

Effect of Molecular Chain Structure of the Cured Epoxy Resin Containing Hyperbranched (3-Hydroxyphenyl) Phosphate on Expansion and Flame Retardance

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ABSTRACT: Melamine is widely used as a blowing agent in intumescent flame-retardant systems. However, when it was blended into the epoxy resin cured with hyperbranched (3-hydroxyphenyl) phosphate (HHPP), neither greater expansion nor improved limiting oxygen index (LOI) was obtained during combustion compared with that without melamine addition. When a portion of HHPP was replaced by polyethylene glycol (PEG), both the expansion degree and the LOI increased, along with the content of PEG, even if the same amount of melamine was blended. This phenomenon shows that the molecular chain structure of the cured epoxy resin based on HHPP has a substantial effect on the flame retardance. Only when the degraded products are sufficiently viscous, at the decomposition temperature of the blowing agent, can the material be bubbled to form an expanding charred crust. The morphologic structure of the

crust of the epoxy resin cured with HHPP shows that there were many holes on the surface because the degraded products were too rigid to be bubbled, from which the gases formed by melamine evolved. With increasing PEG content, the degraded products became increasingly viscous and bulged more easily with the gases. No holes appeared on the charred crust of the sample cured with the mixture of HHPP and PEG at a ratio of 3:1. In this case, most of the gases were entrapped and caused the material to expand, resulting in the increases of expansion degree and LOI. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 2065–2070, 2004

Key words: hyperbranched; flame retardance; differential scanning calorimetry (DSC); mass spectrometry; thermal properties

INTRODUCTION

With increasingly stringent requirements on fire safety of materials, searching for new flame-retardant polymers and studying their flame-retardant mechanisms have attracted many research activities.

The intumescent materials containing phosphorus and nitrogen have become increasingly attractive in various industrial applications in recent years because of the absence of toxic gases and smoke during combustion compared with that generated by halogen-type flame retardants. This technology is derived from intumescent coatings that have been in use for more than 40 years.^{1,2} Generally, three kinds of chemicals are incorporated into formulations to obtain intumescent flame retardancy: (1) inorganic acid or precursors, such as phosphorous-containing compounds; (2) a carbon-rich polyhydric compound, such as pentaerythritol; and (3) a blowing agent, such as melamine

and polyamides, to yield gaseous products. During combustion, the intumescent system forms an expanding charred crust as a barrier between the flame and the underlying polymeric material. This crust has a low thermal conductivity,³ which attenuates the transfer of heat to protect the underlying polymeric material from further attack from flame or heating. Furthermore, the formed crust is very compact,⁴ which limits the diffusion of oxygen to the underlying material of the char, and prevents the transfer of degraded products of the material to the fire as fuel. All these factors result in a prolonged burning time or extinguishing a fire.

Melamine is well known as a blowing agent used in intumescent systems,^{5–7} and decomposes at around 335°C,⁸ resulting in the release of gases such as ammonia, which plays an important role in forming an expanding charred crust.

In our previous study, a novel hyperbranched (3-hydroxyphenyl) phosphate (HHPP) with high functionality was synthesized.⁹ The limiting oxygen index (LOI) of the thermally cured epoxy resin with HHPP was increased, and the heat release rate was substantially decreased, compared with that of epoxy resins cured with conventional curing agents such as resorcinol. However, it is interesting that, when 10 wt %

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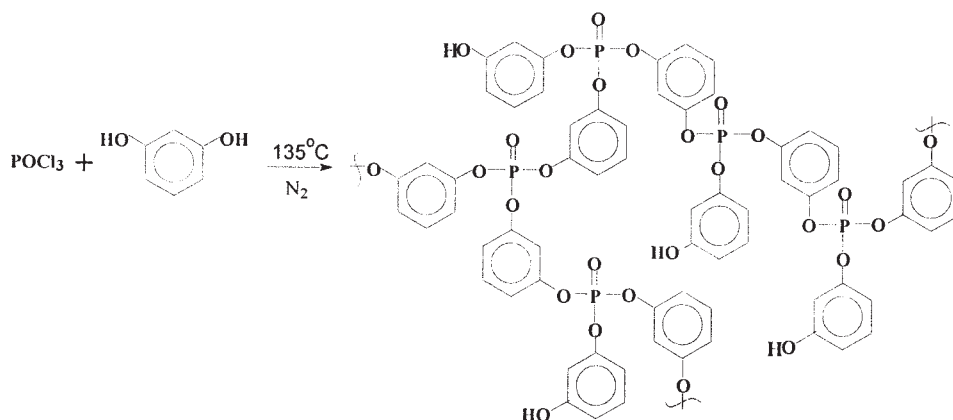


Figure 1 Schematic outline of the synthesis of HHPP.

melamine was blended into the epoxy resin cured with HHPP, neither LOI enhancement nor greater expansion of the cured product was observed. The reason for this change is probably attributable to the formed degraded material, which is too rigid to expand at the temperature at which the melamine decomposed. To verify this explanation, polyethylene glycol (PEG) was introduced into the above melamine-containing epoxy resin as a curing agent together with HHPP. The expanding degrees, combustion behaviors, and morphologic structures of the formed chars with different PEG contents in the presence of melamine after combustion were investigated in this work and reported herein.

EXPERIMENTAL

Materials

The synthesis of hyperbranched (3-hydroxyphenyl) phosphate (HHPP, phenol value = 6.3 mmol/g) was reported elsewhere⁹ and the schematic outline of the synthesis is shown in Figure 1. Diglycidyl ether of bisphenol A [WSR618, epoxy equivalent weight (EEW) = 196 g/equiv] was obtained from Blue Star New Chemical Materials Co. (Beijing, China). Polyethylene glycol 400 (PEG), melamine, *N,N*-dimethylbenzylamine (DBA), isopropanol, *n*-butyl acetate, and triphenyl phosphine were purchased from Shanghai First Reagent Co. (China). An aliphatic urethane acrylate, with a molecular weight of around 1500 g/mol (Ebecryl 270), and UV-curable monomers such as trimethylolpropane triacrylate (TMPTA) and 1,6-hexamethyldiol diacrylate (HDDA) were supplied by UCB Chemicals, Radcure Specialties (Brussels, Belgium). 1-Hydroxy-cyclohexyl-phenyl ketone (Irgacure 184), supplied by Ciba-Geigy (Summit, NJ) was used as a photoinitiator.

Sample preparation

The different contents of HHPP and PEG were used as combined curing agents. WSR618 was blended sepa-

rately with the above complexes at 80°C. Triphenyl phosphine (0.2 wt %) and DBA (2 wt %) were added to each formulation as a curing accelerator¹⁰ and a catalyst for the reaction of PEG with WSR618, respectively. The above mixtures were poured separately into a hot aluminum mold, and then thermally cured at 130°C for 60 min, followed by 170°C for 180 min and 200°C for 180 min. The cured products were denoted as HHPP/PEG₀, HHPP/PEG₁₀, HHPP/PEG₁₅, HHPP/PEG₂₀, and HHPP/PEG₂₅, respectively, according to the PEG ratios in the samples. Another series of samples were prepared similar to the described series, except that an additional 10 wt % (total amount) of melamine was blended into each sample before being poured into aluminum molds. The samples obtained were denoted as HHPP/PEG₀/MA, HHPP/PEG₁₀/MA, HHPP/PEG₁₅/MA, HHPP/PEG₂₀/MA, and HHPP/PEG₂₅/MA, respectively. To obtain a highly crosslinked polymer, one EEW of epoxy resin was cured with one functional equivalent weight of the curing agent. The compositions of the samples are listed in Table I. The curing condition was determined from differential scanning calorimetry (DSC), shown in Figure 2.

Measurements

The DSC thermograms were recorded with a TA Shimadzu DSC-50 instrument (Shimadzu, Kyoto, Japan) at a heating rate of 10°C/min under nitrogen atmosphere. Thermogravimetric analysis (TGA) was carried out on a Shimadzu TG-50 instrument at a heating rate of 10°C/min in air. The LOI values were measured on a ZRY-type instrument (made in China) on 120 × 60 × 3-mm³ sheets, according to the standard "oxygen index" test ASTM D2863. Each datum was obtained from three samples as an average value. SEM micrographs of the charred layers were obtained using X650 scanning electron microscopy (Hitachi X560 scanning electron microanalyzer; Hitachi, Osaka, Japan). The specimens were previously coated with a conductive gold layer. The expansion degree of the

TABLE I
Compositions, LOI, and Expansion Degrees of the Samples

Sample	Composition (g)						LOI	Expansion degree
	HHPP	WSR618	PEG	DBA	PPh ₃	MA		
HHPP/PEG ₀	2	2.471	—	—	0.009	—	27.0	139.2
HHPP/PEG ₁₀	2	3.018	0.558	0.011	0.010	—	26.7	160.1
HHPP/PEG ₁₅	2	3.406	0.954	0.019	0.011	—	26.5	151.6
HHPP/PEG ₂₀	2	3.923	1.481	0.030	0.012	—	26.3	147.0
HHPP/PEG ₂₅	2	4.641	2.214	0.044	0.013	—	26.0	110.0
HHPP/PEG ₀ /MA	2	2.471	—	—	0.009	0.497	27.0	139.7
HHPP/PEG ₁₀ /MA	2	3.018	0.558	0.011	0.010	0.620	27.3	185.1
HHPP/PEG ₁₅ /MA	2	3.406	0.954	0.019	0.011	0.713	27.5	202.2
HHPP/PEG ₂₀ /MA	2	3.923	1.481	0.030	0.012	0.823	28.3	208.7
HHPP/PEG ₂₅ /MA	2	4.641	2.214	0.044	0.013	0.984	29.0	236.1

cured samples during combustion was defined as the ratio of the volume after combustion to the original one. To eliminate the turbulence from the voids and the adsorbed gases on the surface of the formed chars after combustion, the volumes of the chars were measured by the following method. First, the char was coated with a UV-curable formulation (Table II) by a spray gun, and then exposed to a UV lamp (1 kW; Blue Sky Special Lamps Development Co., Beijing, China) to form a continuous compact film. The volume of the sample was measured by the volume of water excluded from a flask at 25°C, which has a capillary on the top similar to that of a density bottle, and calculated by the formula

$$V_{\text{char}} = \frac{W_1 - (W_2 - W_3)}{\rho_1} - \frac{W_3 - W_4}{\rho_2}$$

where V_{char} is the volume of the char; W_1 is the weight of the flask filled with distilled water; W_2 is the weight of the flask containing the coated char and the filled water; W_3 and W_4 are the weights of the chars after

and before being coated, respectively; and ρ_1 and ρ_2 are the densities of the water and the cured UV coating at 25°C, respectively. The latter was tested by a density bottle. Direct pyrolysis/mass spectrometry (DP-MS) analysis was carried out with a Micromass GCT-MS spectrometer (Waters Corp., Milford, MA) using the standard direct insertion probe for solid polymer materials, at a heating rate of 20°C/min in the range of 30–600°C. The mass data were continuously acquired at a scan rate of 0.1 s. Electron impact (EI) was used for the mass spectra with 70 eV and the mass range of 10–1000 m/z .

RESULTS AND DISCUSSION

Intumescent behavior of the samples

The formation of an expanding charred crust is the crucial requirement of an intumescent system. It is generally achieved by the addition of blowing agents such as melamine, urea, urea-formaldehyde resins, and polyamides. These compounds decompose to yield gaseous products, causing the char to expand and hence provide insulating crusts.

The expansion degree strongly influences the flame retardance of a material. The higher the expansion degree, the thicker the insulating layer to protect the underlying material. Figure 3 shows the expansion degrees of samples, and the data are listed in Table I. It is interesting that the expansion degree of HHPP/PEG₀/MA is almost the same as that of HHPP/PEG₀,

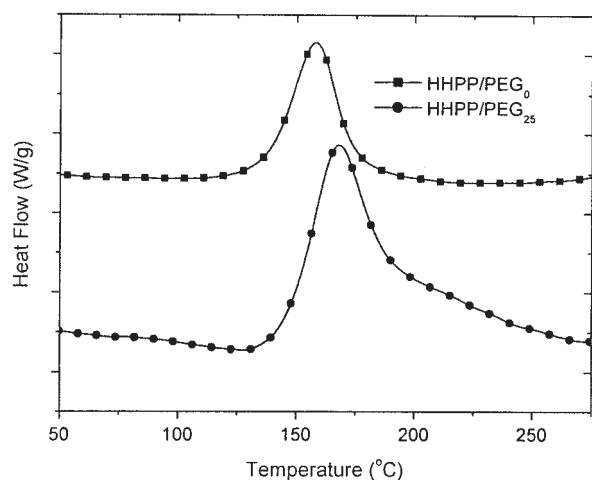


Figure 2 DSC thermograms of the curing reactions of HHPP/PEG₀ and HHPP/PEG₂₅.

TABLE II
Formulation of the UV Curable Coating

Constituent	Parts by weight
EB270	60
TMPTA	25
HDDA	15
Isopropanol	40
<i>n</i> -Butylacetate	60
Irgacure 184	5

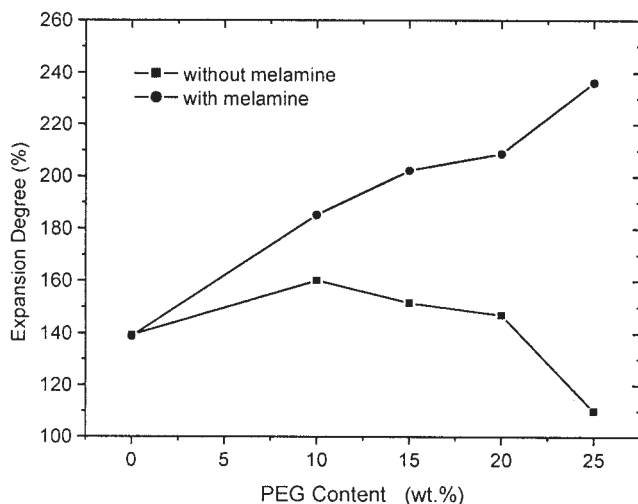


Figure 3 Expansion degrees of samples with different PEG contents.

although the former contains 10 wt % of melamine. Furthermore, with increasing PEG content, the difference in the expansion degrees of samples with and without the presence of melamine increases from 25% between HHPP/PEG₁₀ and HHPP/PEG₁₀/MA to 126.1% between HHPP/PEG₂₅ and HHPP/PEG₂₅/MA, which is shown in Figure 4. Consequently, the efficiency of the melamine as a blowing agent was improved with further PEG addition.

To obtain a high expansion degree, it is supposed that the decomposition of the blowing agent, and the degraded products of the material must be sticky enough or be in the melting state at the degrading temperature of the blowing agent. Only in this case are the gases evolved by blowing agent able to cause the degraded products to expand, and then further to form a cellulose crust to protect the underlying material.

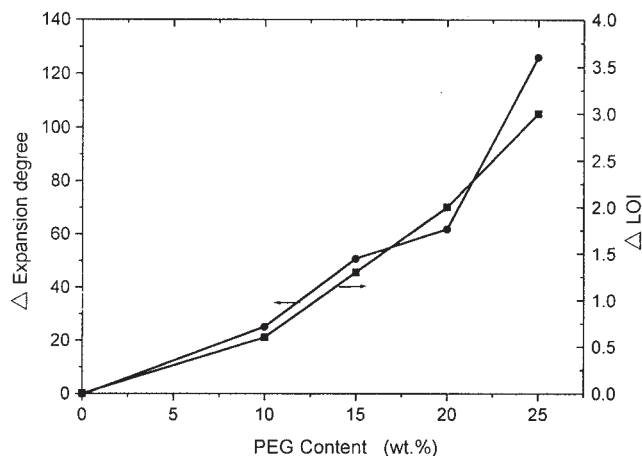


Figure 4 Differences of expansion degrees and LOI values between samples with and without melamine at different PEG contents.

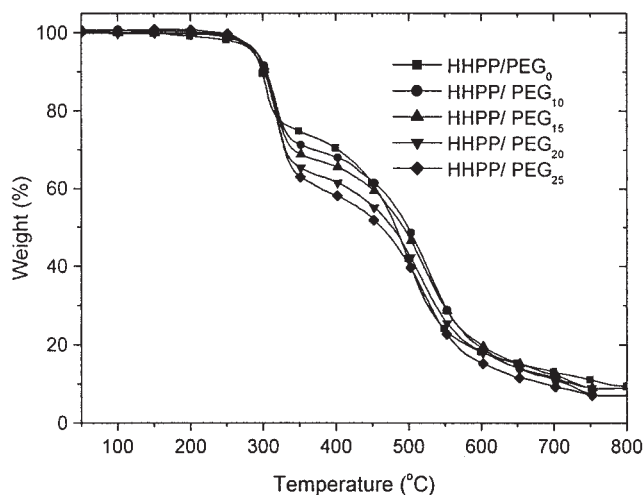


Figure 5 TGA thermograms of samples cured with HHPP and PEG in the absence of melamine.

The thermal degradation behaviors of the samples without melamine were studied to show the degradation states at the decomposition temperature of melamine. The TGA thermograms and the DTG curves are shown in Figures 5 and 6, respectively. All samples have two degradation stages. The first is between 250 and 400°C, with the DTG peak at around 320°C. The second is between 400 and 750°C, with the DTG peak at around 520°C. All the samples degrade a similar amount of masses at below 320°C, at which temperature most of the phosphorus-containing moieties have degraded.¹¹ At the degradation temperature of 335°C for melamine, the mass losses are 23.9, 26.5, 28.5, 31.8, and 33.0% in the sequence of HHPP/PEG₀ to HHPP/PEG₂₅, corresponding to the increasing content of PEG. This indicates that PEG segments in the material began to degrade at around 320°C, and the various

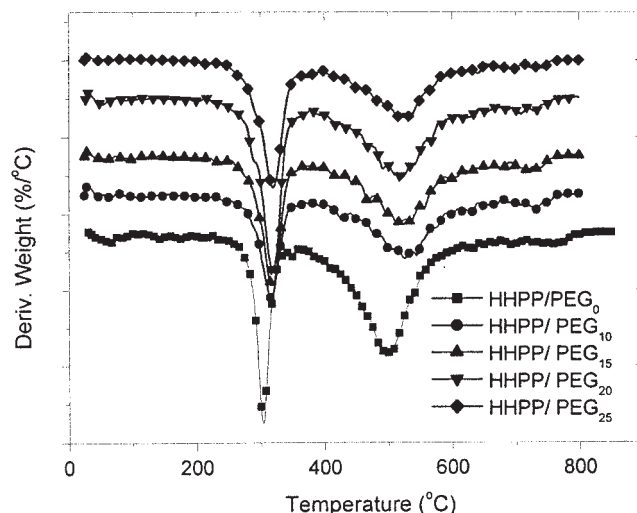


Figure 6 DTG curves of samples cured with HHPP and PEG in the absence of melamine.

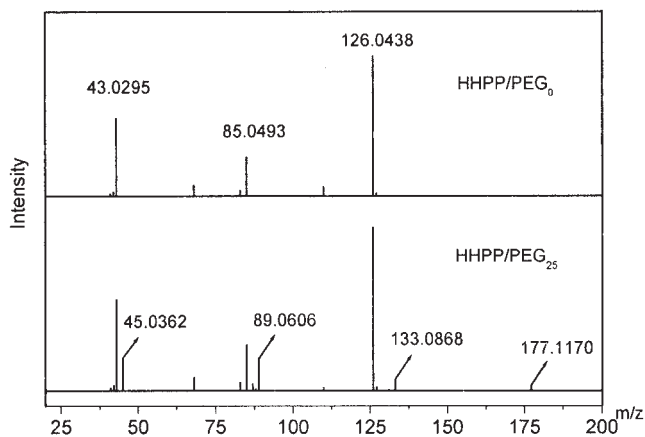


Figure 7 EI mass spectra of HHPP/PEG₀ and HHPP/PEG₂₅ at 320°C.

contents of PEG addition result in different degrees of degradation.

Because the samples lost much mass at the temperature at which melamine decomposed, various expansion degrees were obtained. This difference in the expansion degrees may be attributed to the states, stickiness or rigidity, of the degradation products in the condensed phase. The degraded products of HHPP/PEG₀/MA are rigid because most of them are aromatic or polynuclear aromatic carbons. The gases formed by melamine evolved through the cracks on the char surface during combustion because the char structure had no elasticity and was hard to be bubbled. As a result, melamine cannot act effectively as a blowing agent in this case, and the expansion degree of HHPP/PEG₀/MA remains the same as that of HHPP/PEG₀. On the contrary, the degraded products of HHPP/PEG₂₅/MA are sticky because PEG has decomposed at the decomposition temperature of melamine and forms many short segments in the condensed phase. Figure 7 shows the mass spectra of HHPP/PEG₀ and HHPP/PEG₂₅ at 320°C, which correspond to the first DTG peak of HHPP/PEG₂₅. The major difference between them is that there are four peaks in the mass spectrum of HHPP/PEG₂₅ located at 45.0362, 89.0606, 133.0969, and 177.1170, respectively, which correspond to PEG fragments of (CH₂CH₂O)_nH ($n = 1-4$). The polyether fragments decomposed by PEG segments at high temperature conferred a greater degree of stickiness the degraded to the mixture. It was also clearly observed that the sample containing more PEG was much softer, if squeezed with nippers, when the samples were heated in a muffle oven for the same time around 330°C. Because the mixture of the degraded products of HHPP/PEG₂₅/MA was sufficiently viscous to trap most of the gases formed by the decomposition of melamine, the volume was expanded by these gases, leading to a much higher expansion degree than that of HHPP/PEG₂₅.

Flame retardance of the samples

LOI, which ranks the flammability of materials, is the minimum concentration of oxygen in an oxygen/nitrogen mixture that will just support combustion. Figure 8 shows the LOI values of the samples. It decreases from HHPP/PEG₀ to HHPP/PEG₂₅ with increasing content of phosphorus, which is attributed to the easy flammability of the PEG segment, and the lowered crosslinking density of the material caused by PEG, which caused the material to degrade more easily. On the contrary, the LOI value increased from HHPP/PEG₀/MA to HHPP/PEG₂₅/MA, although they contained the same amount of melamine and a similar phosphorus content. The difference in the LOI values of the samples with and without melamine increased from 0 between HHPP/PEG₀ and HHPP/PEG₀/MA to 3.0 between HHPP/PEG₂₅ and HHPP/PEG₂₅/MA, as shown in Figure 4.

The contribution of PEG to the LOI enhancement may be explained as follows: with increasing PEG content, the expansion degree increased in the presence of melamine as discussed above, resulting in the formation of a thicker insulating char. It separated the flame from the inner material more efficiently, substantially improving the flame retardance. Another reason is that more compact chars were formed in the presence of PEG, which is discussed in the next section.

Morphologic structures of the charred crusts

An intumescent system usually forms an expanding crust during combustion, which acts as an insulating barrier. To separate oxygen more efficiently from the degraded volatile component, the crust's surface should be compact enough to prevent penetration of gases.

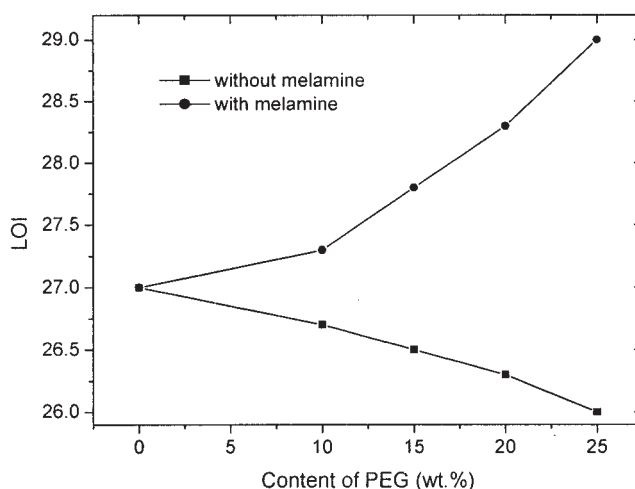


Figure 8 LOI values of samples with different PEG contents.

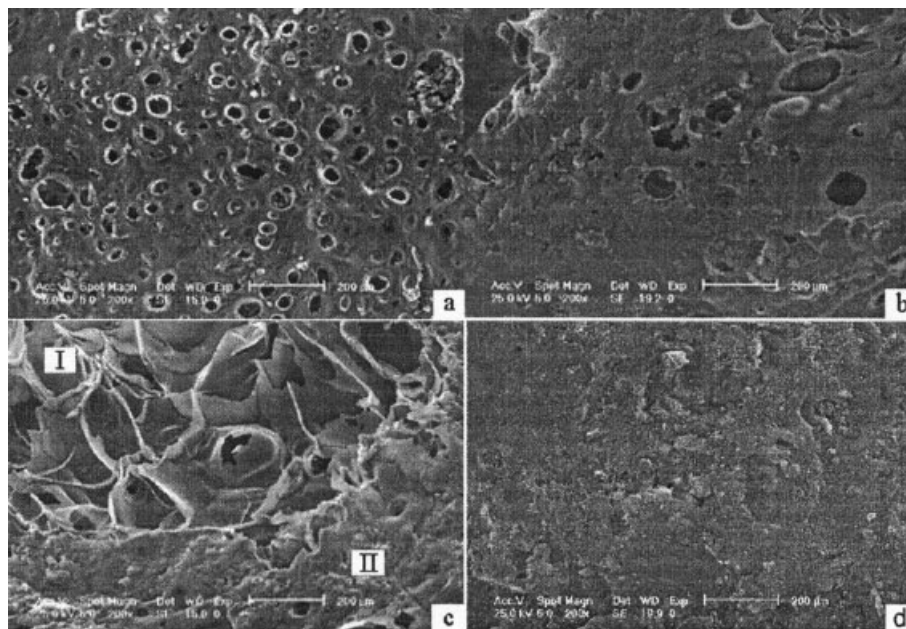


Figure 9 SEM micrographs of the charred crusts: (a) HHPP/PEG₀/MA, (b, c) HHPP/PEG₁₅/MA, (d) HHPP/PEG₂₅/MA.

Figure 9 shows the SEM micrographs of the charred crusts of samples magnified at $\times 200$. Figure 9(a) shows the image of the crust of HHPP/PEG₀/MA, and it can be seen that there are many small holes on the surface, which are explained by the fact that, at the temperature when the ammonium was formed by the degradation of melamine, the degradation product of HHPP/PEG₀/MA was too rigid to be bubbled. The gases could not be entrapped and then evolved from the material, leaving many holes on the crust's surface. The porous layer was less effective in separating oxygen from the degraded volatile component. Consequently, melamine cannot act efficiently as a blowing agent, resulting in a low expansion degree and thus inefficiency in flame retardance when added to HHPP/PEG₀.

With respect to the crust of HHPP/PEG₁₅/MA, which is shown in Figure 9(b), there are considerably fewer holes compared with those in HHPP/PEG₀/MA. As discussed above, the presence of PEG promotes greater viscosity of the degraded products, which facilitates easier bubbling. Most of the gases formed by melamine were entrapped by the degraded products, and the material was forced to expand. Both the expansion degree and LOI value increased correspondingly. Figure 9(c) also shows the image for the crust of HHPP/PEG₁₅/MA, where part of the surface char was peeled off. The inner part is denoted as area I and the surface part as area II. There are some semiballs in area I, showing that the degraded product of HHPP/PEG₁₅/MA has a tendency to trap the gases, so the char crust is bubbled by the evolved gases. However, there are still some gases that evolve from the material, leaving some holes on the surface.

Figure 9(d) shows the image of the crust of HHPP/PEG₂₅/MA. With increasing PEG content, the surface

of the formed crust is more compact. Almost no holes remain on the surface. Correspondingly, both the expansion degree and the LOI value are the highest among the samples.

CONCLUSIONS

The molecular chain structure of a crosslinked film has a substantial effect on the expansion degree and flame retardance of an intumescent system. The expansion occurs only with difficulty if the degraded product is too rigid to be bubbled at the temperature at which the blowing agent decomposed. In this case, the gases will evolve from the crust, leaving numerous holes on the surface, and the blowing agent cannot act effectively. The introduction of compounds with soft segments such as PEG can promote greater viscosity of the degraded products, which can be bubbled and form cellulose crusts. Both the expansion degree and the flame retardance can be effectively improved.

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