

Studies and Characterization of RESOL/VAc-EHA/HMMM IPN Systems in Aqueous Medium

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ABSTRACT: Resol was solution-blended with vinyl acetate-2-ethylhexyl acrylate (VAc-EHA) resin in an aqueous medium, in varying weight fractions, with hexamethoxymethylmelamine (HMMM) as a crosslinker and the data were compared with a control. The present work was aimed to obtain an optimum combination of high-temperature resistance 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. FTIR spectra of the blends of resol/VAc-EHA/HMMM indicated the formation of new stretching, which was generated due to crosslinking reactions among VAc-

EHA and the crosslinker HMMM. TGA showed that, with an increase in the VAc-EHA percent in semi-IPNs, the decomposition temperature decreased gradually, whereas in case of full-IPNs, the decomposition temperature increased with increase in the VAc-EHA percent. However, the full-IPNs had a higher decomposition temperature than that of the semi-IPNs, at the same resol/(VAc-EHA) ratio. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 3581–3588, 2002

Key words: interpenetrating networks (IPN), FT-IR; differential scanning calorimetry (DSC); thermogravimetric analysis (TGA)

INTRODUCTION

The physical and chemical combination of two or more structurally dissimilar polymers has gained much academic interest for a number of years. Polymer blends encompass many different kinds of materials, containing two or more polymer components and mostly 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 remarkably reduced by arresting the morphologies of the participating components. Based on the crosslinking type, IPNs are classified under two headings—semi-IPN and full-IPN. In a semi-IPN, one of the polymers is in a crosslinked form and the other is in a linear form, while in a full-IPN, both networks are crosslinked and the morphology is fixed and well defined.^{1,2}

Thermoset phenolic resin is one of the earliest synthetic resins to possess good fire retardancy and a low smoke and toxicity index.^{3–5} It is widely used in construction, electrical, and other industries. However, unmodified phenolic resin is a brittle material, with limited application. Much research has been conducted to improve the mechanical properties and to toughen the phenolic resin. The polyester-phenolic

copolymer has been synthesized to improve the mechanical and heat-resistance properties.⁶ The flexural strength improves when phenoxy resin is blended with resol-type phenolic resin.⁷ The present study aimed at improving the properties of the resol by blending a vinyl acetate-2-ethylhexyl acrylate copolymer (VAc-EHA) by an IPN technique.

EXPERIMENTAL

Materials

Resol was prepared by the method cited in the literature.^{9,10} The hardener for resole was *p*-toluenesulfonic acid (PTSA), 0982 H from Bakelite AG (Tennenlohe, Germany). The VAc-EHA copolymer in the emulsion form was obtained from Macromoles (Calcutta, India). Hexamethoxymethylmelamine (HMMM) was prepared in the laboratory using a standard procedure.¹¹

FTIR

Infrared spectra were obtained on a Perkin-Elmer 1600 Series FTIR spectrophotometer. Sixty-four scans at a resolution of 4 cm⁻¹ were signal-averaged.

DSC

A DuPont 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.

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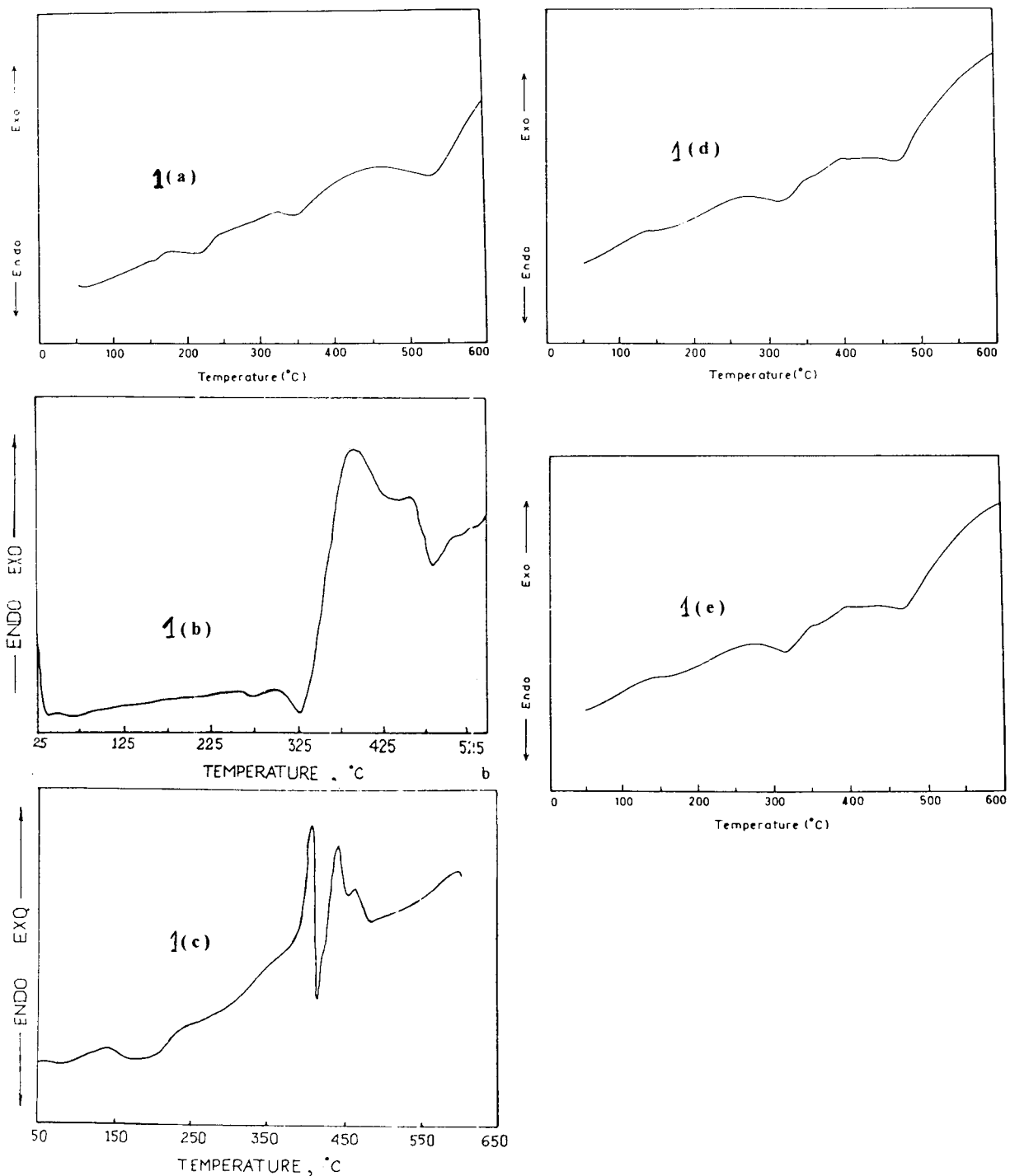


Figure 1 DSC thermograms of (a) resol, (b) VAc-EHA, (c) HMMM, (d) S-5, (e) S-10, (f) S-20, (g) S-30, (h) F-5, (i) F-10, (j) F-20, and (k) F-30.

TGA

Thermogravimetric analysis (TGA) thermograms were obtained on a DuPont thermogravimetric analyzer under a nitrogen atmosphere at a heating rate of 20°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.

Procedure

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 resol was placed in a three-necked, round-bottomed flask and thoroughly mixed with 7% by weight¹² (based on resol)

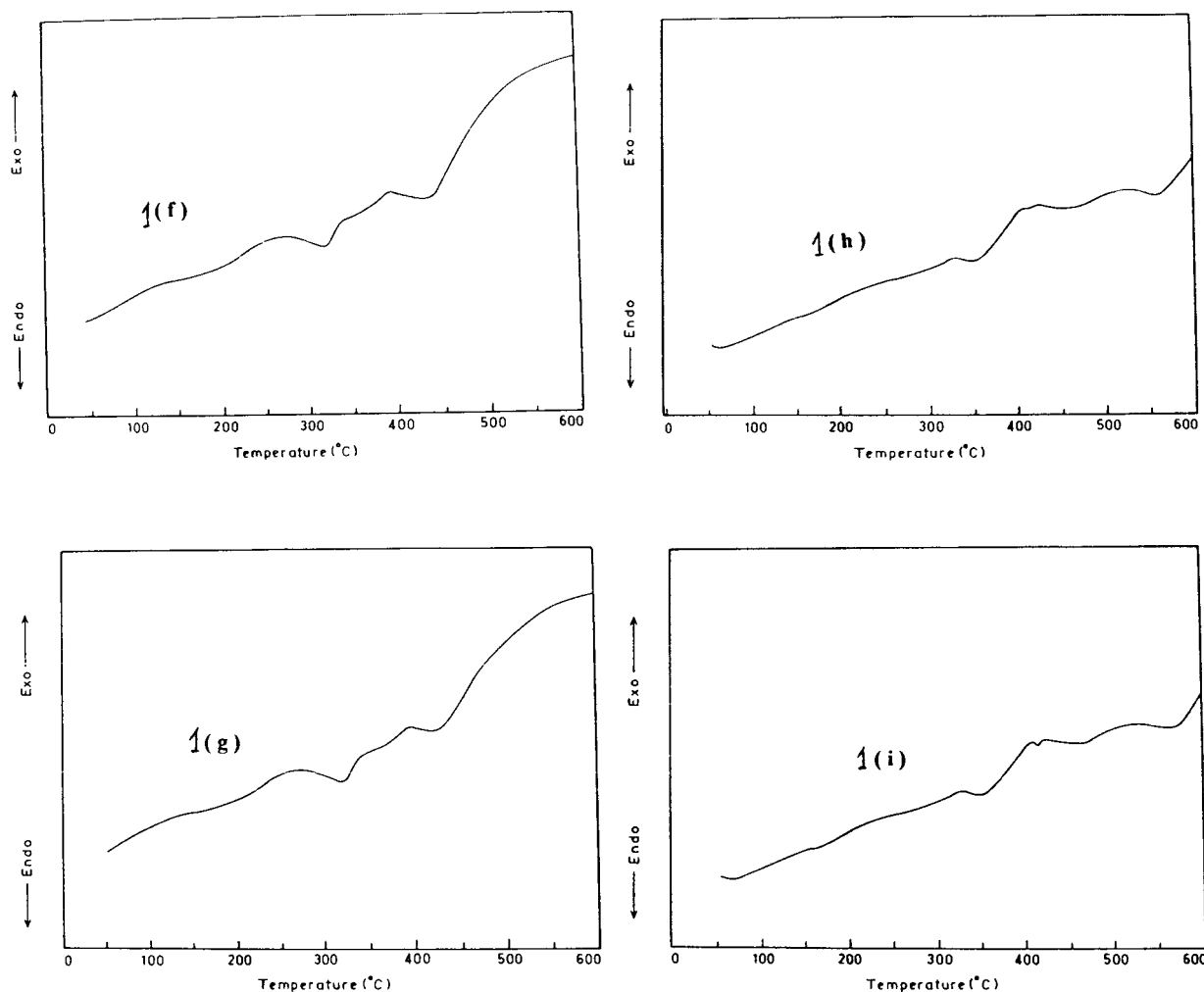


Figure 1 (Continued from the previous page)

of PTSA for 20 min. The VAc-EHA copolymer was then accurately weighed and introduced into the flask. The contents of the flask were then stirred well to give a homogeneous mixture. When the formation of bubbles ceased, the viscous mass was poured into a glass mold prepared by clipping together two glass plates with a Teflon gasket in between them. The thickness of the Teflon gasket controlled 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 1 h, to produce semi-IPNs. The samples of semi-IPNs are referred to as S-5, S-10, S20, and S30, where S denotes semi and 5, 10, 20, and 30 denote the percentages of VAc-EHA in the IPNs.

To obtain full-IPNs, a crosslinker for the acrylic copolymer, namely, HMMM, was added to the mixture at the final stage. In all cases, the concentration of HMMM was kept constant at 20% by weight based on the VAc-EHA copolymer. All other operations were

identical to those followed for semi-IPNs. The samples of full-IPNs are referred to as F-5, F-10, F-20, and F-30, where F denotes full and 5, 10, 20, and 30 denote the percentages of VAc-EHA in the IPNs. The samples produced were used for carrying out DSC, TGA, and FTIR studies.

RESULTS AND DISCUSSION

DSC

The DSC thermograms of the virgin components and the blends are shown in Figure 1 (a-c) and in figure 1(d-k), respectively. Figure 1(a) shows the DSC curve for pure resol. VAc-EHA [Fig. 1(b)] shows a small endotherm around 325°C, followed by an exotherm about 380°C and final degradation around 475°C.

For HMMM [Fig. 1(c)], an endothermic depression is observed about 180°C, where elimination of water and methanol take place. This is followed by an exothermic peak about 400°C, then an endothermic one

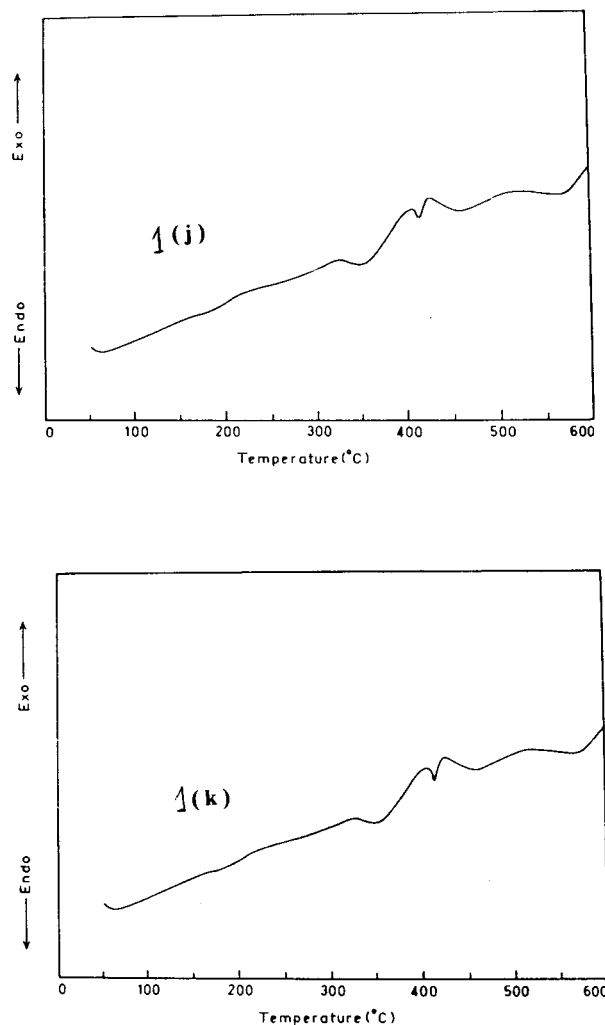


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about 415°C, and, again, an exotherm around 450°C. The exotherms relate to the crosslinking reactions occurring via the trans-etherification mechanism and the endotherms relate to the occurrence of condensation reactions.^{11,13,14} Thus, the extensive crosslinking reactions taking place in the HMMM leads to the formation of two prominent exothermic peaks. Finally, decomposition takes place around 550°C.

In the semi-IPN blends [Fig. 1(d–g)], all the endothermic and exothermic peaks of pure resole and pure VAc–EHA appeared, but they are at a 5–10°C higher-temperature zone and the depth of the peaks vary with the VAc–EHA content in the blend, as shown in Table I.

In the full-IPN blends [Fig. 1(h–k)], it is seen that a second endotherm appears due to decomposition and condensation–elimination reactions about 355°C, followed by exothermic crosslinking around 400°C, as in case of pure HMMM, but the depth or energy of the endothermic and exothermic peaks increase with increase of the VAc–EHA percent, as shown in Table II.

The crosslinking takes place between VAc–EHA and HMMM via transesterification, copolymerization, and self-condensation reactions.¹¹ Decomposition occurs around 550°C.

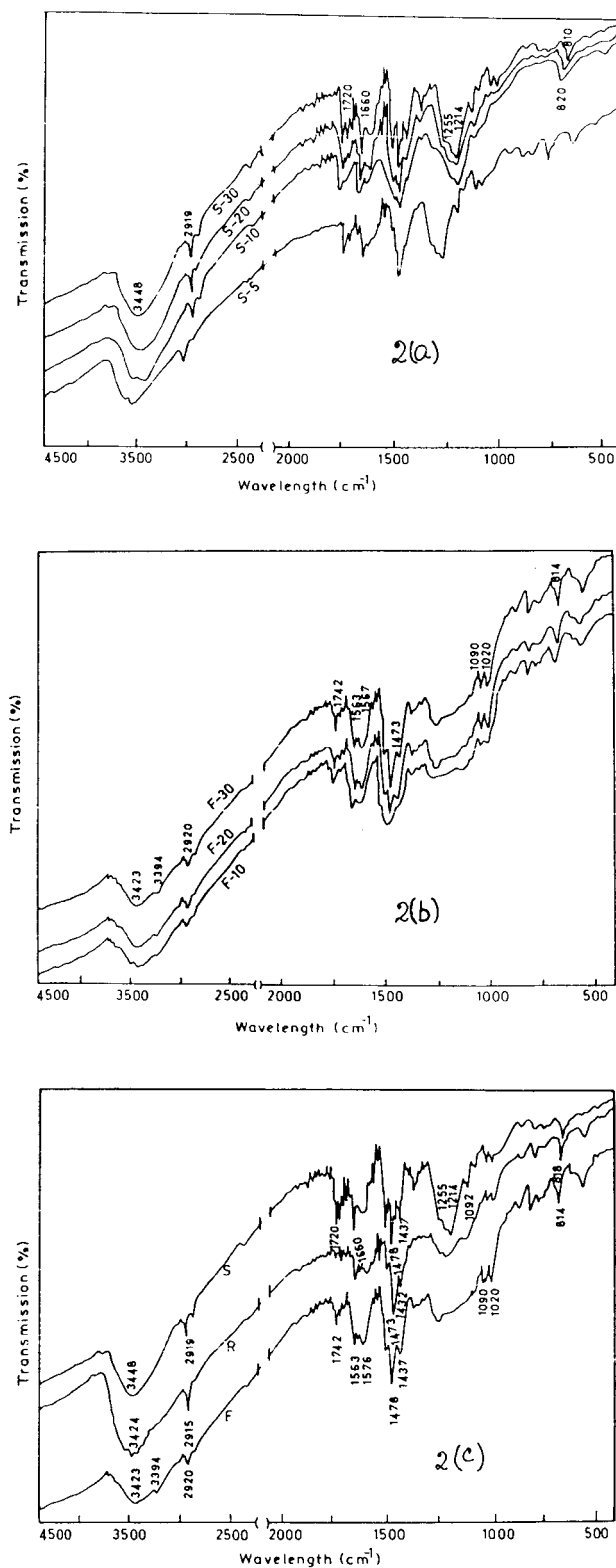


Figure 2 FTIR spectra of (a) semi-IPN systems, (b) full-IPN systems, and (c) resole, S-20, and F-20 systems.

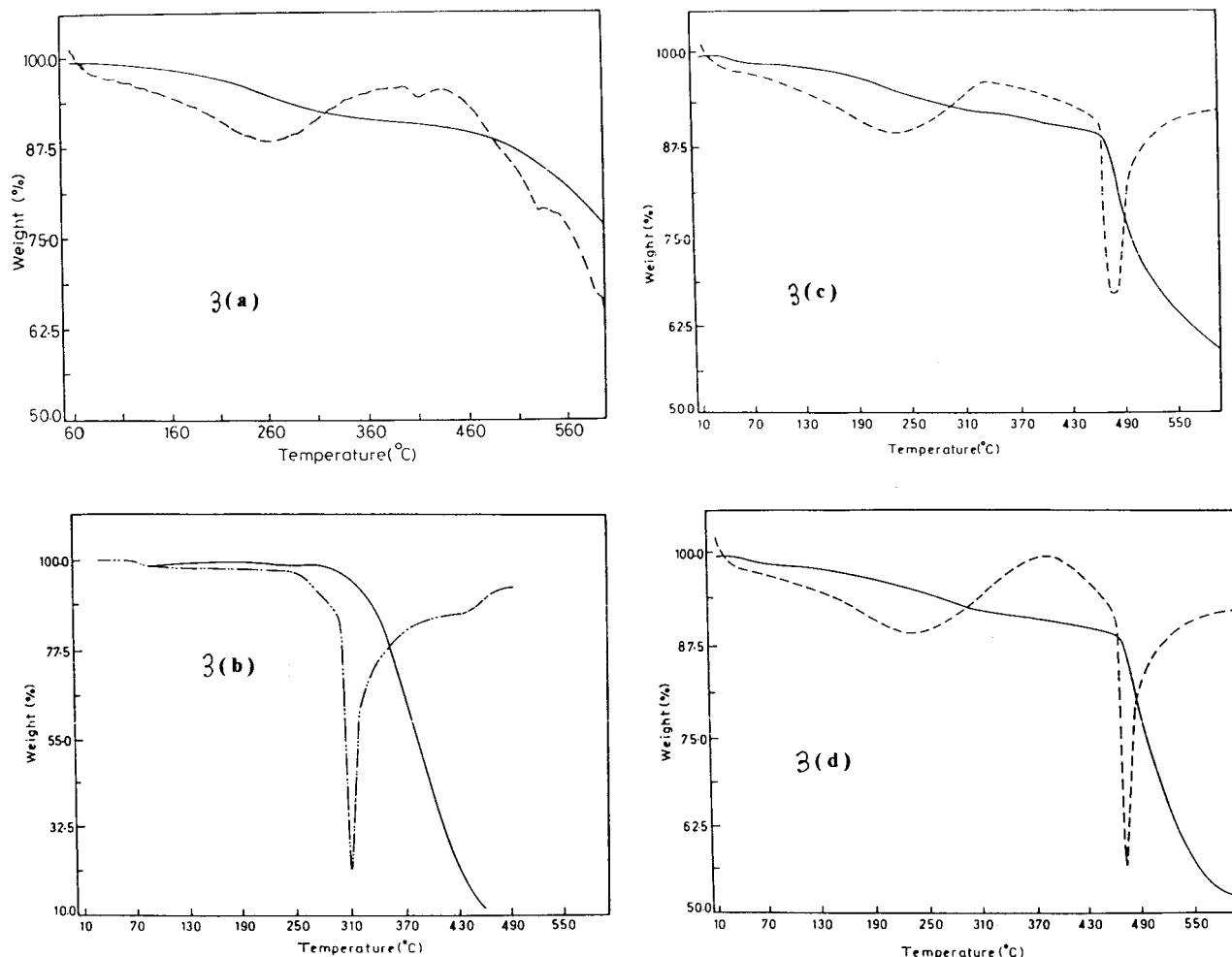
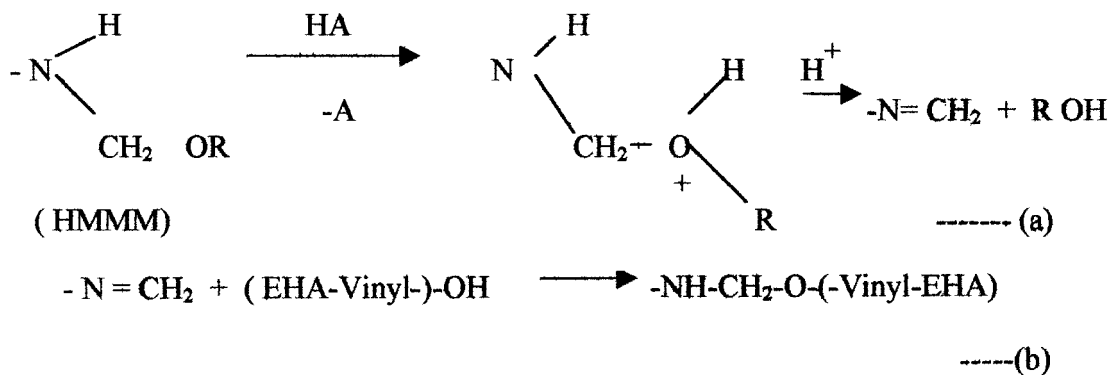


Figure 3 TGA curves of (a) resol, (b) VAc-EHA, (c) S-5, (d) S-10, (e) S-20, (f) S-30, (g) F-5, (h) F-10, (i) F-20, and (j) F-30. (—) TGA; (-----) DTGA.

The crosslinking mechanism between VAc-EHA and HMMM is not certain. The probable mechanism can be explained in the following way: In aqueous medium in

the presence of acid (at pH < 6), the acetate group partially hydrolyzed to alcohol. These —OH groups then reacted with the melamine derivative in the following way:



Equation (a) explains the general acid-catalyzed curing of HMMM and equation (b) explains the

crosslinking reaction between VAc-EHA and the HMMM derivative produced from reaction (a).

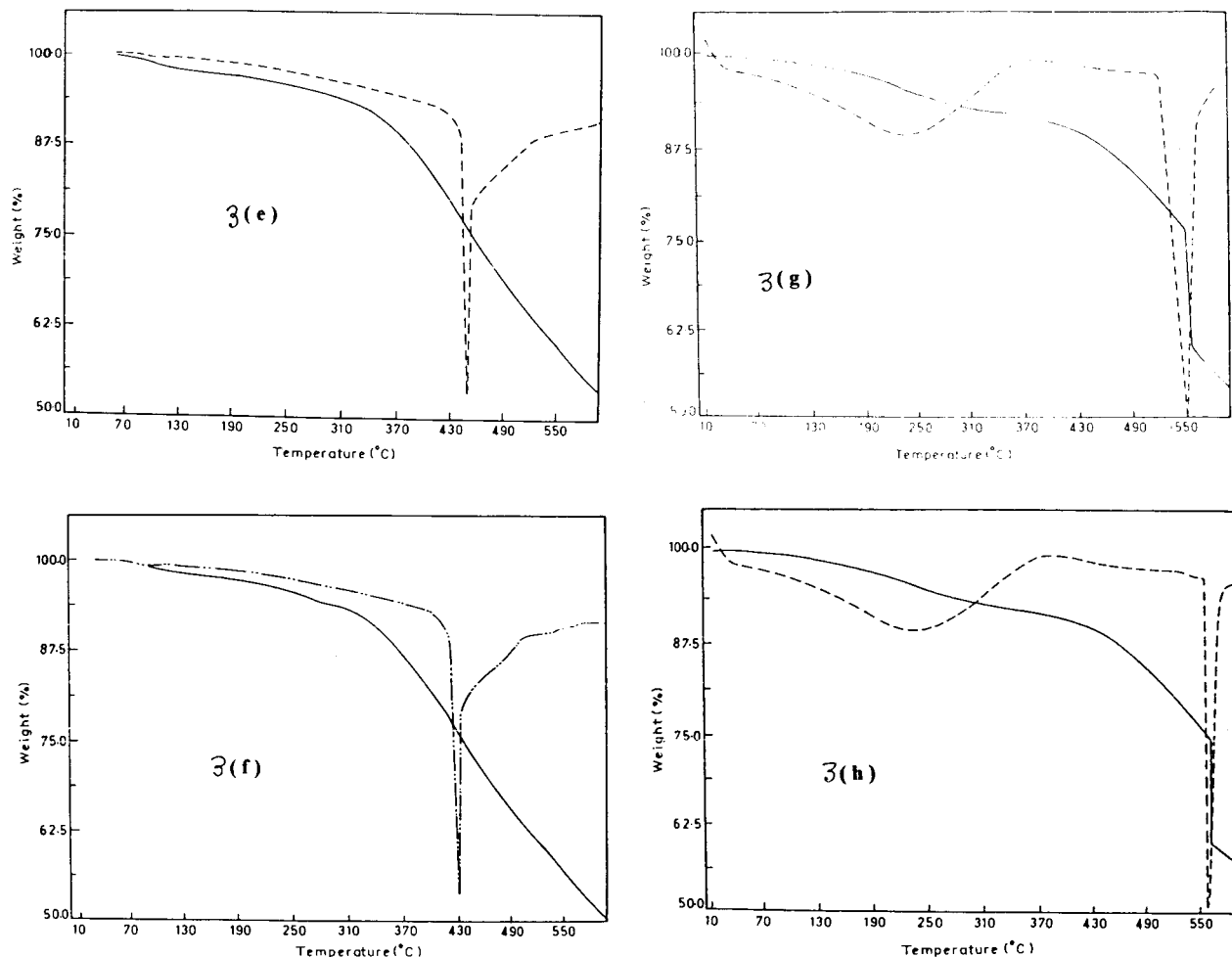


Figure 3 (Continued from previous page)

FTIR

The FTIR studies investigated the specific interactions involved in blend miscibility. Resol showed characteristic stretching for the hydrogen bond of the OH group at 3424 cm^{-1} , the C—H of alkene at 2915 cm^{-1} , and the aromatic C=C at 1473 and 818 cm^{-1} for *para*-substitution [Fig. 2(c)].

On blending resole and VAc-EHA (semi-IPNs), only characteristic stretching for the vinyl ester at 1720 cm^{-1} and for the acrylic ester at 1660 cm^{-1} appear, along with other characteristic peaks of resole [Fig. 2(a)]. But on blending of resole and VAc-EHA/HMMM (full-IPNs), new characteristic stretching bands around 3394 cm^{-1} for imines ($=N-H$), around $1563-1576\text{ cm}^{-1}$ for secondary N—H vibrations, and around 814 cm^{-1} for the trisubstituted alkenes appear, but the characteristic stretching for vinyl ester at 1720 cm^{-1} disappears, indicating the involvement of such groups in the crosslinking reactions [Fig. 2(b)]. All these observations firmly establish the occurrence of

crosslinking reactions between VAc-EHA and HMMM.

TGA/DTGA

The crosslinking efficiency and the extent of IPN formation in the resol/VAc-EHA/HMMM blends increased with increase in the VAc-EHA/HMMM percent. This was supported by the TGA and DTGA data [Fig. 3(a-j)]. The endothermic peak at the higher temperature in the DSC curve coincides with the temperature of the maximum weight loss rate in the DTGA curve. Again, for full-IPNs, at the final decomposition temperature region, the weight loss is drastic and the weight loss increases with increase of the VAc-EHA/HMMM content. These facts establish, beyond doubt, that IPNs are formed and both thermosetting networks are broken down at the final decomposition temperature simultaneously. This is due to that HMMM, after curing, produces $-CH_2-NH-$ linkage, giving a complicated crosslinked structure¹⁵, this

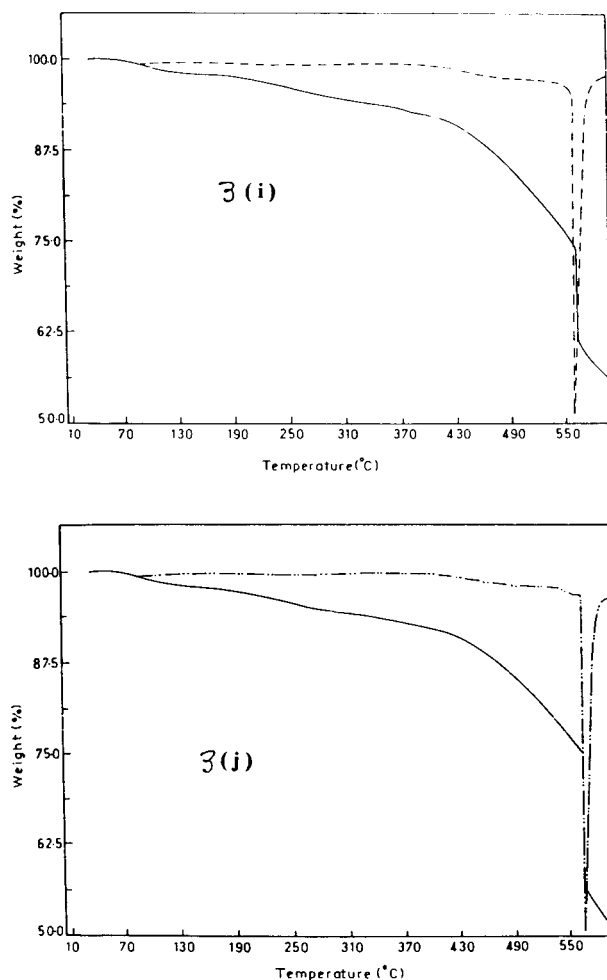


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network structure along with the phenolics network structure form an interpenetrating polymeric network and make the IPN system more thermostable.

Contrary to the above facts, the weight loss for semi-IPNs at the final decomposition temperature region are not so drastic, which establishes the fact that

TABLE I
Energies of Endothermic and Exothermic Peaks and Final Decomposition Temperatures of Resol/VAc-EHA Semi-IPNs

VAc-EHA (wt %)	Energy of endothermic peak at higher temperature (cal/g)	Energy of exothermic peak at higher temperature (cal/g)	Final decomposition temperature (°C)
5	14.9	1.2	479
10	15.4	1.4	472
20	17.1	1.5	454
30	18.2	1.6	430

TABLE II
Energies of Endothermic and Exothermic Peaks and Final Decomposition Temperatures of Resol/VAc-EHA/HMMM Full-IPNs

VAc-EHA (wt %)	Energy of endothermic peak at higher temperature (cal/g)	Energy of exothermic peak at higher temperature (cal/g)	Final decomposition temperature (°C)
5	9.2	2.7	549
10	10.6	5.6	560
20	12.4	9.8	562
30	15.6	11.3	565

only resol was crosslinked, whereas VAc-EHA is just dispersed within that network. With increase in the VAc-EHA percent in the semi-IPNs, the final decomposition temperature also decreases, as obtained from the DSC data.

CONCLUSIONS

Resol was solution-blended with VAc-EHA resin in an aqueous medium, in varying weight fractions, with HMMM as the crosslinker and the data were compared with a control. 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. FTIR spectra of the blends of resol/VAc-EHA/HMMM indicated the formation of new stretching, which was generated due to crosslinking reactions between the VAc-EHA and the crosslinker HMMM.

TGA showed that, with increase in the VAc-EHA percent in the semi-IPNs, the decomposition temperature decreased gradually, whereas in the case of full-IPNs, the decomposition temperature increased with increase in the VAc-EHA percent due to the presence of HMMM within the system. However, the full-IPNs, due to a higher amount of crosslink density, have a higher decomposition temperature than that of the semi-IPNs at same resol/(VAc-EHA) ratio. This fact was supported by the DSC data as well.

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