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Microencapsulated Ammonium Polyphosphate with Polyurethane Shell: Application to Flame Retarded Polypropylene/Ethylene-propylene Diene Terpolymer Blends

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Microencapsulated Ammonium Polyphosphate with Polyurethane Shell: Application to Flame Retarded Polypropylene/Ethylene-propylene Diene Terpolymer Blends

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Microencapsulated ammonium polyphosphate with polyurethane resin (PUMAPP) was prepared by *in situ* polymerization and characterized by X-ray photoelectron spectroscopy (XPS). The flame retardation of PUMAPP/dipentaerythritol(DPER) and ammonium polyphosphate (APP)/DPER flame retarded polypropylene (PP)/ethylene propylene diene rubber (EPDM) composites were studied using limiting oxygen index (LOI), UL-94 test and cone calorimeter. Results demonstrated that the flame retardancy of the PP/EPDM/PUMAPP/DPER composites was better than that of the PP/EPDM/APP/DPER composites at the same additive loading. Real time Fourier transform infrared (FTIR) and thermogravimetric analysis (TG) were used to study the thermal degradation and stability of the PP/EPDM/PUMAPP/DPER composite. The hydrolytic stability of the flame retarded PP/EPDM composites was studied. It was found that the microencapsulation of APP with the PU resin led to a decrease in the particle's water solubility. Moreover, the synergistic effect of vinyltrimethoxysilane (VTMS) on the PP/EPDM/PUMAPP/DPER composite was also investigated.

Keywords: Microencapsulation, ammonium polyphosphate, polyurethane, PP/EPDM, intumescent flame retardation and

1 Introduction

Plastics/rubber blends have gained significant attention due to the ease of tailoring the required properties and the simple preparation method. Among different kinds of plastics/rubber blends reported, the polypropylene (PP)/ethylene propylene diene rubber (EPDM) blends play an important role (1). PP/EPDM blends are extensively used in many fields, for example, cars, electric casings, interior decoration, insulation, etc. Nevertheless, the drawbacks of PP/EPDM blends, like relatively lower thermal stability and flammable properties, restrict the range of its application.

Traditionally, halogen-containing flame retardants produce large amounts of smoke and corrosive and irritating gases on burning, and thus limit their use in some occasions (2). In the search for halogen-free retardants, increasing attention is being given to intumescent flame retardant (IFR) systems. A typical intumescent system comprises an acid source—a dehydration catalyst for char formation, a carbon source—a carbonization agent and a gas source—a blowing agent (3). The compounds used as an acid source are generally inorganic acids or precursor of the acids, for example, ammonium polyphosphate (APP). Carbonization agents are mainly hydroxyl-containing compounds, such as pentaerythritol (PER) and starch, and blowing agents are the compounds which can produce gases on heating, for example, melamine (MEL), urea, and so on. In recent years, many papers have been published on the APP/PER/MEL intumescent flame retardation of polyolefins (4–6).

Unfortunately, most IFR systems have some problems such as moisture sensitivity and poor compatibility with polymer matrix. In fact, ammonium phosphates are water-soluble and they have a poor compatibility with the

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Table 1. The formulation of the untreated and flame retarded PP/EPDM.

Sample	PP/EPDM	PUMAPP (phr)	APP (phr)	DPER (phr)	DCP (phr)	DBTDL (phr)	VTMS (phr)
PE	100	—	—	—	—	—	—
PEAD1	100	—	12.5	12.5	—	—	—
PEAD2	100	—	16.5	16.5	—	—	—
PEAD3	100	—	21.5	21.5	—	—	—
PEA	100	—	43	—	—	—	—
PEPD1	100	12.5	—	12.5	—	—	—
PEPD2	100	16.5	—	16.5	—	—	—
PEPD3	100	21.5	—	21.5	—	—	—
PEP	100	43	—	—	—	—	—
PEVPD	100	21.5	—	21.5	0.1	0.1	2

polymer. Thus problems of migration and solubility may occur. To deal with the problems of moisture absorption and poor compatibility with polymers, the technique of microencapsulation is a good choice.

Microencapsulation is a process of enveloping microscopic amounts of matter in a thin film of polymer, which forms a solid wall (7). This core/shell structure allows isolation of the encapsulated substance from the surroundings and thus protects it from any degrading factors such as water. Melamine–formaldehyde (MF) and urea–formaldehyde (UF) resins are commonly used in the microencapsulation, for example, red phosphorus (8), epoxy resins (9), etc. Recently, Kun Wu and coworkers have done a great deal of work on the microencapsulated APP with MF and urea–melamine–formaldehyde (UMF) resin (10, 11). However, very few publications have been found on the microencapsulation of APP with polyurethane resin and its application in polymers, especially in PP/EPDM.

In the present work, the microencapsulated ammonium polyphosphate with polyurethane resin (PUMAPP) was prepared by in situ polymerization and characterized by XPS. The flame retardation, thermal and hydrolytic stability of the PUMAPP/DPER and APP/DPER flame retarded PP/EPDM composites were studied by LOI, UL 94 test, cone calorimeter, TG and SEM, respectively. Real time FTIR was used to investigate the thermal degradation mechanism of the PUMAPP/DPER flame retarded PP/EPDM composite. The mechanical properties of the materials were also studied. Moreover, the synergistic effect of vinyltrimethoxysilane (VTMS) on the PP/EPDM/PUMAPP/DPER composite was investigated.

2 Experimental

2.1 Materials

Polypropylene (F401, MFI = 2.0 g/10 min, density = 0.9 g/cm³) was provided by Yangzi Petroleum Chemical Company, China. Ethylene-propylene-diene copolymer (EPDM 5565) containing 50 wt% ethylene and 7.5 wt%

ethylidene norbornene (ENB) was supplied by DuPont Dow Elastomer Co. Ltd., USA. APP with a average degree of polymerization ($n > 1,000$) was kindly supplied by Shandong Shian Chemical Engineering Corporation, China. Pentaerythritol (PER), DPER, VTMS, dicumyl peroxide (DCP), its half time 175°C is about 1 min), dibutyl tin dilaurate (DBTDL, toluene-2,4-diisocyanate(TDI), 1,4-dioxane, Tween-80, dimethyl sulfoxide (DMSO), were standard laboratory reagents and provided by Sinopharm Chemical Reagent Co. Ltd., China.

2.2 Preparation of Microencapsulated APP

The mixture of 2.04 g PER (0.015mol) and DMSO (30 ml) was first added into 500 ml three-necked, round-bottomed flask and stirred at 1000 rpm for 10 min at 40°C. Then 5.46 g TDI (0.03 mol) of 30 ml 1,4-dioxane was poured into the above solution. 25 min later, put into 60 g APP of 150 ml 1,4-dioxane, 0.375 g (5% of polyurethane) Tween-80 and 0.18 g DBTDL. Then the resulting solution was heated to 85°C and kept for several hours. After that, the bright yellow suspension could be obtained and cooled to the room temperature, filtered, washed with distilled water, and dried at 80°C. The PUMAPP microcapsules were finally acquired.

2.3 Preparation of Flame Retarded PP/EPDM Composites

All flame retarded PP/EPDM composites were prepared in a Brabender-like apparatus at a temperature of about 175°C for 15 min. After mixing, the samples were hot-pressed at about 175°C under 10 MPa for 10 min into sheets of suitable thickness for analysis. The formulations are given in Table 1. It is necessary to note that the weight ratio of PP/EPDM in all the PP/EPDM composites was 3:2.

2.4 Measurements and Characterization

2.4.1 X-ray photoelectron spectroscopy

The PUMAPP was characterized by XPS. The XPS spectra were recorded with a VG Escalab mark II spectrometer

(VG Scientific Ltd, UK), using Al K α excitation radiation (1253.6 eV) and calibrated by assuming the binding energy of carbonaceous carbon to be 284.6 eV.

2.4.2. Limiting oxygen index

LOI was measured according to ASTM D2863 using an HC-2 oxygen index meter (Jiangning Analysis Instrument Company, China). The specimens for the test were of dimensions $100 \times 6.5 \times 3 \text{ mm}^3$.

2.4.3. UL94 vertical burn tests

The vertical burn test was carried out on a CFZ-2-type instrument (Jiangning Analysis Instrument Company, China) according to the ASTM D3801 UL 94 test standard. The specimens used were of dimensions $130 \times 13 \times 3 \text{ mm}^3$.

2.4.4. Cone calorimetry

The cone calorimeter (Stanton Redcroft, UK) test was performed according to ISO 5660 standard procedures. Each specimen of dimensions $100 \times 100 \times 3 \text{ mm}^3$ was wrapped in aluminum foil and exposed horizontally to an external heat flux of 35 kW/m^2 .

2.4.5. Mechanical properties measurement

The tensile strength and elongation at break were measured with a WD-20D Electronic Universal Testing Machine at the crosshead speed of 500 mm/min. The type and rated load of load cell used in the tensile tests were FR-1 and 20000N, respectively.

2.4.6. Thermogravimetric analysis

The thermogravimetric experiments were performed using analyzer STA 409 C TGA apparatus (Netzsch Company, Germany) under air flow at a heating rate of $10^\circ\text{C}/\text{min}$.

2.4.7. Real time FTIR spectroscopy

Real time Fourier transform infrared (FTIR) spectra were recorded using a Nicolet MAGNA-IR 750 spectrophotometer equipped with a ventilated oven having a heating device. The untreated PP/EPDM and flame retarded PP/EPDM composites were mixed with KBr powders, and the mixture was pressed into a tablet, which was then placed into the oven. The temperature of the oven was raised at a heating rate of about $10^\circ\text{C}/\text{min}$. Dynamic FTIR spectra were obtained *in situ* during the thermal oxidative degradation of the polymer and its composites.

2.4.8. Scanning electron microscopy

The samples were fractured in liquid nitrogen first and then immersed into water for 24 h. After that, the fractured surface was sputter-coated with a conductive layer, and then its morphologic structures were observed by scanning electron microscopy AMRAY1000B.

2.4.9. Ageing studies

Sheets of fire retardant polymers were kept in water at 50°C for 24 and 48 h, respectively. The relative hydrolytic stability was monitored in terms of LOI, UL-94 test and SEM for the exposed specimens.

3 Results and Discussion

3.1 Characterization of PUMAPP by XPS

Figure 1 shows XPS spectra of APP and PUMAPP. As shown in Figure 1, the two peaks located at 134.7 and 190.9 eV could be attributed to the absorption of P_{2P} and P_{2S}, respectively. Compared PUMAPP with APP, it is noted that the intensities of the two peaks decrease greatly. Meanwhile the intensities of the C_{1S} peaks centered at 284.7, increase sharply. The changes of the above peaks are due to the coverage of the outside APP particles with the PU resin which indicates that APP was successfully coated by the resin.

3.2 Flame Retardancy

Table 2 presents the LOI values and UL 94 testing results of the untreated and flame retarded PP/EPDM composites. As seen from Table 2, the LOI value of sample PEA is as low as 21. The LOI value of sample PEP is 26, which is higher than that of sample PEA. However, both of the composite cannot pass the UL 94 test. There are no ratings for the composites at all. The above results illustrate that PUMAPP used alone in PP/EPDM also does not have good flame retardancy. When DPER is incorporated into the PP/MP composites, a remarkable improvement of flame retardation is observed. From the data listed in Table 2, at the same loading, i.e., 43 phr flame retardants, the LOI values of sample PEAD3 and PEPD3 are enhanced from 21 to 30.5 and 26 to 32, respectively, in comparison with those of sample PEA and PEP. Moreover, both sample PEAD3 and PEPD3 can reach the V-O rating in UL-94

Table 2. LOI and UL-94 results of the untreated and flame retarded PP/EPDM.

Sample	LOI (%)	UL-94
PE	17.5 ± 0.5	No-rating
PEAD1	23 ± 0.5	No-rating
PEAD2	26.5 ± 0.5	V-2
PEAD3	30.5 ± 0.5	V-0
PEA	22 ± 0.5	No-rating
PEPD1	25 ± 0.5	No-rating
PEPD2	28.5 ± 0.5	V-2
PEPD3	32 ± 0.5	V-0
PEP	26 ± 0.5	No-rating
PEVPD	33.5 ± 0.5	V-0

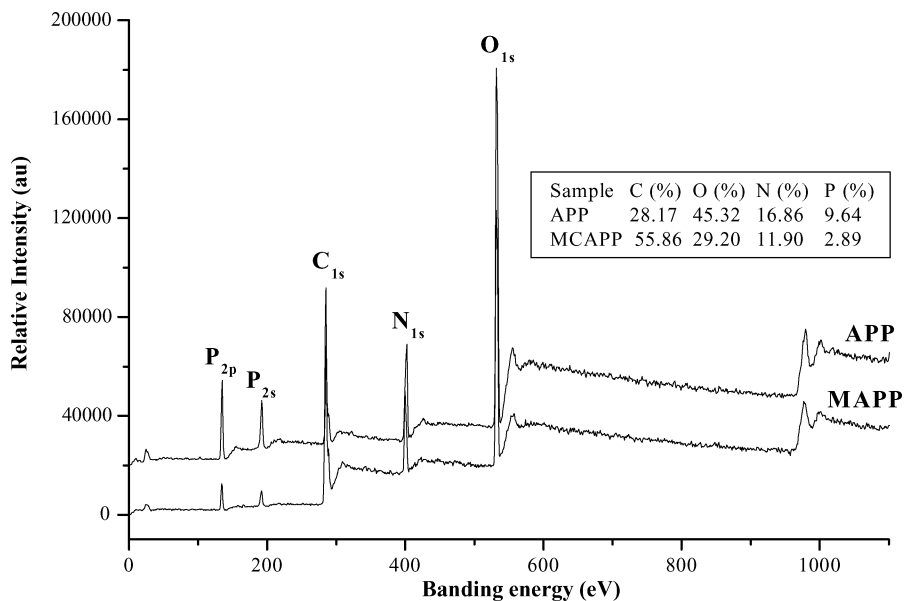


Fig. 1. XPS spectra of APP and PUMAPP.

testing. Of the most interest is the fact that the LOI value of sample PEPD3 is higher than that of sample PEAD3. The explanation for the increase may be due to the fact that when the PP/EPDM composites containing PUMAPP are heated, the PU resin in the coating layer of APP could act as carbonization agent, which makes the material swell to form better intumescent char during the combustion process and thus improve the flame retardancy of the materials. In addition, compared sample PEVPD with sample PEPD3, it is also can be seen from Table 2 that the incorporation of VTMS could enhance the LOI value of the PP/PUMAPP/DPER composite further.

The flame retardancy of the untreated and flame retarded PP/EPDM composites are also investigated by cone calorimeter. Cone calorimeter is a performance based bench scale fire testing apparatus and has been found that its results correlate well with those obtained from large scale fire tests, and thus it has become a reliable indicator of likely performance in a real fire (12). Heat release rate (HRR), especially the peak HRR (PHRR), has been found to be one of the most important parameters to evaluate fire safety. Figure 2 shows the RHR curves of the flame retarded PP/EPDM composites vs. PP/EPDM obtained from the cone calorimeter test. It can be seen that the material without flame retardant burns very fast after igni-

tion and a sharp RHR peak appears with a PRHR value of 1302 kW/m². In the case of sample PEAD3, PEPD3 and PEVPD, their PRHR values are greatly reduced, as shown in Figure 1. Moreover, sample PEPD3 has a much lower PHRR value than that of sample PEAD3, illustrating that microencapsulated ammonium polyphosphate with polyurethane resin is more effective in improving the flame retardancy of the PP/EPDM composite.

It is noted from Table 3 that the ignition time (IT) of the fire retarded PP/EPDM composites is lower than that of the untreated PP/EPDM. This is a typical character of intumescent flame retardant system and has been previously

Table 3. Cone calorimeter data of the untreated and flame retarded PP/EPDM.

Sample	PE	PEAD3	PEPD3	PEVPD
Time to ignition (s)	55 ± 1	47 ± 1	34 ± 1	58 ± 1
Peak RHR (kW/m ²)	1302 ± 65	364 ± 18	303 ± 15	335 ± 16

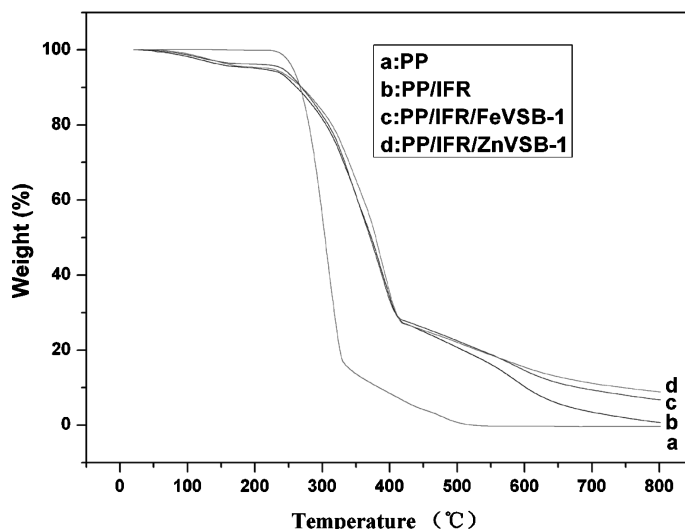


Fig. 2. Effect of the TMIVSB-1 on the thermal stability of PP/IFR systems measured by TGA under air. (PP/IFR/TMIVSB-1 = 75/23/2; IFR:APP/petol = 2/1, by weight).

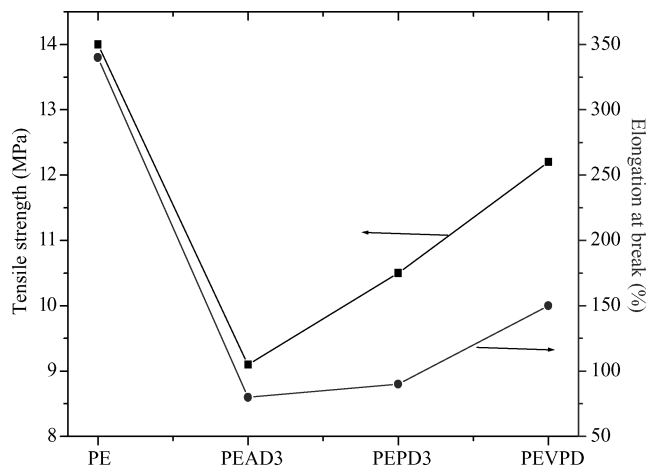


Fig. 3. Mechanical properties of pure PP/EPDM and the flame retarded PP/EPDM composites.

discussed by other researchers (13). As shown in Table 3, it can be found that the ignition time of sample PEPD3 is lower than that of sample PEAD3, indicating that the introduction of PUMAPP into PP/EPDM decreases the apparent stability of the material further and increase the ease of ignition, compared with uncoated APP particles. Nevertheless, it is interesting to see that the introduction of VTMS into the IFR PP/EPDM composites leads to an increase in the IT from 34 (sample PEPD3) to 58 (sample PEVPD).

3.3 Mechanical Properties

Figure 3 shows the mechanical properties of pure PP/EPDM and the flame retarded PP/EPDM composites. It is expected that the tensile strength and elongation at break decrease with adding flame retardants. As seen from Figure 3, the tensile strength and elongation at break of sample PEPD3 increase from 9.0 to 10.5 MPa and 80 to 90%, respectively, in comparison with sample PEAD3, indicating that the mechanical properties of sample PEPD3 is better than that of sample PEAD3. This could be due to the fact that the microencapsulation of APP is beneficial to improve the compatibility of APP in the polymer resin. Moreover, as shown in Figure 3, it is noted that the incorporation of VTMS enhance the mechanical properties of sample PEPD3 further.

3.4 Thermal Behavior

The TG curves of APP and PUAPP in the air atmosphere are shown in Figure 4. As seen from Figure 4, APP mainly has two decomposition processes. It begins to decompose at about 320°C ($T_{-5\%}$). The evolution products in the first process are mainly ammonia and water (about 20% mass loss), and crosslinked polyphosphoric acids are formed simultaneously (14). The second process occurs in the range

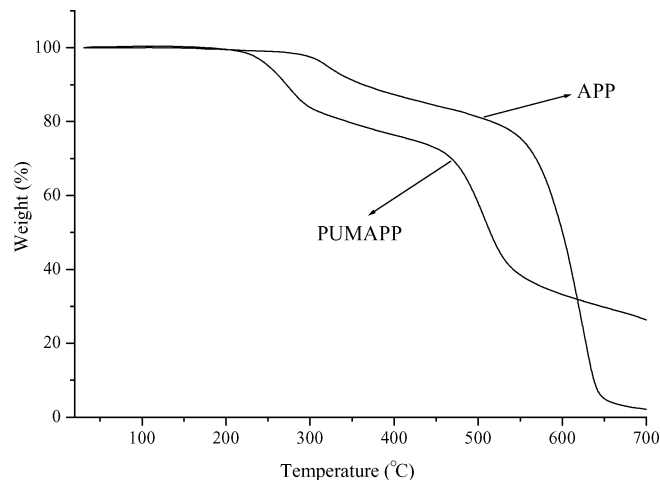


Fig. 4. TG curves of APP and PUMAPP in the air atmosphere.

of 500–700°C, which is the main decomposition process of APP, and weight loss is about 78%. The residual weight of APP is 2.4% at 700°C. It is noted that the initial decomposition temperature of PUMAPP begins around 250°C which is lower than that of APP, resulting from a lesser amount of thermal stability of PU resin in PUMAPP (7). However, when the temperature is up to 618°C, PUMAPP is more thermally stable than APP. Moreover, PUMAPP after the decomposition at 700°C left about 26.5% residue, while for APP, only 6.6% residue is left at the temperature.

Figure 5 shows the TG curves of the untreated PP/EPDM and flame retarded PP/EPDM. It is clear to see that the untreated PP/EPDM begins to decompose at about 259°C and almost decomposes completely at 550°C. As for sample PEAD3, the initial decomposition temperature is enhanced to 270°C and 4.7% residue is left at 700°C. However, with regard to samples PEPD3 and PEVPD, they

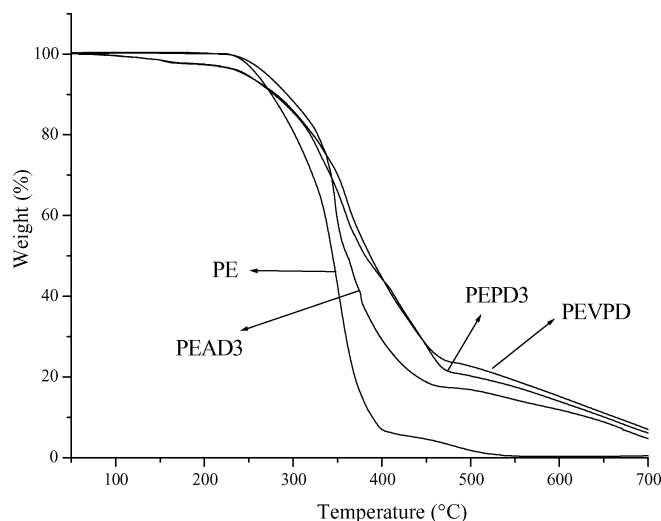


Fig. 5. TG curves of sample PE; sample PEAD3; sample PEPD3 and sample PEVPD in the air atmosphere.

decompose early in comparison with the pure PP/EPDM and sample PEAD3, due to the primal decomposition of the PU resin in PUMAPP. As a matter of fact, the existence of APP could accelerate the decomposition of PU resin (15). Nevertheless, after 340°C, the thermal stability of sample PEPD3 is higher than that of sample PEAD3, which may be caused by the formation of more thermally stable intumescent char at a relatively higher temperature. Moreover, it is noted that the incorporation of VTMS is beneficial to improve the thermal stability of sample PEPD3 further. As seen from Figure 5 and Table 4, when the temperature is under 315 and in the temperature range from 400 to 450°C, the TG curve of sample PEPD3 is almost the same as that of sample PEVPD, however, during the temperature range from 310 to 400°C and 450 to 700°C, sample PEVPD possesses a relatively higher thermal stability.

3.5 Thermal Degradation Mechanism

The thermal degradation behavior of sample PEPD3 is investigated using real time FTIR spectroscopy. Figure 6 shows the changes in the dynamic FTIR spectra obtained from the sample PEPD3 at different pyrolysis temperatures.

As shown in Figure 6, at 25°C, the peaks at 2956 (asymmetric stretch vibration of CH₃), 2924 (asymmetric stretch vibration of CH₂), 2840 (symmetric stretch vibration of CH₂), 1458 (asymmetric deformation vibration of CH₃/CH₂), 1380 (symmetric deformation vibration of CH₃), 1169 (stretch vibration of C-C) and the three peaks at 975 and 840 cm⁻¹, assigned to the wagging vibration of CH₃/CH₂ which are the typical absorption peaks of PP/EPDM. When temperature is up to 400°C, these peaks disappear completely, indicating the entire decomposition of PP/EPDM.

As seen from Figure 6, the band around 1730 and 1650 cm⁻¹, attributed to the C=O and N-H of the urethane function, decreased from 250°C, which is caused by the decomposition of PU resin. Then, at 350°C, the 1730 peak becomes wider, while the peak at 1650 cm⁻¹ disappears. When the temperature is up to 400°C, a wider peak at 1600 cm⁻¹ appears, which may be due to the absorption of N-H in the H-N-C(=O)-O-P groups formed by the reaction between polyphosphoric acid and isocyanate group (15). Af-

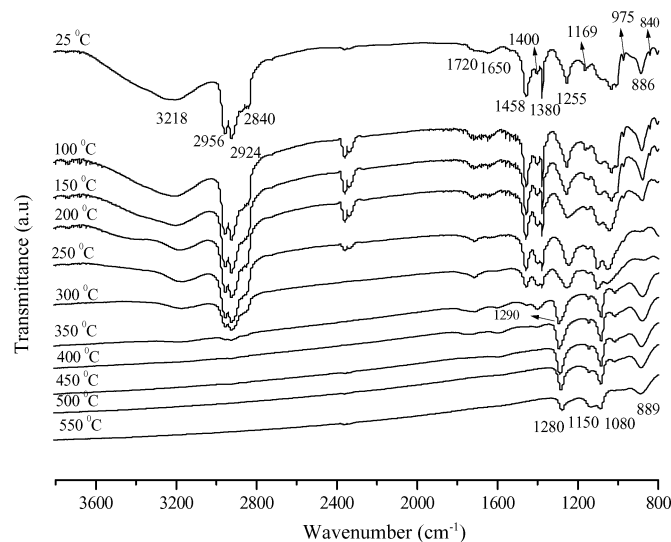


Fig. 6. Dynamic FTIR spectra of sample PEPD3 with different pyrolysis temperatures.

ter 450°C, the H-N-C(=O)-O-P groups decompose, leading to the formation of a charred carbonaceous structure, as well as the disappearance of the two peaks.

The peaks at 3215 and 1400 cm⁻¹ could be assigned to the stretching and deformation vibration of NH₄⁺, respectively. They disappear at 350°C because of the elimination of NH₃ from ammonium salt complexes (16). At 25°C, the peaks at 1255, 1087 and 886 cm⁻¹ were attributed to the O=P, P-O-P absorption of APP. It is clearly seen from Figure 5 that the peak at 1255 cm⁻¹ moves to the relatively higher wave numbers (1290 cm⁻¹) when temperature increases to 350°C. This could be due to the formation of pyrophosphate caused by the dehydration of polyphosphoric acids, as discussed in the above “thermal behavior” part. At 550°C, there are mainly three peaks which existed in the spectra. The absorption peaks at 1150 cm⁻¹ might be assigned to the stretching vibration of P-O-C, as phosphate-carbon complexes (17). The peaks at 1280, 1080 and 886 cm⁻¹ as shown in the spectrum, indicate that the residue also contains P=O and P-O-P groups.

3.6 Hydrolytic Stability

Recently, increasing attention is being given to the hydrolytic stability of intumescent flame retarded polymer composites. This is due to the fact that most intumescent flame retardants tend to migrate to the surface of the composite and dissolve into the water which can deteriorate its flame retardancy and physical properties (18).

Table 5 shows the variation of the LOI values and of the UL-94 rating after immersing the materials. According to the Table 5 results, the fire performance of all the materials are changed, i.e., all the LOI values have decreased after immersion. However, compared with

Table 4. TG data of APP, PUMAPP, the untreated PP/EPDM and the flame retarded PP/EPDM

Sample	$T_{-5\%}$ (°C)	$T_{-50\%}$ (°C)	Residual mass (at 700°C) (%)
APP	320	599	6.6
PUMAPP	250	515	26.5
PE	259	344	0
PEAD3	270	360	4.7
PEPD3	245	380	6.2
PEVPD	245	387	7.0

PP/EPDM/APP/DPER composites, it is seen that the water treatment has less impact on the LOI values and UL-94 ratings of the PP/EPDM/PUMAPP/DPER composites. As shown in Table 5, when the samples are immersed into 50°C water for 24 h, regardless of the decrease in the LOI values of the PP/EPDM/PUMAPP/DPER composites after treated, a good maintenance of the UL-94 ratings is observed (still V-0 rating). As a consequence, the conclusion can be drawn that the water re-

sistance of PUMAPP is much better than that of APP in PP composites. Moreover, when VTMS is incorporated into the PP/EPDM/PUMAPP/DPER composite, a better flame retardancy could be obtained after immersion. For example, when the immersion time increases to 48 h, the formulation without VTMS is no-rating for the UL-94 test, while the formulation containing the synergistic agent maintains a V-0 classification. This is possibly explained by the fact that the Si-O-Si three dimensions network formed

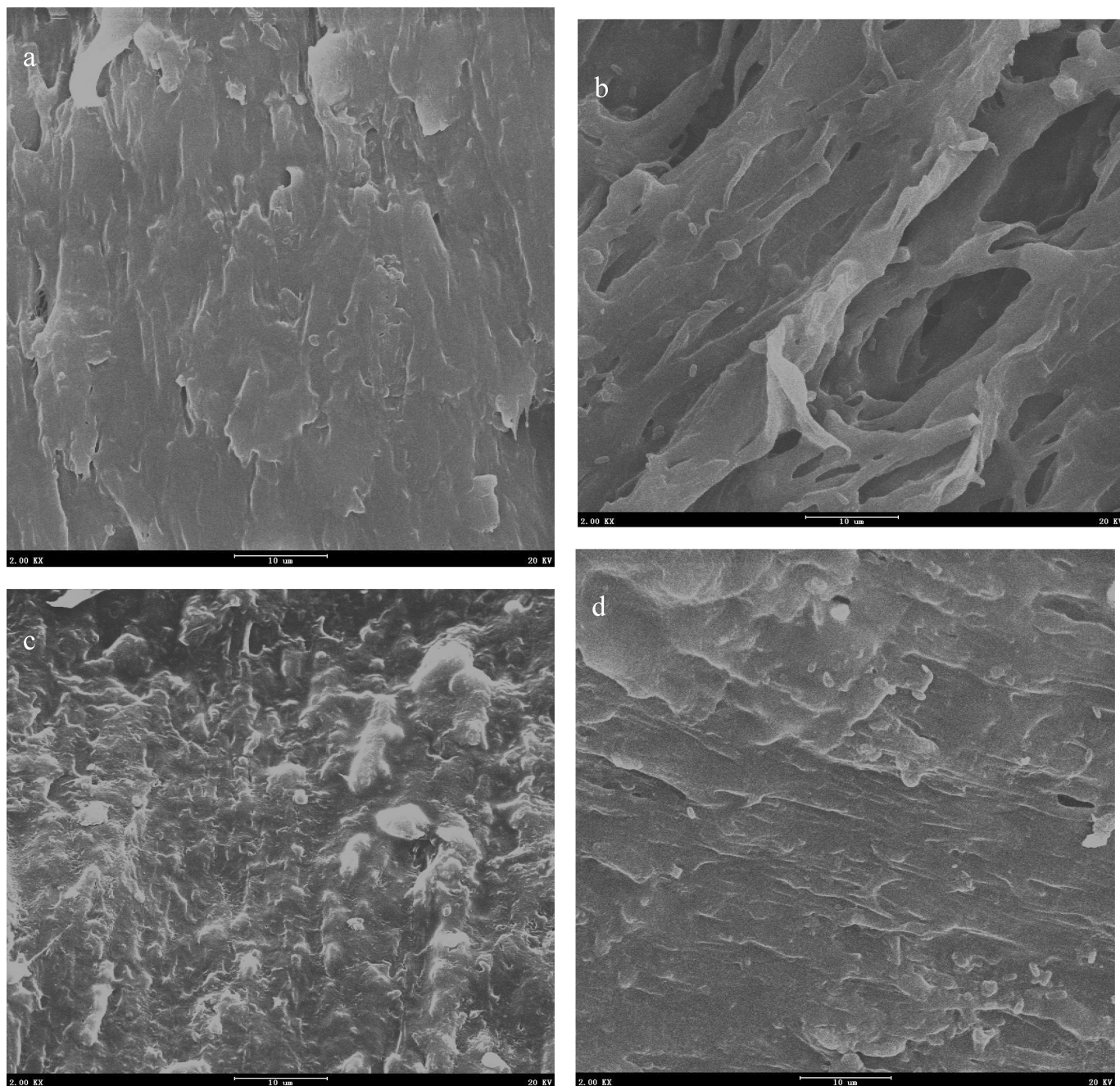


Fig. 7. SEM micrographs of the fractured surfaces of sample PEAD3 (a, b), PEPD3(c, d) and PEPVD (e, f) before and after water treatment (50°C, 24 h), magnified by 2000 times. (*Continued*)

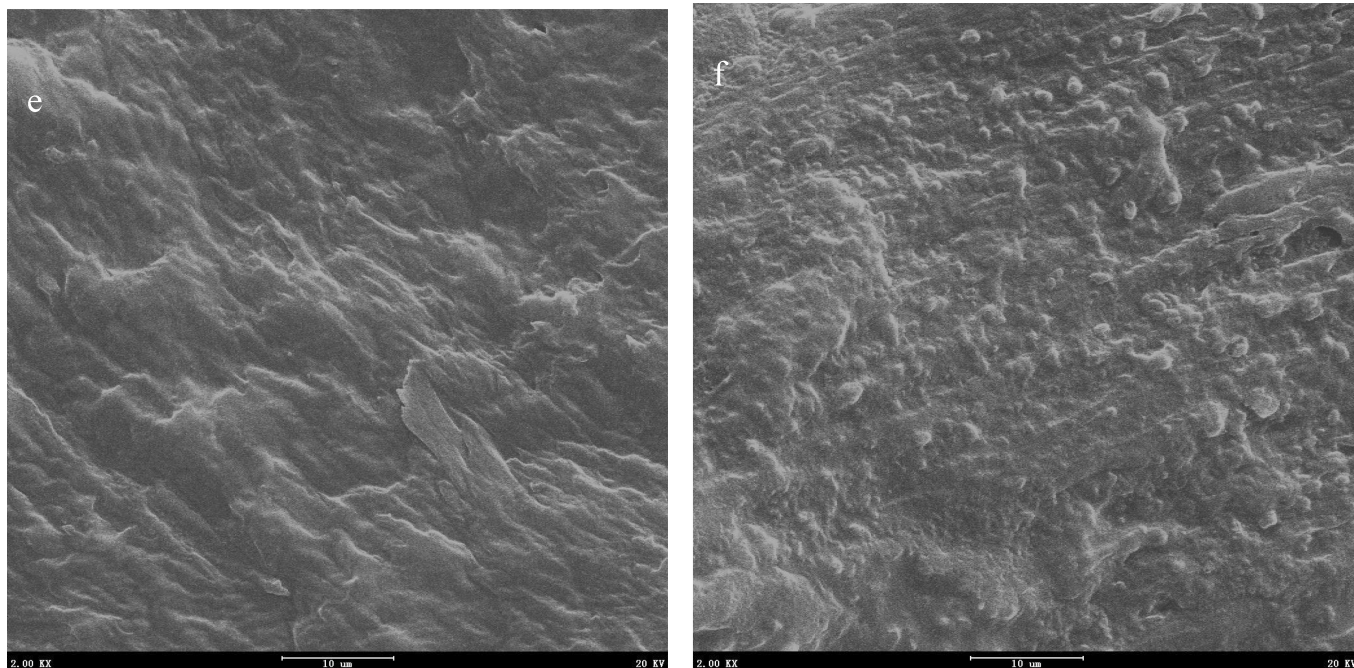


Fig. 7. (Continued)

by the water crosslinking of VTMS could slow down the leakage of flame retardants and thus, keep the flame retardancy of the materials (19).

The fractured surfaces of sample PEAD3, PEPD3 and PEPVD, before and after water treatment, are observed by SEM, as shown in Figures 7(a–f). When the composites containing APP are exposed to hot water medium at 50°C for 24 h, nearly all APP particles are eluted, leaving some defects on the fractured surface as shown in Figure 7(b). As for the composites in the presence of PUMAPP treated in 50°C hot water for 24 h, fewer holes are found in Figure 7(d) in comparison with that in Figure 7(b), indicating that the microencapsulation has a remarkable effect on the water resistance of APP in the PP composites. Moreover, as can be seen from Figure 7(f), it is obvious that almost no holes could be found, which is consistent with the results of the flame retardancy study.

4 Conclusions

In this paper, APP is microencapsulated with PU resin by a *in situ* polymerization method. TG results show that the initial decomposition temperature of PUMAPP is advanced, while it possesses a relatively higher thermal stability when temperature is up to 618°C. According to LOI values, UL-94 test and cone calorimeter results, it has been found that the PP/EPDM/PUMAPP/DPER composites possesses a better flame retardancy compared with the PP/EPDM/APP/DPER composite at the same loading.

The testing results of mechanical properties show that the microencapsulation of APP is beneficial to improve the compatibility of APP in the polymer resin. The interest of the use of VTMS as synergistic agent in the formulations is also investigated. The addition of a small quantity of VTMS results in an improvement of the fire retardant effect. It has also been demonstrated that, under hydrolytic conditions, the crosslinking of VTMS allows reducing the migration of flame retardants and retaining good fire retardant properties.

Table 5. LOI and UL-94 results of the flame retarded PP/EPDM after the water treatment

Immersion Condition Sample	50°C, 24 h		50°C, 48 h	
	LOI (%)	UL94	LOI (%)	UL94
PEAD3	28.5 ± 0.5	V-2	26.5 ± 0.5	No-rating
PEPD3	30 ± 0.5	V-0	28 ± 0.5	No-rating
PEVPD	31.5 ± 0.5	V-0	30 ± 0.5	V-0

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