ±5%.

Impact properties

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

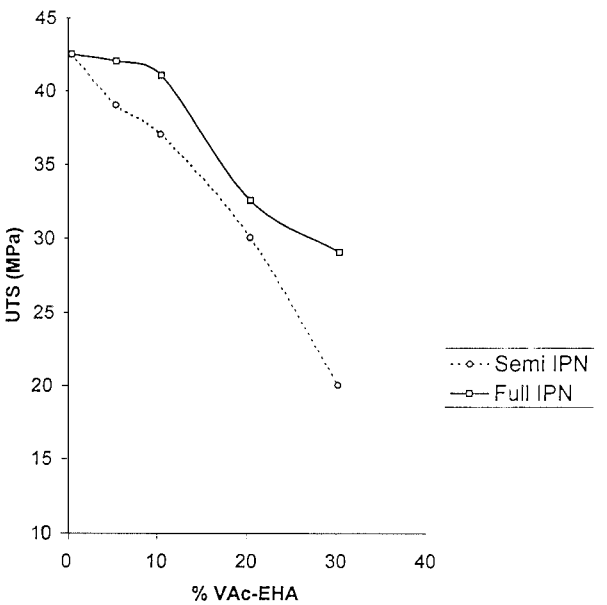


Figure 1 Variation of ultimate tensile strength vs % VAc–EHA of IPN systems.

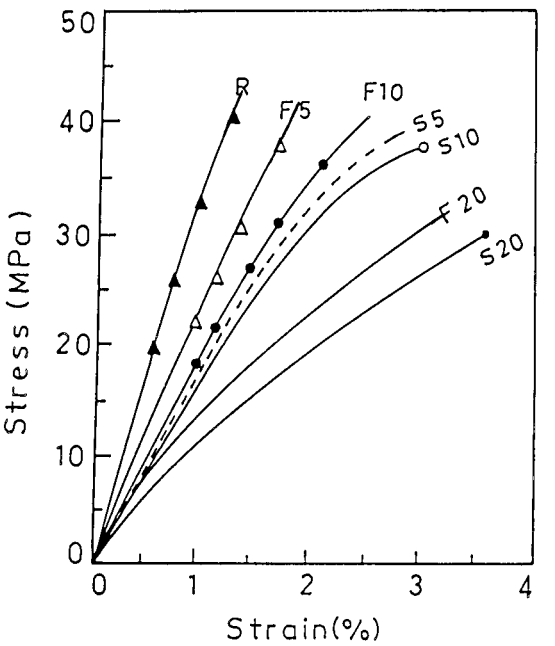


Figure 2 Variation of stress vs strain % of IPN systems.

Hardness

Hardness was measured using Shore-D hardness tester. In all cases, 12 specimens were tested and average values were reported.

Dynamic mechanical properties

The dynamic mechanical properties were measured by using a Dupont 983 DMA. The samples (10 ± 1.7 mm) were tested in resonant frequency mode with oscillation amplitude of 0.2 mm and were mounted in the vertical clamps at a clamping distance to thickness ratio of 11. The analysis was performed in nitrogen at the heating rate of 5°C/min.

In all cases, six specimens were tested and average values were reported.

Morphology

Phase morphology was examined in a Phillips PSEM-500 scanning electron microscope. For scanning electron microscope (SEM) studies, the fractured surfaces of the samples undergoing failure in tensile testing were sputter coated with gold.

RESULTS AND DISCUSSION

Mechanical behavior

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

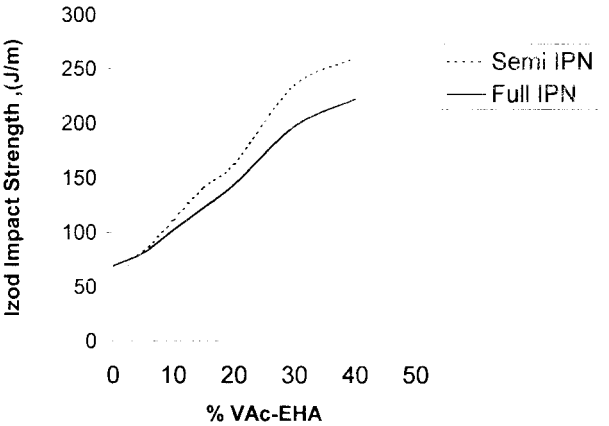


Figure 3 Variation of impact strength vs VAc–EHA % of IPN systems.

resol and VAc–EHA were crosslinked) had been studied as a function of blend ratios of resol and VAc–EHA. The mode of changes in ultimate tensile strength of the semi-IPNs and full-IPNs had been compared in Figure 1. The influence of crosslinking of the dispersed network into the subsequently crosslinked matrix network of phenolics 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 phenolic matrix by shielding the reactive sites of phenolics by the dispersed VAc–EHA matrix; (2) the plasticizing influences of the dispersed VAc–EHA domain.

It was observed that the full IPNs of resol/VAc–EHA system had higher moduli and UTS than the semi-IPNs. This could be possibly explained by the fact that the VAc–EHA moieties had much higher free volume, and there was ample scope of interpenetrating by the linear chains of VAc–EHA copolymer; while in case of full IPNs, the crosslinks within the VAc–EHA chains made them more compacts.

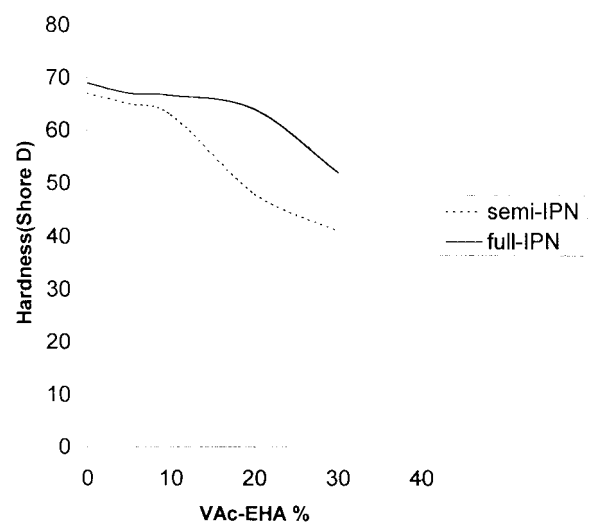


Figure 4 Variation of hardness vs VAc–EHA % of IPN systems.

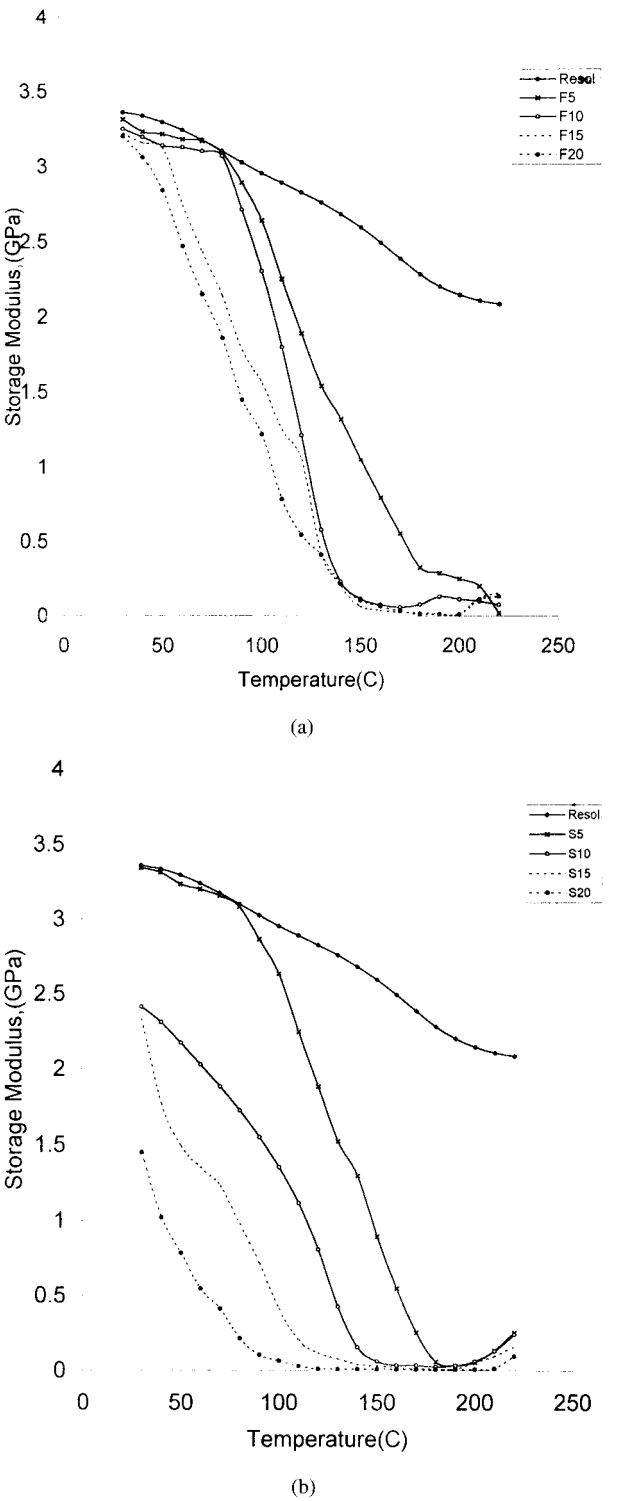
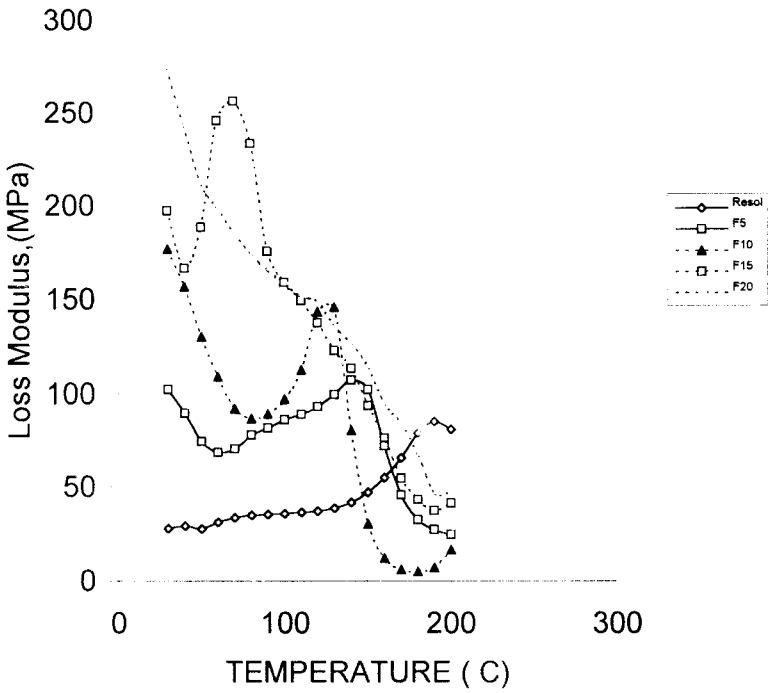
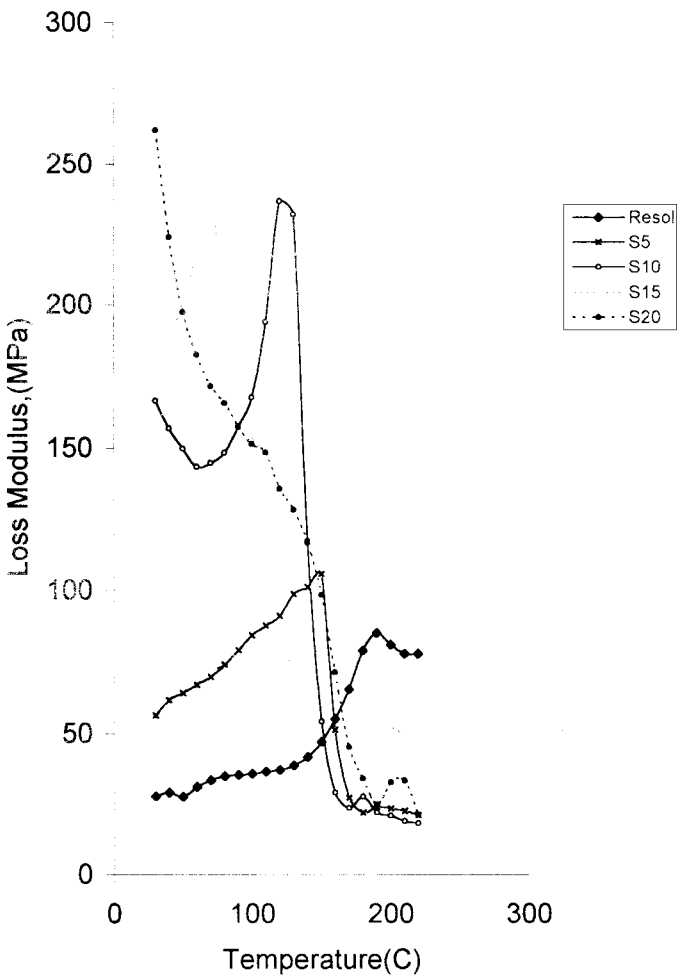


Figure 5 (a) Variation of storage modulus with temperature of full IPN systems. (b) Variation of storage modulus with temperature of semi-IPN systems.



(a)



(b)

Figure 6 (a) Variation of loss modulus with temperature of full IPN systems. (b) Variation of loss modulus with temperature of semi-IPN systems.

TABLE I

Sample designation	Temp. at E'_{max} (°C)	Temp. at tan δ_{max} (°C)	Tan δ_{max}
Resol	190	208	0.0378
F5	140	150	0.4876
F10	121	146	0.4971
F15	70	80	0.5874
F20	35	60	0.6522

Figure 2 shows the stress vs strain % curves for some of the representative samples of IPNs of resol/VAc–EHA. By virtue of higher extent of interpenetrating as discussed earlier strain percent of semi-IPNs are less than the full IPNs. The curves display a 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 which is due to increase in plastic deformation as understood from Figure 2.

Figure 3 shows the impact strength vs VAc–EHA % of IPNs of resol/VAc–EHA. The degrees of improvement in terms of strain % and impact strength depend on the sizes of the dispersed phase. Thus, the impact strength may be expected to increase with increasing proportions of the VAc–EHA copolymer.

Hardness

Figure 4 shows the hardness vs VAc–EHA %. The curve shows a decreasing trend for both semi-IPNs and full-IPNs. The hardness of the semi-IPNs lies above those for full-IPNs of same percentage of the VAc–EHA copolymer content, which also explains our earlier observations.

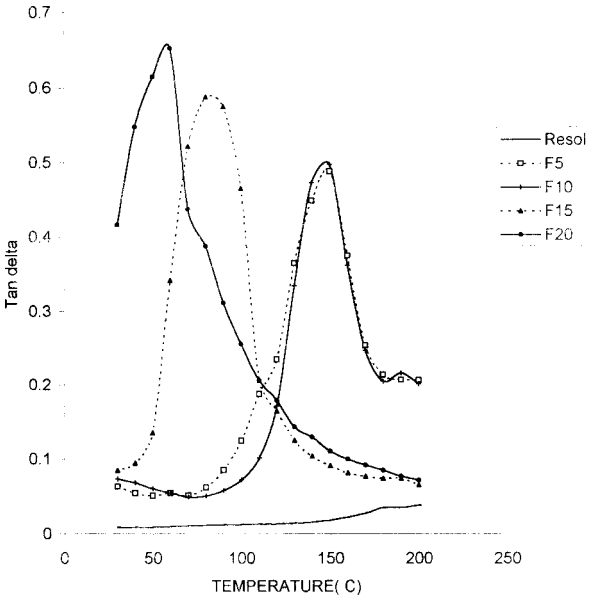
Dynamical mechanical analysis

Storage modulus

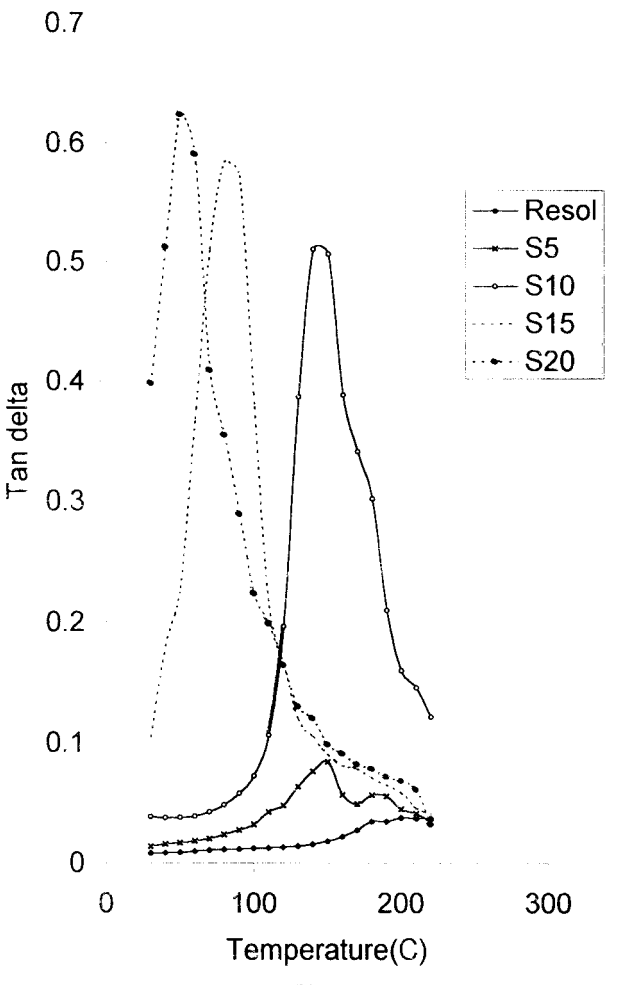
The importance of the dynamic storage modulus in many structural applications is well known. A clear understanding of the storage modulus–temperature curve obtained during a dynamic mechanical test provides valuable insight into the stiffness of a material as a function of temperature. Figures 5(a) and (b) show the storage modulus–temperature curves of resol, semi-IPN systems, and full IPN systems, respectively.

TABLE II

Sample designation	Temp. at E'_{max} (°C)	Temp. at tan δ_{max} (°C)	Tan δ_{max}
Resol	190	208	0.0378
S5	138	147	0.499
S10	119	140	0.5102
S15	65	76	0.5987
S20	30	50	0.6673



(a)



(b)

Figure 7 (a) Variation of tan δ with temperature of full IPN systems. (b) Variation of tan δ with temperature of semi IPN systems.

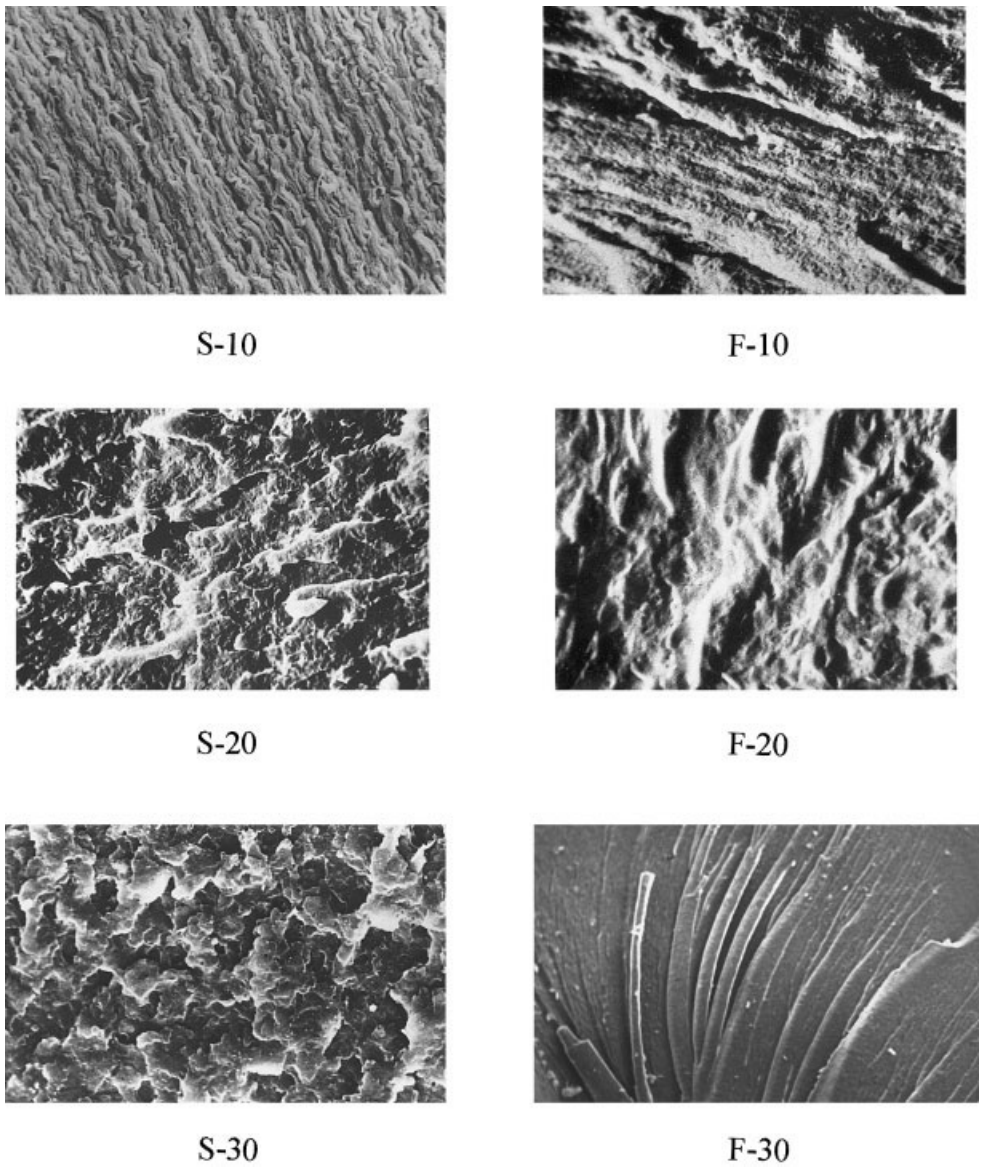


Figure 8 SEM of the IPN systems of magnification (×500).

Full IPN systems have higher E' than semi-IPN systems at the same VAc–EHA content.

Loss modulus

Figure 6 shows the loss modulus (E'')–temperature curves of resol, semi-IPN, and full IPN systems. The T_g value decreases gradually with increase in VAc–EHA content in both systems. Full-IPN systems have higher T_g values than semi-IPN systems (Tables I and II). This is due to the fact that crosslinking efficiency and the extent of interpenetrating network formation in resol/VAc–EHA/HMMM blend increase with increase in VAc–EHA/HMMM percent.[20]

Tan δ

Figure 7 shows the tan δ vs temperature curves of resol, semi-IPN, and full-IPN systems. Tan δ is a damping term that can be related to the impact resistance of a material.[21] The higher the peak tan δ value, the greater the degree of molecular mobility. On comparing the temperature corresponding to maximum tan δ peak values of Figure 7, it can be seen that resol has the higher value than semi-IPNs and full IPNs.

Scanning electron microscopy

The SEMs of both semi-IPNs and full- IPNs for different compositions of each are shown in Figure 8. The change in fracture mechanics from a predominantly shear yielding to crazing with increasing concentration of VAc–EHA can be easily 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 fea-

tures 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.

Sometimes, the parabolic features interact and overlap, and produce complex geometrical patterns. The macroscopically rough surface 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. Resol was solution blended with VAc–EHA resin in aqueous medium, in varying weight fractions, with HMMM as crosslinker, and data was compared with a control.
2. Full IPNs of the resol/VAc–EHA system had higher moduli and UTS than the semi-IPNs.
3. DMA studies showed that full-IPN systems have higher T_g values than semi-IPN systems. The impact strength increases with increasing proportions of the VAc–EHA copolymer.

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