DSC, FTIR, and TGA Studies on Crosslinking and Thermal Behavior of Vinyl Acetate–2-Ethylhexyl Acrylate Copolymer and Hexamethoxymethylmelamine Blends

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ABSTRACT: Vinyl Acetate–2-Ethylhexyl acrylate copolymer (VAc–EHA) was solution blended with hexamethoxymethylmelamine (HMMM) resin in aqueous medium using varying proportions. The films were dried at room temperature and under reduced pressure at 65°C. The DSC studies showed endothermic peaks where condensation reaction took place and exothermic peaks pointing toward the possibility of crosslinking reactions. The energy of the endotherms and exotherms increased with increasing HMMM content. These facts were also justified and supported by TGA and FTIR results. The FTIR spectra of the blends indicated the formation of a number of new stretchings, which were generated due to the crosslinking reactions. TGA showed that the higher the HMMM content, the higher the final degradation temperature and the char yield. The temperature of the larger endotherm of the DSC coincided with the region of maximum weight loss rate of the differential TGA curves. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **65:** 2075–2080, 1997

Key words: polymer blends; aqueous medium; surface coating; fire hazard; char yield

INTRODUCTION

Two of the most challenging problems facing scientists today are pollution and fire hazards. Surface coatings, which constitute an indispensible part of modern life, contribute to both problems because of the presence of toxic volatiles and flammable ingredients used in their formulations. The present work deals with the preparation of water-borne surface coatings that exhibit environmentally friendly and fire-retardant properties as well. The recent trend of frontier technologists is to use an aqueous medium in a surface coating instead of an organic solvent medium. Here an aqueous emulsion of vinyl acetate–2-ethylhexyl-acrylate (VAc–EHA) copolymer was used as the base resin in water-borne surface coatings in tune with the present outlook.[1] This being a thermoplastic polymer, it melts and drips on exposure to fire and does not possess any fire-retardant characteristics. To compromise this, the copolymer was blended with a water soluble etherified derivative of methylol melamine (hexamethoxymethylmelamine, HMMM).[2]

EXPERIMENTAL

Materials

VAc–EHA copolymer was obtained from Macromoles, India. HMMM was prepared in the laboratory using the standard procedure.[3]

Method

The individual polymers were first separately diluted with distilled water to maintain a solid con-
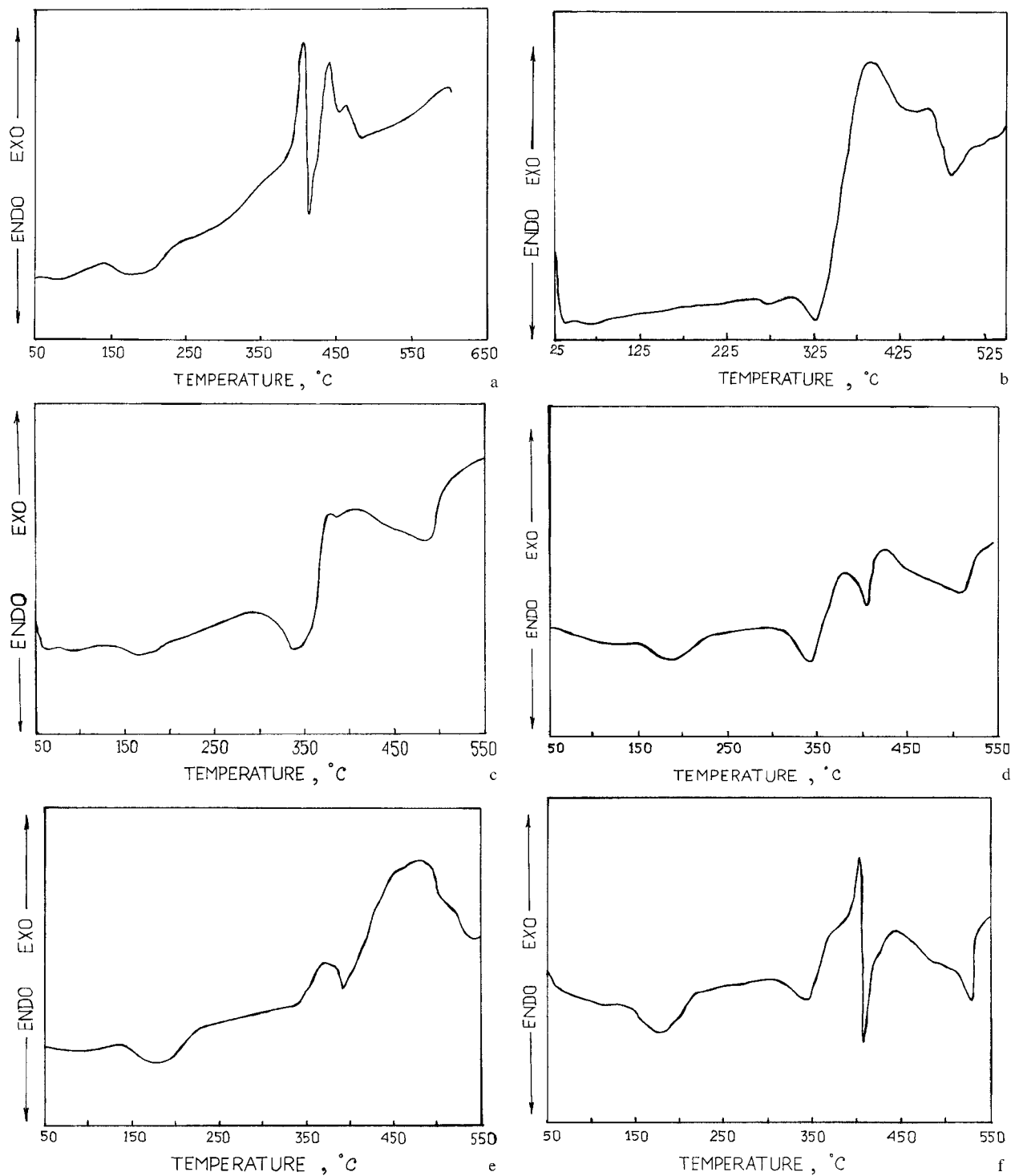
Figure 1 Differential scanning calorimetric curves for VAc–EHA, HMMM, and VAc–
EHA/HMMM blends: (a) HMMM; (b) VAc–EHA; (c) 90/10; (d) 80/20; (e) 70/30; (f)
60/40; (g) 50/50; (h) 40/60.

tent of 50% by weight for convenience, under a
well stirred condition. The blends were then pre-
pared by mixing the components in appropriate

proportions (0–60% of HMMM by weight) in 500-
mL conical flasks using a magnetic stirrer for 45
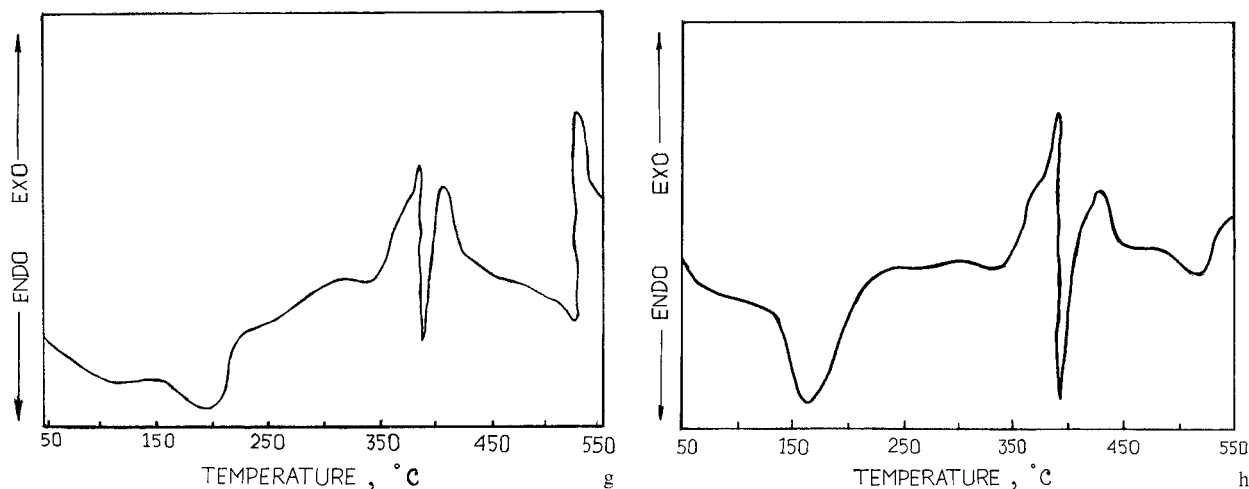min at ambient temperature (∼ 30°C). Films

Figure 1 (*Continued from the previous page*)

were then cast from the freshly prepared aqueous solutions onto a mercury surface under a controlled rate of evaporation of solvent, maintaining a constant dry film thickness of about 1.5 mm. Each film was then dried at room temperature for 30 days, followed by vacuum drying at 65°C for 48 h. The films were used for carrying out the DSC, TGA, and FTIR studies.

The DSC thermograms of the pure components and the blends are shown in Fig. 1(a–h). For HMMM [Fig. 1(a)] an endothermic depression is observed at about 180°C, where elimination of methanol and water take place. This is followed by an exothermic peak at about 400°C, then an endothermic one at about 415°C, and again an exotherm at around 450°C. The exotherms show the crosslinking reaction occurring via the trans-etherification mechanism and the endotherm results from the occurrence of condensation reac-

tions. Thus, the extensive crosslinking reaction taking place in the pure HMMM leads to the formation of the two prominent exothermic peaks. Finally decomposition takes place around 550°C.

Figure 1(b) shows a small endotherm around 325°C followed by an exotherm at about 380°C and final degradation at around 475°C for VAc–EHA.

In the blends it is seen that an endothermic depression at about 180°C, as in case of pure HMMM, appears for all blend proportions; but the depth or energy of the endothermic zone increases with an increase in HMMM percent. The probable reason is that the higher the percentage of HMMM, the higher will be the elimination of methanol. In the 90/10 (VAc–EHA/HMMM) blend [Fig. 1(c)], a second endotherm appears due to decomposition and condensation–elimination reactions at about 350°C, followed by exother-

Table I Energies of Endothermic and Exothermic Peaks Obtained from DSC and Final Decomposition Temperatures of VAc–EHA/HMMM Blends

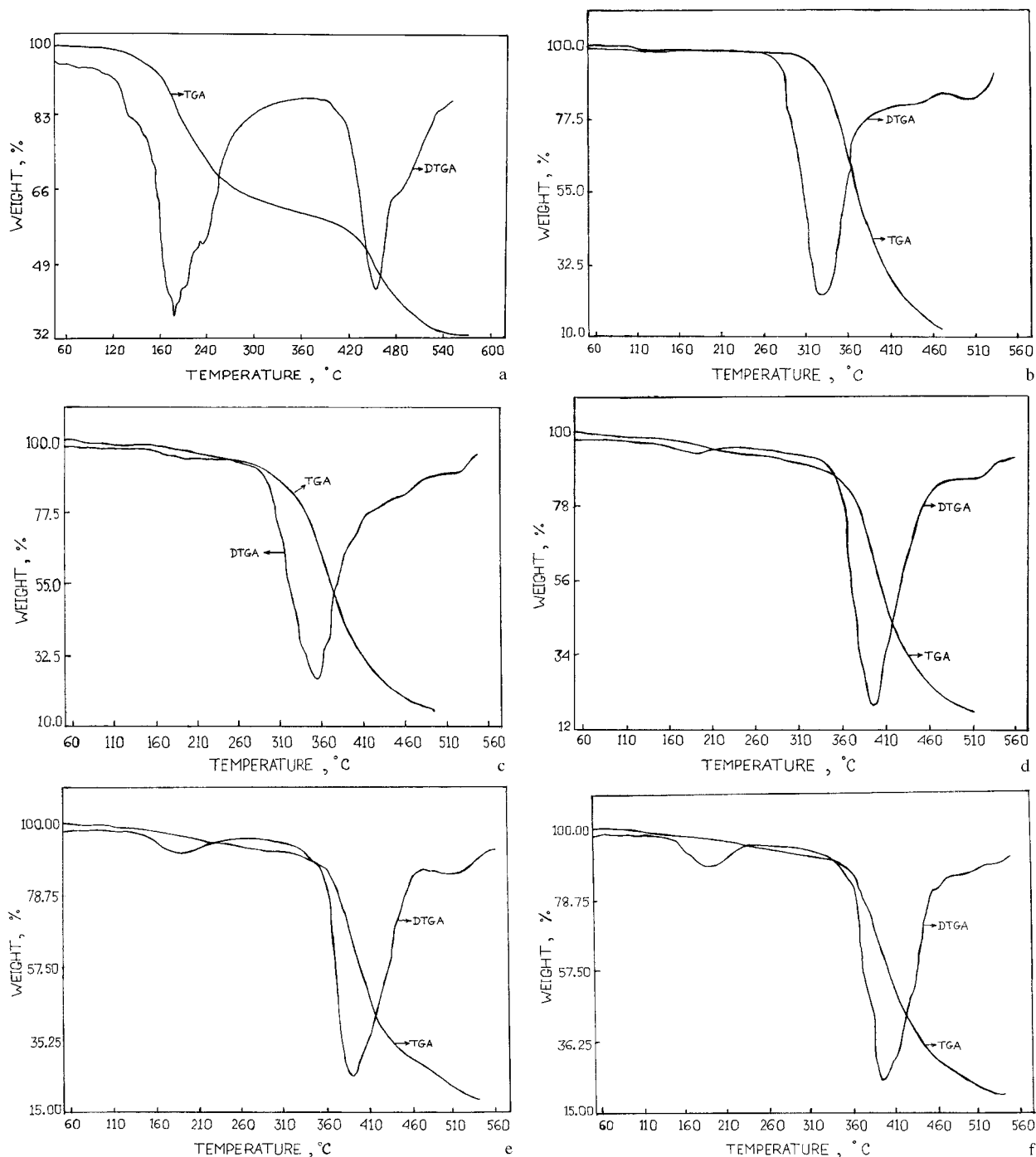| VAc–EHA (wt %)	HMMM (wt %)	Energy of Endothermic Peak at Higher Temperature (cal/g)	Energy of Exothermic Peaks (cal/g)	Final Decomposition Temperature (°C)
90	10	6.3	12.3	500
80	20	6.6	16.8	520
70	30	7.0	26.7	540
60	40	10.7	28.2	542
50	50	12.2	28.9	546
40	60	12.8	32.7	548

Figure 2   Thermogravimetric and differential thermogravimetric analysis of HMMM, VAc–EHA, and VAc–EHA/HMMM blends: (a) HMMM; (b) VAc–EHA; (c) 90/10; (d) 80/20; (e) 70/30; (f) 60/40; (g) 50/50; (h) 40/60.

mic crosslinking at around 400°C. The crosslinking takes place between VAc–EHA and HMMM via transetherification, copoly, and self-condensa-

tion reactions.[4] Decomposition occurs at 500°C. For the blend containing 20–60% HMMM, the second endotherm appears in the same tempera-
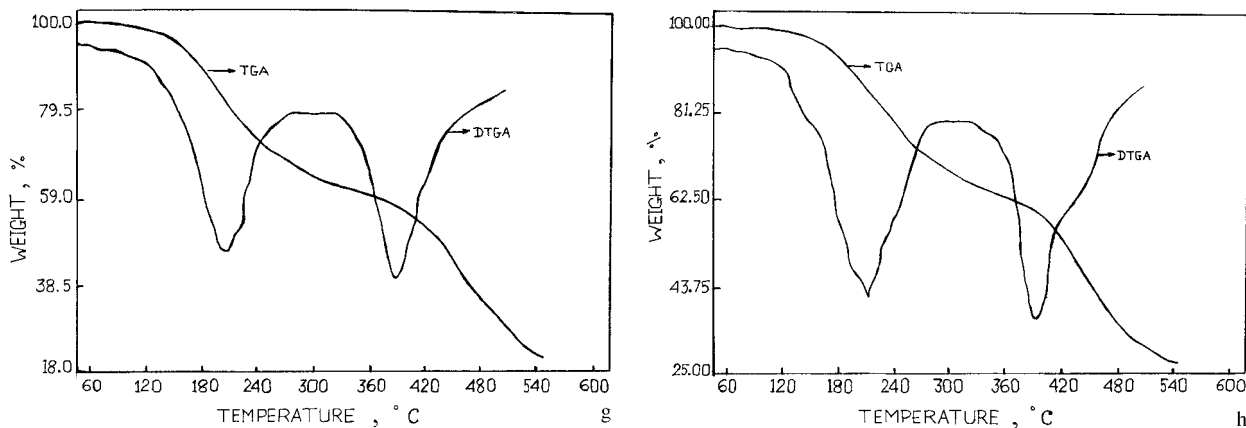
Figure 2 (*Continued from the previous page*)

ture region, around 350°C; this is followed by an exotherm, then an endotherm, and again an exotherm [Fig. 1(d–h)].

The most significant feature of the DSC study is that the energy of exothermic and endothermic peaks increases with increasing HMMM content indicating that the higher the HMMM percent, the higher the crosslinking density. The final decomposition temperature also improved with increasing HMMM percent (Table I).

The DSC data are well supported by FTIR and TGA results of the blend samples.

The FTIR studies investigated the specific interactions involved in blend miscibility.[5] HMMM showed characteristic stretchings for the methylol group at 1020 cm^{-1}, the methyl ether group at 1080 cm^{-1}, the C—O stretching in —CH_2—O—CH_2— linkage at 1127 cm^{-1}, and also a stretching band at 1650 cm^{-1} for the primary amine. The pure copolymer VAc–EHA showed characteristic stretching for the vinyl ester at 1720 cm^{-1} and for the acrylic ester at 1660 cm^{-1}.

But on blending, new characteristic stretching bands occur. For all compositions of blend films the characteristic stretching for the methyl ether group at 1080 cm^{-1} disappeared, but the 1020 cm^{-1} stretching for methylol always appeared. This may be due the presence of excess residual methylol groups due to the higher functionality of HMMM. For blends containing higher proportions of amino resin, the characteristic stretching for the vinyl ester at 1720 cm^{-1} disappeared, indicating the involvement of such groups in crosslinking reactions. The new stretching bands that appeared on blending were in the range of 3408–3427 cm^{-1} for free secondary amines, around 3394

cm^{-1} for imines (=N—H), 1741–1749 cm^{-1} for α-ketoesters, 1560–1578 cm^{-1} for secondary N—H vibrations, and around 821 cm^{-1} for the trisubstituted alkenes.

All these observations firmly establish the occurrence of crosslinking reactions between VAc–EHA and HMMM.

The fact that crosslinking efficiency increases with an increase in HMMM percent is supported by TGA and differential TG (DTG) analysis data. The endothermic peak at the higher temperature in DSC analysis coincides with the temperature of maximum weight loss rate in the DTG analysis. The extent of the condensation reaction and the rate of weight loss both increase with HMMM percent, which definitely points toward improving crosslinking density. Now it is quite evident that crosslinked thermosetting polymers produce a carbonaceous char at higher temperatures and the higher the char content is, the higher the fire retardanry power.[6] Thus, it is observed in Figure 2(a–h) that char yield increases with HMMM percent and the maximum decomposition temperature also shifts toward higher values. These degradation temperatures obtained from TGA coincide with those obtained from DSC analysis.

CONCLUSION

A very good waterborne coating formulation with minimal pollution hazard and good fire-retardancy characteristics can be obtained by using the blend of VAc–EHA with HMMM. But because drying time of the film with more than 40% of HMMM is found to be high, the 60 : 40 (VAc–

EHA : HMMM) blend may be considered as the ideal one.

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