

Simultaneous Improvement in the Flame Retardancy and Water Resistance of PP/APP through Coating UV-curable Pentaerythritol Triacrylate onto APP*

Cheng-liang Deng, Cong Deng^{**}, Jing Zhao, Rui-min Li, Wen-han Fang and Yu-zhong Wang^{**}

Center for Degradable and Flame-Retardant Polymeric Materials, College of Chemistry, State Key Laboratory of Polymer Materials Engineering, National Engineering Laboratory of Eco-Friendly Polymeric Materials (Sichuan), Analytical and Testing Center, Sichuan University, Chengdu 610064, China

Abstract To improve the flame-retardant efficiency and water resistance of ammonium polyphosphate (APP), the UV-curable pentaerythritol triacrylate (PETA) was used to microencapsulate APP *via* the UV curing polymerization method. The prepared PETA-microencapsulated APP (PETA-APP) was characterized by Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), and thermogravimetric (TG) analysis. PETA-APP was used as intumescent flame retardant (IFR) alone to flame retard polypropylene (PP). The water resistance of PP/PETA-APP composites was investigated, and the effect of PETA on the combustion behaviors of PP/APP composites was studied through limiting oxygen index (LOI), vertical burning test (UL-94) and cone calorimeter (CC) test, respectively. With 40 wt% of PETA-APP, the PP/PETA-APP system could achieve a LOI value of 30.0% and UL-94 V-0 rating after treatment in hot water for 168 h, while the LOI value of the system containing 40 wt% uncoated APP was only 19.2%, and it failed to pass the UL-94 rating. CC test results showed that the heat release rate (HRR), mass loss rate (MLR) and smoke production rate (SPR) of PP/PETA-APP system decreased significantly compared with PP/APP system, especially the peak of HRR was decreased by 51.4%. The mechanism for the improvement of flame retardancy for PP/PETA-APP composites was discussed based on FTIR and X-ray photoelectron spectroscopy (XPS) tests. All these results illustrated that simultaneous improvement of flame retardancy and water resistance for PP/APP was achieved through coating UV-curable PETA onto APP.

Keywords: Microencapsulation; Pentaerythritol triacrylate; Ammonium polyphosphate; Intumescent flame retardant; Water resistance.

INTRODUCTION

Ammonium polyphosphate (APP, $(\text{NH}_4)_{n+2}\text{P}_n\text{O}_{3n+1}$) is an extensively-used inorganic phosphorus/nitrogen flame retardant due to its low cost, low toxicity and higher thermal stability^[1]. Generally, APP can improve the flame retardancy of cured epoxy resins when it is used alone, but it has low flame-retardant efficiency on polyolefin without the introduction of charring agents^[2, 3]. In addition, APP has some shortcomings, such as its low water resistance and poor compatibility with polymer matrix^[4, 5]. In order to solve these problems, the technique of microencapsulation such as microencapsulation with melamine-formaldehyde resin^[6], urea-formaldehyde resin^[7], polyurethane^[8] *etc.* has been applied in industrial and academic fields. However, some encapsulated flame retardants are associated with health risks. For example, formaldehyde and 2,4-diisocyanatotoluene may

* This work was financially supported by the National Natural Science Foundation of China (Nos. 50933005, 51121001) and the Program for Changjiang Scholars and Innovative Research Team in Universities (IRT1026).

^{**} Corresponding authors: Cong Deng (邓聪), E-mail: dengcong@scu.edu.cn

Yu-zhong Wang (王玉忠), yzwang@scu.edu.cn

Received April 3, 2014; Revised May 7, 2014; Accepted May 13, 2014

doi: 10.1007/s10118-015-1575-5

decompose and produce some harmful substances during being manufactured or applied^[9].

As a derivative of pentaerythritol, pentaerythritol triacrylate (PETA) could act as a char-forming agent to enhance the flame retardancy of APP^[10], and its cured product exhibits excellent adhesive properties to a variety of substrates, good chemical and corrosion resistance, outstanding electrical insulation, high tensile, flexural and compressive strength and hardness^[11–13]. In this work, the UV-curable PETA, as a shell material, was used to microencapsulate APP *via* UV irradiation towards simultaneously improving the water resistance and flame-retardant efficiency of APP when used alone. The prepared PETA-microencapsulated APP (PETA-APP) was used as intumescent flame retardant (IFR) to flame retard polypropylene (PP). The flame retardancy and water resistance of PP/PETA-APP systems were investigated and a possible flame-retardant mechanism of PETA-APP was proposed according to the results of FTIR and XPS spectra.

EXPERIMENTAL

Materials

APP (form II, $n > 1000$) was supplied by Taifeng New-Type Flame Retardants Co., Ltd. (Shifang, China). PETA was provided by Sigma-Aldrich Trading Co., Ltd. (Shanghai, China). Triethanolamine (TEA), benzophenone (BP) and acetone were provided by Kelong Chemical Reagent Co. (Chengdu, China). Commercial PP (T30S) with a melt flow index of 2.6 g/10 min (230 °C, 2.16 kg) was provided by PetroChina Lanzhou Petrochemical Co., Ltd. (Lanzhou, China).

Preparation of PETA-APP

The mixture of 30.0 g PETA and 30.0 g acetone was first stirred for 10 min at room temperature. Then, 50.0 g APP was dispersed into the solution under stirring. Next, the polymerization mixture was prepared by adding 5 wt% photoinitiator (TEA and BP, 1:1), and the thin uniform films of the mixture were laid on glass plates. The samples on the glass plates were put in the UV irradiation apparatus and were irradiated for about 3 min, and then dried in a vacuum oven at 80 °C. Finally, cured PETA-APP was obtained. In order to obtain PETA-APP with uniform size, the prepared PETA-APP was grinded in a mortar, and then sifted to get particles with about 70–80 μm size.

Preparation of Flame Retardant PP Samples

All the formulations of flame retardant PP (FR-PP) are shown in Table 1. PP blends were extruded by a twin-screw extruder (Kebeilong Keya Nanjing Machinery Co., Ltd, Nanjing, China) at a temperature protocol of 190, 195, 200, 195, 190 and 185 °C from the feed zone to the die, and the extrudates were cut into pellets, then, the samples for combustion tests were molded by compression molding at 170 °C.

Table 1. FR-PP formulations

Samples	PP (wt%)	APP (wt%)	PETA-APP (wt%)
PP	100	0	0
PP/APP20	80	20	0
PP/APP30	70	30	0
PP/APP40	60	40	0
PP/PETA-APP20	80	0	20
PP/PETA-APP30	70	0	30
PP/PETA-APP40	60	0	40

Determination of Water Resistance

Water solubility test of APP and PETA-APP

10 g sample was put into 100 mL distilled water at room temperature (or 70 °C) and stirred for 60 min. The suspension was then filtered. Next, the obtained solid was dried to a constant weight at 100 °C. Finally, the solubility of the sample in water was obtained.

Water resistance of FR-PP composites

Each specimen (the weight of M_0) was put into distilled water at 70 °C, and kept at this temperature for 168 h (the water was replaced at each interval of 24 h). And then the treated specimens were taken out, and dried to a constant weight at 100 °C. The weight of the dried sample was M_1 , so the weight loss can be calculated based on the following equation: $[(M_0 - M_1)/M_0] \times 100\%$.

Measurements

The ultraviolet light source used for irradiation is a lamp (INTELLI-RAY 400, Uvitron Co., US), which emits light with the characteristic wavelength of 315–400 nm. The UV irradiation was carried out under air atmosphere, and the distance between the samples and the UV lamp was about 10 cm.

FTIR spectra were recorded on a Nicolet FTIR 6700 apparatus (Nicolet, US) in the wavenumber range of 4000–400 cm^{-1} . The powdered samples were mixed with KBr, and then pressed into slices for the measurement of FTIR.

SEM was used to study morphological feature on a Philips XL-3 scanning electron microscope (JEOL, JSM 5900LV, Japan) under an accelerating voltage of 20 kV. The specimens were frozen in liquid nitrogen for 1 h, and then the brittle fracture surfaces of specimens were coated with a conductive layer before being examined.

The LOI values were measured on an HC-2C oxygen index meter (Jiangning, China) with dimension of 130 mm $\times$ 6.5 mm $\times$ 3.2 mm according to ASTM D2863-97.

The UL-94 tests were performed on a CZF-2 type instrument (Jiangning, China) with dimension of 130 mm $\times$ 13 mm $\times$ 3.2 mm, according to ASTM D3801.

CC tests were carried out on an FTT Standard Cone Calorimeter (Fire Testing Technology, UK) at a heat flux of 50 kW/m^2 with dimension of 100 mm $\times$ 100 mm $\times$ 6 mm according to ISO 5660 standard procedures.

TG tests were performed using a NETZSCH TG 209 F1 (NETZSCH, Germany) thermal analyzer with a constant scanning rate of 10 K/min in the temperature range of 40–700 °C under air atmosphere.

XPS spectra were recorded by an XSAM80 (Kratos Co., UK), using Al $K\alpha$ excitation radiation ($h\nu = 1486.6 \text{ eV}$).

RESULTS AND DISCUSSION

Characterization of PETA-APP

The FTIR spectra of APP and PETA-APP are presented in Fig. 1. For APP, the peaks at 3180 and 1105 cm^{-1} correspond to the asymmetric deformation vibration of NH_4^+ and O–P–O in H_2PO_4^- , respectively; the peaks at 1075 and 1016 cm^{-1} are ascribed to the symmetric deformation vibration of PO_3 in HPO_4^{2-} , and O–P–O in PO_3^- , separately; at 1252 and 800 cm^{-1} , the two peaks represent the symmetric stretching vibration of P=O and

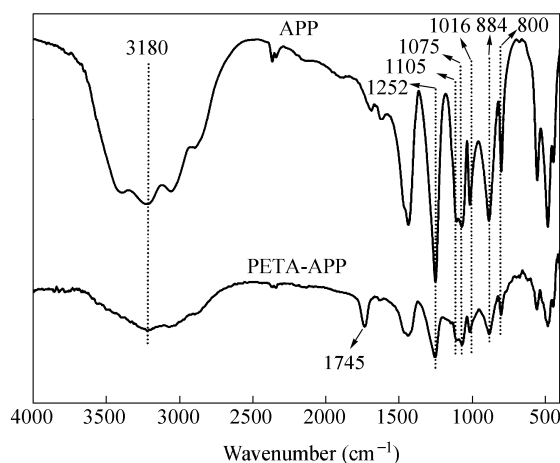


Fig. 1 FTIR spectra of APP and PETA-APP

P—O—P, respectively; in addition, the peak at 884 cm^{-1} should be from the asymmetric stretching vibration of P—O in P—O—P^[1, 14, 15]. For PETA-APP, its spectrum is similar with that of APP except for the difference at 1745 cm^{-1} , which is ascribed to the stretching vibration of ester-carbonyl groups^[14, 16, 17]. The appearance of this new peak for PETA-APP suggests that the PETA might be successfully coated on the surface of APP.

Figures 2(a) and 2(b) show the surface morphology of APP and PETA-APP. It was observed that the surfaces of APP particles were quite smooth. After being modified by PETA, the surfaces of PETA-APP particles were changed, and it seemed that some particles clung to each other. Obviously, both the surface morphology and connection status of PETA-APP particles are rather different from those of APP, suggesting that APP should be coated by PETA.

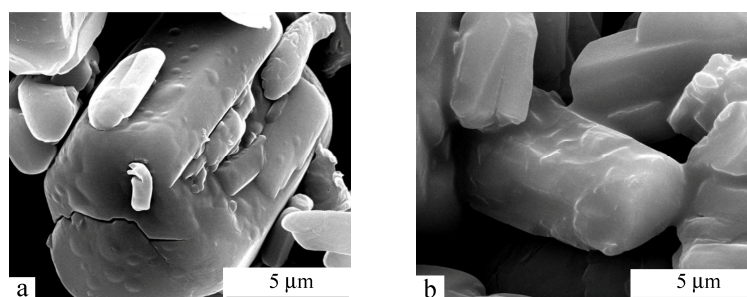


Fig. 2 SEM micrographs of APP (a) and PETA-APP (b)

Water Resistance of both PETA-APP and Its PP Composites

In order to evaluate the effect of microencapsulation on the water solubility of APP, the water solubilities of APP and PETA-APP with different percentages of PETA were tested, and the results are presented in Fig. 3. The solubilities of APP at $25\text{ }^{\circ}\text{C}$ and $70\text{ }^{\circ}\text{C}$ were $0.56\text{ g}/100\text{ mL H}_2\text{O}$ and $10.00\text{ g}/100\text{ mL H}_2\text{O}$ (all the APP particles dissolved easily in hot water), respectively, suggesting that APP can be easily attacked by water, especially at high temperatures^[1, 2]. After the microencapsulation, the solubility of APP decreased. When the percentage of PETA resin was beyond $17.5\text{ wt}\%$, the solubility of PETA-APP decreased a lot. These results demonstrate that a hydrophobic shell on APP particle can effectively protect the core (APP) from water.

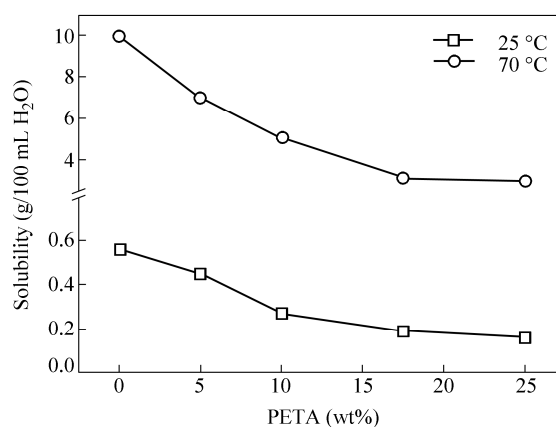


Fig. 3 Water solubility of neat APP and PETA-APP with different percentages of PETA

Figure 4 shows the SEM micrographs of fractured surfaces of PP/APP and PP/PETA-APP composites before and after water treatment ($70\text{ }^{\circ}\text{C}$) for 7 days. From Fig. 4(b), it can be seen that most of APP particles were hydrolyzed when the composites containing APP were exposed to hot water at $70\text{ }^{\circ}\text{C}$ for 168 h, leaving some defects at the fracture surface. The hydrophobicity of PETA shell could greatly decrease the water solubility of APP, and thus many PETA-APP particles still existed in PP matrix after the water treatment at

70 °C for 168 h, as shown in Fig. 4(d). Table 2 shows the weight loss percentage of the FR-PP composites. It is noted that the weight loss of the PP/PETA-APP composites decreased greatly compared with that of PP/APP composites. For example, the weight loss of the PP/PETA-APP40 decreased to 1.89%, compared with 7.68% for PP/APP40. These results demonstrate that the microencapsulation of APP has a positive effect on the water resistance of PP/APP composites.

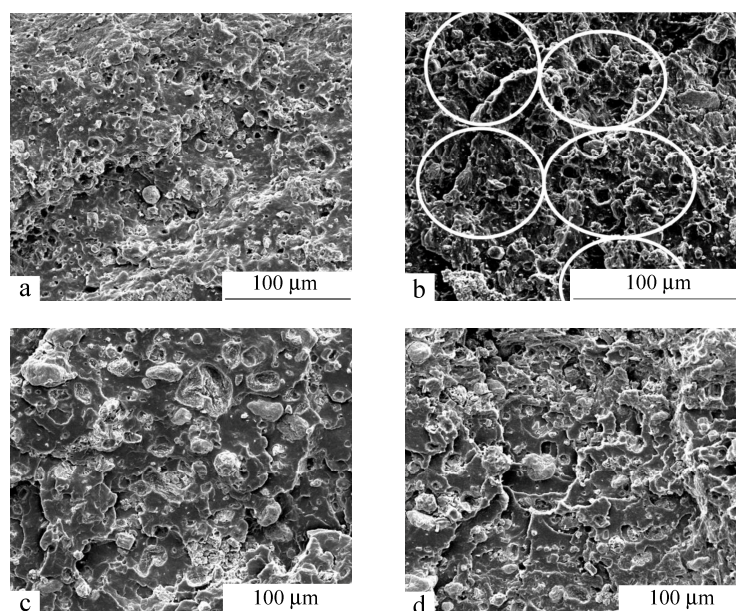


Fig. 4 SEM micrographs of fracture surfaces of FR-PP composites: (a) PP/APP, (b) PP/APP (treated for 168 h in 70 °C water), (c) PP/PETA-APP and (d) PP/PETA-APP (treated for 168 h in 70 °C water)

Table 2. Weight loss of PP composites after water treatment (70 °C, 168 h)

Samples	Weight loss (wt%)	Samples	Weight loss (wt%)
PP/APP20	5.72 ± 0.05	PP/PETA-APP20	1.62 ± 0.03
PP/APP30	6.84 ± 0.07	PP/PETA-APP30	1.75 ± 0.05
PP/APP40	7.68 ± 0.04	PP/PETA-APP40	1.89 ± 0.06

Flame Retardancy of PP/PETA-APP Composites

To understand the flame retardancy of FR-PP samples before and after water treatment (70 °C, 168 h), the LOI values and UL-94 ratings of FR-PP samples were measured, and the results are shown in Table 3. Clearly, neat PP had a low LOI value (17.0%), and it was no rating in UL-94 test, accompanied by serious melt-dripping. The LOI value of PP/APP20 was 19.7%, which was decreased to 19.0% after water treatment. However, with the increasing of APP, the LOI value of the PP/APP composite only increased slightly. When the content of the APP was 40 wt%, the LOI value of the composite was only 20.8% and decreased to 19.2% after water treatment. The PP/APP composite still failed to pass the UL-94 rating and had an obvious dripping even though the addition of the APP reached 40 wt%. These results indicated that APP was not very effective to improve the flame retardancy of PP, and the water treatment had a great impact on the LOI values for PP/APP composites. For PP/PETA-APP composites, when the addition of the PETA-APP was 20 wt%, the LOI value of the PP/PETA-APP composite reached 26.2%, and it only decreased slightly after water treatment. With further increasing the PETA-APP, the LOI value of the PP/PETA-APP composite increased significantly. When the content of PETA-APP was 40 wt%, the LOI value of the PP/PETA-APP composite reached 30.5%, which increased by 46.6% compared with APP at the same loading. Furthermore, the PP/PETA-APP40 composite could pass UL-94 V-0 rating after water treatment while PP/APP40 composite was still no rating. Obviously, PETA-APP is much more effective to promote the flame retardancy of PP than APP. Wu *et al.*^[1, 5] reported that the LOI value of

PP/DPER/APP (the mass percentage of DPER/APP is 30%) was about 28.0, and the UL-94 rating was V-1. According to the results listed in Table 3, the composite PP/PETA-APP30 could achieve the same effect on the flame retardation as PP/DPER/APP at the same loading of flame retardant, suggesting that the PETA on the surface of APP could act as the carbonization agent to improve the flame retardancy of PP/APP composites. Furthermore, the LOI value of PP/DPER/APP decreased to 23.0% after the water treatment and it failed to pass the UL-94 rating. However, the corresponding results are 27.5% and V-2 rating respectively in our research. So the microcapsulation method should be better to improve the flame retardancy of PP/APP treated by hot water than blending APP with the same loading of charring agent.

Table 3. LOI and UL-94 results of PP composites before and after water treatment (70 °C, 168 h)

Samples	Untreated		After water treatment	
	LOI (%)	UL-94 rating	LOI (%)	UL-94 rating
PP	17.0	NR ^a	—	—
PP/APP20	19.7	NR	19.0	NR
PP/APP30	20.5	NR	19.0	NR
PP/APP40	20.8	NR	19.2	NR
PP/PETA-APP20	26.2	NR	25.7	NR
PP/PETA-APP30	28.1	V-1	27.5	V-2
PP/PETA-APP40	30.5	V-0	30.0	V-0

^aNR: no rating in UL-94 test

In order to further investigate the effect of PETA-APP on the combustion performances of PP, CC test was performed in this study. The heat release rate (HRR) and total release rate (THR) curves of neat PP and PP composites are shown in Figs. 5(a) and 5(b), and the corresponding data are presented in Table 4. For neat PP, the peak of HRR (PHRR) was 837 kW/m², and the THR was 212 MJ/m². At 40 wt% APP, the PHRR and THR of PP/APP composite were 440 kW/m² and 186 MJ/m², respectively, which were lower than those of neat PP. At the same loading of PETA-APP, the PHRR and THR of the PP/PETA-APP composite significantly reduced, which were 214 kW/m² and 183 MJ/m², respectively, and the PHRR value decreased by 51.4 % compared with PP/APP40. Based on the HRR curves, FGR has been calculated to assess the fire hazard of the composite according to the following equation^[18]:

$$FGR = PHRR/t_{PHRR}$$

Generally, a lower FGR value indicates that the time to flashover is delayed, which allows enough time to evacuate for person in distress and/or arrive for fire extinguishers^[19]. When 40 wt% APP was introduced into PP, the FGR was increased from 3.28 kW/m²·s to 3.38 kW/m²·s. With the incorporation of 40 wt% PETA-APP, the t_{PHRR} was prolonged to 370 s, the FGR of PP/PETA-APP40 composite significantly decreased to 0.58 kW/m²·s, which was greatly decreased by 82.8% compared with that of PP/APP40. The results presented above proved that the microencapsulation by PETA greatly reduced the FGR of PP/APP composites, consequently could significantly extent the time to escape in the accident^[20].

The smoke production rate (SPR) and mass loss (ML) curves of PP and PP composites are presented in Figs. 5(c) and 5(d). It is noticeable that the SPR peak values of both PP/APP40 and PP/PETA-APP40 composites significantly reduced compared with that of neat PP. The SPR peak of neat PP was 0.106 m²/s. Compared with neat PP, the SPR peak of PP/APP40 decreased to 0.078 m²/s, and the value of PP/PETA-APP40 further reduced to 0.044 m²/s. These results illustrated that both PETA-APP and APP could play a role in restraining the produce of smoke. Moreover, the smoke suppression effect of PETA-APP was significantly better than that of APP. Figure 5 shows that the average MLR of PP/APP and PP/PETA-APP composites also decreased markedly at 40 wt% flame retardant. For the PP/APP40 composite, the average MLR decreased to 0.067 g/s from 0.089 g/s of neat PP, and it further reduced to 0.035 g/s for the PP/PETA-APP40 composite.

The digital photos of the residues for PP/APP40 and PP/PETA-APP40 after CC tests are shown in Fig. 6. There was no residue left for neat PP after CC test; while a small amount of residue was left for PP/APP40, and

an unexpanded char layer was formed after CC test. For PP/PETA-APP40 composite, a continuous intumescent char layer was formed after combustion. Generally, the intumescent char layer could slow the heat and mass transfer between gas and condensed phases, and could also protect the underlying materials from further burning^[21–24]. So the formation of intumescent char layer should be the most important factor to achieve the much better flame retardancy of PP/PETA-APP.

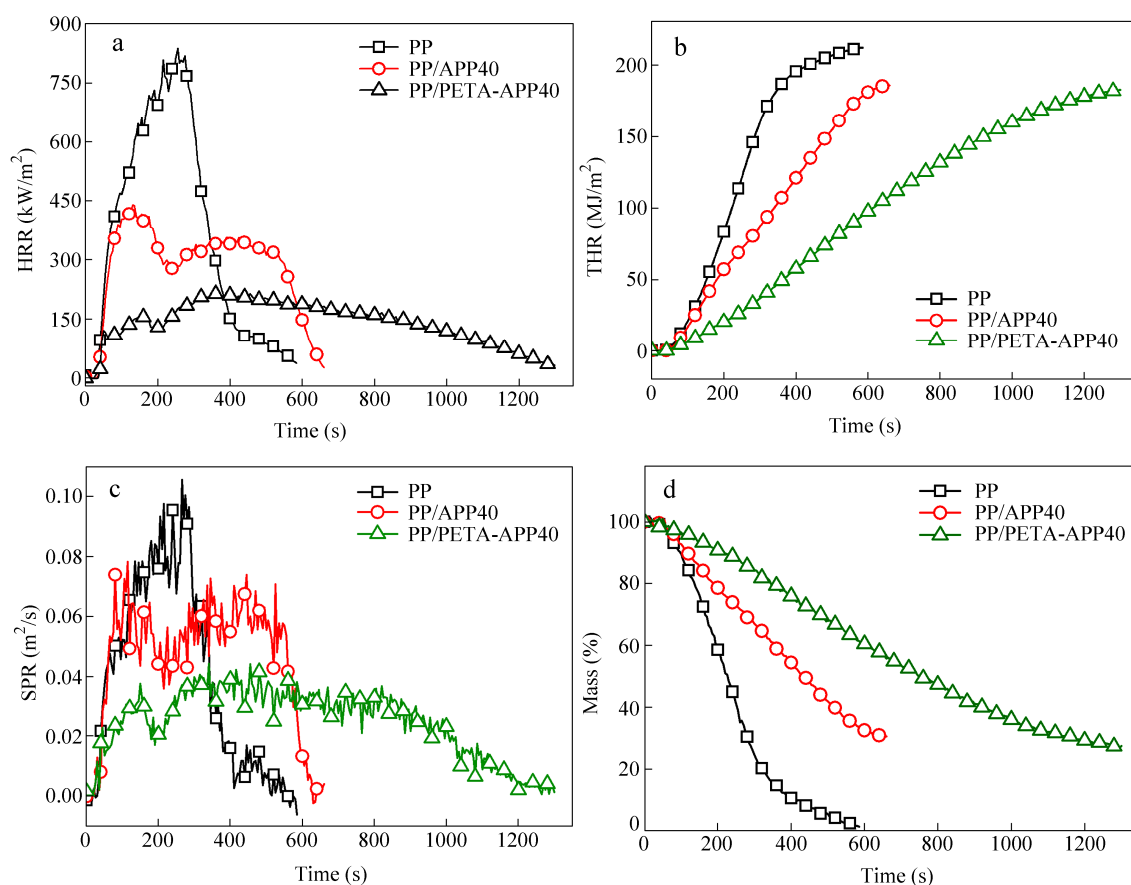


Fig. 5 HRR (a), THR (b), SPR (c) and ML (d) curves of neat PP, PP/APP40 and PP/PETA-APP40 composites

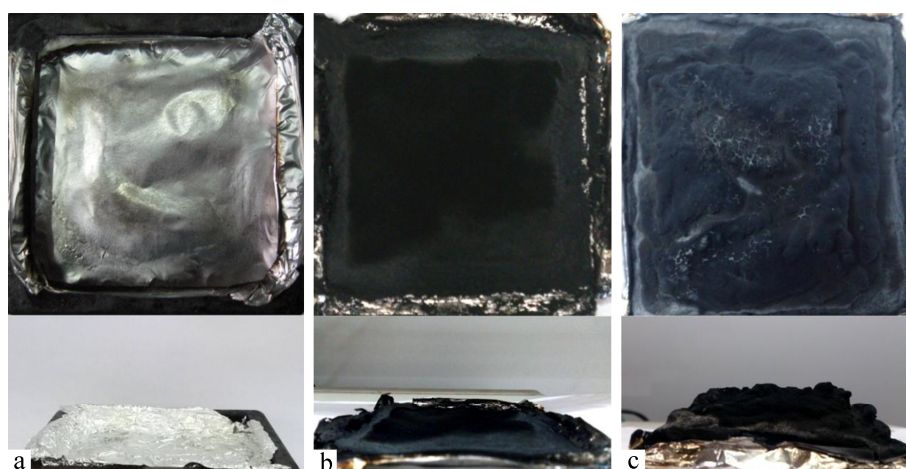


Fig. 6 Digital photographs of the residue chars after CC test: (a) neat PP, (b) PP/APP40 and (c) PP/PETA-APP40

Table 4. The main data from cone tests for neat PP and its composites

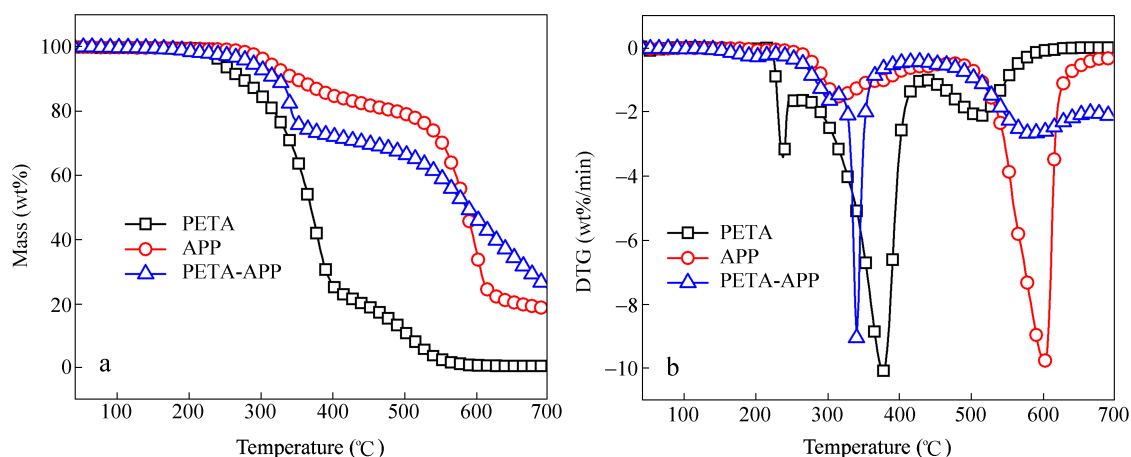
Samples	TTI ^a (s)	PHRR (kW/m ²)	t_{PHRR} ^b (s)	FGR (kW/m ² .s)	THR (MJ/m ²)	Av-MLR ^c (g/s)	PSPR (m ² /s)
PP	33	837	255	3.28	212	0.089	0.106
PP/APP40	30	440	130	3.38	186	0.067	0.078
PP/PETA-APP40	32	214	370	0.58	183	0.035	0.044

^a TTI represents the time to ignition; ^b t_{PHRR} represents the time to PHRR; ^c Av-MLR represents the average ML rate.

Thermal Decomposition Behavior

TGA is one of the commonly utilized techniques for rapid evaluation of the thermal stability of different materials, and it can indicate the decomposition of polymers at various temperatures^[28]. The decomposition curves of APP and PETA-APP are shown in Fig. 7, and the corresponding data are presented in Table 5. APP decomposed in the range of 312–700 °C, including two main processes. In the first process, the onset decomposition temperature (T_{onset}) of APP was about 312 °C, and then the weight loss was about 14.7 wt% from 312 to 480 °C. Here, T_{onset} is defined as the temperature at 5 wt% of mass loss (ML). The volatile in this process mainly included NH₃ and H₂O. Meanwhile, cross-linked polyphosphoric acid was formed during this period^[29]. The maximum ML rate was 1.5 wt%/min at 315 °C. The second process started at about 480 °C, which was the main decomposition process of APP. The 61.7 wt% of weight loss was detected from 480 °C to 700 °C. The maximum mass loss rate in this process was 9.8 wt%/min at 601 °C.

PETA-APP has the similar TG behavior with APP under the same conditions. At the first stage, the weight loss resulting from some volatiles was about 25.2 wt% in the range from 287 to 450 °C. The T_{onset} of PETA-APP was about 287 °C, which is less than that of APP, due to the initial decomposition of PETA shell. The second stage started at 450 °C and ended at 700 °C with a 44.9% weight loss. Above 580 °C, PETA-APP was more stable in comparison with APP. Compared with APP, PETA-APP had a lower maximum ML rate at this stage, and the char residue of PETA-APP had an increment of 34% compared with that of APP, indicating that PETA-APP possessed better thermal stability at high temperatures.

**Fig. 7** TG (a) and DTG (b) curves of cured PETA, APP and PETA-APP under air**Table 5.** TG and DTG data of cured PETA, APP and PETA-APP under air

Samples	T_{onset} (°C)	T_{max} ^a (°C)		The rate of T_{max} (wt%/min)		The char residue (wt%)		
		Peak1	Peak2	Peak1	Peak2	500 °C	600 °C	700 °C
PETA	248	238	376	3.4	10.1	11.4	0.6	0.3
APP	312	315	601	1.5	9.8	79.2	36.3	18.6
PETA-APP	287	340	581	8.9	2.7	66.7	46.6	24.9

^a T_{max} : the temperature at the maximum ML rate

In order to investigate the effect of the microencapsulation of APP on the thermal behavior of PP composites, the thermal degradation behaviors of PP composites were investigated in this work, and the results are shown in Fig. 8 and Table 6. Neat PP began to decompose at 265 °C; when the temperature further increased, the weight loss increased rapidly until PP decomposed completely at about 500 °C, finally no residual char was left. The thermal decomposition of the PP/APP40 composite included three processes^[1]. In the first process, the sample of PP/APP40 decomposed at about 285 °C, which was delayed by the decomposition of APP, compared with neat PP. The second process of ML in the temperature range from 300 to 420 °C was the main decomposition process of PP/APP40 composite, and its corresponding maximum decomposition rate was 9.3 wt%/min. In the third process, the further decomposition of the char occurred at above 420 °C, and the residue left at 700 °C for PP/APP was about 2.9 wt%. In comparison with PP/APP, the T_{onset} of PP/PETA-APP40 was 289 °C, higher than that of PP/APP. As mentioned in Table 5, the T_{onset} of APP (312 °C) was much higher than that of PETA/APP (287 °C), while the T_{onset} of PP/APP40 (285 °C) was lower than that of PP/PETA-APP40 here. The reason might be that the shell of PETA prevents the contact between APP and PP matrix, and then postponed the acid catalyzed decomposition when the temperature was below 289 °C, consequently caused that the T_{onset} of PP/APP40 was lower than that of PP/PETA-APP40^[27, 28]. The char residues at 700 °C was 3.5 wt% for PP/PETA-APP40, which was higher than that of PP/APP40, indicating that the thermal stability of PP/PETA-APP40 was improved a little at high temperatures after being microencapsulated by PETA.

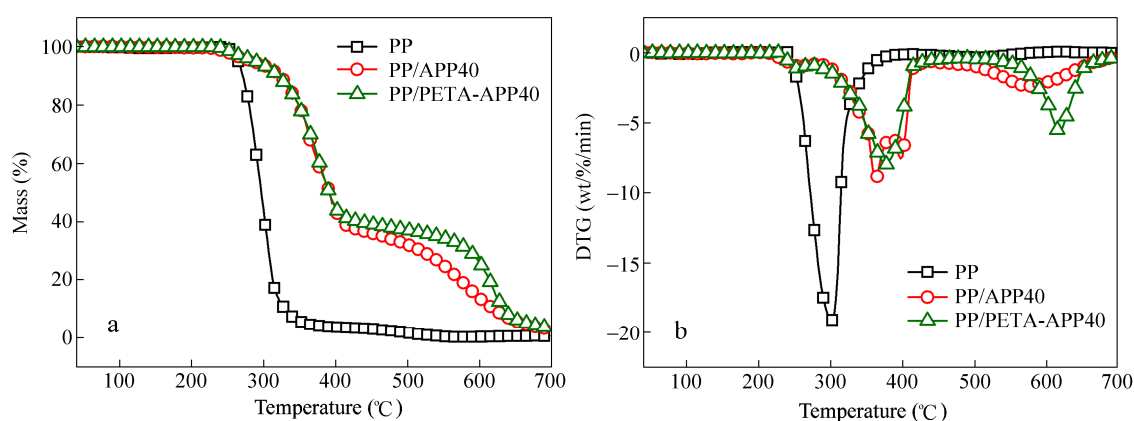


Fig. 8 TG (a) and DTG (b) curves of neat PP and PP composites under air atmosphere

Table 6. TG and DTG data of neat PP and PP composites under air atmosphere

Samples	T_{onset} (°C)	T_{max} (°C)		The rate of T_{max} (wt%/min)		The char residues (wt%)		
		Peak1	Peak2	Peak1	Peak2	500 °C	600 °C	700 °C
PP	265	301	—	19.2	—	1.7	0.2	0.2
PP/APP40	285	363	582	9.3	2.4	32.1	13.8	2.9
PP/PETA-APP40	289	375	618	8.0	5.7	37.1	26.0	3.5

Flame Retardant Mechanism of PETA-APP

The flame-retardant mechanism of PETA-APP might include the co-contribution of the gas phase and the condensed phase. It was reported that the gas products from APP/pentaerythritol (or its derivatives) system during the thermal degradation process were NH_3 , CO , CO_2 and H_2O , similar to the gas products from APP only^[29, 30]. So the contribution of the gas phase for PETA-APP to the flame retardancy should be similar to APP. Therefore, the condensed phase mechanism may play the key role for the better flame retardancy of PETA-APP than APP. To understand the contribution of the condensed phase of PETA-APP to the flame retardancy, FTIR test of the condensed products at different temperatures was carried out. Here, it should be noted that this test was conducted with the samples exposed to air for 10 min in a muffle furnace. Several literatures^[20, 26, 31] have studied the condensed products of APP at different temperatures during the thermal degradation. First, APP

tends to dissociate and release ammonia above 300 °C, and the free condensed hydroxyl groups give cross-linked structures containing “P—O—P” (ultraphosphate) with the elimination of water. Above 410 °C, the thermal degradation of the ultraphosphate is limited and followed by the formation of a relatively stable residue. Figure 9 shows the FTIR spectra of the condensed products of PETA-APP at 287, 340 and 580 °C, corresponding to the initial decomposition, the first and second maximal degradation of PETA-APP, respectively. The strong and broad absorbing peak at 3200 cm⁻¹ could be attributed to the stretching vibration of N—H bond of NH₄⁺, and it gradually decreased with increasing temperature, meaning that amount of NH₃ was released during the thermal degradation. This process was accompanied by the formation of ultra-, pyro- or poly-phosphoric acids with free acidic hydroxyl groups by thermal dehydration^[14, 32]. The phosphoric acid(s) could react with the side group —OH on PETA and facilitate the formation of char^[27, 33]. At 287 °C, the new absorption peaks appeared at 1640 and 1400 cm⁻¹, indicating the formation of species containing C=C and C—H in the carbonization process, respectively^[34, 35]. The peaks at 1000 cm⁻¹ and 900 cm⁻¹ corresponding to the stretching vibration of the P—O—C and P—O—P groups could also be observed in the whole heating process, and they became much stronger at 340 °C, suggesting that more and more phosphorus-rich cross-linked structures were formed with increasing of temperature^[20]. It is well-established that the P—O—C cross-links can further form the thermal stable charring residues by aromatization at relatively high temperatures (580 °C)^[32]. FTIR test demonstrated the main reactions between APP and PETA at the temperature range of 287–580 °C, in which the formation of the phosphorus-rich cross-links should play a positive role on enhancing the flame retardancy^[21].

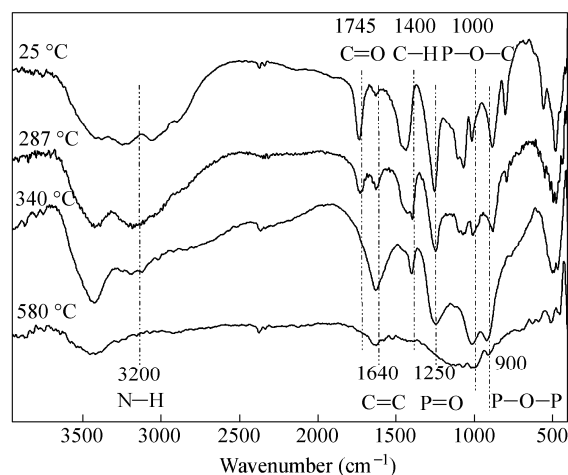


Fig. 9 FTIR spectra of the condensed residues of PETA-APP at different temperatures

XPS data for the condensed products of PETA-APP at different temperatures are presented in Table 7. This test was also conducted with the samples exposed to air for 10 min in a muffle furnace. The content of C decreased to 30.0 wt% from 42.7 wt% with increasing temperature mainly because of the oxidization of unstable C^[32], indicating that PETA was engaged in the formation of char layer. The content of N was also reduced as the result of the volatilization of NH₄⁺/NH₃ during heating, while the contents of O and P increased, which should be associated with the formation of the P—O—P and P—O—C structure in this case^[32, 36]. In general, the XPS results are in accordance with the FTIR results.

Table 7. Element content of the condensed products of PETA-APP during heating

	C (wt%)	N (wt%)	O (wt%)	P (wt%)
287 °C	42.7	4.9	38.9	13.5
340 °C	34.5	4.4	42.9	18.2
580 °C	30.0	3.4	44.9	21.6

On the basis of the experimental data presented above, a potential flame-retardant mechanism of PETA-APP is shown in Fig. 10. First, APP was thermally decomposed into ultra-, pyro- or poly-phosphoric acids with free acidic hydroxyl groups^[32, 37]. The phosphoric acid(s) could react with PETA chains or another molecular of poly-phosphoric acid by the dehydration reaction of the side group $-\text{OH}$. During this process, cross-linked reaction might occur, and then lead to the formation of a three-dimensional network structure. PETA containing hydroxyl groups could promote the dehydration reaction in PETA-APP, which facilitated the stabilization of APP and reduced the volatility of phosphorus, and thus more APP would be available for phosphorylation and the formation of char^[27, 38]. This would certainly enhance the stabilization of the three-dimensional network structure. Consequently, the flame retardancy of PP composite containing PETA-APP was improved compared with that of PP containing APP uncoated.

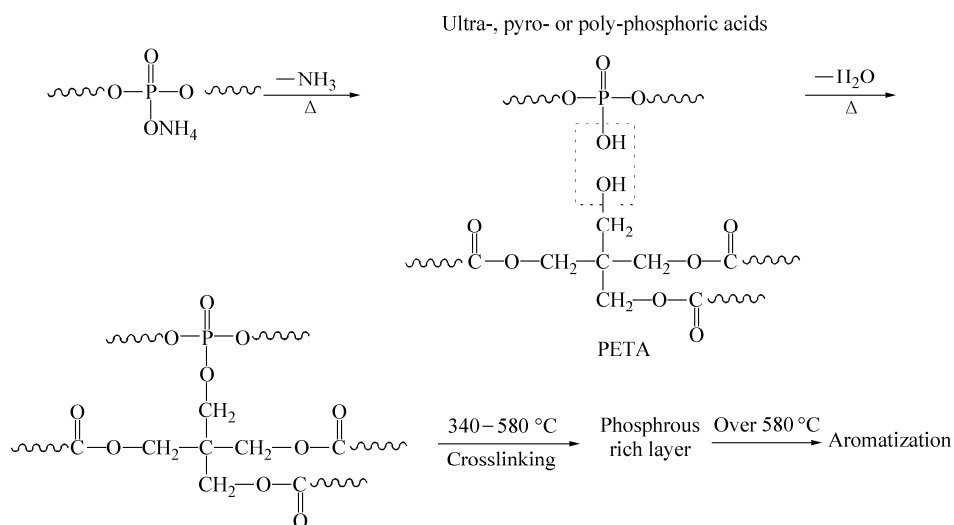


Fig. 10 Possible flame-retardant mechanism for PETA-APP

CONCLUSIONS

APP was microencapsulated through PETA shell by the UV curing polymerization method. FTIR and SEM tests confirmed that the surfaces of APP particles were microencapsulated by PETA. The microencapsulation of APP resulted in the decrease of water solubility. The water resistance test demonstrated that the shell of PETA could effectively restrain the extraction of APP in the FR-PP composites. TG data illustrated that the thermal stability of APP and its FR-PP composites was affected by the microencapsulation through PETA. The LOI value of PP/PETA-APP40 was higher than that of PP/APP40 at the same loading before and after the water treatment. Moreover, the PP/PETA-APP40 composite could pass UL-94 V-0 rating after the water treatment while PP/APP40 composite was still no rating. CC results indicated that PETA-APP had better flame retardant contribution in PP matrix than APP. The HRR, MLR and SPR of the PP/PETA-APP system decreased largely compared with that of neat PP and PP/APP system. The study on the flame-retardant mechanism of PETA-APP demonstrated that PETA containing hydroxyl groups could promote the dehydration reaction in PETA-APP, which facilitated the stabilization of APP and the formation of char residue. Consequently, the flame retardant efficiency of APP was improved by the microencapsulation of PETA shell.

REFERENCES

- 1 Wu, K., Wang, Z.Z. and Hu, Y., Polym. Adv. Technol., 2008, 19: 1118
- 2 Wang, J.S., Wang, D.Y., Liu, Y., Ge, X.G. and Wang, Y.Z., J. Appl. Polym. Sci., 2008, 108: 2644

- 3 Carosio, F., Alongi, J. and Malucelli, G., *Carbohydr. Polym.*, 2012, 88: 1460
- 4 Le Bras, M.L., Bugajny, M., Lefebvre, J.M. and Bourbigot, S., *Polym. Int.*, 2000, 49: 1115
- 5 Yang, K., Xu, M.J. and Li, B., *Polym. Degrad. Stab.*, 2013, 98: 1397
- 6 Wang, G.F., Narita, N. and Takebayashi, T., 2001, U.S. Pat., 6,291,068
- 7 Wata, M., Seki, M., Inoue, K., Takahashi, R., Fukumura, T. and Tanaka, M., 1999, U.S. Pat., 5,945,467
- 8 Ni, J.X., Tai, Q.L., Lu, H.D., Hu, Y. and Song, L., *Polym. Adv. Technol.*, 2010, 21: 392
- 9 Bourbigot, S. and Duquesne, S., *J. Mater. Chem.*, 2007, 17: 2283
- 10 Bourbigot, S., Le Bras, M., Duquesne, S. and Rochery, M., *Macromol. Mater. Eng.*, 2004, 289: 499
- 11 Wang, H.L., Xu, S.P. and Shi, W.F., *Prog. Org. Coat.*, 2009, 65: 417
- 12 Huang, Z.G. and Shi, W.F., *Eur. Polym. J.*, 2006, 42: 1506
- 13 Xing, W.Y., Hu, Y., Song, L., Chen, X.L., Zhang, P. and Ni, J.X., *Polym. Degrad. Stab.*, 2009, 94: 1176
- 14 Colthup, N.B., Daly, L.H. and Wiberley, S.E., *Introduction to infrared and Raman spectroscopy*. Academic press, San Diego, CA, 1990
- 15 Weng, S.P., *Fourier transform infrared spectrometer*. Chemical Industry Press, China, 2010
- 16 Bajpai, M., Shukla, V. and Kumar, A., *Prog. Org. Coat.*, 2002, 44: 271
- 17 Decker, C. and Biry, S., *Prog. Org. Coat.*, 1996, 29: 81
- 18 Breulet, H. and Steenhuizen, T., *Polym. Degrad. Stab.*, 2005, 88: 150
- 19 Richard Hull, T. and Kandola, B.K., "Fire retardancy of polymers-new strategies and mechanisms", *Royal Society of Chemistry, Cambridge*, 2009, p. 184
- 20 Shao, Z.B., Deng, C., Tan, Y., Chen, M.J., Chen, L. and Wang, Y.Z., *Polym. Degrad. Stab.*, 2014, 106: 88
- 21 Liu, Y., Deng, C.L., Zhao, J., Wang, J.S., Chen, L. and Wang, Y.Z., *Polym. Degrad. Stab.*, 2011, 96: 363
- 22 Wang, L.L., Zhang, T., Yan, H.Q., Peng, M., Fang, Z.P., Li, Y. and Hao, W., *Chinese J. Polym. Sci.*, 2014, 32(3): 305
- 23 Hu, X.P., Li, W.Y. and Wang, Y.Z., *J. Appl. Polym. Sci.*, 2004, 94: 1556
- 24 Hu, X.P., Li, Y.L. and Wang, Y.Z., *Macromol. Mater. Eng.*, 2004, 289: 208
- 25 Liu, Y., Wang, J.S., Deng, C.L., Wang, D.Y., Song, Y.P. and Wang, Y.Z., *Polym. Adv. Technol.*, 2010, 21: 789
- 26 Camino, G., Grassie, N. and McNeill, I.C., *J. Polym. Sci. Polym. Chem. Ed.*, 1978, 16: 95
- 27 Wang, J.S., Wang, D.Y., Liu, Y., Ge, X.G. and Wang, Y.Z., *J. Appl. Polym. Sci.*, 2008, 108: 2644
- 28 Wu, K., Zhang, Y.K., Hu, W.G., Lian, J.T. and Hu, Y., *Compos. Sci. Technol.*, 2013, 81: 17
- 29 Levchik, S., Camino, G., Costa, L. and Luda, M., *Polym. Degrad. Stab.*, 1996, 54: 317
- 30 Zhang, K., Wu, K., Zhang, Y.K., Liu, H.F., Shen, M.M. and Hu, W.G., *Polym. Plast. Technol. Eng.*, 2013, 52: 525
- 31 Levchik, S., Levchik, G., Balabanovich, A., Camino, G. and Costa, L., *Polym. Degrad. Stab.*, 1996, 54: 217
- 32 Yan, Y.W., Chen, L., Jian, R.K., Kong, S. and Wang, Y.Z., *Polym. Degrad. Stab.*, 2012, 97: 1423
- 33 Lin, H.J., Yan, H., Liu, B., Wei, L.Q. and Xu, B.S., *Polym. Degrad. Stab.*, 2011, 96: 1382
- 34 Mysen, B.O., Ryerson, F.J. and Virgo, D., *Am. Mineral.*, 1981, 66: 106
- 35 Qian, Y., Wei, P., Jiang, P.K., Zhao, X.M. and Yu, H.Z., *Polym. Degrad. Stab.*, 2011, 96: 1134
- 36 Camino, G., Costa, L. and Trossarelli, L., *Polym. Degrad. Stab.*, 1984, 7: 25
- 37 Laoutid, F., Bonnaud, L., Alexandre, M., Lopez-Cuesta, J.M. and Dubois, P., *Mater. Sci. Eng. R.*, 2009, 63: 100
- 38 Gao, S.L., Li, B., Bai, P. and Zhang, S.Q., *Polym. Adv. Technol.*, 2011, 22: 2609