Study of Fire Retardancy and Thermal Stability of Vinyl Acetate–2-Ethylhexyl Acrylate Copolymer by Blending with Amino Resin in Aqueous Medium

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ABSTRACT: Trimethoxymethyl melamine (TMMM) and hexamethoxymethyl melamine (HMMM) were blended with the widely used acrylic medium, the copolymer of vinyl acetate and 2-ethylhexyl acrylate (VAc–EHA), for preparing water-based blends having improved fire retardancy. The weight fraction of the VAc–EHA copolymer was varied from 40 to 95%, at the pH value of 7 and a solid content of 50% was kept in all cases. The limiting oxygen index (LOI) and char yield of the blends were evaluated and the surface morphology of TMMM, HMMM, and the VAc–EHA copolymer at room temperature and at 110, 340, and 550°C was also studied to explain the improvement in the fire-retardancy behavior of the blends. The LOI and char yield of the VAc–EHA copolymer was found to improve substantially on incorporation of both TMMM and HMMM. But due to the limited stability of TMMM in aqueous medium, HMMM is more suitable for blending with VAc–EHA, to give a water-based coating having good fire-retardancy properties. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **63:** 985–990, 1997

Key words: Blend; water-based coating; fire retardancy; limiting oxygen index; char yield; morphology

INTRODUCTION

The combustible material in most fatal fires is polymeric in nature. Whether natural or synthetic, these solid fuels account for the majority of damage occurring during a fire hazard. Numerous tests have been devised for flammability and many codes and regulations cite them. Thus, significant effort has been devoted to improve the thermal stability and fire retardancy of polymers. The progress relies on understanding the nature of fire, fuel properties, how to measure them, and how to analyze the nature of polymer degradation.

The burning of a solid polymer or a polymer composition involves the following five stages [1]L

1. Heating of the polymer.
2. Decomposition.
3. Pyrolysis or gasification.
4. Ignition.
5. Combustion and flaming.

Heating of the Polymer

The application of a heat source, such as direct flame, increases the temperature of the solid polymer at a rate dependent upon the relative sizes and temperature of the flame and of the polymer. During this initial stage, thermoplastic polymers soften or melt and begin to flow, the temperature of melting having a pronounced effect on the subsequent stages in the process. The thermal behavior of thermoset or crosslinked polymers varies
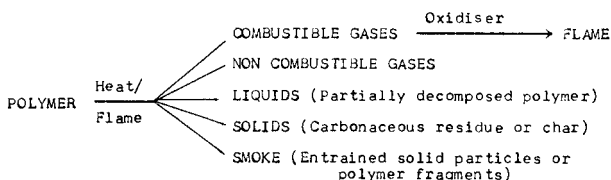
with the degree of crosslinking. Generally, these materials do not melt below the decomposition point.[2]

Decomposition

At some later stage in the heating process, decomposition of the polymer mass occurs with the elimination of volatile gases or chemically degraded polymer fragments according to the following scheme:

The temperature and the rate at which this occurs depend upon the thermal history or stability of the polymer and the chemical decomposition reaction occurring under the existing conditions.

Pyrolysis or Gasification

This is usually an exothermic process in the absence of oxygen and generally proceeds in three closely related phases:

(a) *Between 100 and 250°C:* Low-energy reaction such as functional group elimination, usually from chain ends.[2]
(b) *Between 250 and 500°C:* Sufficient energy is available for scission of the highest energy chemical bonds, leading to unzipping of some polymer chains, producing flammable monomers or random elimination of small chemical fragments. Often, recombination of these fragments leads to aromatic condensed ring systems which are stable under pyrolytic conditions.[2]
(c) *Above 500°C:* These aromatic condensed ring structures are further condensed with the eventual elimination of most elements other than carbon. This resulting carbon char is highly insulative and ignites with difficulty at normal oxygen concentration. If the intermediate composition of the char can be maintained in a viscoelastic state during the final stage of the pyrolysis, the gases evolved will be trapped in the viscous liquid and the char will expand into a carbonaceous foam.[2]

Ignition

As the temperature of the polymer increases and the flammable gases formed reach an appropriate ratio of oxygen to air ignition occurs. This is an exothermic process. The critical factor for polymer ignition is the rate of energy input, which, in turn, determines the rate of chemical decomposition.[3]

Combustion and Flaming

As ignition is an exothermic process, most of the destruction associated with fire occurs during the flaming or combustion phase. In this stage, very few polymers, however treated, can resist combustion.

Clearly, for a polymeric material to act as a fire retardant, it must inhibit one or more of the above-mentioned steps. Now, as evident from the above discussion, the behavior of thermoplastic and thermoset polymers toward fire resistance is entirely different.

In thermoplastics, the bonds in the chain acquire vibrational energy, due to heating, becoming more active, until the solid is transformed into a highly viscous liquid. On further heating, the vibrationally excited bonds begin to break, causing random scission, in which the backbone of the polymer cleaves irregularly along the chain, resulting in a rapid reduction of average molecular weight and melt viscosity. Also, successive ejection of the terminal monomeric unit may occur. This process known as unzipping produces molecular weight distribution concentrated at DP = 1. The monomer is highly volatile at these temperatures.

Although the absorbed energy drives the solid thermoplastic toward gasification, it may have a different effect on thermosets. Because of their crosslinked nature, thermosets generally do not soften or drip when exposed to flame as do many thermoplastics. Generally, most thermosets produce very little flammable fuel when heated by an ignition source. They produce an insulating carbonaceous char that can be oxidized only at extremely high temperatures and or at high oxygen concentration. The porous residue is less rapidly volatile than is the original polymer. It also acts as a diffusion barrier to volatiles leaving the polymer and to reactive oxygen reaching the surface. The thermal-insulating property reduces the transfer of heat to the fresh portion of the sample, thus further reducing decay.[4]
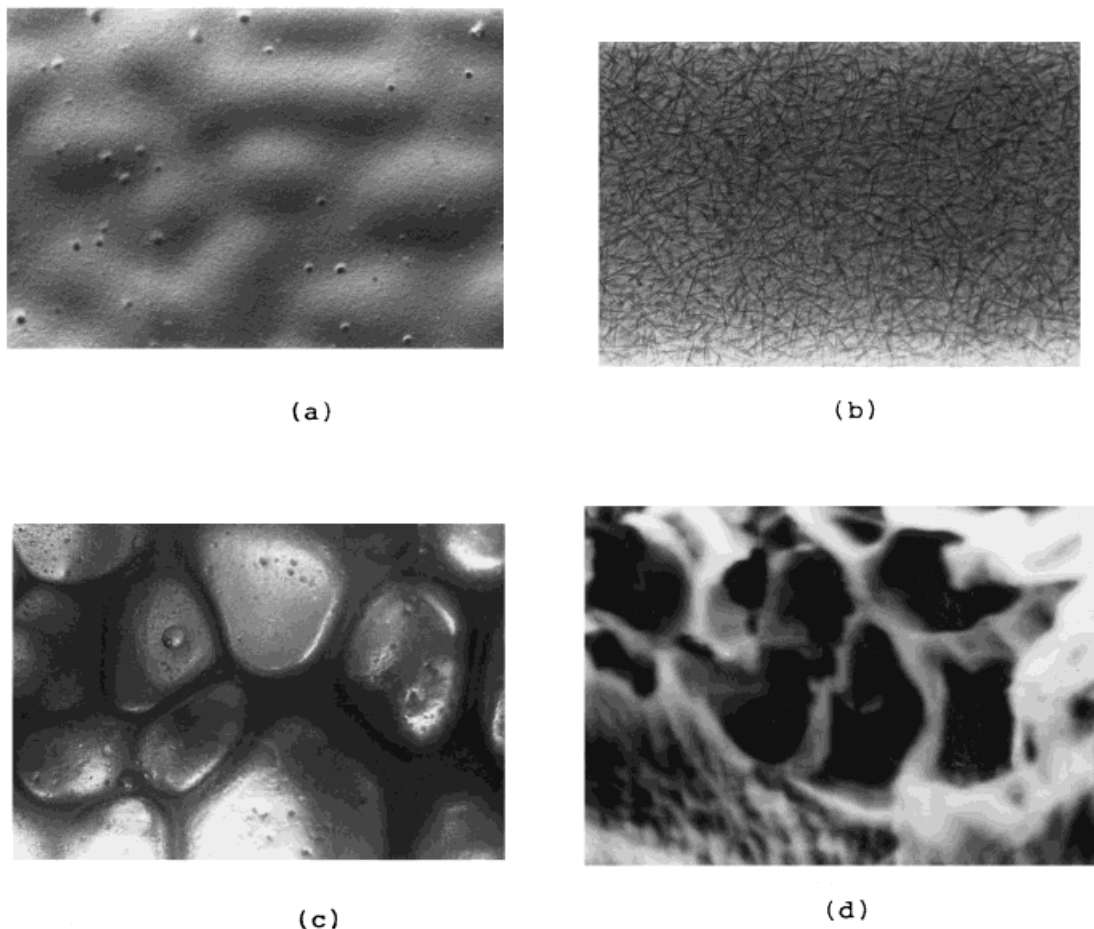
Figure 1 Polarized micrographs of surface morphology of HMMM at (a) room temperature, (b) 110°C, (c) 340°C, and (d) 550°C.

EXPERIMENTAL

Melamine–formaldehyde, a thermosetting resin, having excellent water resistance and thermal stability, on etherification produces hexa and tri derivatives of etherified melamine resin, having limited life in a water-soluble form, depending on the extent of substitution. pH also plays an important role in retaining its longer life as a water-soluble resin. The reaction of melamine and formaldehyde in the presence of excess methanol produces trimethoxymethyl melamine (TMMM) and hexamethoxymethyl melamine (HMMM),[5] of which the latter one is more hydrophillic and has substantial stability in the aqueous phase. These etherified, water-soluble melamine resins are chosen as one of the components for blending with the widely used acrylic medium, such as the copolymer of vinyl acetate (85%) and 2-ethylhexyl acrylate (15%) [VAc–EHA], for water-borne coatings, with a view to improve its fire-retardancy characteristics. The importance of water-based coatings is also undeniable from the point that they totally eliminate the environmental hazards associated with evaporation of organic solvents in the case of solvent-based coatings.

HMMM and VAc–EHA copolymers were blended in distilled water in a high-speed (1000 rpm) blender at different weight fractions (40–95%) of the VAc–EHA copolymer at a fixed pH of 7 for a constant time. The solid content of each composition was maintained at 50%. Films were obtained on polyethylene sheet-covered trays, for controlled drying at an uniform thickness (1.5 mm), and cured at room temperature followed by vacuum drying at 65°C. Films used for limited oxygen index (LOI) testing were cured at 180°C for 30 min using a vacuum oven. The same procedure was followed for the preparation of cast film from the TMMM and VAc–EHA copolymer blend.
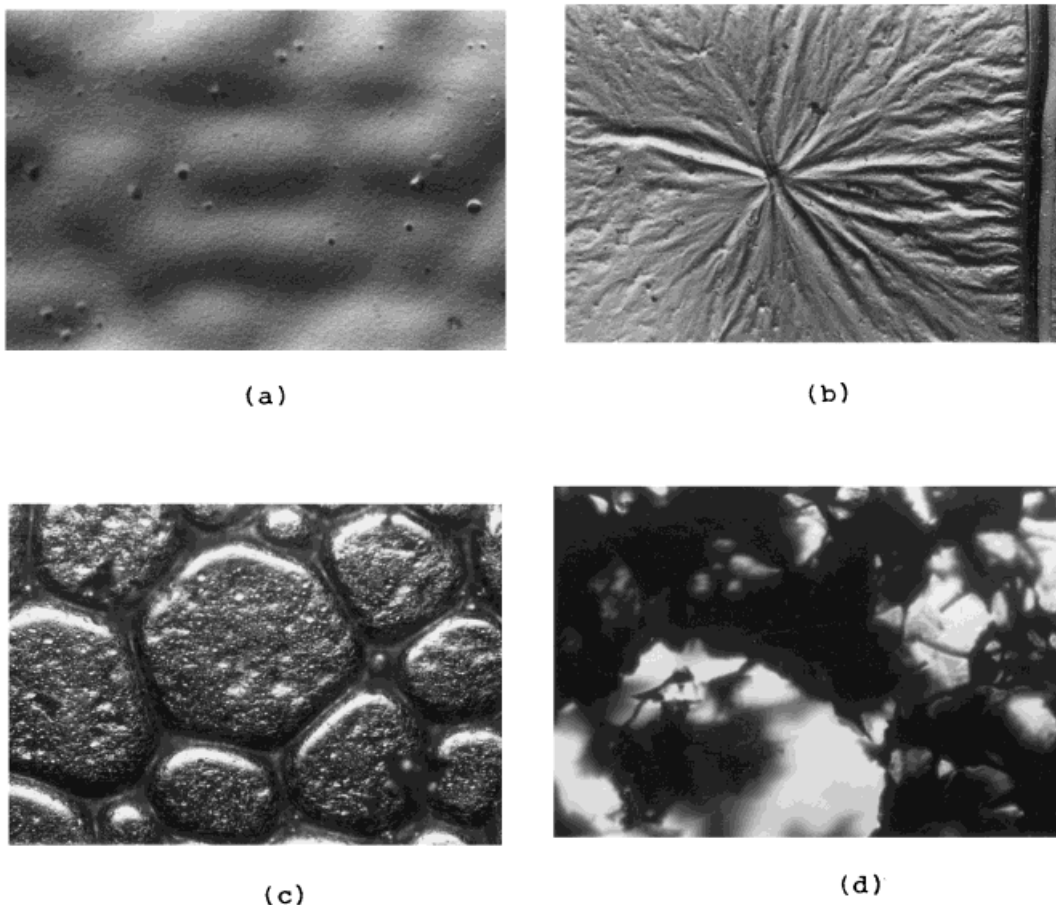
Figure 2 Polarized micrographs of surface morphology of TMMM at (a) room temperature, (b) 110°C, (c) 340°C, and (d) 550°C.

The crosslinking and char-forming phenomenon of HMMM, TMMM, and the VAc–EHA copolymer were studied at different temperatures (room temperature and 110, 340, and 550°C). The morphology of the corresponding thermally transformed surfaces were studied by a polarized microscope and are shown in Figures 1(a)–(d), 2(a)–(d), and 3(a)–(d) for HMMM, TMMM, and the VAc–EHA copolymer, respectively.

Now, to study the thermal behavior and fire retardancy of the HMMM/VAc–EHA and TMMM/VAc–EHA blends, their LOI and char yield at 550°C were evaluated. Stantons Red Craft, Model-FTA, flammability equipment was used for determining the LOI under specified test conditions (ASTM D 2863-74), while Stantons gravimetric balance, TG-750, was used to study the thermal decomposition (char yield) of the blends. The results are tabulated in Tables I and II.

RESULTS AND DISCUSSION

Figures 1(a) and 2(a) show the surface morphologies of HMMM and TMMM films at about 30°C. The bulging nature of the film surfaces in both cases may be attributed to the presence of water retained by the polymer due to their hydrophillic nature. At 110°C, HMMM shows needle-type crystal formation, while TMMM shows spherulitic crystal formation due to a self-condensation reaction[6] [Figs. 1(b) and 2(b)]. At 340°C, HMMM exhibits a foamed network structure having a somewhat oblong-shaped cellular network [Fig. 1(c)], while TMMM exhibits a foamed structure with a hexagonal cellular network [Fig. 2(c)], indicating their thermal stability by the foamed carbonaceous char formation on further heating. At 550°C, as expected, both HMMM and TMMM exhibit a foamed porous carbonaceous char formation [Figs. 1(d) and 2(d)].
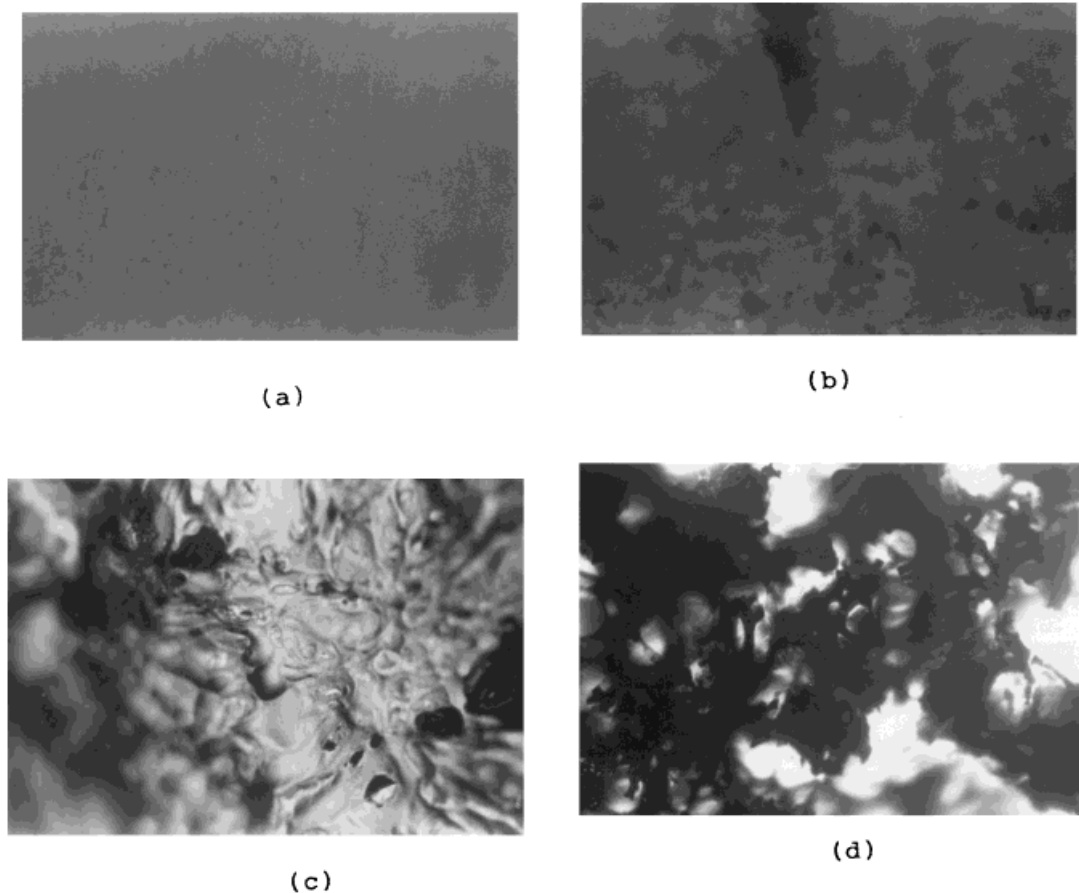
(a)

(b)

(c)

(d)

Figure 3 Polarized micrographs of surface morphology of the VAc–EHA copolymer at (a) room temperature, (b) 110°C, (c) 340°C, and (d) 550°C.

The surface morphologies of the VAc–EHA copolymer samples at room temperature and at 110°C are shown in Figure 3(a) and (b). Unlike HMMM and TMMM, VAc–EHA at room temperature shows a smooth surface, nor does it exhibit any crystalline nature at 110°C. Since VAc–EHA

is a thermoplastic of low thermal stability (T_g = 19°C), it decomposes to produce volatiles of low flash points and low auto ignition temperature. So, at 340°C, VAc–EHA exhibits no foamed structure formation; only an amount of organic residue remained. Also, at 550°C, the phenomenon of po-

Table I LOI and Char Yield at 550°C of HMMM and VAc–EHA Copolymer Blends

HMMM (Wt %)	VAc–EHA (Wt %)	LOI (%)	Char Yield at 550°C (%)
0	100	18	8
5	95	19.2	13.8
10	90	20.4	15.0
20	80	22.6	15.7
30	70	23.4	17.4
40	60	24.2	18.0
50	50	26.8	19.9
60	40	27.1	23.5
100	0	31.1	31.9

Table II LOI and Char Yield at 550°C of TMMM and VAc–EHA Copolymer Blends

TMMM (Wt %)	VAc–EHA (Wt %)	LOI (%)	Char Yield at 550°C (%)
0	100	18	8
5	95	18.9	13.2
10	90	19.8	14.5
20	80	20.2	15.2
30	70	22.1	16.8
40	60	24.1	17.4
50	50	25.0	19.2
60	40	26.0	21.6
100	0	30.0	28

rous char formation as observed in the case of HMMM and TMMM is absent. A small amount of nonporous, agglomerated char [Fig. 3(d)] remained.

Both HMMM and TMMM shows good char yield, but for the VAc–EHA copolymer, the value is quite low. The acrylic copolymer, VAc–EHA, ignites readily (LOI 18) and softens as it burns. In burning, the acrylic copolymer undergoes pyrolysis from the heat of the ignition source. The volatile products of pyrolysis then burn in the gas phase, the heat from the combustion causing additional pyrolysis and consequent continued burning. Depolymerization by unzipping, along with the presence of oxygen in the ester group, probably accounts for the lower gas formation, leaving a very small char residue.

But both HMMM and TMMM after curing produce $-CH_2-NH-$ linkage, giving a complicated crosslinked structure. The polymers are thus difficult to ignite, are self-extinguishing in a horizontal position, generate little smoke during combustion, and ultimately produce a carbonaceous char. Thus, remarkable improvement in the LOI and char yield are observed when HMMM and TMMM are blended with the VAc–EHA copolymer, as expected.

CONCLUSION

The fire retardancy (LOI) of the VAc–EHA copolymer improved by 50.5 and 44.4% of its original valve on incorporation of 60% HMMM and TMMM, respectively. So, the VAc–EHA copolymer, which is widely used in the surface-coating industry, may be blended with a higher percentage of HMMM for use in stoving systems, the drying time at room temperature being very high.

For blends containing 30% HMMM or TMMM, the LOI improved by 30 or 22.7%, respectively. It was observed that tack free time is not much affected in such a proportion and this blend may find utilization as a base for fire-retardant coatings. Due to the limited stability of TMMM in an aqueous medium, the blend of HMMM/VAc–EHA is more suitable for use in any water-borne coating system for improved fire retardancy.

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