

Microencapsulation of Intumescent Flame-Retardant Agent and Application to Epoxy Resins

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ABSTRACT: Phosphate tri (2,6,7-trioxa-1-phosphabicyclo [2.2.2] octane-1-oxo-4-methanol) phosphate (trimer) and its microcapsules with MUF resin shell, respectively, were synthesized. Their structures were characterized by NMR, IR, and SEM analysis. Epoxy resins (EP) were modified with trimer, and its microcapsules to get the flame retardant EP, whose flammability and burning behavior were characterized by UL 94 and limiting oxygen index (LOI). About 20% of the trimer microcapsules were doped into EP to get 30.2% of LOI and UL 94 V-0. Thermal properties of the flame retardant EP were investigated with thermogravimetry (TG) and differential thermogravimetry (DTG).

Weight loss behavior and thermal stability were characterized. For EP containing the trimer microcapsules, compared with EP containing trimer, incorporating melamine group into EP decreased weight loss and the maximum weight loss rate, increased the char yield and thermal stability. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 2025–2030, 2011

Key words: epoxy resins; degradation; flame retardant; synthesis; microcapsules

INTRODUCTION

The safe ecological use of polymer flame retardant has become a major subject in the modern polymer industry, and there is an international demand for the control of polymer flammability without the use of halogenated additives. Consequently, current research is mainly focused on looking for halogen-free additives in the form of intumescent flame retardant (IFR), which are being thought as the alternatives of the halogen containing flame retardants.^{1,2} Generally, IFR contains three main ingredients: acid source, carbon source, and gas source. Phosphorus-containing compounds are often used as an acid source in IFR. They degrade to form char layer before the polymer decomposes during a fire. Nitrogen-containing compounds are used as gases source in IFR system, to produce incombustible gases when they degrade. The heat gases can swell the just formed char. The swollen char can isolate the transfer of mass and heat between the materials and the flame in a fire.³ Among the IFRs, caged bicyclic phosphates have attracted many researches, and much investigation has been done in this field.^{4–5} In recent years, a novel phosphate tri(2,6,7-trioxa-1-phosphabicyclo

[2.2.2] octane-1-oxo-4-methanol) (trimer), a caged bicyclic phosphate, has been reported,⁶ which is an effective flame retardant. However, it lacks nitrogen as an intumescent system, whereas an enhancement of flame retardance was observed by introducing nitrogen into the phosphorus flame retardant system.^{7,8} This problem was approached by the technique of microencapsulation.^{9,10} In this articles, microcapsules of trimer with MUF resin shell were synthesized. The trimer microcapsules were then applied to epoxy resins (EP) to get flame retardant EP, which was analyzed for flame retardance and thermal behavior. Better flame retardance of the trimer microcapsules was obtained compared to trimer.

EXPERIMENTAL

Materials

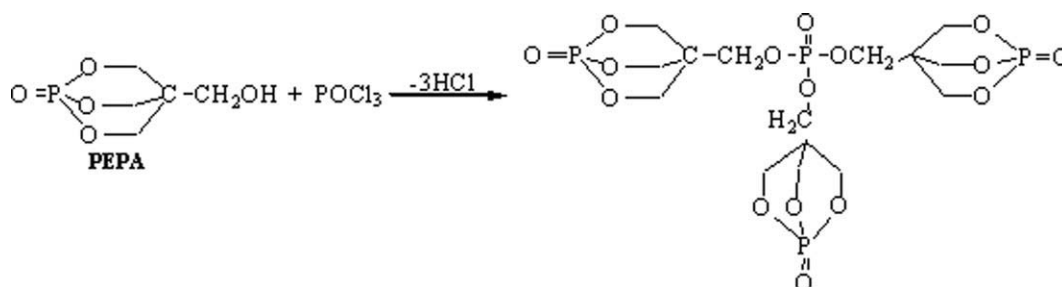
Preparation of 1-Oxo-4-methoxy-2,6,7-trioxa-1-phosphabicyclo[2,2,2]octane (PEPA) was prepared in our laboratory according to previously reported methods.¹¹ Acetonitrile, pyridine, 37% formalin as formaldehyde, melamine, urea, and POCl₃ were received from Beijing Chemical Reagents (Beijing).

Experimental

Synthesis of trimer

A 500 mL four-necked flask was filled with 150 mL of acetonitrile, 50 mL of pyridine, and 108 g (0.6 mol)

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Scheme 1 Synthesis of trimer.

of PEPA. Reaction mixture was heated with stirring to reflux. When PEPA dissolved, 18.2 mL (0.2 mol) of POCl_3 was slowly dropped in. Thereafter the mixture was heated to 80°C under reflux. The reaction was kept for about 10 h at the temperature until no HCl was released. Successively, the reaction mixture was cooled, filtered, and the precipitate was washed with water and then dried at 60°C under reduced pressure, giving 94.2 g of trimer (white powder). The synthesis of trimer is shown in Scheme 1.

Prepolymer synthesis

A volume of 50 ml of distilled water and 37% formalin as formaldehyde with a mole ratio of 3 : 1 were brought to pH 8–8.5 with 10% Na_2CO_3 solution in a three-necked flask. Then mixture (10 g) melamine and urea (mass ratio of 1 : 1) were added to the above solution, stirred until dissolved, and heated to 80°C under reflux for 1 h to get a transparent MUF prepolymer, which was now ready for use of the microencapsulation.

Trimer microcapsules synthesis

Microcapsules are synthesized as reference.¹² About 20 g of trimer was first dispersed in 90 mL of water, stirred for 30 min, then 8 mL of the above MUF resin prepolymer was added into the mixture, and the pH of the mixture was adjusted to 5–6 with sulfuric acid. The resulting mixture was heated at 80°C for 2 h. After that, the mixture was cooled to room temperature, filtered, washed with distilled water, and dried at 105°C . This trimer microcapsules powder was further used.

A schematic illustration of preparation procedure of trimer microcapsules is shown in Scheme 2.

Characterization of trimer and trimer microcapsules

FTIR spectroscopy

The IR spectra were measured on a NEXUS-470 FTIR (Nicolet) spectrophotometer in the range $4000\text{--}600\text{ cm}^{-1}$ at a resolution of 0.5 cm^{-1} . Samples were ground and mixed with KBr to form pellets.

$^1\text{H-NMR}$ spectroscopy

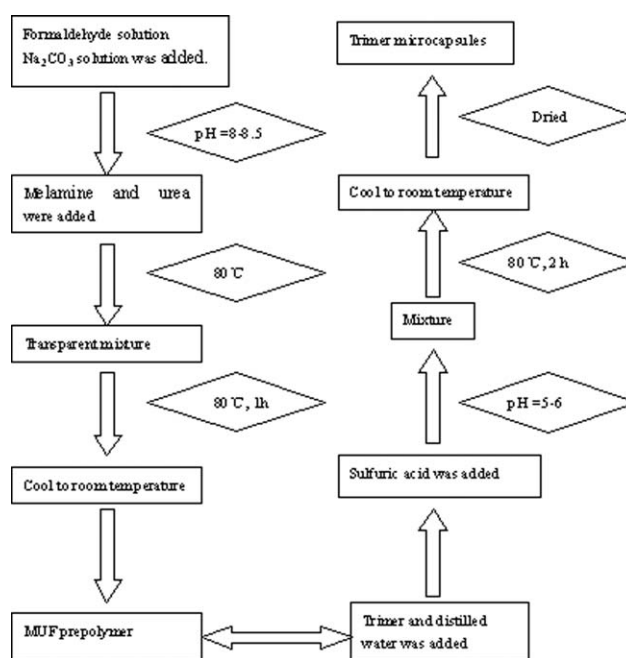
The $^1\text{H-NMR}$ spectra were recorded on a Bruker ARX-400 spectrometer using deuterated acetone as solvent and tetramethylsilane as internal reference.

Limiting oxygen index (LOI)

The LOI value is the minimum amount of oxygen in oxygen-nitrogen mixture required to support combustion over 3 min or till specimen is consumed for more than 5 cm from the top. LOI values were determined in accordance with ASTM D2863-70 by means of a General Model HC-1 LOI apparatus. The results are given in Table I.

Vertical burning test

Vertical burning tests were conducted on a vertical burning test instrument (CZF-2-type) with sheet dimensions of $130 \times 13 \times 3\text{ mm}$ according to ASTM D3801.



Scheme 2 Preparation procedure of trimer microcapsules.

TABLE I
Flame Retardant Properties of EP Containing Different Contents of Microcapsules

Sample No.	Microcapsules (%)	P, Wt (%)	N, Wt (%)	LOI (%)	UL 94 rating
EP-1	0	—	—	20.6	not rated
EP-2	10	0.96	1.38	24.2	not rated
EP-3	15	1.44	2.07	27.8	V-1
EP-4	20	1.92	2.76	30.2	V-0
EP-5	25	2.40	3.45	32.9	V-0
EP-6	20 (trimer)	4.20	—	28.4	V-0

Scanning electron microscopy

Trimer microcapsules were observed with a JSM-5600LV scanning electron microscopy (SEM) using 15 kV and 60 mA of electric current. The samples were gold-coated using an IB-3 Ionic sputtermeter.

Thermal analysis

Thermogravimetry (TG) and differential thermogravimetry (DTG) were carried out on a DTA-2950 thermal analyzer (Dupont) under a dynamic nitrogen (dried) atmosphere at a heating rate of $10^{\circ}\text{C min}^{-1}$. The reference material was $\alpha\text{-Al}_2\text{O}_3$.

Elemental analysis

The elemental analysis was carried out using a Carlo Ersa 1102 Elemental Analyzer.

RESULTS AND DISCUSSION

Characterization of trimer

The prepared trimer was characterized by the $^1\text{H-NMR}$ spectroscopy (Fig. 1). The peaks between 4.61 and 4.66 ppm corresponds to the $-\text{CH}_2-$ (18H, d) on the caged bicyclic phosphates. The peak of $-\text{CH}_2-$ (6H, c), which is near phosphates, was observed at 3.94 ppm.

Figure 2 shows the FTIR spectra of trimer and trimer microcapsules. Absorption of CH_2 from PEPA was observed at 2989 and 2912 cm^{-1} . The peaks at 1308 and 1279 cm^{-1} were associated with the stretching mode of $\text{P}=\text{O}$ on the bicyclic phosphates and phosphates out of bicycle, respectively. The peaks at 1022 and 997 cm^{-1} can be assigned to $\text{P}-\text{O}-\text{C}$ in the phosphate. The absorptions at 850 cm^{-1} are assigned to the skeleton vibration of caged bicyclic phosphates.

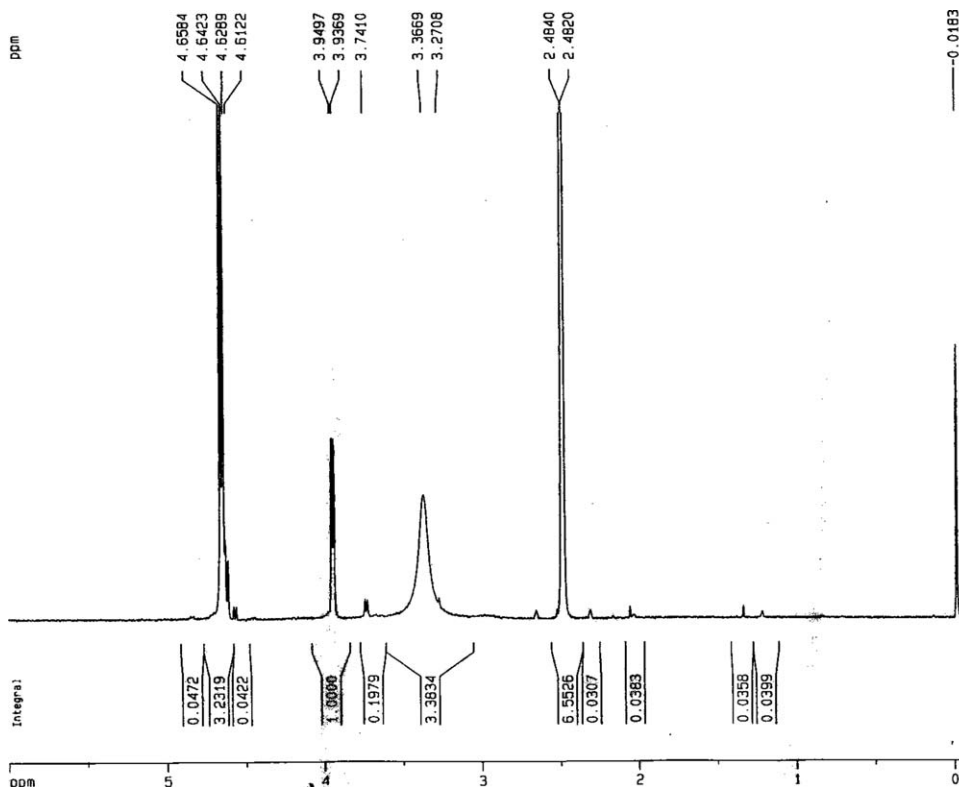


Figure 1 The $^1\text{H-NMR}$ spectra of trimer.

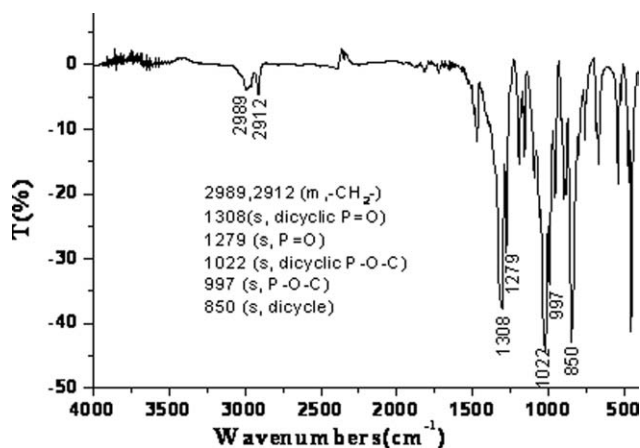


Figure 2 The FTIR spectra of trimer.

The data of trimer ($C_{15}H_{24}O_{16}P_4$) element analysis is as following:

$\omega(C, \%) = 30.28(30.84)$, $\omega(H, \%) = 4.17(4.14)$,
 $\omega(P, \%) = 21.05(21.22)$. The obtained data much correspond to theoretic data.

All these facts allowed us to conclude that the target products were synthesized successfully.

Characterization of trimer microcapsules

Figure 3 shows the FTIR spectra of trimer microcapsules. For trimer microcapsules, the typical absorption peaks include 2989 cm^{-1} , 2912 cm^{-1} (m, CH_2), 1308 cm^{-1} (s, dicyclic $\text{P}=\text{O}$), 1279 cm^{-1} (s, $\text{P}=\text{O}$), 1022 cm^{-1} (s, dicyclic $\text{P}-\text{O}-\text{C}$), 997 cm^{-1} (s, $\text{P}-\text{O}-\text{C}$), 850 cm^{-1} (s, dicycle) become broad. The absorptions of $1558\text{--}1472\text{ cm}^{-1}$ are because of the ring vibration of MEL group from the MUF resin. The absorption of 3406 cm^{-1} is because of the vibration of $\text{N}-\text{H}$. The spectrum of trimer microcapsules reveals not only well-defined absorption peaks of MUF but also the characteristic bands of trimer, indicating that the MUF resin exists in the trimer microcapsules.

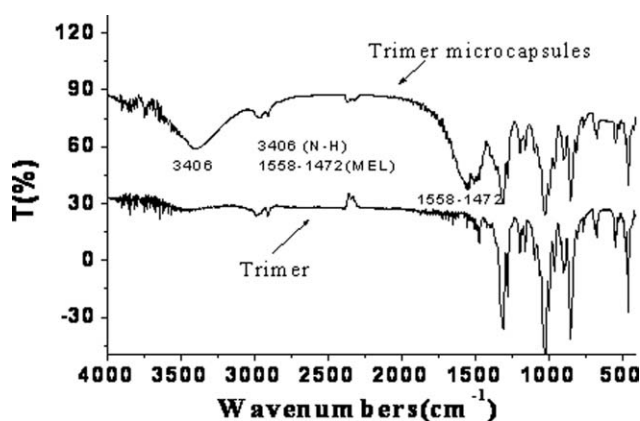


Figure 3 The FTIR spectra of trimer microcapsules.

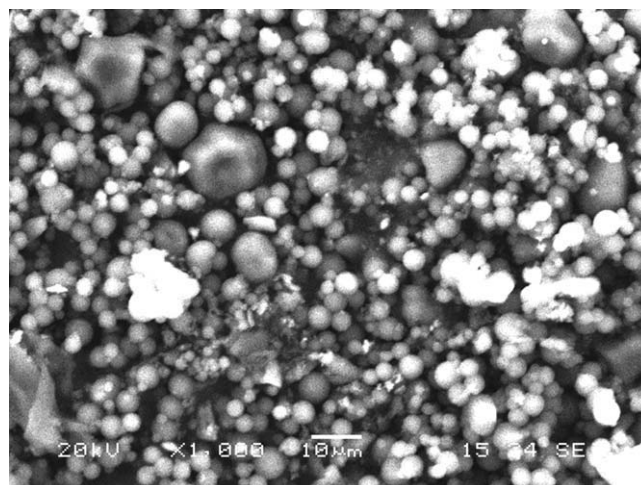


Figure 4 SEM of the trimer microcapsules.

The SEM of the trimer microcapsules (Fig. 4) show that they are almost spherical, without clear edges and corners, which shows that MUF resin penetrates through in the surface of trimer to reach and surround the trimer microcapsules. Microcapsules are sometimes slightly stuck between them. The microcapsule size is approximately between 2 and 5 μm .

Flame retardance of EP

Flame retardant properties of EP containing different content of microcapsules are listed in Table I. From these values, we can see good flame retardance of the trimer microcapsules. The EP obtained qualified for the UL 94 V-0 rating at low phosphorus contents between 1.92 and 2.40% with a LOI of up to 32.9%. For EP's containing trimer (EP-6), 28.4% of LOI and UL 94 V-0 were observed in the 20% microcapsules while much higher LOI (30.2%) was observed in the same addition for EP containing the trimer microcapsules (EP-4), although with a lower content of phosphorus (1.92%). This enhancement of flame retardance is attributed to import of nitrogen,

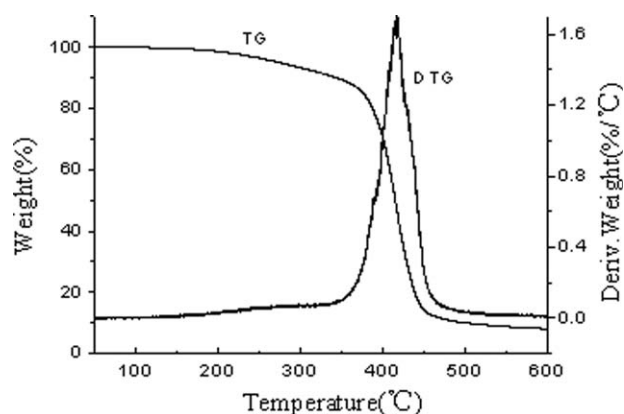


Figure 5 TG and DTG curves of EP-1.

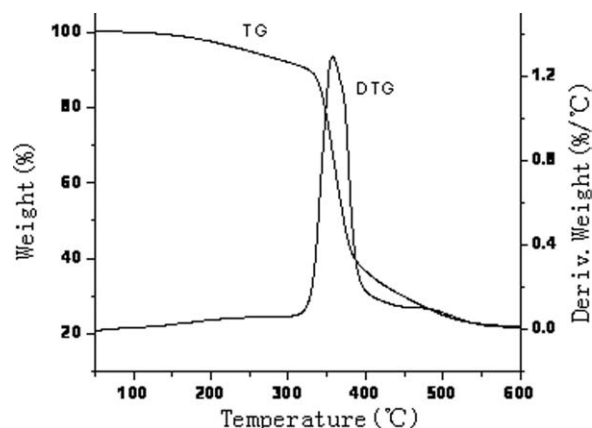


Figure 6 TG and DTG curves of EP-4.

suggested as flame retardant synergism between phosphorus and nitrogen, which is supported by Refs. 7 and 8.

Degradation of EP

When the flame retardant elements are incorporated into polymeric materials, the weight loss pattern of the polymers is altered. Phosphorus groups decompose at relatively lower temperatures to form a heat-resistant char, retarding the weight loss rate of the polymers at higher temperatures.^{8,13,14} Melamine groups decompose at temperatures above 350°C releasing noncombustible ammonia gas and forming highly thermally stable melam and melem products.^{8,15} This constitutes a critical role in flame retarding polymeric materials through condensed-phase mechanisms as well as gas-phase mechanism.

Figures 5–7 show some TG thermograms of EP investigated in this study. It can be seen that there is a main and quick decomposition stage between 300–500°C. The initial decomposition temperature (IDT), integral procedure decomposition temperature (IPDT), the weight loss (WL) at IDT, char yield (CY) at 600°C, temperatures at the maximum weight loss rate (T_{max}) and the value of the maximum weight loss rate (R_{max}) have been measured and are listed in Table II. The weight loss behavior of these EP containing flame retardant elements is found to follow the patterns discussed above. For flame retardant EP (EP-4, EP-6), compared with EP-1, the weight losses at IDT (10.9%, 11.2%), T_{max} (350°C, 365°C), and R_{max} (1.21% per °C, 1.38% per °C) are decreased,

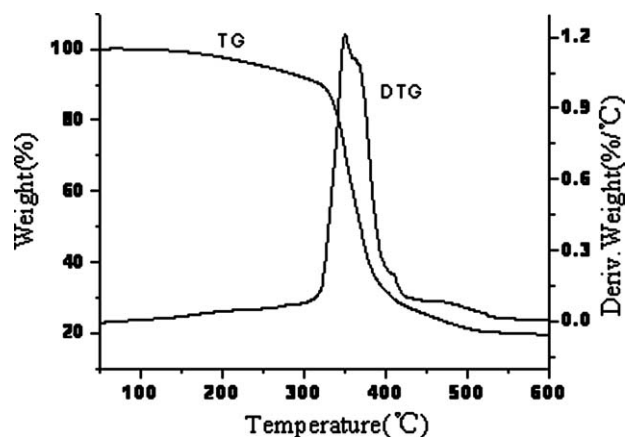


Figure 7 TG and DTG curves of EP-6.

char yields (23.8%, 19.6%) are increased. Moreover, it is especially noteworthy that EP containing the trimer microcapsules (EP-4) exhibits a good efficiency. Introducing melamine groups into EP shows significant effect on increasing char yields, because melamine groups form melam and melam based chars with very high thermal stability. Nitrogen in EP-4, used as synergist, serves as a blowing agent and char-reinforcing component, leading to the production of intumescent chars, which protect the underlying combustible substrate because of the good thermal insulating characteristics.¹⁶ Moreover, the decrease significant weight loss rates lowers the amount and rate of release of combustible products from the decomposition of EP, consequently depressing the flammability of EP.

Thermal stability of EP

The thermal stability of the EP is assessed by two parameters: IDT and IPDT. IDT indicates the apparent thermal stability of the EP, that is, the failure temperatures of the resins in processing and moulding. However, IPDT exhibits the inherent thermal stability of the resins, that is, the decomposition characteristics of the volatile composition. From Table II, phosphorus-containing EP (EP-4, EP-6) show relatively lower IDTs than do the phosphorus-free resin (EP-1), as phosphorus-groups decompose at low temperatures. Incorporation of melamine group makes it much lower. However, the existence of melamine (EP-4) exhibits higher IPDT than the EP containing only phosphorus (EP-6), exhibiting a

TABLE II
Thermal Data of the Epoxy Resins from Thermogravimetric Analysis

Sample No.	IDT (°C)	IPDT (°C)	WL (%)	CY (%)	T_{max} (°C)	R_{max} (%/°C)
EP-1	378	448	16.3	8.1	415	1.69
EP-4	328	403	10.9	23.8	350	1.21
EP-6	345	381	11.2	19.6	365	1.38

higher thermal stability. The high IPDT implies the EP potential application in highly anti-thermal coatings and thermal insulating materials.

CONCLUSIONS

We succeeded in synthesizing trimer and its microcapsules. About 20% of the trimer microcapsules are doped into EP to get 30.2% of LOI and UL 94 V-0. Comparing EP containing the trimer microcapsules, compared with EP containing only trimer, incorporating melamine groups into EP alters thermal stability and degradation characteristics, which decreases weight loss and the maximum weight loss rate. It also increases the char yield and thermal stability. In the thermal degradation of EP containing the trimer microcapsules, nitrogen serves as a blowing agent and char-reinforcing component, leading to the production of intumescent chars, which protects the underlying combustible substrate to get good flame retardance.

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