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Synthesis and effect of hyperbranched (3-hydroxyphenyl) phosphate as a curing agent on the thermal and combustion behaviours of novolac epoxy resin

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Abstract

A novel type of hyperbranched (3-hydroxyphenyl) phosphate (HHPP) with high functionality as a curing agent of epoxy resins was synthesized and characterized by FTIR, ^{1}H NMR and vapor phase osmometry (VPO). The cured epoxy resin with HHPP possessed improved glass transition temperature. The thermostability and flame retardancy of *O*-cresol novolac epoxy resin cured with different contents of HHPP were investigated by thermogravimetric analysis (TGA), limiting oxygen index (LOI) and cone calorimetry. The obtained results show that the samples containing a higher percentage of HHPP exhibit relatively lower thermostability at lower temperature while higher thermostability at elevated temperature and more char was formed compared with those containing a lower percentage of HHPP. The LOI value increased from 22.0 to 30.0 when HHPP, instead of 1,3-dihydroxybenzene, was used as a curing agent. The 25 wt% addition of HHPP in the curing agent complex effectively decreased the heat release rate and improved the char yield to the content nearly similar as those of the epoxy resin cured with pure HHPP.

Keywords: Epoxy resin; Hyperbranched polymer; Phosphorus; Flame retardancy; Thermal property; Combustion behaviour

1. Introduction

Epoxy resins have been commercially widely used in modern industries because of their advantages of low shrinkage on cure, good adhesion to substrates, superior electrical and mechanical resistance, etc. However, some disadvantages such as poor flame resistance of epoxy resins limit their usage in some fields, such as special adhesives and coatings, advanced composites in aerospace and electronic industries. It demands the development of flame retardant systems to reduce fire hazards.

Most flame retardants commercially used are inorganic compounds or halogen-based organic compounds, which can, however, give rise to toxic gases and corrosive smoke during combustion that can choke people exposed to the toxic and acidic fumes and damage costly equipment [1]. The stringent conditions set by statutory governmental regulations for the use of flame retardants demand the development of halogen-free flame retardant materials, in which phosphorus-based intumenscent systems used as substitutes for halogenated flame retardant additives seem to be most attractive. In the case of fire, the intumenscent system forms an expanding charred crust on the surface of substrate, which has a low thermal conductivity and attenuates the transference of heat [2,3]. Some new anti-flammable polymer materials have been reported in recent years [4,5].

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The general technique to prepare flame retardant polymeric materials is to blend additive-type flame retardants with resins [6] or using reactive-type flame retardants. As to the former case, the addition of a mass of flame retardant additives will adversely affect their mechanical properties. Moreover, a small quantity of flame retardants may be leached out or lost from the materials during using and aging, thus leading to the decrease of flame retardant ability [7–11].

Among various phosphorus-based flame retardants, triphenyl phosphate (TPP) is well known to be one of the most effective flame retardants for many polymers. It was reported that TPP could generate phosphoric acid during thermal degradation, and the reaction among phosphoric acids, in succession, takes place to give rise to pyrophosphoric acid, which acts as a heat transfer barrier in condensed phase [12]. It has been also proved that reactive-type flame retardants as components of resins are more effective in fire retardant behaviour compared with those as additives incorporated into resins [13]. However, as phosphate groups in polymeric chain can increase the flexibility of the segments, the glass transition temperature (T_g) of the polymer will decrease with the introduction of phosphate group. To maintain, or even improve, the T_g of epoxy resin cured by phosphate-containing curing agent, hyperbranched (3-hydroxyphenyl) phosphate (HHPP) was designed and used. The highly branched structure provides the compound with high functionality and rich phosphorus groups.

Generally, hyperbranched polymers are synthesized with multifunctional monomers, mostly AB_2 type monomers [14]. Another kind of products described as $A_2 + B_3$ type hyperbranched polymer, which are obtained from the reaction of di- and trifunctional monomers, were designed by Fréchet and coworkers [15]. The obtained resins have high degrees of branching, leading to multifunctional end-groups.

In this work, HHPP was synthesized with 1,3-dihydroxybenzene and phosphoryl trichloride by $A_2 + B_3$ reaction mode. The reaction process was monitored by FTIR and the final product was characterized by ^{1}H NMR. The thermal behaviour and flame retardancy of novolac epoxy resin cured with HHPP was investigated by TGA, LOI and cone calorimeter measurements, respectively.

2. Experimental

2.1. Materials

Ethyl alcohol, 1,3-dihydroxybenzene (DHB), sodium sulfate and triphenyl phosphine as a curing accelerator were used as received. Phosphoryl trichloride ($POCl_3$) and triethylamine (TEA) were distilled prior to use. All chemicals mentioned above were purchased from Shanghai First Reagent Co., China. *O*-cresol novolac epoxy resin (F44, EEW = 227 g/eq) was obtained from Blue Star New Chemical Materials Co., Ltd, China.

2.2. Synthesis of HHPP

34.940 g (0.318 mol) DHB was added to a 500 ml three-necked flask equipped with a reflux condenser and an over-head mechanical stirrer, and heated to 120 °C under a dry nitrogen atmosphere. Then 19.431 g (0.127 mol) $POCl_3$ was added dropwise into the flask after DHB was melted. The evolution of HCl was detected immediately by test paper. The reaction mixture was further heated to 135 °C and maintained for 24 h with continuous stirring. After that, ethyl alcohol was added into the resultant as a solvent, and then the freshly distilled triethylamine was added dropwise into to neutralize the residual HCl until no white smoke was observed. The formed triethylamine hydrochloride salt was removed by filtration, and then the solvent was distilled out. The obtained product was washed with water until the peaks around 2700 cm^{-1} in the FTIR spectrum disappeared. The obtained product was dried under vacuum at 90 °C to a constant weight. IR (NaCl): 1236, 1130 and 993 cm^{-1}, stretching vibration of P–O–Ph; 1270 cm^{-1} stretching vibration of P=O; 3500–3200 cm^{-1}, stretching vibration of Ph–OH. ^{1}H NMR (400 MHz, CD_3COCD_3) (ppm): 6.7–7.5 (Ph–**H**), 3.3 (–**OH**), 2.05 (CD_3COCD_2**H**).

2.3. Curing of epoxy resins

The mixtures of HHPP with DHB in the ratios of 0/100, 25/75, 50/50, 75/25, 100/0 were used as combined curing agents. F44 was mixed separately with above complexes at 100 °C. 0.2 wt% triphenyl phosphine (total amount of HHPP and DHB) was added to each formulation as a curing accelerator [16]. The mixtures were poured into hot aluminum molds, and then thermally cured at 130 °C for 60 min, following by 170 °C for 180 min and 200 °C for 180 min. The cured products were denoted as $HHPP_{100}/DHB_0$, $HHPP_{25}/DHB_{75}$, $HHPP_{50}/DHB_{50}$, $HHPP_{75}/DHB_{25}$, and $HHPP_0/DHB_{100}$, respectively.

2.4. Measurements

FTIR spectra were recorded with a Nicolet MAGNA-IR 750 spectrometer. ^{1}H NMR spectrum was recorded with an AVACE 400 Bruker spectrometer using CD_3COCD_3 as a solvent. DSC thermograms were recorded with a TA Shimadzu DSC-50 instrument at a heating rate of 10 °C/min under nitrogen atmosphere. TGA was carried out on a Shimadzu TG-50 instrument at a heating rate of 10 °C/min in air. The limited oxygen index (LOI) values were measured on a ZRY-type instrument (made in China) on sheets of 120×60×3 mm^3 according to the standard "oxygen index" test ASTM D2863, each sample was tested for three times, and the average value was defined as LOI value. Vapor phase osmometry (VPO) measurement was performed on a QX-08 apparatus at 35 °C, and acetone was used as a solvent.

Cone calorimeter (Stanton Redcroft type, England) was used to measure the combustion behaviours of the cured samples under a heat flux of 35 kW m^{-2} according to the ASTM E-1356-90 standard.

3. Results and discussion

3.1. Synthesis of HHPP

In this study, the synthesis of HHPP was performed by starting from DHB and phosphoryl trichloride in the ratio of 2.5:1, which is presented in Fig. 1. The reaction process was monitored by FTIR, as shown in Fig. 2. As the reaction between $POCl_3$ and DHB proceeded, the distinctive absorption around 1300 cm^{-1} corresponding to the stretching vibration of P=O in $POCl_3$ decreases gradually until disappeared completely after 24 h reaction. The acid value of the final product was measured to be lower than 3 mg KOH/g by titration, which implies that almost all phosphoryl chloride groups have been consumed during the reaction. The number average molecular weight measured by VPO is 4000 g mol^{-1}, and the ^{1}H NMR spectrum (Fig. 3) shows that all the distinct peaks can be assigned to the hydrogen in HHPP.

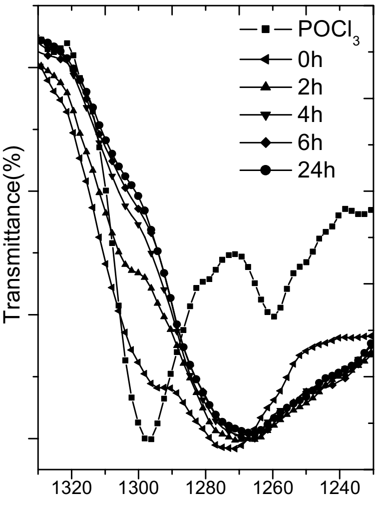

Fig. 2. FTIR spectra of the reactants during the reaction.

3.2. Thermal properties

DHB was selected as a control compound to study the contribution of phosphate group of HHPP to the thermal behaviour and flame retardance, as it has similar hydroxyphenyl structure with HHPP while the main structural difference between them is the presence of the phosphate structure in HHPP. The curing processes of F44 with HHPP and DHB determined from differential scanning calorimetry (DSC) as the traces of reactions are shown in Fig. 4, respectively. The different exothermic peaks and T_gs of these two systems are obtained.

T_g is a very important parameter for epoxy resins and epoxy matrix composites. It varies widely with the structures, molecular weights and other thermodynamic parameters of the polymers, such as intermolecular force and chain flexibility [17]. It has been reported that incorporating phosphate-containing compounds in epoxy chains would decrease the T_gs compared with those of their phosphorus free counterparts. It is because

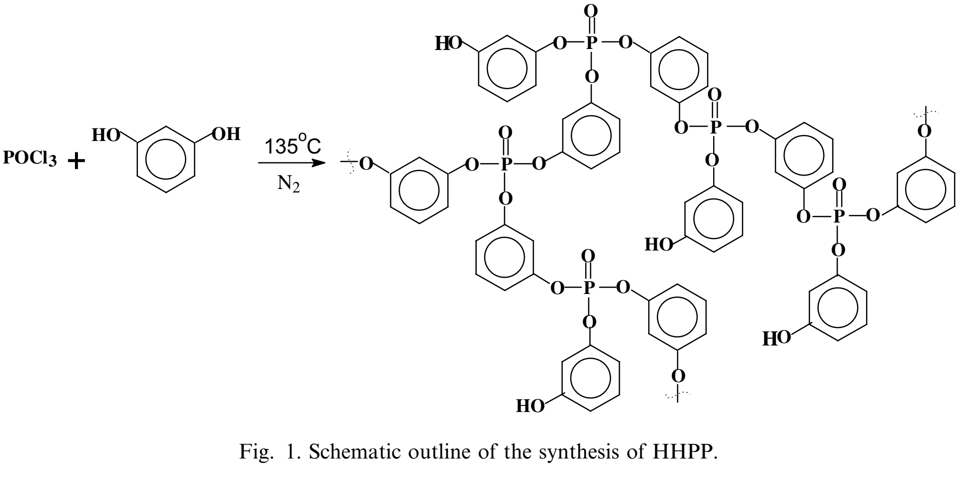

Fig. 1. Schematic outline of the synthesis of HHPP.

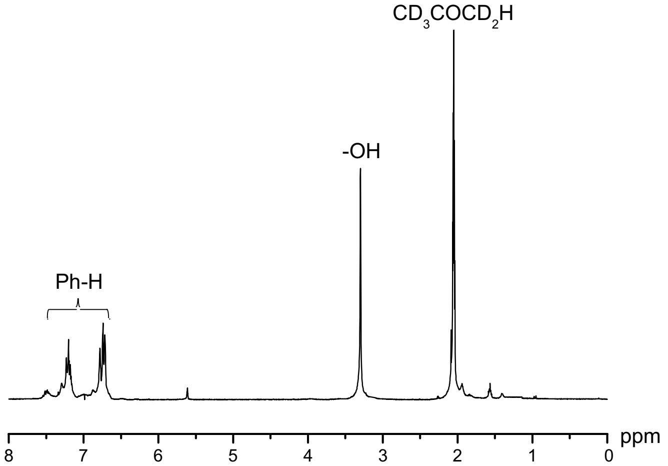

Fig. 3. ^{1}H NMR spectrum of HHPP.

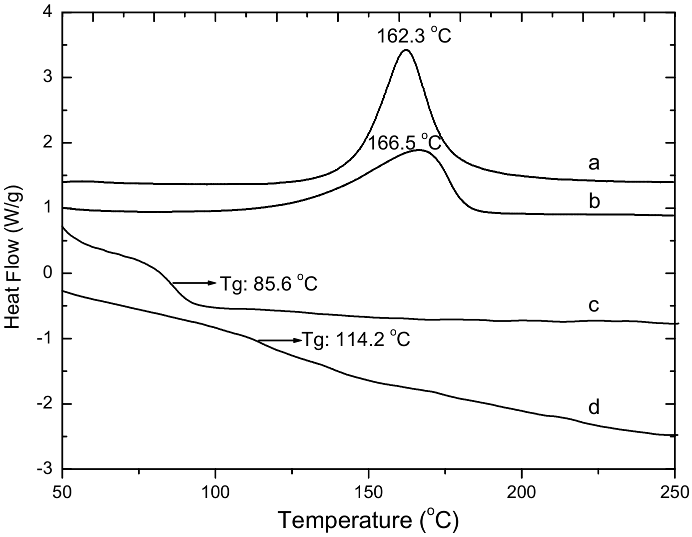

Fig. 4. DSC thermograms of (a) curing reaction of HHPP/F44, (b) curing reaction of DHB/F44, (c) cured product of DHB/F44, and (d) cured product of HHPP/F44.

that the flexible –P–O– groups in the backbones of the cured polymers decrease the rotational barrier [18]. However, an opposite tendency in T_gs of the HHPP and DHB-cured epoxy resins was observed in the present study (Fig. 4). The T_g of the cured film of epoxy resins with HHPP was found to be higher than that cured with DHB. This result might be understood by the effect of crosslinking density, which can increase the T_g of the cured film [19]. The equivalent ratios of 1:1 for phenol to epoxy groups are used in the epoxy resins cured with HHPP and DHB. However, HHPP is a multifunctional compound which acts as crosslinker, resulting in a much higher crosslinking density. The effect of crosslinking density to T_g is greater than that of chain flexibility, leading to a higher T_g of the epoxy resin cured with HHPP.

The thermal degradation behaviours of F44 cured with different ratios of HHPP and DHB were further investigated by TGA in air. Fig. 5 shows the thermogravimetric traces of these products. The TGA data as the degradation temperatures at different weight losses together with the final char yields at 800 °C are listed in Table 1. It can be clearly seen that the temperature at 5 wt% loss decreases with increasing the ratio of HHPP to DHB. This result can be explained by the fact that the resin with higher phosphorus content has less thermo-

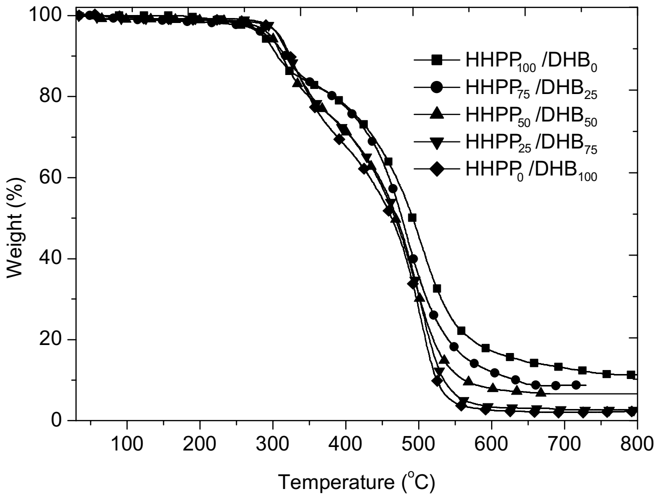

Fig. 5. TGA thermograms of the cured F44 with different ratios of HHPP and DHB.

Table 1
Thermogravimetric data of the cured F44 with different ratios of HHPP and DHB

Materials	Temperature recorded at specific weight loss (°C)			Residue (%), 800 °C
	5%	25%	50%	
HHPP	240	387	619	23.0
$HHPP_{100}/DHB_0$	286	415	492	11.3
$HHPP_{75}/DHB_{25}$	291	412	477	8.7
$HHPP_{50}/DHB_{50}$	297	380	468	6.6
$HHPP_{25}/DHB_{75}$	307	380	470	2.6
$HHPP_0/DHB_{100}$	309	366	463	2.3

stability at the beginning of thermodegradation because the O=P—O bond is less stable than –C–C– bond [20]. The degradation of phosphate group at relatively low temperature range plays an important role in enhancing flame retardance, because the degraded products of phosphate unit have great contributions to the formation of phosphorus-rich crosslinking carbonization char at high temperature. The char formed acts as a protective layer on the polymer surface against heat and oxygen diffusion, and prevent the further decomposition of epoxy resins [19,21,22]. As a result, the epoxy resin cured with higher content of HHPP is more stable at high temperature and yields more char after degradation. This can be verified by the data in Table 1, which show that the temperature of 25% weight loss increases with increasing the content of HHPP. The same trend can be seen from the temperatures of the samples with 50% weight loss. The final char yield increases from 2.3% of $HHPP_0/DHB_{100}$ to 11.3% of $HHPP_{100}/DHB_0$. Consequently, the high char yield limited the production of flammable gases, thus decreased the exothermicity of pyrolysis reactions and inhibited the thermal conductivity of the burning materials, so that leveled up the flame retardancy of the epoxy resins.

3.3. Combustion behaviour

The flammability of the cured phosphorus-containing epoxy resins has also been assessed by the LOI test, and the results are given in Table 2. It can be seen that the incorporation of 25 wt% HHPP in the curing agent complex increased the LOI from 22 of that cured with pure DHB to 27, which is almost the same as the value, 27.5, of the resin cured with 50 wt% HHPP. The LOI further increased to 30.0 when the ratio of HHPP was raised to 75 wt% in the curing agent complex. The increase of LOI is nonlinearly with the content of HHPP, which is because that 25 wt% HHPP in the curing agent complex is enough to form crosslinking char as a protective layer on the polymer surface during degradation.

As well known, the LOI test is a useful tool to rank the flammability of a material in a small-scale fire, while cone calorimetry is regarded as one of the most effective bench-scale methods to measure many important parameters of a real fire. The results, such as ignition time (T_{ig}), heat release rate (HRR) and mass loss rate, correlate well with those obtained from a large-scale test.

The results obtained by cone calorimeter for the samples are shown in Figs. 6 and 7, and the data are listed in Table 2. T_{ig} is the time required for the entire surface of a sample to burn with a sustained flame, which can be measured from the onset of a HRR curve. From Table 2, the T_{ig} decreases gradually with increasing the content of P. The result indicates that phosphate unit is thermally unstable, and degrades at low temperature, which makes the samples with more P content has

Table 2
Data from the cone calorimetric measurements

Sample	T_{ig} (s)	Peak HRR (kW m^{-2})	Avg. HRR (kW m^{-2})	THR (MJ m^{-2})	Avg. EHC (MJ kg^{-1})	Char yield (%)	LOI
$HHPP_0/DHB_{100}$	125	724	163	94.0	24.0	22.3	22.0
$HHPP_{25}/DHB_{75}$	89	369	114	64.7	22.1	41.2	27.0
$HHPP_{50}/DHB_{50}$	83	389	96	54.7	20.9	43.7	27.5
$HHPP_{75}/DHB_{25}$	79	290	100	51.4	20.4	44.6	30.0
$HHPP_{100}/DHB_0$	67	443	97	38.6	18.6	47.2	30.0

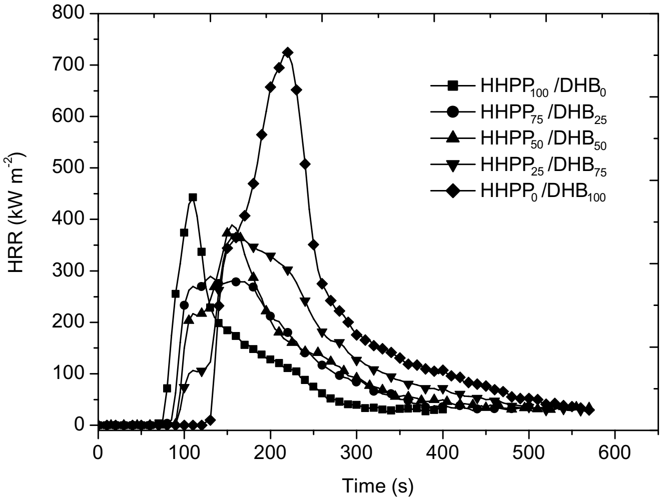

Fig. 6. HRRs of the cured F44 with different ratios of HHPP and DHB.

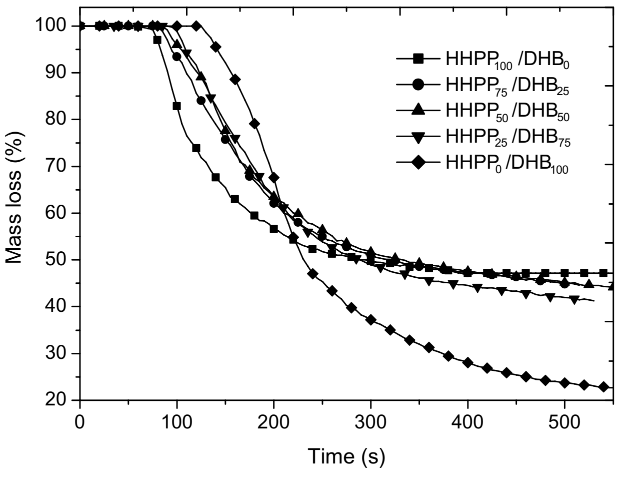

Fig. 7. Mass loss of the cured F44 with different ratios of HHPP and DHB.

shorter T_{ig} under a constant heat flux. HRR during combustion is generally considered to be one of the most important parameters for characterizing the intensity of a fire, which in turn determines other parameters such as the mass loss rate and the fire growth rate [23]. The peak value of HRR represents the maximum intensity of a fire. The HRR of the samples versus burning time are shown in Fig. 6. The peak and avg. HRR values of all phosphorus-containing samples are significantly smaller than those of phosphorus-free resin, which are also listed in Table 2. Meanwhile, the total heat release (THR) and average effective heat of combustion (EHC) decrease gradually with increasing the phosphorus content. In summary, it is obvious that the higher the phosphorus content of a epoxy resin system, the less the heat released, because the shortening of burning time can improve the flame retardancy of epoxy resins. However, it can be seen that the incorporation of a small quantity of HHPP effectively decreases the maximum intensity of a fire, but it cannot further decrease by increasing the HHPP content although less heat was released. This is because that 25 wt% of HHPP in the curing agent mixture is enough to form complex crosslinking char as a protective layer on the polymer surface during degradation.

Fig. 7 shows the mass losses of the samples versus combustion time. Similar as the results obtained from TGA, the sample containing higher phosphorus content lost its weight earlier and faster during combustion, and spent less time to reach a constant level of char yield. However, there is a significant difference compared with the results obtained from TGA and cone calorimeter measurements. The degradation process observed by TGA is more distinct as the heating rate is much lower than that in cone calorimeter where the obtained result correlates better with that in a real fire. From Table 2, the char yield for $HHPP_{25}/DHB_{75}$ measured by cone calorimeter is as high as 41.2%, which is nearly as double as that of epoxy resin cured with pure DHB. It is interesting that the char yields of the samples only increase slightly with increasing the phosphorus content, even for the resin cured with pure HHPP. This is because that, as mentioned above, 25% HHPP is enough to make hydrocarbon crosslink efficiently in a real fire, which leads to a high char formation. This result further demonstrates the above explanation on the reason of low HRR for $HHPP_{25}/DHB_{75}$.

4. Conclusions

A novel hyperbranched (3-hydroxyphenyl) phosphate with high functionality has been synthesized, which act as a curing agent of epoxy resin and can improve the T_g of the final product.

The cured novolac epoxy resin with higher HHPP content is less stable at the beginning of degradation, and the degraded phosphate groups make a great contribution to form crosslinking char as a barrier to protect the material from further burning. The presence of 25 wt% HHPP in the curing agent complex for the curing of F44 is sufficient to form crosslinking char, decrease the heat release rate and improve the char yield to the level similar as those of F44 cured with pure HHPP.

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