Research Article

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Synthesis of a novel modified chitosan as an intumescent flame retardant for epoxy resin

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Abstract: According to the concept of fire life cycle assessment (LCA), a new type of intumescent flame retardant was designed and synthesized by chemically bonding chitosan, phosphorus pentoxide and melamine. The resultant compound, chitosan ethoxyl melamine phosphate (CEMP), was characterized by FTIR, ^1H NMR, ^{31}P NMR, XRD and SEM. The performance of CEMP and organic montmorillonite (OMMT) was evaluated in the substrate of epoxy resin (EP) with limited oxygen index (LOI), UL-94, cone calorimetric test (CCT), TGA and TG-IR. As a result, intumescent flame retardant EP (EP3) containing 30.6% LOI and V-0 rating was prepared by adding 3 wt% OMMT and 15 wt% CEMP. The CCT results indicated that CEMP and OMMT reduced the peak of heat release rate (PHRR) to about one fourth that of pure EP and total heat release (THR), 1/2. Decomposition of EP and EP3 was traced from 100 to 600°C by TG-IR.

Keywords: chitosan, OMMT, intumescent flame retardant, EP, chemical bond

1 Introduction

It is undoubtable that we have been living in the times of synthetic materials since the first synthetic fiber, Nylon, was born in Dupont lab in 1940s. Various synthetic materials that mostly originated from the paraffin have

improved our life greatly to be more comfortable and convenient. However, meanwhile, the flammability of synthetic materials has caused lot of trouble to the human being. Every year, millions of lives are lost in the fire incidents. Hence, great efforts and endeavors have been made to develop new technology and new compounds to improve the flammability of synthetic materials. However, nowadays the main issues in the development of a new flame retardant are not limited in the range of technology, but rather in the field of environmental protection, namely how to relieve the environmental stress (1–5). The reason may date back to the last century. Since the 1960s, flame retardants (FRs) are invented and applied in synthetic materials, i.e., chemicals enable to both prevent combustion and delay the spread of fire after ignition. Among them, halogen-based fire retardants are very effective in reducing fire risk, i.e., the probability of occurrence of a fire, but there is a high fire hazard, that is, the probability of producing toxic, corrosive, obscuring smokes while performing the fire retardant action or when involved in a fully developed fire, beyond flashover, when the fire can no longer be extinguished (6–11). The halogen radicals access the vapor of combustion zone to quench the active radicals of H and OH, thereby stopping the oxidation reaction, and in turn preventing the heat generation (8,12).

Therefore, at the end of last century, the consumption of halogenated FRs occupied 50% of total FRs. However, in fact, the amount of FRs burnt in the incident fire is negligible. A large portion of FRs is finally disposed of as wastes accompanying its host goods of synthetic materials. Leachate of FRs from wastes and its derivatives created by various reactions in the environment are hazardous to animals and plants. Therefore, poly FR became a research hot spot, which was launched by the Dow Chemical Co. in 2011. It was a butadiene styrene brominated copolymer (13,14), a stable high molecular weight, non-PBT additive that can be used in XPS and expanded polystyrene (EPS) foams (12,15–17). Anyway, a ban on the halogenated FRs boosts the

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dramatic increase in organophosphate FR consumption. Alerting the potential hazards to the environment bore a new concept of fire life cycle assessment (LCA). LCA is applied to assess the overall environmental impact throughout the life of products containing flame retardants (18–21). Besides taking into account detection and extinction issues, smoke opacity and toxicity of effluents, it focuses on safety risks induced by flame retardants during process. These flame retardants migrated from goods are induced by the exposure via skin contact, risks by inhalation of substances emitted into the atmosphere during the life of product, by emission of toxic gases during incineration and by emanation of gaseous effluents during combustion in the event of accidental fire. These risks have now become the main issues in the development of new FRs in order to achieve the required high level of protection for health and safety.

Nevertheless, phosphorus is the unique element that is comprehensively evaluated as the best composition of FRs (12,22). Radicals of phosphorus oxides may act as the halogen radicals to quench the high-energy radicals of H and OH in the gas of combustion zone. Moreover, phosphorus oxides may form polyphosphate at high temperature, which is a nonflammable shell segregating the substrate and fire (23–27). However, according to LCA requirements, FRs with a high level of protection for health and safety should be highly efficient, eco-friendly, show no migration and certainly be nontoxic. Hence, in terms of migration, the small molecules of organophosphate compounds are first excluded from the recipes of FRs due to their migration property. Additionally, the use of inorganic phosphate salts, e.g., ammonium phosphate, should be avoided due to their water solubility, which will be leached in the life of products, thereby lowering the efficiency of FRs.

In terms of high efficiency, the technique of intumescence is a plausible one. The intumescent agent produces nonflammable and nontoxic gas, usually nitrogen, at high temperature. Nitrogen gas expands and volatilizes at the expense of heat to lower the temperature. Meanwhile, nitrogen gas may dilute the concentration of flammable reagents. Besides, an additional effect is that nitrogen gas can foam the char and polyphosphate layer. Acidic phosphorus compounds created at high temperature catalyze the dehydrogenation reaction of polyolefin to form the nonflammable char. Sponge like char and polyphosphate layer are more effective at segregating substrate and fire, and weaken the transportation of mass and energy between the substrate and fire. Certainly, adding mineral particles is always an economic, eco-friendly and effective way to improve the efficiency of FRs.

The main function of mineral particles in FRs is to dilute the concentration of polyolefin in the substrate. The lower concentration of decomposable polyolefin, the lower the concentration, or the slower the supply rate of flammable substances is. Therefore, the mineral particles are effective at suppressing the occurrence of smoke due to the full combustion. At last, a readily neglected factor is the compatibility of composition in the intumescent FR (IFRs), which severely impacts the efficiency of IFRs (28,29). It is said, if the intumescent agent and phosphorus compounds were simply mixed into substrate, the efficiency of FRs would be diminished due to the nonuniformity of components' dispersion. Finally, in terms of eco-friendly aspects, the natural polymers are the best, e.g., cellulose, chitosan and alginate.

By far, a lot of intumescent flame retardants have been explored. However, few of them are satisfactory to the LCA requirements. For example, Fang *et al.* (30) synthesized polyhexamethylene guanidine phosphate and then physically mixed ammonium polyphosphate (PHMGP-APP) as the IFRs for cotton fabric. Chen *et al.* (31) used polyethylenimine (PEI) as intumescent agent to fabricate IFRs by physically mixing ammonium polyphosphate (APP) and fluorinated-decyl polyhedral oligomeric silsesquioxane (F-POSS). In these cases, the small molecule of phosphate compound was used. Hassan *et al.* (32) explored a chitosan-based IFR. The chitosan was first phosphate esterified, and then utilizing the surplus P-OH to form melamine phosphate salt. In this case, melamine ions will be easily leached during the life of products. Most recently, Borreguero *et al.* (33) developed a new method to synthesize IFR for the polyurethane foam. In this method, diethyl-*N,N*-bis(2-hydroxyethyl) aminomethyl phosphonate (Fyrol-6) was employed as initiator to conduct the ring opening polymerization of epoxy resin. The aminophosphate polyol exhibited good performance in the flame retardant polyurethane (PU) foam. The char residue increased from 7.79 to 22.13 wt% with the increase of polyol from 25 to 50 pph. Amazingly, Malucelli *et al.* (34) utilized the phosphoric acid in DNA to synthesize SiO₂@DNA as IFR for cotton fabric. Reviewing these literatures, it can be found that LCA is gradually guiding the development of IFRs.

Chitosan is a natural material abundant in the nature. It has been widely used as a carbon resource in IFRs because it is a type of polyol (35–37). However, so far to our best knowledge, the chitosan-based IFRs satisfying LCA requirements have not been found. Therefore, in this paper, a new type of chitosan-based IFR will be prepared by covalently bonding melamine into chitosan via phosphoric covalent bridge, chitosan

Scheme 1: Synthetic route of chitosan ethoxyl melamine phosphate (CEMP).

ethanol melamine phosphate (CEMP). The synthetic route of CEMP is shown in Scheme 1. Ethyl phosphoric ester (EPA) is also introduced to hydrophobilize the polymer, so as to increase the compatibility with polyolefins. Such a chemical structure is anticipated to be highly efficient due to the integrity of functional groups, no migration in the life of products, no toxicity and eco-friendly nature. The flame retardancy will be evaluated with epoxy resin (EP), which is the main material of glass composites.

acid was bought from Aladdin Co. Ltd (Shanghai, China). Organic montmorillonite (OMMT, average particle size 70–80 nm) was purchased from Zhejiang Fenghong New Material Co. Ltd. Melamine was supplied by Maclean Biotechnology Co. Ltd. Ethanol, methanol, diethyl ether, acetone, toluene, pyridine and *N,N*-dimethylformamide were all provided by Sinopharm Chemical Reagent Co. Ltd (Shanghai, China). These reagents were of analytical grade and directly used without further purification.

2 Experimental

2.1 Materials

Chitosan (CS, viscosity 50–800 mPa s, degree of deacetylation 80–95%) was supplied by Zhengzhou Wanbo Chemical Products Co. Ltd (Henan, China). Epoxy resin (EP, DGEBA, commercial name: E-51, epoxy value: 0.51) and curing agent (polyether amine) were purchased from Hefei Jiangfeng Chemical Industry Co. Ltd (Anhui, China). Methyl sulfonic

2.2 Synthesis of CEMP

CEMP was synthesized according to the literature (38–42). At first, chitosan (CS, 2.0 g) was immersed in methyl sulfonic acid (12 mL) in a 100 mL four-necked round-bottomed flask equipped with a magnetic stirrer and a reflux condenser. The flask was placed in an ice-water bath under an inert atmosphere of N_2 . Then, phosphorus pentoxide (P_2O_5 , 2.0 g) was slowly added under stirring for 3 h. The obtained phosphorylated chitosan (PCS) was washed successively with diethyl ether, acetone

and methanol in order to remove the unreacted P_2O_5 and dried in a vacuum oven at 60°C for 12 h. Second, PCS (2.0 g) was dispersed in about 5 mL toluene in a 100 mL four-necked round-bottomed flask and subsequently thionyl chloride (1.0 mL) was added dropwise for 2 h under nitrogen atmosphere at 40°C. After ethanol was added, the reaction took place for 2 h. Washed with toluene and ethanol, the product was then dried in a vacuum oven at 60°C for 12 h. Third, acetylated chitosan (ACS) (2.0 g) and melamine (2.0 g) were charged into a 100 mL four-necked round-bottomed flask containing 20 mL of *N,N*-dimethylformamide (DMF) and 10 mL of the base pyridine. The reaction was carried out at 140°C for 4 h under nitrogen atmosphere. CEMP was obtained by washing the product with DMF and methanol.

2.3 Preparation of flame retardant EP

The recipe of flame retardant EP is shown in Table 1. It should be remarked that OMMT is usually used as inherent flame retardant additive because of its good fire resistant features (42,43), so OMMT was also used in this paper. Normally, the steps for preparing a flame retardant epoxy resin were as follows (44,45): at room temperature and pressure, the epoxy resin after adding a curing agent, CEMP and OMMT were completely blended with a small mixer according to the mass ratio of each component and then were injected into a custom-sized polymethyl methacrylate (PMMA) mold. Then the samples were put in a vacuum oven to defoam and polymerize at 60°C for 24 h. Finally, the obtained EP spline after drying was corrected by removing the corner burrs.

2.4 Characterizations

CEMP was characterized by FTIR spectroscopy (Nicolet 6700, USA) using KBr disk and the scanning speed was 32 s^{-1} . ^1H and ^{31}P NMR was conducted on the NMR

spectrometer (AVANCE III HD 600 MHz, Bruker Instrument Corp., Germany) using dimethyl sulfoxide (DMSO-d_6) as the solvent. Scanning electron microscopy (SEM, FEI Inspect F50, USA) was used to analyze its surface morphology and structural features of the modified product after the sample was sprayed with gold. The X-ray diffraction (XRD, Hitachi Instrument Corp., Japan) was performed on Ultima IV to analyze the crystal form of the product. The thermal stability of the sample was analyzed by thermogravimetry (TG, TG209 F3, Netzsch Instrument Corp., Germany) and the test temperature range was 25–800°C with a heating rate of 20°C/min under nitrogen atmosphere. The limiting oxygen index (LOI) values were measured on a JF-3 oxygen index meter from Jiangning Analysis Instrument Company. According to GB/T 2406-2008, the specimen dimensions were $100 \times 6.5 \times 3\text{ mm}$. Vertical burning test (UL-94) was carried out on a CFZ-2-type instrument (Jiangning Analysis Instrument Company, China) and the specimens used for UL-94 were of dimensions $130 \times 12.7 \times 3\text{ mm}$. Cone calorimetry (FTT2000, Suzhou Phoenix Instrument Company, China) was used to investigate the combustion behavior of flame retarded EP. According to ISO 5660, the size of samples was $100 \times 100 \times 3\text{ mm}$ and the heat flux was 35 kW/m. Thermogravimetry-infrared spectrometry (TG-IR) of flame retarded samples was measured on TG 209 F3 thermogravimeter (Netzsch Instrument Corp., Germany) which was interfaced to the Nicolet WAS10 FTIR spectrophotometer (Nicolet 6700, USA) to track and detect small molecules released during thermal degradation and the test temperature range was 25–600°C with a heating rate 20°C/min in an inert atmosphere. The morphology of char residue was analyzed by the FEI Inspect F50 SEM instrument (FEI, USA).

3 Results and discussion

3.1 FTIR analysis

In view of the previous studies on the attribution of the infrared spectrum of chitosan, which was a product of the de-*N*-acetylation of chitin and its degree of de-*N*-acetylation and crystallization was different, the infrared spectrum was slightly different (46,47). The FTIR mainly has two large spectral regions: the high frequency region with the wavenumber between 4,000 and $1,330\text{ cm}^{-1}$ is the characteristic frequency region. The low frequency

Table 1: Mass ratio of each component

Samples	EP (%)	CEMP (%)	OMMT (%)
EP	100	0	0
EP1	92	5	3
EP2	87	10	3
EP3	82	15	3

Figure 1: FTIR spectra of CS, PCS, ACS and CEMP.

region with a wavenumber of $1,330\text{--}500\text{ cm}^{-1}$ is referred to as a fingerprint region. In this paper, the infrared spectra of CS, PCS, ACS and CEMP were studied. It can be seen from Figure 1 that the CS had a strong absorption peak at $3,421\text{ cm}^{-1}$, which can be classified as the overlapping stretching vibration absorption peaks of O–H and N–H. The peak at $2,940\text{ cm}^{-1}$ belonged to the asymmetric stretching vibration absorption of C–H. The peak at $1,630\text{ cm}^{-1}$ is ascribed to the amide I stretching absorption. There were various peaks in the fingerprint area and the absorption peaks from $1,046$ to $1,160\text{ cm}^{-1}$ coincided with the C–O stretching vibration absorption. There was a ring stretching vibration absorption peak at around 854 cm^{-1} and the out-of-plane bending of O–H was shown at 645 cm^{-1} . After phosphorylation, the spectrum of PCS hardly changed. There was a new peak that appeared at $1,647\text{ cm}^{-1}$ due to the formation of NH_3^+ . An absorption peak that appeared at $1,208\text{ cm}^{-1}$ may be a P=O stretching vibration absorption peak. It may be caused by P–O single bond stretching vibration absorption at $1,070\text{ cm}^{-1}$. There was a strong absorption peak at 778 cm^{-1} due to the in-plane bending of the P–O single bond. For the ACS after further acid chloride chlorination, it can be seen from Figure 1 that the absorption peaks of PCS and ACS showed no significant change. The absorption peak became stronger at 568 cm^{-1} , indicating that it may be a stretching vibration absorption peak of P–Cl. As for CEMP, there was a stretching vibration absorption peak of N–H on melamine at $3,135\text{--}3,498\text{ cm}^{-1}$. The peaks at $1,627$, $1,561$ and $1,417\text{ cm}^{-1}$ were characteristic absorption peaks of the triazine ring. The absorption peak of P–Cl disappeared at 568 cm^{-1} and the above infrared characterization results can preliminarily determine that the target product probably has been synthesized.

3.2 ^1H and ^{31}P NMR

In order to analyze the structure of the modified product, the ^1H and ^{31}P NMR of CS, CEMP was performed, respectively. As shown in Figure 2, there are many peaks corresponding to the various protons of hydroxyl groups and methylene groups in CS. However, when CS was esterified, only a broad peak was left in CEMP. The peaks at 2.50 and 3.36 ppm belonged to the absorption peak of solvent $\text{d}_6\text{-DMSO}$. Two peaks at 6–7 ppm were characterized by the protons of NH_2 . It is clear that in CS, two peaks were ascribed to the coupling of adjacent methylene proton, whereas in CEMP, the two peaks of CS disappeared and a new peak at 6.35 ppm appeared. The peak at 6.35 ppm should be assigned to melamine. In order to further confirm the structure of reaction products, ^{31}P NMR of PCS and CEMP was carried out, respectively (32,47–49). As shown in Figure 3, for PCS, the peak positions are negative, i.e., -0.17 and -1.07 ppm . These peaks are the characteristic peaks of phosphorylate esters. The peak at -1.07 ppm indicated the pure alkyl group linked to $-\text{O}-\text{P}$, while the peak at -0.17 ppm referred to the polarized alkyl group, thus showing that the chemical shift moved to the low field. According to the molecular structure of CS, it became clear that the esterified points were C-3 and C-6, respectively. In the ^{31}P NMR of CEMP, those two peaks moved to -0.68 and 0.46 ppm . This result implied that there were strong polar groups attached on phosphorus atoms. All these results implied that CEMP was prepared successfully.

3.3 SEM analysis of CEMP

In a heterophase system, the specific area of additives is fairly important to the effective mixture. The big specific area is favorable to enlarge the contact area, in turn to improve the performance of additives. As shown in Figure 4, the surfaces of various compositions used in this paper were observed with SEM. The surface of pure chitosan was relatively smooth, whereas melamine had a regular crystal form. As the phosphorylation proceeded, the porous surface gradually appeared. The surface of CEMP became rougher, which was beneficial to generate noncombustible gas and stop the combustion further. Moreover, the porous network structure facilitated the formation of a porous carbon layer in the condensed phase and showed distinct flame retardant effect (50,51).

Figure 2: ¹H NMR spectra of CS and CEMP.

Figure 3: ³¹P NMR spectra of PCS and CEMP.

Figure 4: SEM photographs of CS, melamine, and CEMP.

Figure 5: XRD graphs of CS and CEMP.

3.4 XRD analysis

It is well known that a large number of hydroxyl functional groups inside the chitosan resulted in the crystallization of CS. Therefore, the degree of crystallization is another index indirectly indicating the degree of phosphorylation (52,53). As shown in Figure 5, there were lots of sharp diffraction peaks indicating the high crystallinity of chitosan. However, for the target product CEMP, only a broad peak appeared at $2\theta = 20^\circ$. It indicated that the crystalline structure of CS was completely destroyed due to the phosphorylation. It further proved that CEMP was successfully prepared.

3.5 TG analysis of CS and CEMP

It was analyzed by TGA in order to characterize the thermal behaviors of CS and CEMP, the relative experimental data of 5%, 50% and the maximum weight loss is shown in Table 2. It was clearly observed from Figure 6 that there was a platform at about 161°C because of the water evaporation process. For pure chitosan, its mass decreased sharply with increasing temperature. At 311°C the thermal degradation weight of CS reached 50%. The

Figure 6: TGA curves of CS and CEMP.

thermal degradation process of CS tended to be gentle at 528°C . However, there was a slight downward trend at about 800°C , at this time, the residual carbon content was about 26.8%. As for the modified chitosan, the weight of CEMP was also gradually reduced to a stable stage at 161°C like CS due to insufficient drying, and then, as the temperature increased, the magnitude of the sharp decrease in mass was smaller than that of unmodified chitosan. The temperature of 50% mass loss was 369°C , which was 58°C higher than that of CS. The residual carbon content of CEMP was about 31.2% at 800°C , which was 4.4% higher than that of CS. The possible reason was that the grafted phosphate and melamine groups were first cleaved, releasing HPO and PO radical groups during the thermal degradation of CEMP, and thus the chain reaction was interrupted by combining the H and OH released from the pyrolysis of the sample. In summary, it was certified that the overall thermal stability of chitosan after the modification was improved.

Table 2: TG data of CS and CEMP

Samples	$T_{5\%}$ ($^\circ\text{C}$)	$T_{50\%}$ ($^\circ\text{C}$)	$T_{\max}$ ($^\circ\text{C}$)	Char residue at 800°C (%)
CS	161	311	528	26.8
CEMP	161	369	602	31.2

Table 3: LOI and UL-94 test results for flame retarded EP

Samples	Flame retardant ratio (%)	LOI (%)	t_1 (s)	t_2 (s)	UL-94 rating	Dripping
EP	0	20.5 ± 0.1	>30	>30	NR	Yes
EP1	8	23.8 ± 0.2	16.4	19.8	V-1	No
EP2	13	26.4 ± 0.2	14.8	16.5	V-1	No
EP3	18	30.6 ± 0.2	0.6	1.4	V-0	No

t_1 is the first ignition and t_2 is for the second. NR is no flame retardant rating.

3.6 LOI and UL-94 vertical burning tests

The performance of EP in the presence of CEMP and OMMT or not was evaluated by LOI and UL-94 vertical burning tests (44,45,54). The results are summarized in Table 3. In the absence of flame retardant, flame retardant grade of EP fell off the standard, accompanied with a heavy black smoke and severe deformation in combustion. The cotton wool was ignited by the droplets of EP. The LOI was only 20.5%. However, the addition of CEMP and OMMT greatly improved the performance of EP in combustion. As shown in Table 3, first of all, the dripping was stopped. The LOI increased from 23.8 to 30.6%, as the amount of flame retardant additives increased from 8 to 18 wt%. Meanwhile, the flame retardant grade increased from V-1 to V-0 and the time of flame combustion of EP3 after two ignitions was both less than 2 s, far below that of pure EP showing that the reaction of burning was interrupted in time and had a better self-extinguishing effect in comparison to EP without flame retardant additives.

Figure 7 shows the actual burning situation of samples after LOI and UL-94 tests. It was observed that, without CEMP and OMMT, the residue of EP completely disappeared due to dripping in the LOI test. The residue of EP containing CEMP and OMMT remained as porous char. The situation of samples was illustrated in the post UL-94 test. As shown in Figure 8, the sample of pure EP was seriously deformed and owing to smoke smudging, the surface became black. However, with the increase of CEMP, the combustion situation significantly

improved. For example, sample deformation of EP3 was hardly observed after burning. It suggested that CEMP and OMMT interrupted the combustion reaction in a quick and effective manner. Many intumescent flame retardants have been reported. Qian *et al.* (55) prepared organic/inorganic IFRs with different phosphorus/nitrogen ratios through the sol-gel process and investigated the performance of the flame retardancy of epoxy resin, where the highest LOI value was only 29.5% with 10% portion of additives and it decreased with the addition of flame retardant. Moreover, the salt easily leaked into the substrate materials, in turn to result in the difficulty of distribution, again emphasizing the importance of the polymer type. Yan *et al.* (45) synthesized pentaerythritol phosphate melamine salt (PPMS)-functionalized expandable graphite (EG), a novel mono-component, as intumescent flame retardant for epoxy resin. However, the highest LOI value was only 27.5% with 20% PPMS-EG, in addition to inferior mechanical properties. Utilizing the physical blends of various FR components as IFR was advantageous for the sake of convenience. However, it was reported that the size and its distribution of each component in the substrate significantly affected the performance of both FR and mechanical property (56). The main reason was that the functional compositions could not come into contact with each other sufficiently, which was the disadvantage compared with the chemical bonding process. Meanwhile, it was proved that the flame retardant effect after adding OMMT and CEMP was greatly enhanced, thus reducing the fire risk.

Figure 7: Photographs of the samples after LOI and UL-94 tests (a: EP, b: EP1, c: EP2, and d: EP3).

Figure 8: Digital photographs of the char residues of flame retarded EP after the cone calorimetric test (a: EP, b: EP1, c: EP2, and d: EP3).

3.7 Cone calorimetric test

Digital photographs of EP residues after the cone calorimetric tests are shown in Figure 9. It is clear that pure EP was completely burned without any swelling phenomenon and there were black and oily substances

(Figure 8a) (41,57,58). With the addition of CEMP and OMMT, different degrees of expanded char layer appeared. As the amount of CEMP attained 15%, the expanded char layer increased significantly (Figure 8c and d). On the other hand, the smoke was also significantly suppressed. These results, at least apparently, indicated the flame retardant effect exhibited on EP.

The combustion process was evaluated by a cone calorimeter. Figure 9 depicts the heat release (HRR), total heat release (THR), smoke release (SPR) and the total smoke emission (TSP) during the combustion of flame retardant modified EP. The relevant parameters including the average yields of CO (av-COY) and CO₂ (av-CO₂Y) as well are listed in Table 4. It is obvious that, as shown in Table 4, the overall parameters of pure EP were significantly higher than those of composite EP. Figure 9a and b indicate that, once the pure epoxy resin was ignited, a lot of heat was released in a very short time, ca. 200 s. PHRR was 603.1 kW m⁻² and THR, 86.4 MJ m⁻². It implied that the temperature was high, which accelerated the decomposition of PE. In contrast, PHRR of samples, EP1, EP2 and EP3, were 159.7, 152.5 and 133.0 kW m⁻², almost one fourth of HRR of EP. Correspondingly, THR were 49.9, 44.6 and 35.1 MJ

Figure 9: Cone calorimetry curves (a: HRR, b: THR, c: SPR, and d: TSP).

Table 4: Cone calorimeter data of flame retarded EP

Samples	TTI (s)	PHRR (kw m^{-2})	THR (MJ m^{-2})	av-COY (kg/kg)	av-CO ₂ Y (kg/kg)	TSP (m^2)
EP	108 ± 5	603.1 ± 28	86.4 ± 7.0	0.01 ± 0.01	0.84 ± 0.01	15.4 ± 0.2
EP1	22 ± 2	159.7 ± 25	49.9 ± 6.5	0.05 ± 0.01	0.74 ± 0.01	9.3 ± 0.2
EP2	21 ± 2	152.5 ± 25	44.6 ± 6.8	0.06 ± 0.01	0.59 ± 0.01	6.8 ± 0.2
EP3	20 ± 2	133.0 ± 25	35.1 ± 6.9	0.08 ± 0.01	0.58 ± 0.01	5.0 ± 0.2

t_1 is the first ignition and t_2 is for the second. NR is no flame retardant rating.

m^{-2} , nearly half of THR of EP. Besides, the heat release of composite EP lasted for about 600 s. These results indicated that the temperature of composite EP was much lower than that of EP during the combustion, thus retarding the decomposition of EP. In principle, the polymer is inflammable. However, it decomposes to the smaller organic molecules due to the high temperature. The small organic molecules evaporate and mix with oxygen in air. Hence, the dramatic oxidation reactions take place and release a huge amount of heat. The heat once again induces the decomposition of polymer, thereby accelerating the combustion. One of the targets of an intumescent flame retardant is to absorb the heat by expansion of the char layer, and the char layer expansion slows down the heat transmission from the gas phase to the decomposing polymer. Accordingly, the above results indicated that the CEMP did work during the combustion.

Addition of the inorganic OMMT is to reflect radiant heat from the flame and act as a catalyst for charring to accumulate on the surface of substrate. The char layer created by the CEMP further blocks the heat transfer in the polymer. Figure 9c and d show SPR and TSP. It is clear that, without OMMT and CEMP, SPR of pure EP reached 15 m^2 , whereas TSP of EP3 with the amount of 15% CEMP and 3% OMMT was only 5.0 m^2 , one third of the pure EP. It indicated that the effect of smoke suppression by OMMT and CEMP was significant. In addition, Table 4 also lists the ignition time (TTI) of EP and its composites. The ignition time of pure EP was 108 s, in contrast, after adding the flame retardant, the ignition time was drastically reduced to 20–30 s. One of the functions of CEMP was to accelerate the thermal decomposition of CS and EP, so as to create an expanded char layer as early as possible. The short TTI indicated that the thermal decomposition reaction of CS and EP took place readily under the catalysis of phosphoric acid. The high av-COY and low av-CO₂Y supported the above results. As shown in Table 4, the values of av-COY and av-CO₂Y of pure EP were 0.01 and 0.84 kg/kg, respectively, whereas av-COY of EP composite increased as the amount of CEMP increased. It indicated that the

combustion of EP composite was incomplete due to the low temperature of combustion. All these results of experiment suggested that CEMP were effective at suppressing the combustion further.

3.8 TG analysis

The thermal stability of EP composites was evaluated by TGA. Figure 10 shows TG curves with the amount of intumescent flame retardant at 8, 13, and 18 wt%. The temperatures of 5%, 50% and the maximum weight loss are listed in Table 5 (59). It is clear that the temperature of both 5% and the maximum weight loss of pure EP were lower than those of EP composites, whereas the temperature of 50% weight loss inverted. The temperature of 5% weight loss is mainly ascribed to the dehydration process, while the temperature of 50% weight loss is corresponding to the pyrolysis. The high pyrolysis temperature of pure EP was expected, completely consistent with the initial anticipation to CEMP.

The temperature of maximum weight loss refers to the difficulty in polymer degradation. As shown in Table 5, the temperature of EP3 was 508°C , 72°C higher than that of pure EP. It indicated that heat transfer was

Figure 10: TGA curves of flame retardant EP.

Table 5: TG data of flame retarded EP

Samples	$T_{5\%}$ (°C)	$T_{50\%}$ (°C)	$T_{\max}$ (°C)	Char residue at 800°C (%)
EP	120	370	436	3.6
EP1	136	352	475	14.1
EP2	141	358	490	17.1
EP3	153	362	508	22.2

effectively blocked by the char layer created by the CEMP and EP matrix. The amount of char residues supported this result. At the temperature of 800°C, the content of residual char increased, as the amount of CEMP increased. The char residue of EP3 was 22.2%, almost more than five times as much as that of pure EP.

3.9 TG-IR analysis

In order to further trace the pyrolysis process and elucidate the flame retardant mechanism, the volatile substances of decomposition were simultaneously evaluated with IR during TG measurement. The IR spectra of pure EP and flame retardant modification at different temperatures are shown in Figure 12. It should be noticed that the spectra were automatically calibrated by machine, subsiding the peak of CO₂ absorption that inevitably existed in air, while the peaks of other absorption were going up and down due to the volatile substances including a lot of CO and CO₂, even though it did not affect the results of the analysis. The assignment of main peaks was listed as follows (60): O–H and N–H stretch vibrations (3,400–4,000 cm^{−1}), –CH₃ and –CH₂ (2,800–3,000 cm^{−1}), CO₂ symmetric vibration (2,300–2,400 cm^{−1}), CO stretch vibration (2,100–2,200 cm^{−1}), carbonyl stretch vibration C=O (1,640–1,840 cm^{−1}), C–O ether bond (1,140 cm^{−1}) and aromatics (1,300–1,800 cm^{−1}, typically 1,600 cm^{−1}). For OMMT and CEMP, the noticeable peaks are: Si–O (664 cm^{−1}), P=O double bond (1,252 cm^{−1}) and the asymmetric stretching vibration of P–O–P (1,180 and

899 cm^{−1}). Characteristic expanding peak of triazine ring in melamine (1,400–1,630 cm^{−1}) overlapped with those of benzene in EP (61).

As shown in Figure 11, the peaks at 3,400–4,000 cm^{−1} disappeared at the lower temperature, <300°C, together with the disappearance of 2,300–2,400 cm^{−1} (CO₂ and CO). Typically, the peaks reflecting the existence of alkyl group at 2,879 and 2,918 cm^{−1} also disappeared. This result is coincident with the above results that EP combusted quickly. In contrast, as for EP3, those peaks appeared even at 600°C. Especially, the peaks in the vicinity of 2,357 cm^{−1} were very high during the decomposition and moved to 2,200 cm^{−1} as the temperature increased. It implies that the concentration of CO increased as the temperature increased. CEMP decomposed at 100–200°C because the P–O–P band at 1,180 cm^{−1} appeared at that temperature. It abated as the temperature increased, while the peak at 1,252 cm^{−1} (P=O) gradually appeared. The peak at 899 cm^{−1} reflects the substituent benzene or triazine. It is the highest at 300°C, indicating that the benzene and triazine rings appeared in the volatile gas at 300°C (11,62,63). Multiple peaks (1,300–2,000 cm^{−1}) reflected the alkyl, benzyl, melamine, etc. of various substances. These peaks attained the maximum value accompanying the appearance of the highest peak at 899 cm^{−1}. It implies that the sublimation of melamine took place at 300°C.

Comprehensively, the above results indicated that (1) the pyrolysis of pure EP took place completely because little CO was observed. Decomposition of pure EP gave rise to black smoke that consisted of short chains. (2) Decomposition of pure EP was completed at 300°C because the detectable volatile substances disappeared at that temperature. (3) Phosphoric ester of CEMP decomposed at first to produce phosphoric acid at 100°C. (4) Sublimation of melamine occurred at 300°C. It not only absorbed heat, but also decreased the concentration of combustible gas. (5) The thermal degradation of EP containing CEMP and OMMT was incomplete because a huge amount of CO₂ was released. Hence, it was favorable to form a char layer so as to suppress the release of smoke. These results further confirmed that the addition of CEMP increased the thermal stability of EP and suppressed the occurrence of smoke.

Figure 12: SEM images of EP and EP3 char residues.

3.10 SEM analysis of char residue

Intumescent effect was exhibited in char residues at post-combustion. Hence, the morphology of char residues was observed by SEM (64,65). The micrographs of char residues are shown in Figure 12, where the char

Figure 11: TG-IR curves of pure EP and EP3.

residues of pure EP exhibited smooth surfaces, whereas there were many minipores that appeared on the surfaces of EP3 char residues. It confirmed the intumescent effect of CEMP.

4 Conclusions

According to the concept of fire life cycle assessment (LCA), i.e., assess the overall environmental impact throughout the life of products containing flame retardants, a new type of intumescent flame retardant was designed and synthesized by chemically bonding chitosan, phosphorus pentoxide and melamine to prevent the flame retardant components from leaking into the environment in the application. The structure of chitosan ethoxyl melamine phosphate was characterized by FT-IR, ^1H NMR and ^{31}P NMR. ^1H NMR indicated that many sharp OH proton peaks disappeared in the CEMP ^1H NMR spectrum, instead, a big broad peak appeared. A similar phenomenon was observed in the XRD diagrams of chitosan and CEMP, indicating that the crystalline structure of chitosan was destroyed during the phosphorylation reaction. In the ^{31}P NMR spectrum, two peaks, i.e., 0.46 and -0.46 ppm, appeared in CEMP. Both of them reflected that the polar group was adjacent to the P–O bond. All results indicated that CEMP was successfully prepared. Due to the hardly soluble substrates, the surface of CEMP beads was observed with SEM. The porous surface was confirmed, implying the good miscibility with substrate.

The performance of intumescent flame retardant chitosan ethoxyl melamine phosphate (CEMP) and OMMT was evaluated in the epoxy resin (EP) substrate.

As a result, with the addition of 3 wt% OMMT and 15 wt% CEMP (EP3), LOI and UL-94 tests evaluated the flame retarded EP to possess smoke suppression with LOI value, 30.6%, and rank V-0 rating without dripping. The results of cone calorimetric test (CCT) indicated that adding CEMP and OMMT significantly reduced PHRR, THR, TSP and CO emission. For example, with EP3, PHRR was one fourth that of pure EP, while THR was just 1/2. These results implied that the intumescent effect did work in the combustion. TGA showed that the char residue yield of EP3 at 800°C was 22.2%, whereas EP gave 3.6%. TG-IR traced the release of volatile substances stemming from the decomposition of EP. Accordingly, it was suggestive that CEMP decomposition commenced at 100°C to create phosphoric acid and sublimation of melamine occurred at 300°C. Intensive peaks of alkyl groups and a faint peak of CO_2 implied that incomplete combustion of pure EP gave rise to smoke that consisted of decomposed short chains. In contrast to the completed combustion of EP below 300°C, EP3 exhibited a strong thermal stability, namely even at 600°C, the volatile substances were detectable. This result was consistent with TGA results that T_{max} of EP3 was 508°C, much higher than 436°C of EP. The intumescent effect of CEMP was confirmed by SEM of char residues at post CCT. The surface of EP3 char residues clearly showed the porous structure, in contrast, the surface of the EP char residue was smooth.

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