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Mechanism on flame retardancy of polystyrene/clay composites-The effect of surfactants and aggregate state of organoclay

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ABSTRACT

Effects of organically modified montmorillonites (OMMTs) with different type and amount of modifiers on flame retardancy of polystyrene (PS) have been studied. The results from morphology analysis, gas chromatography–mass spectrometry and cone calorimeter have showed different mechanisms for the flame retardancy of PS/OMMTs composites, depending on surface property of OMMTs. One is the catalysis of acid sites formed on the surface of octadecylammonium modified MMT (c-MMT) via Hoffman decomposition on the carbonization of degradation products, which promotes the formation of clay-enriched char barrier. The other is related to chemical effect of inherent properties of MMT sheets on reactive intermediates during combustion, which work in PS/Na-MMT and PS/sodium dodecylsulfonate modified MMT (a-MMT) composites. Furthermore, the effect of the aggregate states of a-MMT on the flame retardancy of PS/a-MMT composites was studied. In the case of a-MMTs from spraying drying, a good protective layer with foam-like aggregate state of MMT sheet was formed in the residue, which results in low peak value of heat release rate of PS/a-MMT composites.

1. Introduction

Many attentions have been focused on polymer/clay nanocomposites (PCNs) for their outstanding combination properties, for instance, improved mechanical properties, a remarkable increase in thermal stability as well as flame retardancy for flammability and the reduction in the permeability of gases [1]. PCNs have been believed as a revolutionary new and environmentally benign flame retardant approach. However, the main disadvantage of PCNs is that they do not extinguish and burn slowly until most of the fuel has been burnt. In order to further develop and transfer this method into commercial success, it is crucial to really and completely understand the related mechanism of PCNs, for example, physical effect and chemical effect of organoclay on polymer matrix at high temperature.

As one of the commonly invoked mechanisms, the barrier model suggests that a clay-enriched char layer built on the polymer melt surface provides the mass and heat transfer barrier. An increase in the concentration of clay on the surface of polymer melt has been detected experimentally and explained theoretically [2–4]. In a recent work, Kashiwagi et. al. have found that the formation of a network structure of nanoparticles (including organoclay and carbon nanotubes) within a polymer matrix can significantly reduce the flammability of polymer nanocomposites [5]. Meanwhile, more and more evidences have shown that the chemical effect of organoclay in polymer matrix plays a key role on the flame retardancy. Incorporation of clay in polymer matrix might change degradation process of a polymer, depending on chemical structures of polymer chains [6], which probably change the composition of degradation products and also has a significant effect on flame retardancy of PCNs. Recently researchers have found that acid sites from the decomposition of cationic organic modifiers could catalyze the carbonization of degradation products, which is a main reason for the formation of a clay-enriched char layer. As a result, the flame retardancy of polymer composites is improved, such as poly[ethylene-co-(vinyl acetate)]/organically modified montmorillonite (OMMT) [3], polypropylene (PP)/OMMT [7,8] and polyamide 12 (PA12)/OMMT nanocomposites [9].

Interestingly, a radical trapping model of the structural iron in the clay has also been proposed to explain why the addition of a small amount of OMMT can reduce the peak value of heat release rate (HRR) of polystyrene (PS)/clay nanocomposites [10]. However, some questions have been raised. First, OMMT from the modification

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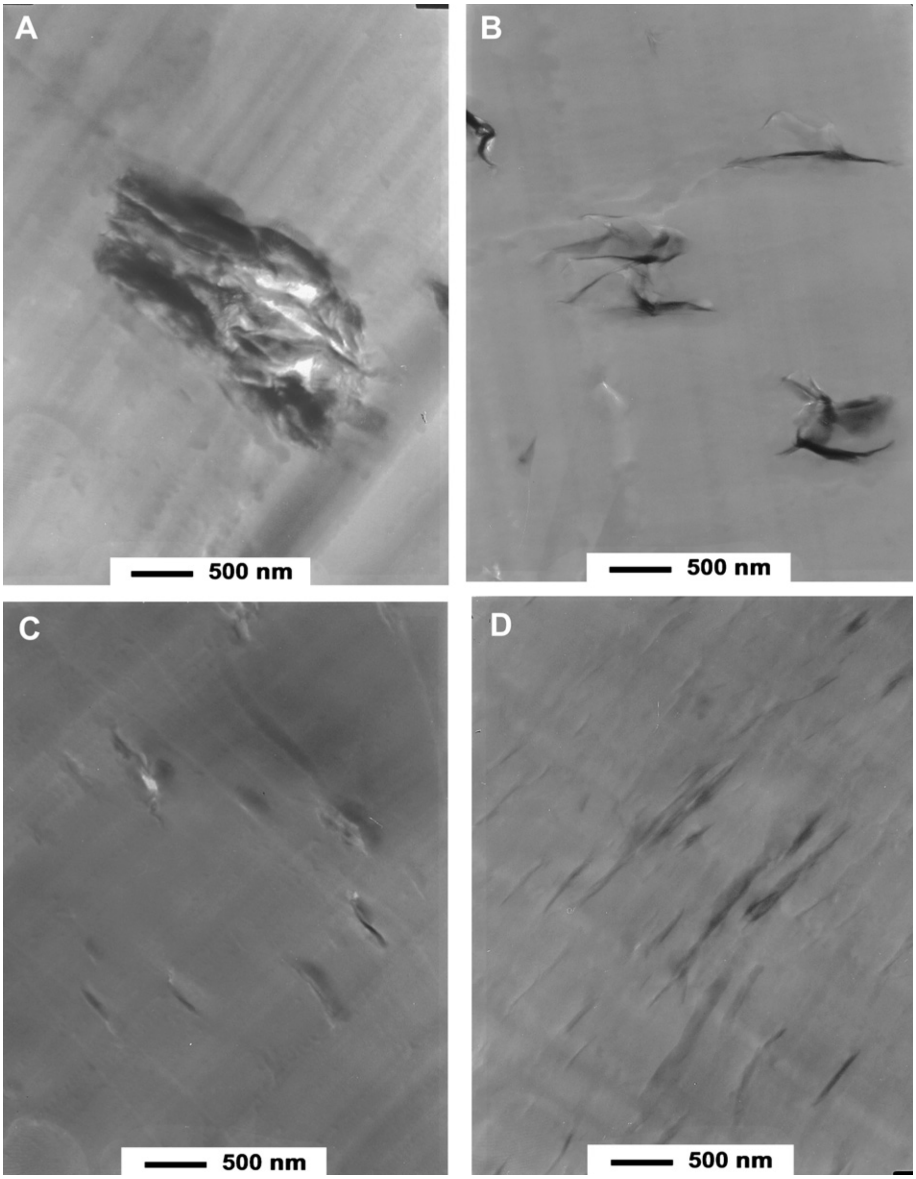

Fig. 1. TEM images of PS/Na-MMT and PS/OMMT composites containing 5 wt% of Na-MMT or OMMT. (A) PS/Na-MMT; (B) PS/a-100MMT; (C) PS/c-80MMT; (D) PS/c-150MMT.

using cationic organic modifier will form acid sites on the surface of MMT sheets, of which the catalysis probably influences the flame retardancy of PS. Secondly, different OMMTs in which the structural iron is included show different behavior on the flame retardancy of PS [10], meaning that the microstructures of PS nanocomposites also play a role in the flame retardancy at least. Meanwhile the OMMTs containing various modifiers may have different ion-exchange loading, resulting in different amount of acid sites on the surface of MMT sheets at high temperature. Thirdly, adding a small amount of OMMTs, in spite of presence of structural iron, leads to the reduction in the peak value of HRR of PS [10], which seems no strong dependence on structural iron [11].

Although the previous reports provide important insights into the combustion behavior of PCNs, the fundamental effects of silicate clay and the included modifier on the observed enhancements of flame retardancy are not yet well understood, as polymers with different chemical structures show various decomposition behavior at high temperature. In this study, we report our efforts to investigate physical effect (such as aggregate states of MMT sheets in the burned residues) and chemical effect (such as acid sites) of MMT sheets with different surface properties on the flame retardancy of PS/clay composites. Here we choose Na^+-montmorillonite (Na-MMT), two kinds of octadecylammonium modified MMT (c-MMT) with different loading of the modifier and three kinds of sodium dodecylsulfonate (SDSo) modified MMT (a-MMT) with different loading of SDSo to explore the impact of OMMT on the flame retardancy of PS. More importantly, a-MMTs with different aggregate states, opened hollow microspheres of a-MMTs prepared by spraying drying [12] and common planar aggregates of a-MMTs prepared by naturally drying at room temperature, were used to investigate the effect of aggregate states of a-MMTs on the flame retardancy of PS/clay composites. Interestingly, it is found that the addition of Na-MMT and a-MMT can reduce the peak value of heat release rate (PHRR) of PS, especially in the case of a-MMT prepared by spray drying. According to the results obtained from PS composites containing different kinds of modified MMTs, we have found different mechanisms for the flame retardancy of PS/clay composites, depending on the surface property of MMT sheets and aggregate states of MMT sheets on the burning surface.

2. Experimental section

2.1. Material and preparation of samples

Polystyrene (PS, MFR = 8 g/10 min) was purchased from Daqing Petroleum & Chemical Corporation. Na-MMT with a cation exchange capacity (CEC) of 119 meq/100 g used in this work was from Kunimine Co. Octadecylamine was from Wako Pure Chemical Industries Co. Sodium dodecylsulfonate (SDSo) from Yingyuan Chemical Co. Ltd (Shanghai, China) was used without further purification.

Octadecylammonium modified montmorillonite (c-MMT) and SDSo (as an anionic surfactant) modified montmorillonite (a-MMT) were synthesized as described in our previous papers [12,13]. Under the same conditions, the loading of octadecylammonium with 80% (or 150%) CEC of Na-MMT was added into Na-MMT suspension at 80 °C in the process of modifying Na-MMT. The obtained c-MMT is named as c-80MMT (or c-150MMT). The factual contents of the modifier are 11.0 wt% (38.5% with respect to CEC) in the c-80MMT and 26.3 wt% (111.1% with respect to CEC) in the c-150MMT (estimated by thermogravimetric analysis (TGA)), respectively. Three kinds of a-MMTs with opened hollow microspherical structure were prepared by adding 60%, 100% and 150% CEC of SDSo into Na-MMT suspension, respectively; and the mixtures were vigorously stirred for 3.5 h at 80 °C. The resultant sols were spray dried using WP-1.5 spray drying instrument. Final spray dried powders were further dried in a vacuum oven at 75 °C for more than 24 h. The obtained samples were named as a-60MMT, a-100MMT and a-150MMT, respectively. As a control, a part of the resultant sol containing 100% CEC of SDSo was naturally dried at room temperature, followed by drying in a vacuum oven at 75 °C for more than 24 h. The obtained sample was named as a-100MMTN. The preparation of PS composites containing 5 wt% different MMTs was carried out in a Brabender mixer with a rotating speed of 100 rpm at 180 °C for 10 min.

2.2. Characterizations

The morphologies of PS/Na-MMT composites and PS/OMMT composites were observed using transmission electron microscope (TEM, JEOL2010) operating at 200 kV accelerating voltage with LaB6 filament. Ultrathin sections were cryogenically cut using a Leica Ultracut and a glass knife at −80 °C. The sample was collected onto carbon-coated copper grids. Field emission scanning electron microscope (FESEM, XL303SEM) was used to observe the morphologies of the burned residue. Samples were coated with an ultrathin film of gold to make them conductive before analysis. TGA was carried out using TA SDT600 at a heating rate of 20 °C/min from ambient to 800 °C under air or nitrogen.

Cone calorimeter was performed according to ISO5660 standard at a heat flux 35 kW/m^2. Exhaust flow rate was 24 L/s and the spark was continuous until the sample ignited. The specimens with the sizes of 6 × 100 × 100 mm square plaques for combustion testing were prepared by the compression molding at 180 °C.

Gas chromatography–mass spectrometry (GC–MS, AGILENT 5975 MSD) was used to analyze the composition of liquid degradation products of the samples. For collecting the degradation products, 10 g of a sample was put into a quartz tube and pyrolyzed under nitrogen at 700 °C that was close to the temperature measured by cone calorimeter at heat flux of 35 kW/m^2. The condensable evolved products were collected using a cold trap.

3. Results and discussion

Fig. 1 shows TEM images for dispersion states of PS composites. Large and unevenly dispersed Na-MMT aggregates were observed in PS/Na-MMT composite. Comparatively, the dispersion states of OMMT in all the PS/OMMT composites become better, but a-100MMT was poorly dispersed in PS matrix comparing with both c-80MMT and c-150MMT. Furthermore the dispersion degree of c-150 was higher than that of c-80MMT in PS matrix. More small particles could be observed in PS/c-150 composite (Fig. 1C vs Fig. 1D). FTIR spectra for adsorbed pyridine after desorption at 150 °C could provide insights into the existence of acid sites in different MMTs [14]. Two bands at 1549 cm^{-1} and 1443 cm^{-1} were characteristic of Brønsted and Lewis acid sites, respectively. In our previous works, Brønsted and Lewis acid sites had been observed in the c-80MMT and c-150MMT after decomposition of octadecylammonium at high temperature [8,9]. Brønsted acid site was originated from the decomposition of octadecylammonium, thus the amount of Brønsted acid site depends on the content of cationic surfactant that exchanges with sodium ion in the modified MMTs. The content of the cationic surfactant in c-150MMT (111.1% with respect to CEC) was higher than that in c-80MMT (38.5% with respect to CEC). However, the excess amount of the cationic surfactant (11.1% with respect to CEC) in c-150MMT would enter the interlayers of MMT together with its counterion [13]. These surfactant molecules did not contact with the surface of MMT sheets and will release HCl during combustion. As a result, the excess cationic surfactant had no contribution to the formation of acid site on the surface of MMT sheets. In this case, however, the content of Brønsted acid site of c-150MMT is still much higher than that of c-80MMT (Brønsted acid site content: c-150MMT/c-80MMT = 2.6). In contrast, no such bands were observed in the Na-MMT and a-100MMT.

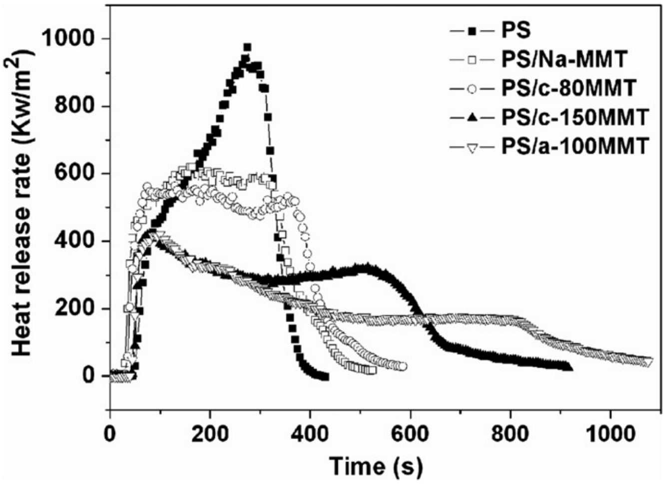

Fig. 2. Comparison of heat release rate (HRR) plots for PS and PS composites (measured by cone calorimeter at an external radiant flux of 35 kW/m^2).

Combustion behavior of the above-mentioned PS composites is compared by means of cone calorimeter (Fig. 2). At the continuous heat flux of 35 kW/m^2, all the samples turned soft and some of volatile gases were generated. Compared to pure PS, PHRR of four kinds of PS composites were decreased. Moreover, it could be seen that the PHRR in PS/c-150MMT composite was lower than that in PS/c-80MMT composite. This may result from the differences in the dispersion states of OMMT and the content of acid sites in the samples [8]. On one hand, a high dispersion degree of OMMT in polymer matrix will be profitable to fire retardancy of polymers. On the other hand, although there are the same weight percentage (5 wt%) of OMMT in both PS/c-80MMT and PS/c-150MMT composites, the absolute content of MMT in the former is higher due to the lower content of surfactant in the c-80MMT. As the decomposition of cationic surfactant results in the formation of acid

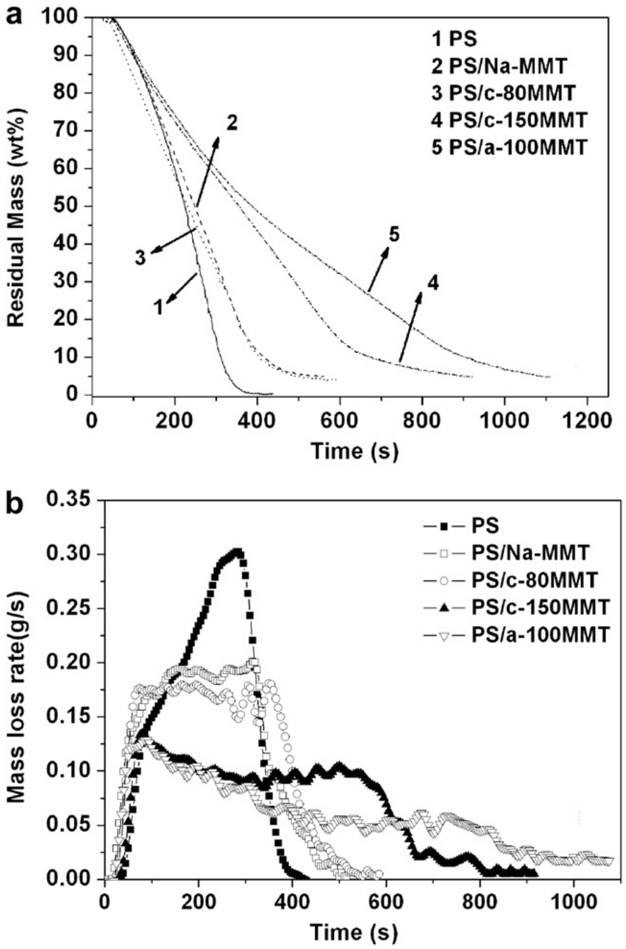

Fig. 3. (a) Mass loss curves of PS and its composites measured by cone calorimeter at an external radiant flux of 35 kW/m^2; (b) Mass loss rate of PS and its composites measured by cone calorimeter at an external radiant flux of 35 kW/m^2.

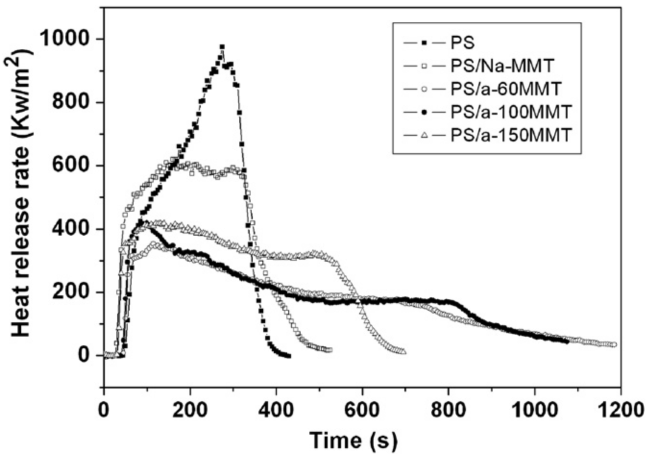

Fig. 4. Comparison of heat release rate (HRR) plots for PS and PS/a-MMT composites with different content of SDSo (measured by cone calorimeter at an external radiant flux of 35 kW/m^2).

sites on MMT sheets, more acid sites will be formed in PS/c-150MMT composite during combustion, which can provide a stronger catalysis on the carbonization of the degradation products of PS and lead to the formation of more carbonaceous products during combustion [8]. Considering the existence of a little amount of octadecylammonium chloride in the c-150MMT, a comparative experiment was done by studying the effect of the cationic surfactant on the flame retardancy of PS. The results showed that the addition of a little amount of NH_4Cl in PS matrix did not reduce the PHRR. Therefore, a lower PHRR of PS/c-150MMT composite should be ascribed to a higher dispersion degree of c-150MMT and a higher content of acid sites of c-150MMT in PS/c-150 composites.

Fig. 3a shows the change of the residual mass of the samples with combustion time. Addition of c-80MMT in PS matrix could decrease the mass loss rate (MLR) comparing with that of PS matrix alone (Fig. 3b). Comparatively, adding c-150MMT into PS matrix led to a dramatic decrease in the MLR during combusting PS/c-150MMT composite. This shows that there are relatively fewer pyrolytic flammable gases to eliminate during combustion in this case. As a result, the HRR of PS/c-150 MMT composite can be further reduced comparing with that of PS/c-80MMT composite.

Interestingly it is observed that adding Na-MMT or a-100MMT in PS matrix could also decrease the PHRR of PS (Fig. 2), although the dispersion states of both fillers in PS matrix were poorer than those of c-80MMT and c-150MMT. Especially in the case of a-100MMT, the flame retardancy of PS/a-100MMT composite was similar to that of PS/c-150MMT composites (Fig. 2). Addition of a-100MMT led to a dramatic increase in the residual mass (Fig. 3a). This means that the release rate of pyrolytic flammable gases toward flame region is small in this case during combustion. Its MLR was even smaller than that in the case of PS/c-150MMT composite at the combustion time between 300–600 s (Fig. 3b). This phenomenon is completely different from those of PA12/a-100MMT [9], in which the addition of Na-MMT did not reduce the PHRR of PA12, and the reduction of the PHRR after adding a-100MMT was smaller comparing with the cases containing cationic surfactant modified MMT. A phenomenon similar to PA12 system was observed in polyethylene (PE)/clay composites in our laboratory. It should be mentioned that both Na-MMT and a-100MMT can not form acid sites on the MMT sheets at high temperature [9]. Thus it is probable that another chemical effect on the flame retardancy acts in PS/Na-MMT and PS/a-100MMT composites. In order to confirm the effect of a-MMTs, a-MMTs with different loading of SDSo were added into PS matrix. Fig. 4 presents the plots of the HRR of three PS/a-MMT composites. The PHRR of PS/a-60MMT composite was 350 Kw/m^2 (about 64% reduction compared to that of pure PS), which is lower than those of PS/a-100MMT, PS/a-150MMT and even PS/c-150MMT composites. The above results confirm solidly that the addition of a-MMT can obviously reduce the PHRR of PS composites.

Moreover a comparative experiment showed that the PHRR of PS/Na-MMT/SDSo = 95/4/1 (by weight) composite, of which the composition is the same as that of PS/a-100MMT composite, was slightly higher than that of PS/Na-MMT = 95/5 (by weight) composite (Fig. 5). This means that the difference between PS/a-100MMT and PS/Na-MMT composites in the PHRR does not result from the contribution of SDSo itself. The other control showed that the PHRR of PS/a-100MMTN = 95/5 (by weight) composite, in which the a-100MMT was prepared by naturally drying the resultant sol containing 100% CEC of SDSo at room temperature, was almost the same as that of PS/Na-MMT composite (Fig. 5). The morphology observation showed that the dispersion degree of a-100MMTN in PS/a-100MMTN composite was slightly lower than that of a-100MMT in PS/a-100MMT composite. The above results imply that the special aggregate states of a-100MMT in PS/a-100MMT composites may play a key role in the reduction of the PHRR.

Fig. 6 presents digital photographs for the residual surfaces of burned samples. Pure PS burned out, and nothing was left behind in the sample pan. There was a carbonaceous protective layer in the

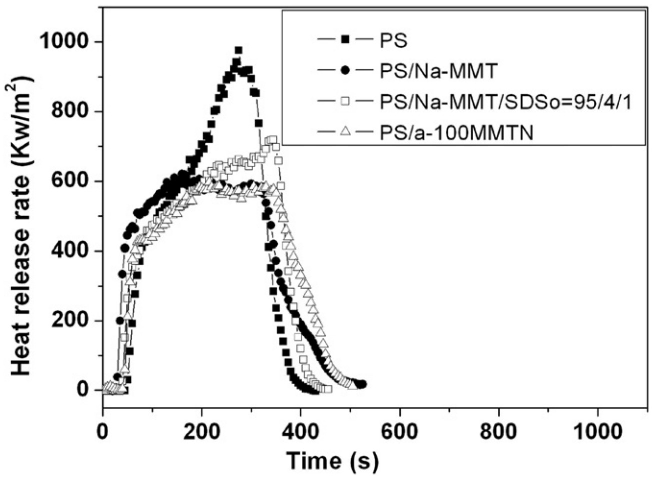

Fig. 5. Comparison of heat release rate (HRR) plots for PS, PS/Na-MMT, PS/Na-MMT/SDSo = 95/4/1 (by weight) and PS/a-100MMTN composites (measured by cone calorimeter at an external radiant flux of 35 kW/m^2).

residues of PS/c-80MMT and PS/c-150MMT composites, and the residue surface of PS/c-80MMT composite was more perfect compared to that of PS/c-150MMT composite. In contrast, without catalytic effect of acid sites, only gray ash was left in PS/Na-MMT composite. Comparatively, the clay sheets in PS/a-100MMT composite, in which a-100MMT was in the form of opened hollow microspheres, have formed a gray and compact protective layer on the sample surface during combustion. However, the strength of this protective layer was lower than those of carbonaceous protective layers in the residues of PS/c-80MMT and PS/c-150MMT composites. The morphologies of residual surfaces from PS/a-60MMT and PS/a-150MMT composites were very similar to that of PS/a-100MMT composite. In contrast, PS/a-100MMTN composite just showed a better dispersion of residue in the sample pan comparing with PS/Na-MMT composite.

Fig. 7 shows FESEM images of the residues from PS/a-100MMT, PS/a-100MMTN and PS/c-150MMT composites. The burned residue of PS/a-100MMT was composed of curled small aggregates of MMT sheets which were connected together (Fig. 7b). A lot of curled small aggregates of MMT sheets have accumulated together to form large aggregates (Fig. 7a). There were many a-100MMTN particles aggregated randomly in the residue (Fig. 7c and d). In contrast, the burned residue of PS/c-150MMT was composed of planar MMT sheets, which accumulated randomly to form large aggregates (Fig. 7e and f). Comparatively, there were many small cracks in the large aggregates of the residue of PS/c-150MMT composite. Interestingly, there were obvious large holes in the residues of PS/c-150MMT and PS/a-100MMTN composites. These are probably formed by volatilization of the degradation products during

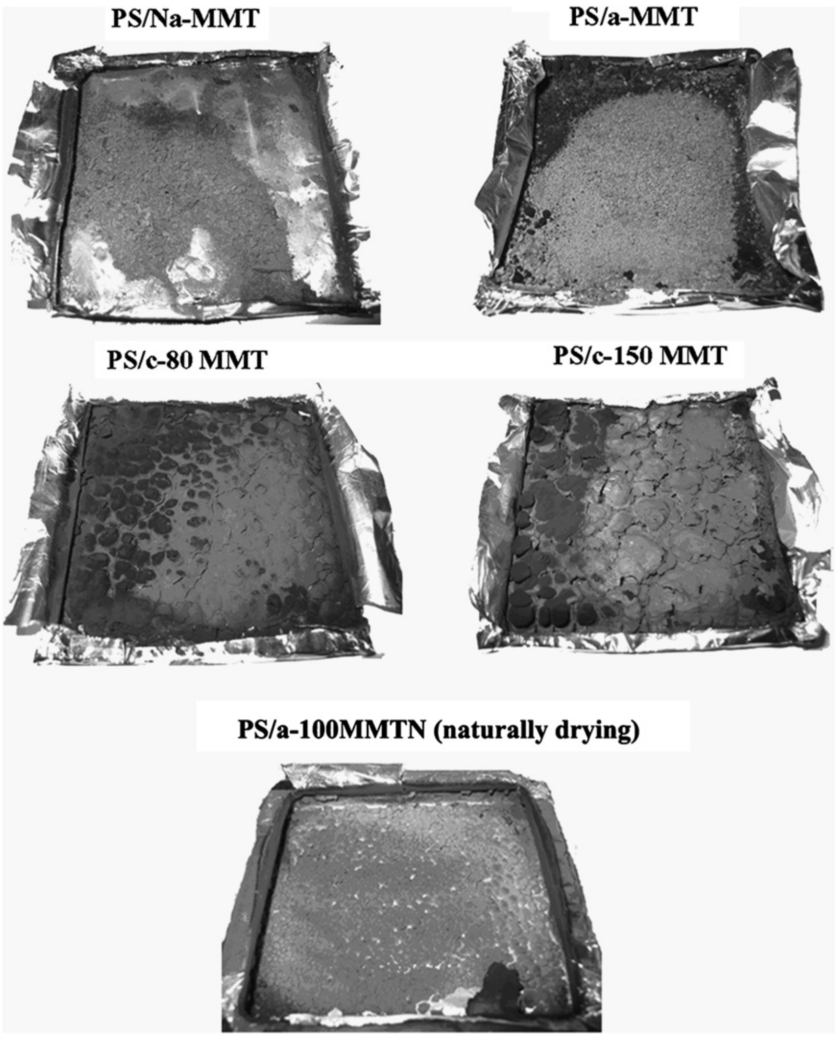

Fig. 6. Photographs of the residue surface at the end of combustion during the measurements of cone calorimeter.

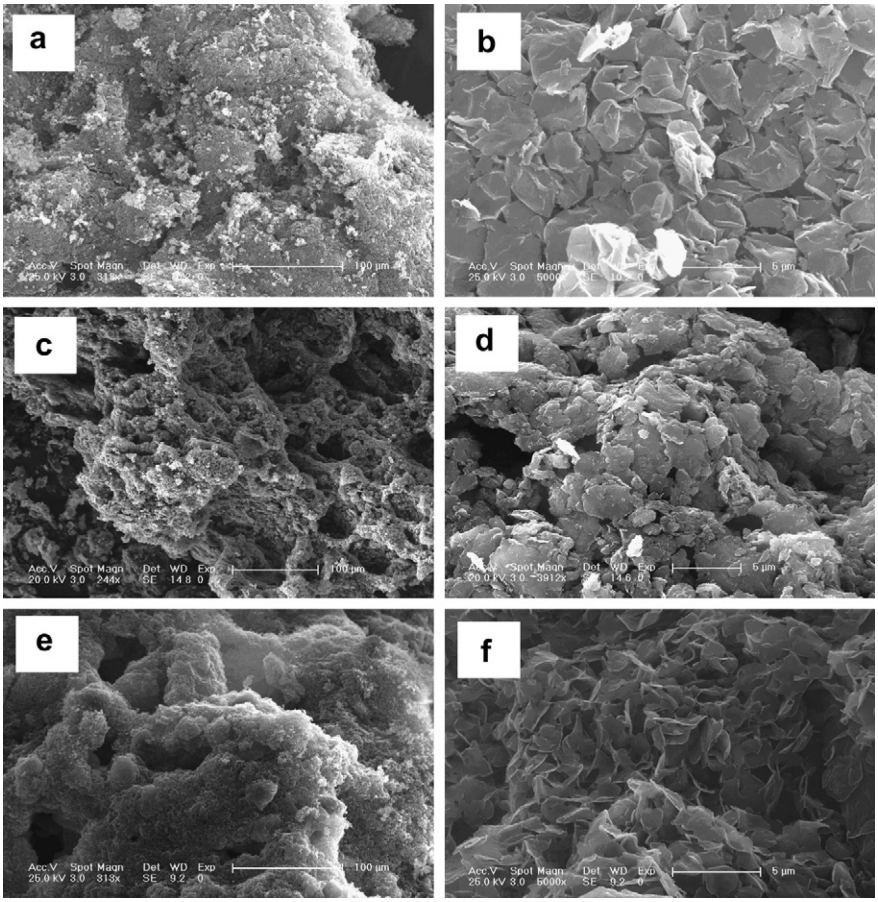

Fig. 7. FESEM images of the residues from PS/a-100MMT (a and b), PS/a-100MMTN (c and d) and PS/c-150MMT (e and f) composites.

combustion. However, this kind of structure is not found in the residue of PS/a-100MMT composite. These results show that the physical barrier of the residue on the surface of PS/a-100MMT composite is probably better than that in PS/c-150MMT composite during combustion. One of the reasons is that the orientation of planar MMT sheets parallel to the burned surface of the materials is necessary to obtain the best physical barrier to the degradation products. Otherwise the random arrangements of MMT sheets will not provide ideal physical barrier. However, it is difficult to make all the planar MMT sheets arranged parallel to the surface during combustion. In contrast, the curled small aggregates of MMT sheets can easily form compact barrier layers in spite of the random arrangements. More importantly, the arrangements of the curled small aggregates of MMT sheets form a foam-like structure, which is similar to the structure of protective layer originated from intumescent flame retardant (IFR) system [15]. In an IFR formulation, usually there is a char forming agent, a catalyst for char formation and a foaming agent. Generally the char forming agent in the IFR will swell when exposed to fire or heat to form a porous foamed carbonaceous mass, which in turn acts as a barrier to heat, air and pyrolysis product. Similarly the foam-like structure of MMT sheets can also provide a better barrier for heat transfer. Compared to PS/a-100MMT composite, a-100MMTN is dispersed as a state of solid particles in PS matrix; as a result, the volume fraction of a-100MMTN is small in the PS composite. Thus a-100MMTN can not form a good protective layer in PS/a-100MMTN composite during combustion in comparison with PS/a-100MMT composite. This is the reason why the flame retardancy of a-100MMT is better than that of a-100MMTN in PS matrix.

The above results demonstrate that there should be different effects of MMT sheets on the flame retardancy of PS, depending on the used MMTs, such as chemical structure of the surfactants and aggregate states. The acid sites are a main chemical factor to significantly improving flame retardancy of PS/c-MMT composites. In the cases without acid sites, such as PS/Na-MMT and PS/a-MMT composites, there is another chemical effect of MMT sheets acting on the flame retardancy of PS, probably resulted from the inherent properties of MMT sheets. It should be mentioned that no acid sites are involved in these composites due to the absence of cationic surfactants, which is different from the situations of the previous reports [10,11]. One of possible reasons is the effect of radical trapping of MMT sheets, which can work in the PS composites containing Na-MMT and a-MMT. The other possible reason is the cross-linking reaction of degradation products via Friedel–Crafts alkylation reaction between benzene ring and vinyl group of styrene (as a main degradation product), which will be catalyzed by MMT sheets [16]. In order to obtain further insight into the chemical effects of MMT sheets on PS matrix at high temperature, GC–MS was used to measure the collected liquid fraction of degradation products from the samples pyrolyzed at 700 °C under nitrogen (Fig. 8). The contents of five degradation products in the liquid fraction from the GC–MS tests are presented in Table 1. Unfortunately, it is difficult to identify the products of Friedel–Crafts alkylation from the GC–MS results. However, the addition of c-MMT led to the formation of more complicated degradation products located at the elution time between 15–20 min due to the catalytic effect of acid sites on the degradation of PS. At the same time, the contents of styrene, dimer and trimer in the liquid fraction

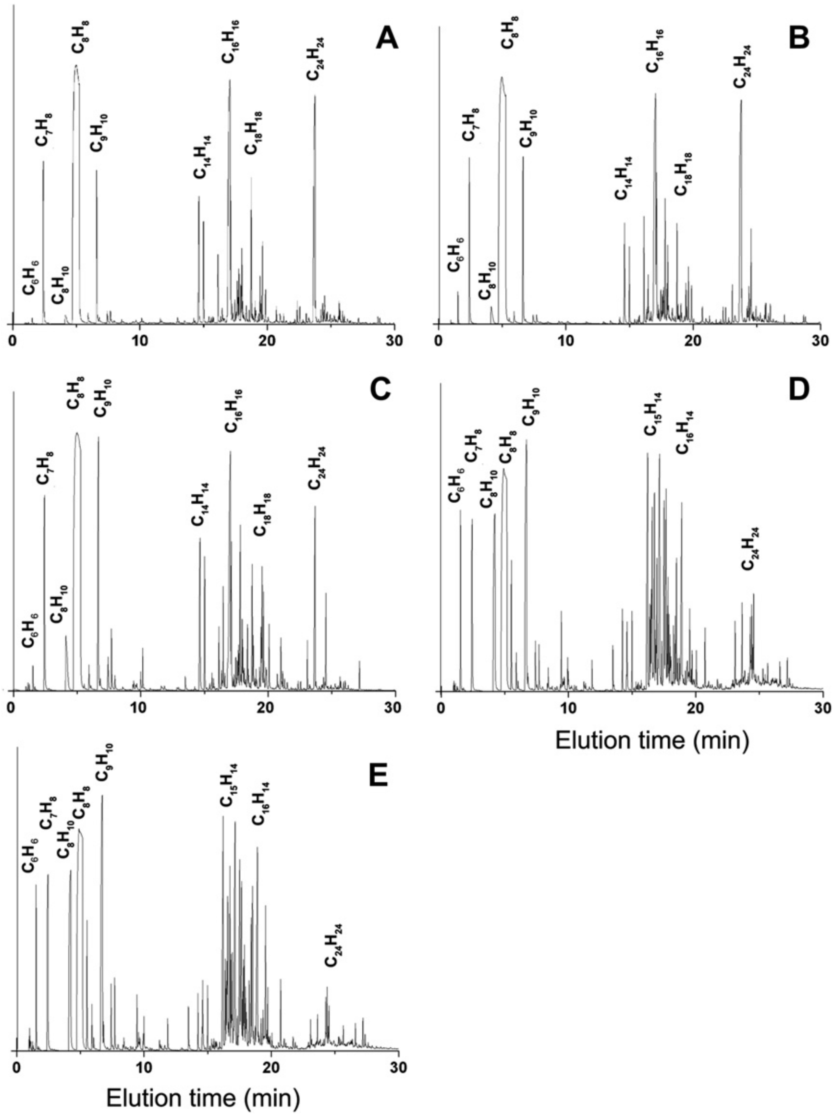

Fig. 8. GC-MS profiles for the collected liquid fractions of the degradation products. (A) PS; (B) PS/Na-MMT; (C) PS/a-100MMT; (D) PS/c-80MMT; (E) PS/c-150MMT.

of degradation products decreased significantly compared to those of pure PS (Table 1). Moreover, it was found that the addition of Na-MMT or a-100MMT in PS matrix slightly changed the composition of degradation products. The contents of benzene, ethylbenzene and some complicated compounds increased a little. In addition, the reduction in the contents of styrene, dimer and trimer was clearly observed in the liquid fraction of degradation products from PS/a-100MMT composite. Although there are not obvious acid sites on the surfaces of Na-MMT and a-100MMT, the composition change of degradation products of PS in the presence of Na-MMT or a-100MMT, especially in the case of a-100MMT, shows that the states of the reactive intermediates may change slightly. Probably the rearrangement of radicals occurs due to the effect of radical trapping of MMT sheets. This chemical effect, combining with physical barrier of dispersed MMT sheets on the surface of burning samples, delays the volatilization of degradation products from the samples.

TGA was further used to investigate effects of various modified MMTs on thermal stability of PS. In the burning process of bulky samples, polymer may endure different degradation process on the surface region and in the middle. Oxidative degradation occurs in the surface region, and the decomposition of PS in the middle is almost a process of thermal degradation, especially PS/OMMT composites, in which the oxygen is hard to permeate into the inside of the samples due to physical barrier of MMT sheets. Fig. 9 shows TGA and DTG curves of PS and PS composites under nitrogen and air. The temperatures for 5 wt% weight loss ($T_{5\ \mathrm{wt\%}}$), 10 wt% weight loss ($T_{10\ \mathrm{wt\%}}$) and the maximum decomposition (T_{max}) for PS and its composites under both air and nitrogen environments are summarized in Table 2. The thermal stability of PS/Na-MMT was a little better than pure PS under nitrogen. However, the addition of Na-MMT did not change the thermal stability of PS under air. The

Table 1
Comparison of the contents of fives degradation products in the liquid fractions by GC–MS measurements.

Sample	Benzene	Ethylbenzene	Styrene	Dimer	Trimer
PS	0.1	0.6	45.8	13.7	9.0
PS/Na-MMT	0.3	0.9	44.3	11.4	10.4
PS/a-MMT	0.3	2.3	40.4	9.6	3.4
PS/c-80MMT	1.6	6.1	24.3	5.3	1.1
PS/c-150MMT	1.2	6.7	24.4	4.9	0.4

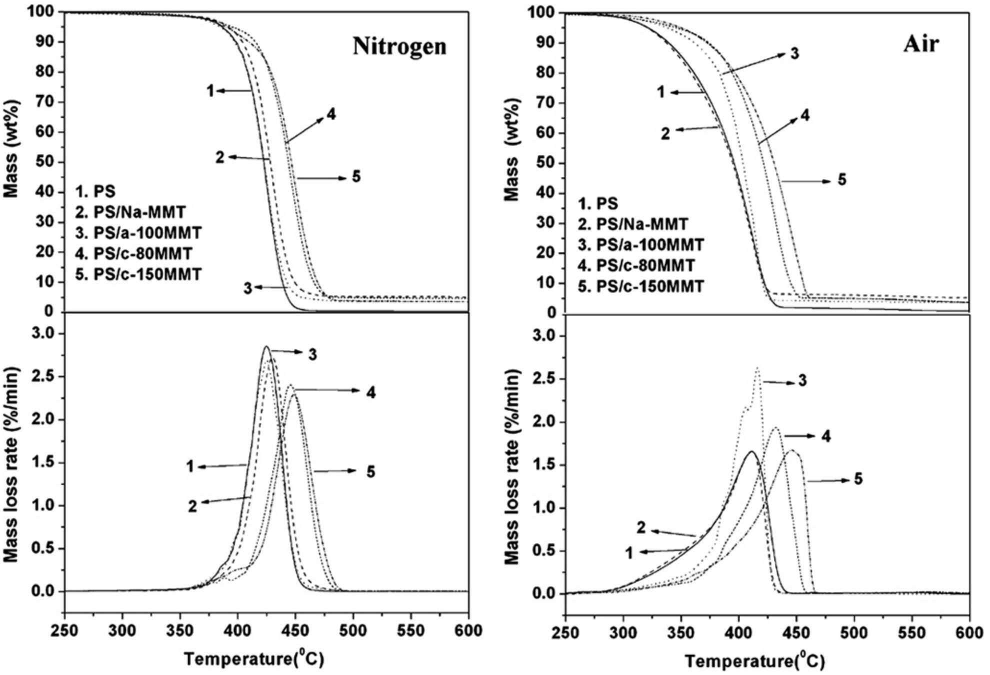

Fig. 9. TGA and DTG curves of PS, PS/Na-MMT and PS/OMMT composites under air and nitrogen on heating ramp of 20 °C/min.

situation of PS/a-100MMT was just contrary to that of PS/Na-MMT, that is, adding a-100MMT in PS matrix resulted in the improvement of thermal stability under air and did not change thermal stability under nitrogen. In contrast, thermal stabilities of both PS/c-80MMT and PS/c-150MMT composites were higher than those of other samples in spite of environmental atmosphere. It is probable that the volatilization delay of the degradation products results from the presence of acid sites on the surface of MMT sheets and the physical barrier of a clay-enriched char protective layer. The above results are different from those of PA12 system [9]. This demonstrates that the effect of modified MMTs on the thermal stability of polymers depends on chemical structure of polymers [6].

It is interesting why the double chemical effects do not act synchronously in PS/c-80MMT and PS/c-150MMT composites. Comparing with thermal degradation via radical intermediates, solid acids will catalyze degradation of PS via cationic intermediates, in which the carbon–hydrogen bonding breaks [17]. More importantly, owing to the lower activation energy, the catalytic degradation of PS can occur preferentially comparing with thermal degradation of PS [17]. In addition, strong catalysis of acid sites controls the carbonization of degradation products via dehydrogenation and aromatization. As a result, the chemical effect from the inherent properties of MMT sheets, such as radical trapping, will not play an important role in the flame retardancy of PS/c-80MMT and c-150MMT composites.

Table 2
Thermal stabilities of PS and PS composites containing different MMTs.

Samples	Air environment			N_2 environment		
	$T_{5\ wt\%}$ (°C)	$T_{10\ wt\%}$ (°C)	T_{max} (°C)	$T_{5\ wt\%}$ (°C)	$T_{10\ wt\%}$ (°C)	T_{max} (°C)
PS	321	339	410	386	398	425
PS/Na-MMT	321	337	410	392	404	430
PS/c-80MMT	345	374	432	394	415	446
PS/c-150MMT	345	374	446	391	409	449
PS/a-100MMT	337	362	416	385	398	425

4. Conclusion

Effects of the modifiers in the OMMT on the degradation and the flame retardancy of PS/OMMT composites have been studied. There are two kinds of chemical effects of OMMT, which depend on the surface property of MMT sheets at high temperature. In the PS/c-MMT (cationic surfactant modified MMT) composites, the acid sites in situ formed by the decomposition of surfactant play an important role in reducing the PHRR of the composites due to their catalysis on the carbonization of degradation products. In contrast, although a-MMT (anionic surfactant modified MMT) and Na-MMT can not form acid sites on the MMT sheets at high temperature, both can reduce the PHRR of PS due to the effect of the inherent properties of MMT sheets. Moreover, in the case of a-MMTs from spraying drying, a special aggregate state of MMT sheets, which is similar to foam-like structure, has been formed in the residue. As a result, the addition of a-MMT results in a significant decrease in the PHRR of PS, which is even lower than the addition of c-150MMT in PS matrix. As the effects of Na-MMT and a-MMT are different in various polymer matrices, such as PA12, PE and PS, it is possible that the chemical effect of the inherent properties of MMT sheets on the flame retardancy of polymers depends on the presence of conjugation structural unit (such as styrene) in polymer chains. Our further work is focused on styrene-containing polymers (such as ABS).

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