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Effect of microencapsulated ammonium polyphosphate on the durability and fire resistance of waterborne intumescent fire-retardant coatings

Zhitian Liu, Mengqin Dai, Qinghua Hu, Shi Liu, Xiang Gao, Fan Ren, Qi Zhang

Abstract Large-scale addition of hydrophilic solid filler (i.e., ammonium polyphosphate) into waterborne intumescent fire-retardant coatings can cause many problems such as poor compatibility, easy absorption of moisture, and poor durability. In this work, microencapsulated ammonium polyphosphate with melamine formaldehyde resin (MFAPP) was prepared and applied in intumescent fire-retardant coatings to solve the problems mentioned. Due to the hydrophobicity of melamine formaldehyde (MF) resin, MFAPP exhibited better water resistance, thermal stability, and compatibility with polymer matrix, which was confirmed by Fourier transform infrared spectra, scanning electron microscopy (SEM), particle size test, water solubility, water contact angle, and thermogravimetric analysis (TGA). The effect of the MFAPP on durability and fire resistance of the fire-retardant coatings test were investigated by the static immersion test, fire resistance test, TGA, and SEM. Even immersed in distilled water for 12 h, the coatings containing MFAPP did not show obvious damage, indicating microencapsulation improved the water resistance of coatings. Furthermore, the fire-resistant time and thermal stability of the waterborne intumescent fire-retardant coatings were also improved remarkably by utilizing the microencapsulation of ammonium polyphosphate.

Keywords Microencapsulation, Ammonium polyphosphate, Intumescent fire-retardant coating, Fire resistance, Durability

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Introduction

Structural steel has been widely used in the construction industry due to its high strength-to-weight ratio, high ductility, short manufacturing process, and construction time, etc.[1–3] However, the load-carrying capacity of steel decreases significantly in a fire when its temperature exceeds 500 °C, which threatens human lives and assets.[4–10] Therefore, the protection of steel materials against fire has become an important issue in the construction industry.

Intumescent fire-retardant coatings have been widely used to protect steel structures.[11–14] Usually, intumescent fire-retardant coatings are composed of a char-forming material, a mineral acid catalyst, a blowing agent, and a binder resin.[15] During the process of combustion, these components work synergistically to form a honeycomb-like char that thermally insulates the underlying steel substrate and establishes a protective barrier against oxygen.[16–21] Since intumescent fire-retardant coatings are normally used as decorative coatings and endure for a long time before a fire

actually breaks out, the durability of the coatings is quite important.[22,23] On the other hand, to achieve promising fire resistance, the content of solid fillers such as fire-retardant additives in fire-retardant coatings is generally high, sometimes even up to 60 wt%.[23,24] However, the high content of solid fillers is detrimental to processability, mechanical properties, and durability of the fire-retardant coating.[24] Furthermore, the conventional intumescent flame retardant (IFR) additives, typically ammonium polyphosphate (APP), are hydrophilic solid materials which have some disadvantages, such as moisture sensitivity, poor compatibility with the coating resin, and migration to the surface of coatings in moist and corrosive environments.[25–32] These disadvantages significantly decrease the fire protection ability and durability of the intumescent fire-retardant coatings. To overcome these problems, utilizing microencapsulated ammonium polyphosphate as fire-retardant additives has been regarded as an effective strategy. The microencapsulation of an IFR system has been widely used in the fields of plastics, rubber, and wood–plastic composites.[29–32] However, the application of microencapsulation technology in intumescent fire-retardant coatings has been quite limited, and there is minimal research on the durability and fire resistance of the fire-retardant coating after the static immersion test.[33]

In this work, microencapsulated APP with melamine formaldehyde resin (MFAPP) was prepared and used in the intumescent fire-retardant coating to solve the problems caused by the large-scale addition of hydrophilic solid fillers, such as poor compatibility, easy absorption of moisture, and poor durability. MFAPP was characterized by Fourier transform infrared (FTIR) spectra, scanning electron microscopy (SEM), and particle size test. The fire resistance properties of the fire-retardant coating before and after the static immersion test were characterized by big panel method and thermogravimetric analysis (TGA). The durability of the intumescent fire-retardant coatings was also investigated by the solubility test, contact angle analysis, the static immersion test, and SEM. The experiment data were listed and analyzed.

Experimental

Materials

Ammonium polyphosphate (APP, $n > 1000$), pentaerythritol (PER), melamine (MEL) ethanol, and sodium bicarbonate ($NaHCO_3$) were purchased from Sinopharm Chemical Reagent Co., Ltd. Formaldehyde (37 wt% solution) was purchased from Nanjing Chemical Reagent Co., Ltd. Hydrochloric acid (HCl) was provided by Xinyang Chemical Reagent Factory. Waterborne polyurethane emulsion modified by epoxy resin (E-44) was prepared in our laboratory. Thickener, defoamer, dispersant, and mildew preventive were obtained from Nantong Chemical Co., Ltd. All chemicals were used as received without further purification.

Preparation of samples

Preparation of microencapsulated APP

Preparation of the melamine formaldehyde (MF) prepolymer: 12.6 g of MEL, 18 g of 37 wt% formaldehyde solution, and 100 mL deionized water were added into a three-neck flask with a high-speed mechanical stirrer. The 3–5 wt% $NaHCO_3$ solution was added dropwise to adjust the pH value to 8. After keeping the mixture at 70 °C for 0.5 h, the MF prepolymer solution was obtained.

Preparation of microencapsulated APP (MFAPP): 20 g of APP was dispersed in 80 mL ethanol, followed by the addition of the aforementioned MF prepolymer solution under stirring. Dilute hydrochloric acid solution was added to adjust the pH to 4–5. After heating the mixture to 80 °C for 2 h, it was then cooled to room temperature, filtered, washed with distilled water, and dried at 30–40 °C. The microencapsulated APP with melamine formaldehyde resin (MFAPP) was finally obtained.

Preparation of intumescent fire-retardant coatings

The intumescent coatings were prepared by grinding waterborne polyurethane emulsion modified by epoxy resin (E-44), fire-retardant additives (MFAPP, PER, MEL), promoters, and water for 1 h in an agate mortar. The components of the intumescent coatings are listed in Table 1. The coatings were applied on one side of steel plates with the size of 100 mm × 150 mm × 3 mm and dried at room temperature for 24 h. This process was repeated several times until the film thickness reached 1 ± 0.1 mm.

Fourier transform infrared (FTIR) spectra

The FTIR spectra were obtained between 4000 and 400 cm^{-1} using a Nicolet 6700 FTIR spectrophotometer. Before measurement, powder samples were mixed with KBr powder and then pressed into a tablet.

The particle size and distribution of MFAPP and APP

The particle sizes and distributions of MFAPP and APP were recorded on a Malvern Zetasizer Nano Series Nano-ZS. Before the measurement, the sample was dispersed in distilled water by sonication for 15 min.

Table 1: The formulation of the intumescent fire-retardant coatings

Components (wt%)	Formulation #1	Formulation #2	Formulation #3	Formulation #4	Formulation #5	Formulation #6	Formulation #7
MFAPP	25.0	30.0	35.0	40.0	45.0	38.7	–
MF resin	–	–	–	–	–	–	18.99
APP	–	–	–	–	–	–	19.71

All the intumescent fire-retardant coatings also contain waterborne polyurethane emulsion modified by epoxy resin (E-44), PER, MEL, promoter, and water

Scanning electron microscopy (SEM)

The morphology of APP, MFAPP, and intumescent coatings after the static immersion test was acquired by scanning electron microscopy (AMARY1000 SEM) with an accelerating voltage of 15 kV. The particles were sprinkled onto a double-sided tape and sputter-coated with a thin layer of gold.

Solubility in water of MFAPP and APP

Water solubility of APP or MFAPP at room temperature was determined by adding 10 g of the samples into 100 ml distilled water and stirring at room temperature for 1 h. After the suspension was centrifuged and filtered, 10 ml of the filtrate was taken out and dried to constant weight at 80 °C. Solubility in water was calculated.

Contact angle analysis

Water contact angle was measured by a contact angle goniometer (DSA100, Kruss Company, Germany) at room temperature. Before measurement, approximately 1.5 g powder sample was placed inside a tablet press machine with inner diameter 10 mm and pressed into tablets. The value of contact angle was determined from digitized optical images of the drop equilibrated for 5 s. For each image, the contact angle values were calculated on edges using software supplied with the instrument.

The static immersion test

The static immersion test was used as an accelerated aging test of water on the coating. Before test, coating with different component ratios was applied on one side of steel plates. After sealing the borders with paraffin, the whole plate was dried at room temperature for 72 h. The dry plate was immersed in distilled water at room temperature for 12 h and dried at room temperature for 72 h. Then, the resulting plates were used for subsequent measurements including SEM, fire resistance test, and TGA.

Fire resistance test

Big panel method (GB/T12441-2005 in China) was used to evaluate the fire resistance performance of the intumescent coatings. During this process, the coated side of the steel plates was exposed to a high-temperature flame (about 1000 °C) produced by an alcohol blast burner, and the temperature as a function of time at the back side of the steel plate was recorded by the thermocouple. Fire-resistant time was defined as the time for temperature of the back side of the steel plate to reach 200 °C from room temperature, which was regarded as a standard of evaluating fire resistance of the intumescent coatings.

Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) was performed by using a Netzsch STA409PC LUXX under N_2 atmosphere with a heating rate of 10 °C/min over a temperature range from 40 to 800 °C to study the thermal degradation.

Results and discussion

Characterization of MFAPP

The FTIR spectra of APP, MF resin, and MFAPP are shown in Fig. 1. Typical absorption peaks of APP included 3190 cm^{-1} (N–H), 1264 cm^{-1} (P=O), 1097 cm^{-1} (P–O symmetric stretching vibration), 1014 cm^{-1} (symmetric vibration of PO_2 and PO_3), 880 cm^{-1} (P–O asymmetric stretching vibration), and 802 cm^{-1} (P–O–P), as indicated in Fig. 1.[34] As for MFAPP, the main absorption peaks appeared at 3414, 3190, 1586, 1333, 1264, 1097, 1014, 880, and 802 cm^{-1}. The absorption peaks located at 1586 and 1333 cm^{-1} were attributed to the ring vibration of MEL from the MF resin. The FTIR spectrum of MFAPP not only showed the characteristic absorption peaks of APP but also the absorption peaks originating from MF resin, indicating that both APP and MF resin existed in the MFAPP.

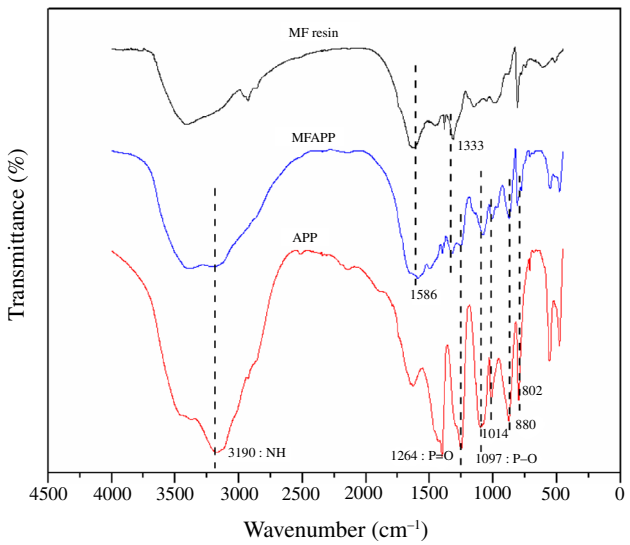

Fig. 1: FTIR spectra of APP, MF resin, and MFAPP

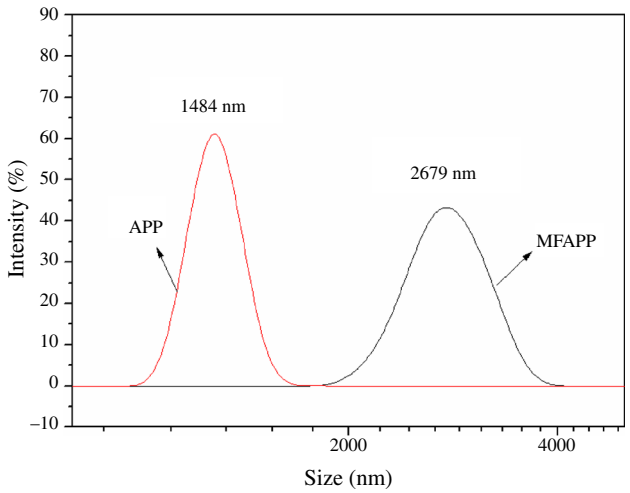

Fig. 2: Particle size distributions of APP and MFAPP

The particle size distribution of APP and MFAPP was measured. As shown in Fig. 2, the average diameter of APP and MFAPP was about 1484 and 2679 nm. Obviously, the particle size of MFAPP was larger than that of APP, indicating that the MF resin was wrapped onto the surface of APP particles. Furthermore, the relatively small (micrometer scale) particle size would be conducive to make coatings with good homogeneity and acceptable mechanical properties.[31]

The surface morphology of APP and MFAPP was investigated by SEM. As shown in Figs. 3a and 3b, the APP particles were irregular cubic solids with partial cracks on the rough surface. However, after the microencapsulation, the MFAPP particles were spherical solids with a smooth surface as shown in Figs. 3c and 3d. This great morphologic change further revealed that APP particles were well covered by the cured MF resin and confirmed the successful formation of microencapsulation, which was consistent with the FTIR results and particle size test. Furthermore, microencapsulation modification may also change the surface properties of APP, which might have a further effect on the interface interaction between APP and coating matrix, and other properties of the coating, such as fire resistance, thermal stability, and durability.

Fire resistance of the coatings

In this work, APP and MF resin (APP & MF resin) or MFAPP was mixed with PER, MEL, polyurethane emulsion modified by epoxy resin (E-44), and promoter to produce intumescent fire-retardant coatings. Figure 4 presents the backside temperature profiles and the fire-retardant time of intumescent coatings containing APP & MF resin or MFAPP under fire resistance test (big panel method). The fire-retardant time for intumescent fire coating based on MFAPP (119.34 min) was much longer than that of the coating based on APP & MF resin (70.77 min), and the heating rate of the coating based on MFAPP was much smaller. This indicated that the microencapsulation of APP can significantly enhance the fire resistance. The improved fire resistance performance may be explained by the following reasons: First, the microencapsulation of APP improved the dispersion of APP in the polymer matrix,[30–32] thereby resulting in high flame retardant efficiency. Second, polyurethane emulsion could act as a carbon source and MF resin could act as gases source. Moreover, melamine and formaldehyde reacted to produce hydroxylated melamine, so MF resin also could play a role of carbon source. The APP, polyurethane, and the MF resin coated at the surface of APP could form a char layer promptly at the initial degradation stages. As a result, the microencapsulation of APP could significantly enhance the fire resistance.

The amount of MFAPP in the fire resistance coating may also affect the fire resistance performance of the coating. The temperature–time curves for coating with different amounts of MFAPP in the fire resistance test are shown in Fig. 5. The backside temperature of the coatings first sped up, then the heating rate decreased, and the backside temperature began to slowly rise. After 5000 s, the backside temperatures were basically stable, namely a platform period. The platform temperature for these coatings decreased with increasing the content of MFAPP from 25 to 40 wt%, while further increasing the content of MFAPP in the coating to 45 wt%, the platform temperature increased. Moreover, the backside temperature of coating containing 40 wt% was lowest when the fire-resistant time reached 100 min. The results indicated that the optimum content of MFAPP in the coating was 40 wt%. It may be attributed to the dense carbon layer formed by an appropriate content of MFAPP reacted with MEL and PER. When the content of MFAPP in the coating

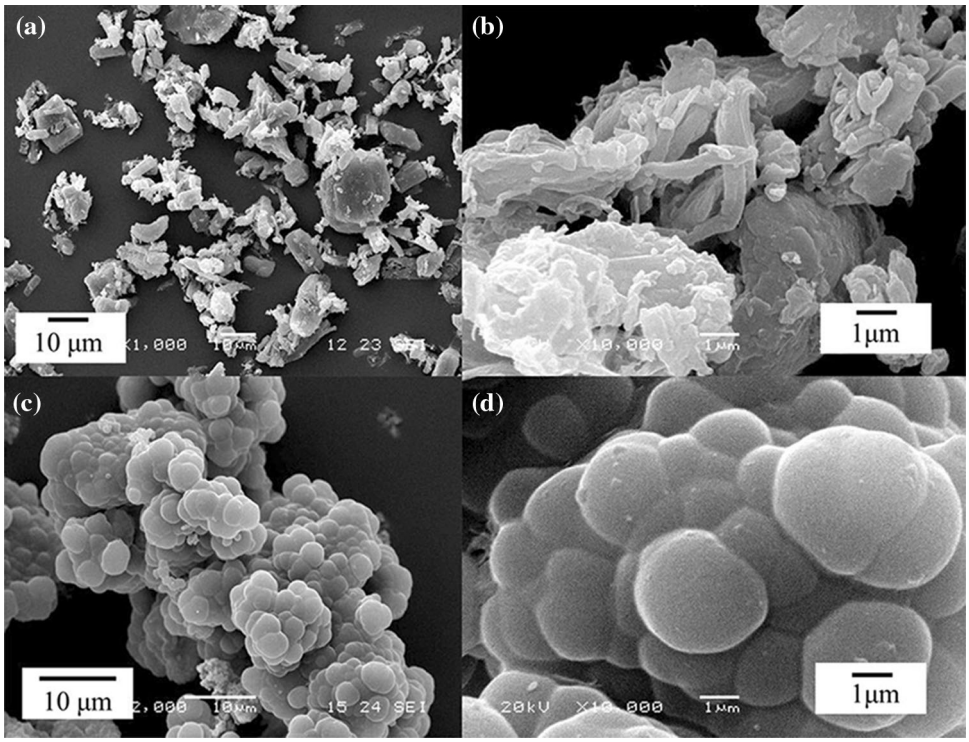

Fig. 3: SEM images of APP (a, b) and MFAPP (c, d)

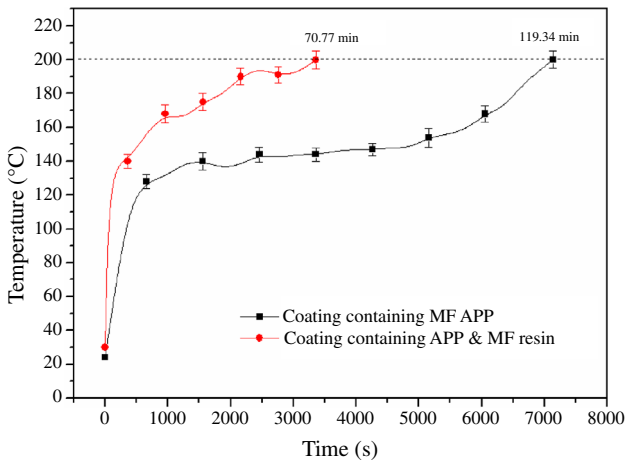

Fig. 4: The influence of the microencapsulation of APP on the fire resistance

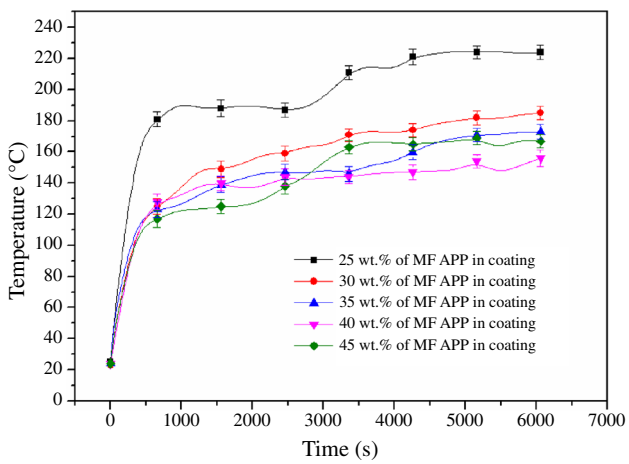

Fig. 5: The influence of the amount of MFAPP on the fire resistance

was too low, the acid source produced by MFAPP was not enough, so they cannot efficiently catalyze the carbon source to form a dense carbon layer, thereby reducing the fire resistance of intumescent fire-retardant coatings. However, when the content of MFAPP in the coating was too high, the excessive amount of MFAPP not only yielded a mineral acid, but also released large amounts of ammonia, water vapor, and other gases, resulting in over-expansion of the carbon layer. The over-expansion of the carbon layer reduced the density and intensity of the carbon layer, thus reducing the fire resistance of the fire-retardant coating.

Thermal properties of MFAPP and fire-retardant coating containing MFAPP

In general, thermal stability of the material reflects its chemical activity under certain conditions.[14,35] Therefore, the thermal stability of acid source APP has great influence on the thermal stability and fire resistance

properties of the fire-retardant coating. The TGA curves of MFAPP and APP & MF resin are shown in Fig. 6. It can be found that the thermal degradation of APP & MF resin was composed of three steps. The first step of mass loss was caused by the evaporation of water in MF resin before 100 °C. The second degradation stage (280–450 °C) was the initial decomposition process of APP, which mainly generated ammonia and water, as well as crosslinked polyphosphoric acids (PPAs).[22] Polyphosphoric acids reacted with hydroxy formed in the process of preparation of MF resin to yield a carbonaceous char. At the same time, MF resin began to decompose and release NH_3 and CO_2, which expanded to form a swollen multicellular char.[13,28] The third step occurred at around 450 °C due to the further decomposition of APP and the char residues. Compared with the APP & MF resin, the degradation of MFAPP was similar to APP& MF resin, but its maximum weight loss rate in every step was lower than that of APP& MF resin, and the initial decomposition temperature in every step was also slightly higher than that of APP& MF resin. Moreover, the char residue of MFAPP was 42.8% at 800 °C, higher than that of APP & MF resin (31.7%). This result demonstrated that the microencapsulation of APP could improve the thermal stability of APP. It may be attributed to the excellent interface interaction between the APP and MF resin when MF resin was wrapped onto the surface of APP particles as it may contribute to the timely formation of char layer at the initial degradation stages.

Since the fire resistance performance of intumescent fire-retardant coating is mainly affected by the interaction between acid source, carbon source, and gas source, it is very important to mix MFAPP with other components to prepare the fire-retardant coating and test its thermal stability. As shown in Fig. 7, the TGA curves of coating containing MFAPP and coating containing APP & MF resin exhibited similar changing trends. However, after 450 °C, the weight loss rate of coating containing MFAPP was greater than that of the coating containing APP & MF resin. This phenomenon indicated the interaction among intumescent flame retardant additives was more complete, resulting in a stage decline of the weight loss. MFAPP increased the char residues of coating, which was the key factor for the improved flame retardant properties at high temperature, as suggested by fire resistance test of the coatings mentioned above. The residue ratios of coating containing MFAPP and coating containing APP & MF resin were 28.7 and 26.1%, respectively. The increased residue at high temperature should be attributed to the formation of more thermally stable carbonaceous char when polyurethane, MEL, PER, and MFAPP inter-reacted to expand.[31,36]

Hydrophobicity of MFAPP and coating

Since the hydrophilic and easy migratory natures of APP greatly decrease the durability and fire resistance of the coating, it is very important to reduce the water solubility of APP.[31–33] Water solubility test of APP and MFAPP gave a clear insight into the influence of microencapsulation on the water solubility of APP. In order to investigate the influence of microencapsulation on the surface properties of MFAPP, the water contact angle on the APP, MFAPP, and two kinds of intumescent fire-retardant coatings were measured. Moreover, the static immersion test was used as an accelerated aging test of water on the coating, which directly reflected the influence of water on coatings in the process of the long-term use.

Figure 8 shows the variations of solubilized APP and MFAPP at different immersion times. At the immersion time of 2 h, the solubility of APP without microencapsulation was 4.03 g/100 ml H_2O, indicating that APP can be easily attacked by the water molecules when exposed in water surroundings. And with

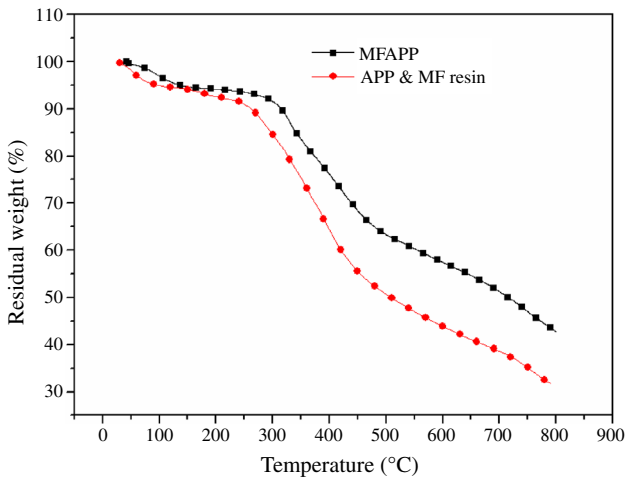

Fig. 6: TGA curves of MFAPP and APP & MF resin

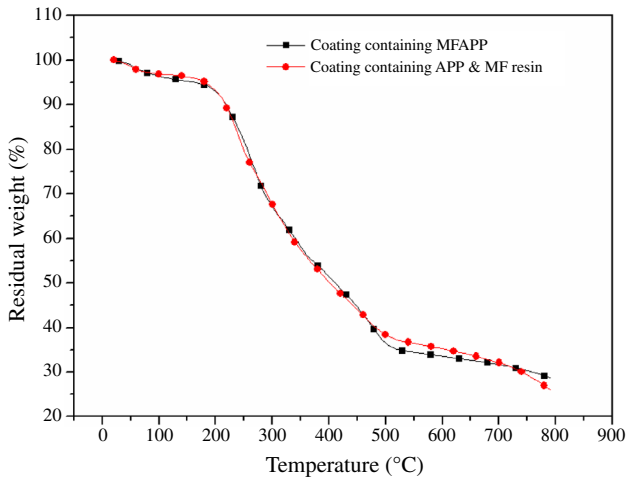

Fig. 7: TGA curves of coating containing MFAPP and coating containing APP & MF resin

increasing the immersion time, the water solubility of APP gradually increased to 5.32 g/100 ml H_2O when immersion time was 10 h. This suggested that APP was extremely able to absorb water under high humidity conditions in long-term use. However, as for MFAPP, the solubility was 0.93 g/100 ml H_2O, which was lower than that of APP. Moreover, the immersion time showed less effect on the solubility of MFAPP when compared with neat APP. It was because the APP was coated by a layer of MF resin which was hydrophobic and prevented APP from being attacked by water. Therefore, the waterproof properties of APP were improved.

The water contact angle of the APP, MFAPP, coating containing APP & MF resin, and coating containing MFAPP is shown in Fig. 9. The relatively small contact angle (15.3°) of APP can be attributed to the hydrophilicity of NH_4^+ in APP.[30,37] The water contact angle of MFAPP was 73.1°, which was much higher than APP, suggesting that the microencapsulation of APP could change the surface properties of APP and improve the waterproof properties. As shown in Figs. 9c and 9d, the water contact angle of the coating containing 40 wt% of APP & MF resin and coating containing 40 wt% of MFAPP was 39.9° and 64.2°, respectively. These results indicated that the microencapsulation of APP may increase the compatibility of APP with polymers when used in coatings, thus improving the dispersibility of additives in the polymer matrix.[30]

In order to directly investigate the influence of moisture on coatings in terms of the long-term use, the static immersion test was carried out as an accelerated aging test of water on the coating. Pictures of two kinds of coatings in the water and after the static immersion

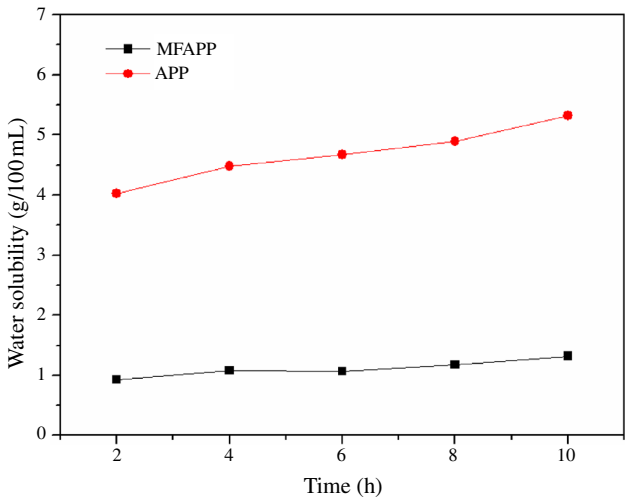

Fig. 8: Water solubility of APP and MFAPP

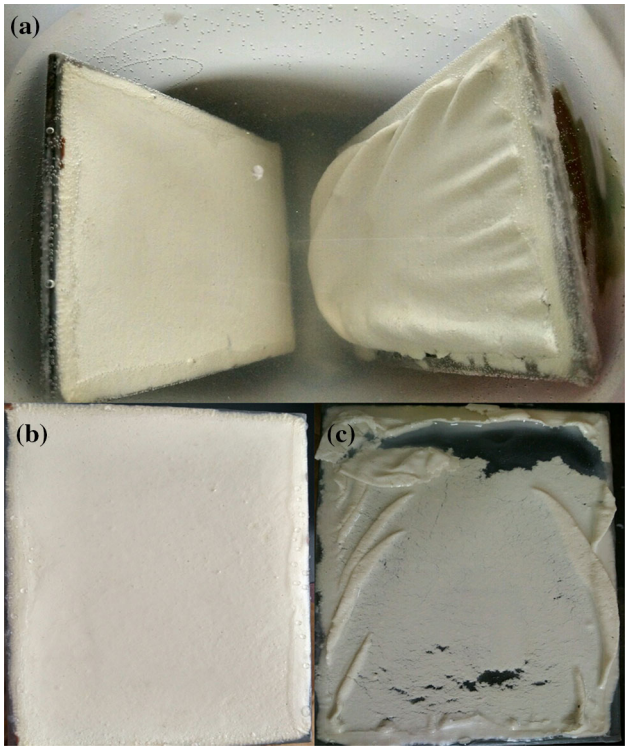

Fig. 10: Pictures of two kinds of coatings immersed in the water (a: left is coating containing MFAPP; right is coating containing APP & MF resin), coating containing MFAPP after the static immersion test (b), and coating containing APP & MF resin after the static immersion test (c)

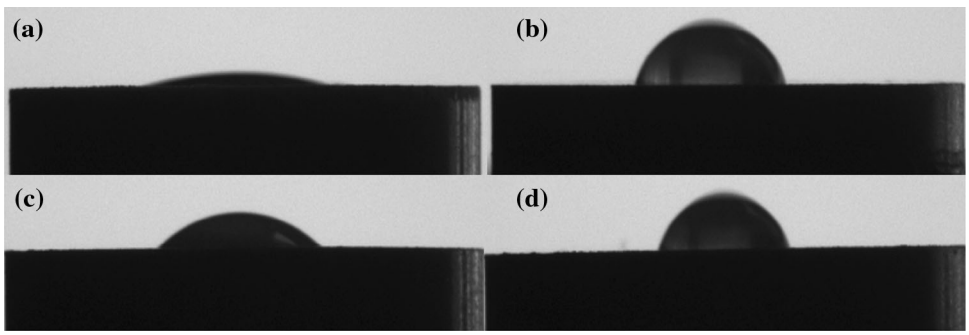

Fig. 9: The water contact angle of the APP (a), MFAPP (b), coating containing APP & MF resin (c), and coating containing MFAPP (d)

test are shown in Fig. 10. During the process of immersion test, the coating containing APP & MF resin began to foam gradually until peeled off completely, while the coating containing MFAPP did not foam at all and the morphology remained throughout the test. After the test samples were immersed in distilled water at room temperature for 12 h, there was no adhesion between the coating containing APP & MF resin and the steel plate. However, the coating containing MFAPP did not show any change. This indicated that the microencapsulation of APP reduces the influence of water on the coating, resulting in distinguished durability of the coating.

The surface morphology of coating containing APP & MF resin and coating containing MFAPP after water treatment was investigated by SEM. As shown in Fig. 11, the two coatings exhibited obviously different surface morphologies. The relatively more ''cavities'' of coating containing APP & MF resin (a, b) was attributed to the aggregation and exfoliation of APP particles in water, resulting from the poor compatibility and water resistance of APP. Compared with Figs. 11a, 11b and Figs. 11c, 11d shows more compact structures and much fewer ''cavities.'' When the coating containing MFAPP was exposed in water, the comparatively better dispersion and less solubility of MFAPP in coating would prevent APP from being exuded, and a certain flame retardancy of the coatings can still be maintained.

Fire protection and thermal properties of coatings after the static immersion test

In order to investigate the influence of microencapsulation on the durability of coatings, the fire resistance and thermal properties of coating containing MFAPP and coating containing APP & MF resin after water immersion were studied. After the static immersion test, the coatings were dried at room temperature for 72 h and then analyzed by fire protection test and TGA. The TGA curves and the temperature–time curves in fire resistance test of the coatings are shown in Figs. 12 and 13. Compared with TGA curves before the static immersion test in Fig. 7, the difference between the TGA curves of two kinds of coatings after the static immersion test became much larger, which was mainly reflected by the difference of the weight loss rate and the residue weight. The weight loss rate of coating containing MFAPP was obviously lower than that of coating containing APP & MF resin. The residue of coating containing MFAPP and coating containing APP & MF resin was 23.4 and 10.9%, respectively. The residue was mainly the carbon layer produced by the interaction between several substances. This indicated that the char layer of coating containing APP & MF resin after the static immersion test was much less and more easily damaged at high temperature. Furthermore, the TGA curves and the residue weight of coating containing APP & MF resin showed great change

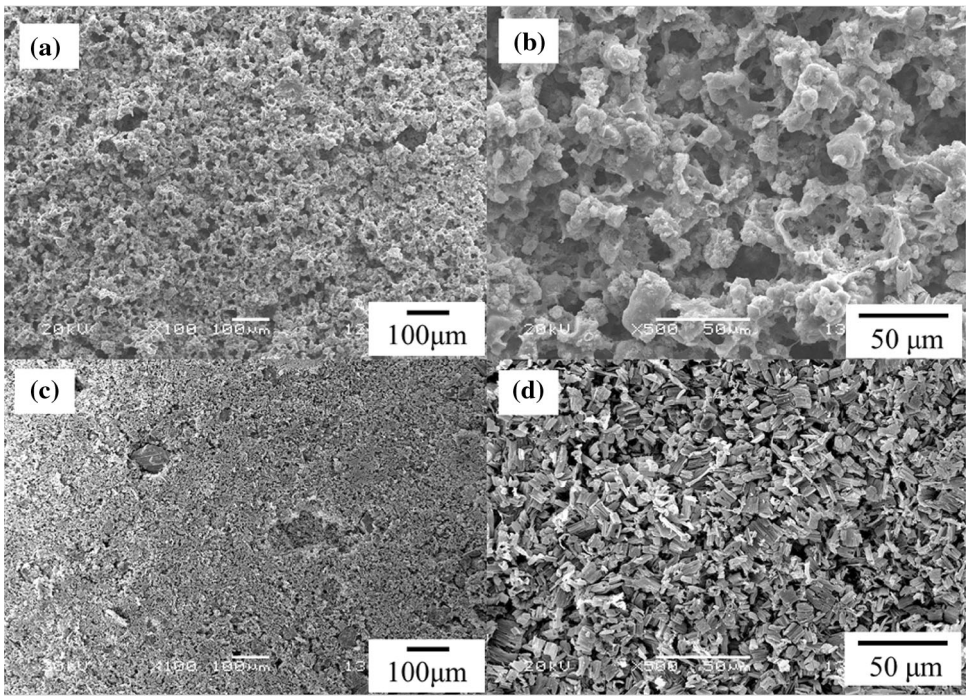

Fig. 11: SEM images of coating containing APP & MF resin (a, b) and coating containing MFAPP (c, d) after the static immersion test

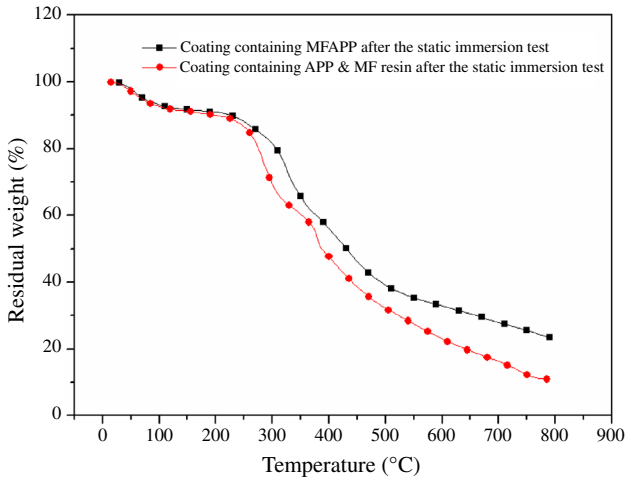

Fig. 12: TGA curves of coating containing MFAPP and coating containing APP & MF resin after the static immersion test

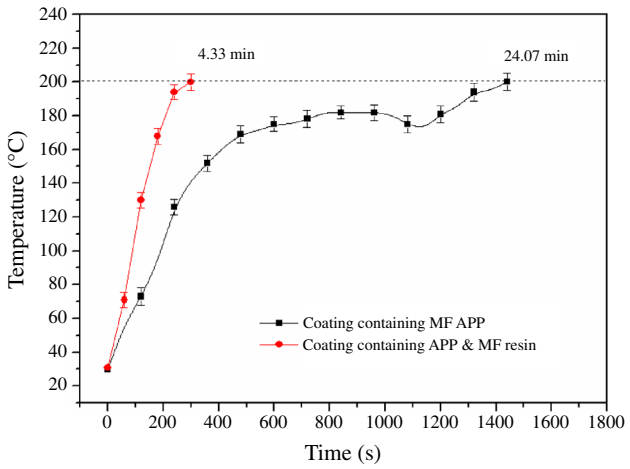

Fig. 13: The backside temperature curves of coating containing MFAPP and coating containing APP & MF resin after the static immersion test

before and after the static immersion test. These results proved that the microencapsulation of APP diminished the effect of water on waterborne intumescent fire-retardant coatings, which will be further confirmed by the fire resistance test below.

As shown in Fig. 13, the fire-resistant time of coating containing MFAPP and coating containing APP & MF resin after the static immersion test was 24.07 and 4.33 min, respectively. These results confirmed that the microencapsulation of APP diminished the effect of water on waterborne intumescent fire-retardant coatings, which was consistent with the thermal analysis results. However, compared with the fire-resistant time before the static immersion test in Fig. 4, the fire-resistant time of coating containing MFAPP and coating containing APP & MF resin after the static immersion test was reduced by 79.83 and 93.88%, respectively. It was attributed to the migration and lose of efficacy of other components during the static immersion test, which will change the fixed composition of the coating; thus, the fire resistance performance declined. Hence, it is of great significance to study the durability of other components in the coating, which will be one of the important research directions of the intumescent fire-retardant coatings.

Conclusion

Microencapsulated APP with melamine formaldehyde resin (MFAPP) was prepared and used in the intumescent fire-retardant coating with pentaerythritol (PER), melamine (MEL), and waterborne polyurethane emulsion modified by epoxy resin (E-44). The FTIR spectra, particle size test, and SEM images indicated that the MF resin has been wrapped onto the surface of APP. Compared with APP, MFAPP has better water resistance, thermal stability, and compatibility with the polymer matrix due to the hydrophobicity of MF resin shell. Moreover, static immersion test results show that after being immersed in distilled water at room temperature for 12 h, there was no adhesion between the coating containing APP & MF resin and the steel plate, while the coating containing MFAPP was almost unchanged. The fire-resistant time and thermal stability of coating containing MFAPP were also enhanced as compared with that of the coating containing APP & MF resin at the same loading before and after the static immersion test. The reason was that MF resin shell improved the dispersion of APP in the polymer matrix, which would help form dense char layer in a timely way. In summary, the microencapsulation of APP not only effectively improved the durability, but also remarkably enhanced the fire resistance of the fire-retardant coating when it was used in fire-retardant coating as acid source.

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