Design, Preparation, and Application of a Novel, Microencapsulated, Intumescent, Flame-Retardant-Based Mimicking Mussel

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ABSTRACT: A novel microencapsulated intumescent flame retardant (TMAPP) was prepared, in which ammonium polyphosphate (APP) is the core and functions as an acid source, melamine−urea formaldehyde (MUF) resin is in the intermediate layer and functions as a blowing agent, and ferric tannin (mimicking mussel) is in the outermost shell layer and functions as a carbonization agent and also as a smoke inhibitor and surface modifier. TMAPP was prepared by treating MUF-microencapsulated APP with tannin acid and FeCl₃. Its structure is characterized by Fourier transform infrared, elemental analysis, and thermogravimetry (TG). TMAPP in epoxy was evaluated for its effect on flame retardancy and mechanical properties. The flame-retardant and smoke suppression performances of EP/TMAPP were studied using cone calorimetry (CONE) and limit oxygen index, and the flame-retardant mechanism was investigated by scanning electron microscopy and TG. The resultant data indicate that EP/TMAPP has very good mechanical properties, flame retardancy, and smoke suppression, whose char residue and thermal stability are increased, and the initial decomposition temperatures are decreased. Meanwhile, the char residue structures were very intumescent and compact. The char residue effectively prevents the underlying materials of EP/TMAPP from further combustion.

INTRODUCTION

In recent years, polymer materials have been widely used in home appliances, building materials, transportation, electronics, electrical appliances, aerospace, and other fields.¹⁻² However, polymeric materials are generally very flammable. Thus, they are generally treated with different flame retardants to decrease the combustibility of polymers,³ and the preparation and application of flame retardants have become an important subject in the polymer field. However, the major problems of polymeric materials containing halogen flame retardants are the generation of corrosive and toxic gases during combustion. Therefore, it is necessary to prepare and use nonhalogenated additives, in which an intumescent flame retardant (IFR) is thought to be an alternative to a halogen additive, in which an intumescent IFR is necessary to prepare and use nonhalogenated polymeric materials containing halogen.

In previous studies, microencapsulation of APP has successfully overcome these problems. The melamine−urea formaldehyde (MUF) resin was commonly used in the microencapsulation of the APP, which not only can improve its poor water resistance, but also increase the flame retardancy, because of the synergistic effect of P−N.¹² However, the melamine−urea formaldehyde APP (MAPP) contains the acid source, blowing agent, but only a little carbonization agent as an IFR.

Mussels are common creatures living in the ocean, which can secrete strong adhesion protein, clinging to the surface of many substances such as bone grafts, plants, glass products, metal components, polymer materials, minerals, and so forth.¹³⁻¹⁶ Many research studies are focused on revealing and mimicking the adhesive materials. The mimicking mussel is widely used in medicine, food, metallurgy, and other fields,¹⁷⁻¹⁹ whose application in the surface modification of the flame retardant
has not been reported. Tannic acid is a complex polyhydric phenol, in which there are multiple phenolic hydroxyl groups, which can be a carbonization agent in IFR and simultaneously form a stable chelate with Fe$^{3+}$. This chelate can form a nanoscale film cling to any substrate interface, which is very similar to the mussel adhesive material.20,21

In this research, a novel microencapsulated IFR via chelation reaction of tannic acid with Fe$^{3+}$ on the surface of MAPP (TMAPP) was prepared. Its compatibility in the polymer matrix and flame retardancy were greatly improved because of its adhesion and making-up carbonization agent. Meanwhile, Fe$^{3+}$ in ferric tannin can be a smoke inhibitor to decrease the generation of the smoke during combustion. TMAPP as a flame retardant was applied to epoxy resin (EP) to obtain very good mechanical properties, flame retardancy and smoke suppression.

**EXPERIMENTAL SECTION**

**Materials.** Epoxy resin (E-44) and a polyamide curing agent were obtained from Nantong Xingchen Synthetic Material Co., Ltd., Shanghai, China, MAPP as a flame retardant was obtained from Hangzhou JLS Flame Retardants Chemical Co., Ltd., Jiangsu, China, and tannic acid and FeCl$_3$ were purchased from an analytical reagent from Tianjin Yongda Chemical Reagent Co., Ltd., China.

**Preparation of TMAPP.** The preparation procedure of TMAPP is shown in Scheme 1 as follows: first, MAPP (100 g), deionized water (250 mL), tannic acid (5 g) solution, and FeCl$_3$ (8.4 g) were mixed during mechanical stirring in a three-necked round-bottom flask. Several minutes later, MAPP (50 g) was put into the flask, and the mixture was adjusted to 8.5 pH with the addition of NaOH. The suspension was reacted for 10 min at 25 °C followed by the addition of deionized water. TMAPP was obtained after centrifuging, washing, and drying.

**Preparation of Epoxy Resin Samples.** First, 63.5 g of epoxy resin and 15 g of MAPP or TMAPP were well mixed for 20 min at 1500 rpm in a dispersion machine. Then, 21.5 g of curing agent was put into the mixture and uniformly stirred for 5 min. Finally, the mixture was added to molds, which were controlled at 25 °C for 24 h. The formulations of EP are presented in Table 1.

**Table 1. Formulations Containing Different Additive Levels**

|            | epoxy resin/g | curing agent/g | MAPP/g | TMAPP/g |
|------------|---------------|----------------|--------|---------|
| EP         | 63.5          | 21.5           |        |         |
| EP/MAPP    | 63.5          | 21.5           | 15     |         |
| EP/TMAPP   | 63.5          | 21.5           | 15     |         |

**Testing.** The MAPP and TMAPP structures were evaluated by a Nicolet iS5 infrared spectrometer (American Nicolet Corporation). The elemental analysis was evaluated by a Carlo Erba 1102 Elemental Analyzer. The sample size for the limit oxygen index (LOI) test was evaluated as 90 × 10 × 3 mm$^3$ by a JF-3 LOI apparatus (Nanjing Jiangning Analytical Instrument Factory) according to ASTM D 2863-97. Vertical burning (UL-94) tests were carried out on a CZF-2-type instrument (Suzhou Feinikesi Quality Inspection Instrument Co., Ltd., China) with a dimension of 130 × 13 × 3 mm$^3$ according to the UL-94 test standard. The mechanical property tests were carried out by a CMT4204 universal testing machine (Meitesi Industrial Systems (China) Co., Ltd) according to GB/T 1040.2-2006 (China). Thermo gravimetry (TG) was evaluated by an HCT-2 thermal analyzer (China) under an air atmosphere at a heating
rate of 10 °C min⁻¹. The sample size for the cone calorimetry experiments was evaluated as 100 × 100 × 3.2 mm³ by PX-07-007 (China) according to ISO5660 under a heat flux of 50 kW·m⁻². The typical results from the mechanical property, LOI, TG, and cone calorimetry tests were the average from the three measurements. The morphologies of the chars were studied by scanning electron microscopy (SEM) (KYKYEM-3200, China).

RESULTS AND DISCUSSION

Characterization of TMAPP. The procedure and schematic of the prepared structure are shown in Scheme 1a. Ferric tannin could be distributed on the surface of MAPP. The SEM images of MAPP and TMAPP are shown in Scheme 1b,c; we can see that there is almost no change after ferric tannin modification. The coordination constant of ferric tannin was lgK = 24.6 in 0.1 M NaCl solution at 20 °C, which demonstrated the reliable stability of the chelate. The structure of MAPP had no obvious change after ferric tannin modification (Scheme 1). The Fourier transform infrared (FTIR) spectra of MAPP and TMAPP are shown in Figure 1.

For MAPP, which includes APP and MUF resin, the main absorption peaks at 3200, 1695, 1564, and 1100 cm⁻¹ are assigned to the stretching vibrations of N–H and –OH, C=O, and C–O groups in the MUF resin, respectively. Meanwhile, the absorption peaks at 1420, 1250, 1000, and 850 cm⁻¹ are assigned to the P=O and P–O groups in APP. For TMAPP, it is obvious that the above typical absorption peaks become broad, which are due to the covering of MAPP by microcapsules. The new absorption peaks at 1615 and 1620 cm⁻¹ are assigned to the stretching vibrations of aromatic ring groups, and the absorption peaks at 3394 cm⁻¹ become larger because of more phenolic hydroxyl groups, which are the characteristic groups of the ferric tannin chelate. The spectrum of TMAPP reveals well-defined absorption peaks of MAPP and characteristic bands of ferric tannin chelate, which indicates that MAPP is successfully microencapsulated by ferric tannin.

The elements of MAPP and TMAPP were determined and presented in Table 2. It can be seen that the amount of elemental N and P of TMAPP was 6.82 and 2.74%, respectively, which was lower than that of MAPP (35.73 and 12.02%). On the contrary, the amount of elemental C and O of TMAPP (44.54 and 30.51%) was much higher than that of MAPP (32.54 and 19.86%). There was a new elemental Fe (15.39%) in TMAPP, from ferric tannin. All these changes may be because of the coverage of MAPP with ferric tannin chelate, which indicates that MAPP was indeed encapsulated by the shell.

The TG and differential thermogravimetry (DTG) of MAPP and TMAPP results are shown in Figures 2 and 3 and Table 3. Degradation of MAPP is mainly composed of two stages. The first stage from 217 to 600 °C with a mass loss of 37.8% and a T_max of 336 °C is due to the degradation of MF resin and cleavage of P–O in MAPP, which releases phosphorus oxides and some nonflammable gases, such as NH₃ and CO₂, as the mentioned gases swell the char to form a “honeycomb” structure. TMAPP mainly degrades in the second stage at above 600 °C with a T_max of 666 °C. The residue of MAPP at 900 °C is only 11.2%, which indicates that some phosphorus oxides can evaporate at higher temperatures.

Degradation of MAPP initially degrades at 217 °C, higher than the initial decompose temperature (T_i) of MAPP, which is due to more thermal stability of ferric tannin than MUF in TMAPP. The T_max of TMAPP is almost the same as MAPP in the first stage but less mass loss for TMAPP at the same temperature, whereas the T_max value in the second stage and the residue at 900 °C is 685 °C and 14.6%, respectively, both higher than...
those of MAPP, which is attributed to the action of ferric tannin as a carbon source in TMAPP.

**Mechanical Properties of EP Samples.** The data of tensile strength and elongation of the EP composites are presented in Table 4. We can see that the mechanical properties of EP composites decrease with the addition of flame retardants, which is in agreement with the previous research. Commonly, the tensile strength and elongation of EP composites are significantly influenced by solid additives. After microencapsulated by the ferric tannin, the elongation at break and tensile strength for EP/TMAPP increase by 27.5 and 13.9%, respectively, compared with those for EP/MAPP. It is suggested that the compatibility of MAPP in EP composites was modified by microencapsulation because the ferric tannin mimicking mussel can readily adhere to the interface between MAPP and EP. The resulting materials had improved mechanical properties because of surface modification, which was also observed in the SEM images of the fracture surface shown in Figure 4.

![Figure 4. SEM results of the microstructure of the failure section of EP with (a) MAPP and (b) TMAPP.](image)

As shown in Figure 4, the sample section of EP/MAPP had obvious MAPP lumps, and there was a distinct phase separation at the interface between MAPP and EP. This indicated that MAPP was more prone to self-aggregation due to the strong polarity interaction of MAPP with itself because of the poor compatibility of MAPP with EP. However, the sample section of EP/TMAPP shows tiny bits of TMAPP and some ductile holes. This indicated that the surface modification of the bioadhesive mussel coating could greatly improve the compatibility between the interfaces of EP and MAPP, resulting in the improvement of their mechanical properties.

**Flame Retardancy of EP.** LOI test is widely used to evaluate the flammability of flame-retardant materials, and the corresponding data are presented in Table 5. As presented in Table 5, EP is flammable with a LOI of only 19.5%, and it cannot pass the UL-94 test, which indicates that the pure EP sample is flammable. With the addition of MAPP or TMAPP contents in the EP composite, the LOI of the EP composites is greatly increased; 35.6% of LOI was observed in 15% of MAPP whereas 37.3% of LOI was obtained in the same content of TMAPP, and their UL-94 rating is V-0. This increase of flame retardancy is due to the intervention of ferric tannin, which can be a good carbonization agent in IFR because of its multihydroxyl phenolic structure.

**Cone Calorimeter Test.** A cone calorimeter can effectively evaluate and compare the combustibility of a polymeric material. Some important parameters of EP composites are shown in Figures 5–8 and listed in Table 5.

![Figure 5. HRR of EP samples.](image)

![Figure 6. THR of EP samples.](image)

![Figure 7. Smoke production rate of EP samples.](image)

**Table 4. Mechanical Properties of EP Samples**

|          | tensile strength/MPa | elongation at break/% |
|----------|----------------------|-----------------------|
| EP       | 71.2±0.19            | 12.5±0.18             |
| EP/MAPP  | 60.2±0.20            | 5.1±0.19              |
| EP/TMAPP | 69.9±0.17            | 6.5±0.20              |

**Table 5. UL-94, LOI, and Cone Test Data of Samples**

|          | EP | EP/MAPP | EP/TMAPP |
|----------|----|---------|----------|
| UL-94    | no rating | V-0  | V-0      |
| LOI/%    | 19.5±0.17 | 35.6±0.18 | 37.3±0.17 |
| time to ignition/s | 44±0.19 | 53±0.20 | 49±0.19 |
| PHRR/kW·m⁻² | 445.9±0.20 | 144.5±0.22 | 115.6±0.22 |
| TPR/kW·m⁻² | 70.116±0.20 | 34.139±0.19 |
| peak SPR/m²·s⁻² | 0.35±0.23 | 0.12±0.18 | 0.10±0.21 |
| TSP/m²·s⁻² | 7281±0.21 | 2768±0.22 | 2663±0.21 |
The heat release for the material on heat is a key parameter to fire. The heat release rate (HRR) and total heat release (THR) curves as functions of combustion time of all samples are shown in Figures 5 and 6. We can see from Figure 5 and Table 5 that the ignition time (time to ignition) for pure EP is 44 s. The HRR of pure EP shows a single peak with a peak HRR (PHRR) of 445.9 kW·m⁻² at 123 s, which indicates that the pure EP burns brightly and gradually. When MAPP is imported, the ignition time becomes longer (53 s) and multipeak phenomena were displayed for EP/MAPP. The greater peak is attributed to the initial burning. The decreasing HRR shows that a swollen char layer is formed on the surface of the EP composites. With further increase of the temperature, part of the char layer is destroyed, and the materials burn again with the back peaks.²₈ For EP/TMAPP, the ignition time decreases from 53 to 49 s compared with EP/MAPP. This may be attributed to the lower content of APP in EP/TMAPP, but also has two main stages, which reveal thermo-oxidative decomposition behavior. The first stage of degradation is due to the cleavage of C–H and O–H and the formation of char, and the second stage can be assigned to further decomposition of the formed char in the action of O₂ at higher temperature. For pure EP, the Tₛ was 318 °C and its residue about 3.4% at 900 °C. In comparison with the pure EP, the Tₛ of EP/MAPP and EP/TMAPP much decreased. This decrease in Tₛ is mainly because of the lower decomposition temperature of the flame retardants, which makes the formation of the protective char easy.³⁵ Therefore, the decomposition of EP/MAPP and EP/TMAPP in the later stage was much decreased, compared with EP. EP/MAPP and EP/TMAPP have similar TG curves. However, EP/TMAPP had a higher residue (18.9%) than EP/MAPP (12.9%), owing to the presence of ferric tannin as a carbonization agent in TMAPP.³⁴–³⁶ Theoretically, the enhancement in char-yielding efficiency is believed to contribute to better flame retardancy.

### SEM and Images of Char Residue
The residues of EP/TMAPP and EP/MAPP after combustion are also considerably increased, which were further proved by SEM and the digital images, as shown in Figure 11. The digital images of the EP composite residues after cone calorimeter tests are shown in Figure 11a–c. From Figure 11a, one can see that there is little residue for EP after the cone calorimeter test. Figure 11b,c shows that the residue left by EP/TMAPP and EP/MAPP was...
intumescent, effectively preventing the inter EP from further combustion. In order to further analyze the residue structure, the SEM images of the residues of EP/TMAPP and EP/MAPP were obtained as shown in Figure 11d,e. For EP/MAPP in Figure 11d, EP/MAPP formed breakable and loose structure, which was easily destroyed in the combustion process. Therefore, the char layer of EP/MAPP only shows the flame retardancy at a low level. We can see from Figure 11e that the carbonaceous layers of EP/TMAPP were more compact, which can effectively prevent the inner EP composites from further combustion.

■ CONCLUSIONS

In this paper, a novel microencapsulated IFR, via chelation reaction of tannic acid with Fe³⁺ on the surface of MAPP (TMAPP), was successfully prepared. TMAPP as a flame retardant was added into EP to obtain a very good smoke suppression and flame retardancy. A high LOI of 37.3% was obtained with the addition of 15% TMAPP for EP. For the thermal decomposition of EP/TMAPP, the Ti decreased and the char residue increased. Its cone calorimeter data showed a drastic improvement in flame retardancy and smoke suppression, as shown by HRR, THR, SPR, and TSP. Tannin acid with a large content of hydroxyl groups can be a good carbonization agent in IFR and ferric tannin as the smoke inhibitor. Therefore, the ferric tannin chelate was inserted into MAPP, which effectively promoted EP/TMAPP form a more compact expanded carbon layer during combustion, effectively preventing the underlying materials from further combustion.

Meanwhile, the ferric tannin chelate can be a good surface modifier for MAPP, which can form a mimicking mussel cling to the interface between MAPP and EP. Therefore, the tensile strength and elongation at the break of EP/TMAPP increased by 13.9 and 27.5%, respectively, compared with that of EP/MAPP.

■ AUTHOR INFORMATION

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