

Chemical effects of cationic surfactant and anionic surfactant used in organically modified montmorillonites on degradation and fire retardancy of polyamide 12 nanocomposites

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Abstract

Three kinds of organically modified Na⁺-montmorillonites (OMMTs), including two kinds of octadecylammonium modified montmorillonite with different contents of octadecylammonium and a kind of sodium dodecylsulfonate (SDSo) modified montmorillonite, were used to prepare polyamide 12 (PA12)/OMMT nanocomposites. Effects of the modifiers on degradation and fire retardancy of PA12/OMMT nanocomposites were investigated. Acid sites formed in cationic surfactant modified MMT via Hoffman decomposition could accelerate degradation of PA12 at high temperature. However, catalytic effect of the acid sites on carbonization of the degradation products promoted char barrier formation, which reduced heat release rate (HRR). Higher content of cationic surfactant in OMMT is beneficial to fire retardancy of PA12 nanocomposites and the dispersion states of OMMT have assistant effects. In contrast, Na⁺-montmorillonite (Na-MMT) and anionic surfactant modified MMT (a-MMT) could not form acid sites on the MMT layers; in this case, fire retardancy of PA12/Na-MMT appears to have no improvement and PA12/a-MMT appears to have limited improvement.

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1. Introduction

Polymer/clay nanocomposites (PCNs) have attracted a lot of attention from both industry and academia for their outstanding combination properties, for instance, the improved mechanical properties, a remarkable increase in thermal stability as well as fire retardancy for flammability and the reduction in the permeability of gases [1–6].

PCNs have been believed as a revolutionary new and environmentally benign flame retardant approach. The reason for the flame retardancy of PCNs is that a carbonaceous silicate layer is formed on the surface during burning. This structure

creates a protective barrier to heat and mass transfer; heat release rate (HRR) of PCNs is significantly decreased [7–9]. Kashiwagi et al. explained the formation of the carbonaceous silicate char on the sample surface during burning by two reasons [9]. One was that the layered silicate was left on the surface by the decomposition of polymer matrix and the other was that the gases and gas bubbles from degradation products propelled the clay particles to the surface region and the associated convection flowed in the melt from the interior of the sample to the surface. Recently, Lewin et al. brought forward an alternative hypothesis to explain the barrier effect of PCNs on the fire retardancy. According to this hypothesis, the clay migrated to the surface due to a difference in the surface free energy (SFE) between clay and polymer before pyrolysis and combustion of polymer take place [10–15].

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Meanwhile, more and more evidences have showed that the chemical effect of modified clay in polymer matrix plays a key role on the fire retardancy. Zanetti et al. pointed out that the modified clay reduced the flammability of EVA due to the formation of acid sites from decomposition of the organic modifier [8]. Recently, Yang et al. have investigated the relationship of acid sites with the flame retardancy of polypropylene (PP)/clay nanocomposites [15] and found that the acid sites could induce the formation of char, which was a main reason for flame retardancy of PP/clay nanocomposites. In addition, incorporation of clay into polymer matrix could change degradation process of a polymer, which probably changes the composition of degradation products and also has a significant effect on fire retardancy of polymer/clay nanocomposites. Iron within the clay could scavenge free radical to prevent degradation of polystyrene [16]. Wilkie et al. systematically studied the thermal degradation behaviour of polymers in the presence of organically modified montmorillonite (OMMT) [17]. They found that the presence of OMMT promoted significantly the intermolecular reactions and inter-chain aminolysis/acidolysis of PA6. Also Davis et al. [18] and Paul et al. [19] proposed that OMMT and water were responsible for the PA6 degradation during processing PA6 nanocomposite at higher temperature.

Although it has been proved that the acid sites are the main reason for flame retardancy of PP/clay nanocomposites [15], it is difficult to speculate that a similar effect should appear in other polymer nanocomposites due to different chemical structures. Furthermore, the intertwined plight between acid sites and barrier effect in the conventional ammonium modified clay containing polymer nanocomposites makes it difficult to determine whether chemical effect or physical barrier mainly controls fire retardancy. In this study, we choose Na-MMT and three kinds of OMMTs, including two kinds of octadecylammonium modified montmorillonite with different contents of octadecylammonium and a kind of sodium dodecylsulfonate (SDSo) modified montmorillonite, to prepare PA12/Na-MMT composites and PA12/OMMT nanocomposites. This provides an opportunity to investigate the effects of acid sites on the MMT layers and physical barrier on fire retardancy of polymer nanocomposites, respectively. Effect of the modifiers in OMMT on the degradation and fire retardancy of PA12 nanocomposites was studied. Acid sites on MMT layers showed catalytic effects on degradation of PA12 and carbonization of the degradation products, which strongly influence fire retardancy of PA12.

2. Experimental part

2.1. Materials

Na^+ -montmorillonite (Na-MMT) with a cation exchange capacity (CEC) of 119 meq/100 g used in this work is from Kunimine Co. Octadecylamine is from Wako Pure Chemical Industries Co. Octadecylammonium modified montmorillonite was synthesized as described in our previous papers [20,21]. Under the same conditions, the loading of octadecylammonium with 60% (or 150%) cation exchange capacity (CEC) of

Na-MMT was added into Na-MMT suspension at 80 °C in the process of modifying montmorillonite. The obtained OMMT is named as c-60MMT (or c-150MMT). The factual contents of the modifier are 8.3 wt% in c-60MMT and 26.3 wt% in c-150MMT (estimated by TGA). Modified MMT by anionic surfactant (a-MMT) was synthesized by adding 100% CEC of sodium dodecylsulfonate (SDSo) into MMT suspension, and this mixture was vigorously stirred for 3.5 h at 80 °C. The resultant sol was spray dried by WP-1.5 spray drying instrument. Final spray dried powder was dried in a vacuum oven at 75 °C for more than 24 h. Polyamide 12 (PA12) with molecular weights ($M_w = 50\,000$) was purchased from Elf Atochem.

2.2. Preparation of samples

The preparation of PA12 nanocomposites containing 5 wt% different MMTs was carried out in a Brabender mixer with a rotating speed of 100 rpm at 210 °C for 10 min. Samples were hot pressed at 200 °C to get the 1 mm thick samples for measurements of TGA.

2.3. Characterizations

The morphologies of PA12/Na-MMT composites and PA12/OMMT nanocomposites were observed by 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 -40 °C. The sample was collected on carboncoated copper TEM grids.

Thermogravimetric analysis (TGA) was carried using Perkin–Elmer at a heating rate of 20 °C/min from ambient to 800 °C in air and nitrogen flow. Cone calorimetry was performed according to ISO5660 Standard at a heat flux 35 kW/m². Exhaust flow rate was 24 L/s and the spark was continuous until the sample ignited. The specimens with the

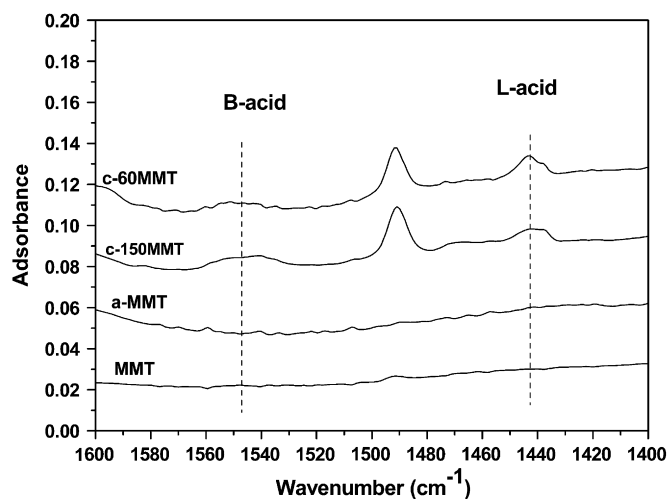


Fig. 1. FTIR spectra of the adsorbed pyridine on c-60MMT, c-150MMT, a-MMT and Na-MMT in the 1600–1400 cm^{-1} range after pyridine adsorption and then desorption at 150 °C.

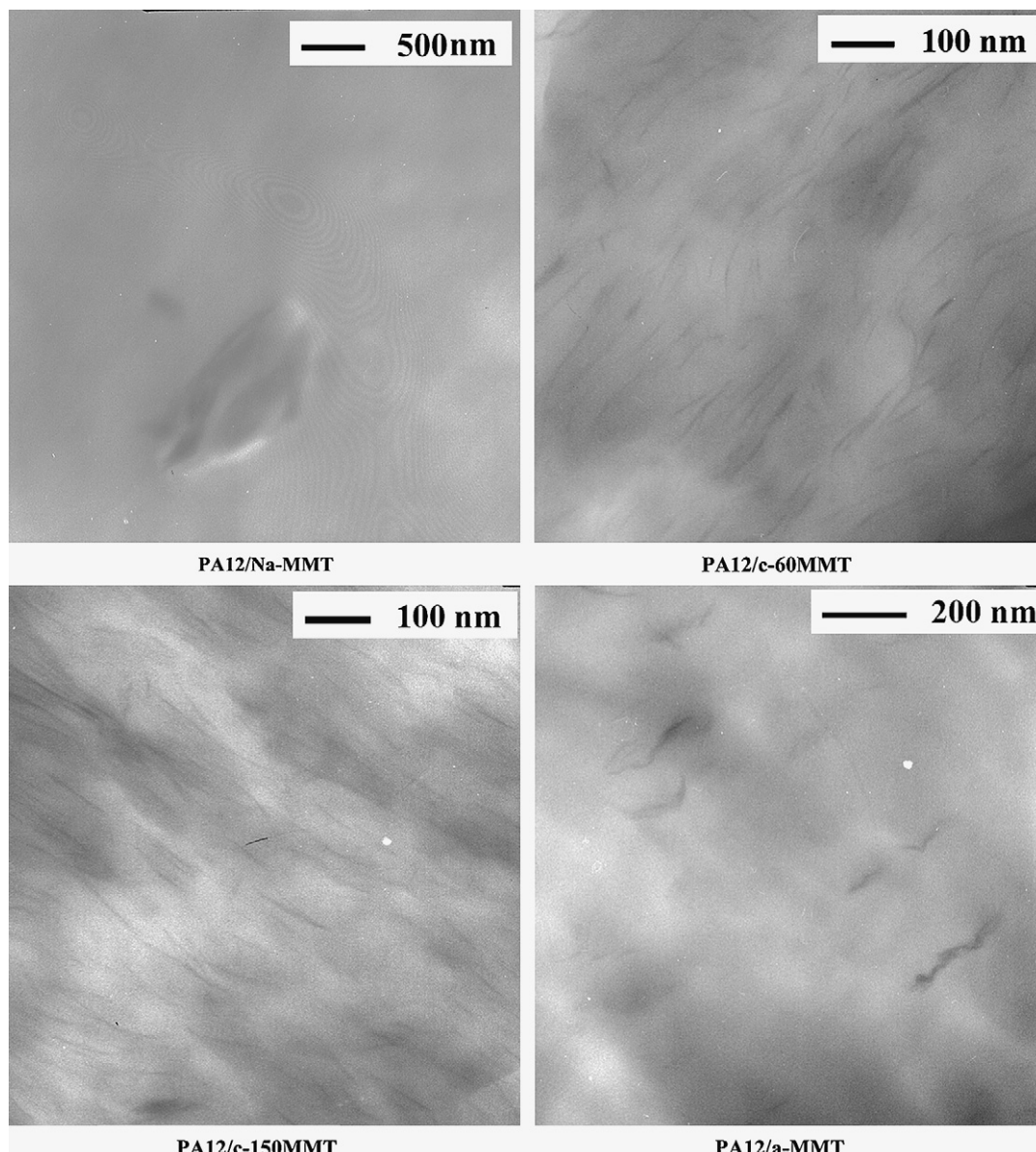


Fig. 2. TEM images of PA12/Na-MMT composites and PA12/OMMT nanocomposites.

sizes of $6 \times 100 \times 100$ mm square plaques for cone calorimetry were prepared by compression molding at 200°C .

Gas chromatography–mass spectrometry (GC–MS, AGILENT 5975 MSD) was used to analyze composition of the degradation products of PA12, PA12/Na-MMT composites and PA12/OMMT nanocomposites. For collecting the degradation products, approximately 10 g of the sample was put into a quartz tube and pyrolyzed at 700°C which was close to the temperature measured by cone calorimeter at a heat flux of 35 kW/m^2 in a N_2 atmosphere. The condensable evolved products were collected using a cold trap.

Acidity testing of MMT was done by pyridine adsorption [22]. Na-MMT and three kinds of OMMTs were treated in air at 550°C until the surfactant burned out. In a sealed tube, about 15 mg of the samples was exposed to the pyridine vapor at 150°C for 1 h. Subsequently, the sample was transferred out

of the pyridine vapor and kept at 150°C for 1 h to remove the physically adsorbed pyridine. The resulting product was pelletized with KBr and characterized by FTIR spectrometer (BRUKER Vertex 70 FTIR).

3. Results and discussion

FTIR spectra for adsorbed pyridine after desorption at 150°C can provide insights into the existence of acid sites in different MMTs. Two bands at 1549 cm^{-1} and 1443 cm^{-1} , which were characteristic of Brønsted and Lewis acid sites, respectively [22], were observed in c-60MMT and c-150MMT after decomposition of octadecylammonium (Fig. 1); however, no such bands were observed in Na-MMT and a-MMT. Fig. 2 shows TEM images for microstructure of PA12/Na-MMT composites and PA12/OMMT nanocomposites. The large and

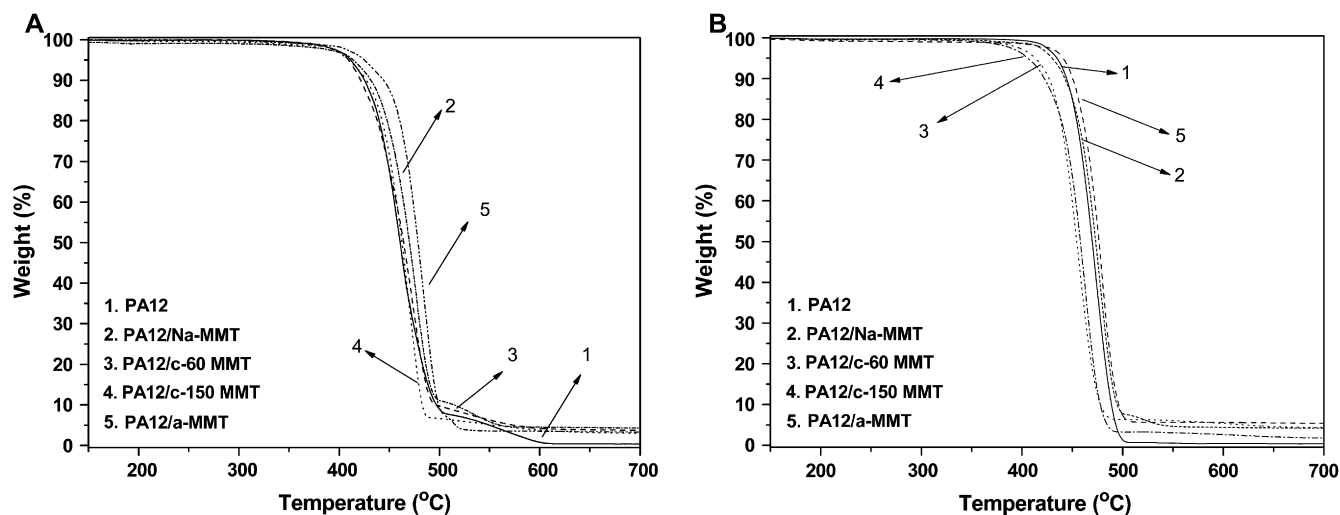


Fig. 3. TGA curves of PA12, PA12/Na-MMT composites and PA12/OMMT nanocomposites (A) in air and (B) nitrogen on heating ramp of 20 °C/min.

unevenly dispersed Na-MMT aggregates were observed in PA12/Na-MMT composites. Dispersion of OMMT layers in PA12/c-60MMT and PA12/c-150MMT nanocomposites is very good. There is no obvious difference in the morphologies between PA12/c-60MMT and PA12/c-150MMT nanocomposites. Comparatively, the size of OMMT layers is larger in PA12/a-MMT nanocomposites. Based on the above results, it is convenient to investigate chemical effect and physical barrier on degradation and fire retardancy of PA12/OMMT nanocomposites.

Bulky sample of polymer may endure different degradation process on the surface region and in the middle. Generally oxidation degradation of polymer on the surface region takes place. In the burning process of bulky sample of PA12/OMMT nanocomposites, the well dispersed MMT layers provide physical barrier effect, thus oxygen is hard to permeate into the middle of the sample. Decomposition of PA12 in the middle is almost a process of thermal degradation. Fig. 3A shows TGA curves of PA12, PA12/Na-MMT composites and PA12/OMMT nanocomposites under air. It is obvious that PA12/a-MMT showed the best thermal stability among the samples. The thermal stability of PA12/Na-MMT is a little better than pure PA12. In contrast, both PA12/c-60MMT and PA12/c-150MMT nanocomposites showed a main degradation process similar to pure PA12 in the range of 200–480 °C. Second degradation process appears in the range of 480–600 °C, which is ascribed to the decomposition of the residual char. TGA curves of PA12/OMMT nanocomposites under nitrogen have been presented in Fig. 3B. The onset temperature of decomposition in both

PA12/c-60MMT and PA12/c-150MMT nanocomposites is much lower than that of pure PA12. However, the thermal stabilities of PA12/Na-MMT composites and PA12/a-MMT nanocomposites are very similar to that of pure PA12. The temperatures for 5 wt% weight loss ($T_{5 \text{ wt\%}}$), 10 wt% weight loss ($T_{10 \text{ wt\%}}$) and the maximum decomposition (T_{max}) for PA12 and its nanocomposites under both air and nitrogen environments are summarized in Table 1. It can be seen from above result that although the physical barrier originated from the well dispersion of MMT layers in polymer nanocomposites can delay release of the degradation products, PA12/c-60MMT and PA12/c-150MMT nanocomposites are easier to degrade than pure PA12 in nitrogen. It can be concluded that degradation of PA12 is accelerated due to the existence of acid sites on the MMT layers originated from the Hoffman decomposition of cationic surfactant.

In order to know insights into catalytic effect of acid sites on the decomposition of PA12, the samples were pyrolyzed at 700 °C and the degradation products were collected. All the collected products contained about 25 wt% gaseous fractions. The other collected products from pure PA12, PA12/Na-MMT composites and PA12/a-MMT nanocomposites were a mixture of liquid fractions and waxy solid at room temperature, but those from PA12/c-60MMT and PA12/c-150MMT nanocomposites were liquid fractions. These degradation products were further analyzed by gas chromatography–mass spectrometry (GC–MS). Fig. 4 shows the GC–MS profiles of the degradation products from PA12, PA12/Na-MMT composites and PA12/OMMT nanocomposites. The composition distribution

Table 1
Comparison of thermal stabilities of PA12, PA12/Na-MMT composites and PA12/OMMT nanocomposites

Samples	Air environment			N ₂ environment		
	$T_{5 \text{ wt\%}}$ (°C)	$T_{10 \text{ wt\%}}$ (°C)	T_{max} (°C)	$T_{5 \text{ wt\%}}$ (°C)	$T_{10 \text{ wt\%}}$ (°C)	T_{max} (°C)
PA12	410	423	462	434	445	472
PA12/Na-MMT	413	431	476	440	450	477
PA12/c-60MMT	409	421	470	413	427	456
PA12/c-150MMT	409	426	467	405	423	462
PA12/a-MMT	424	443	485	430	442	479

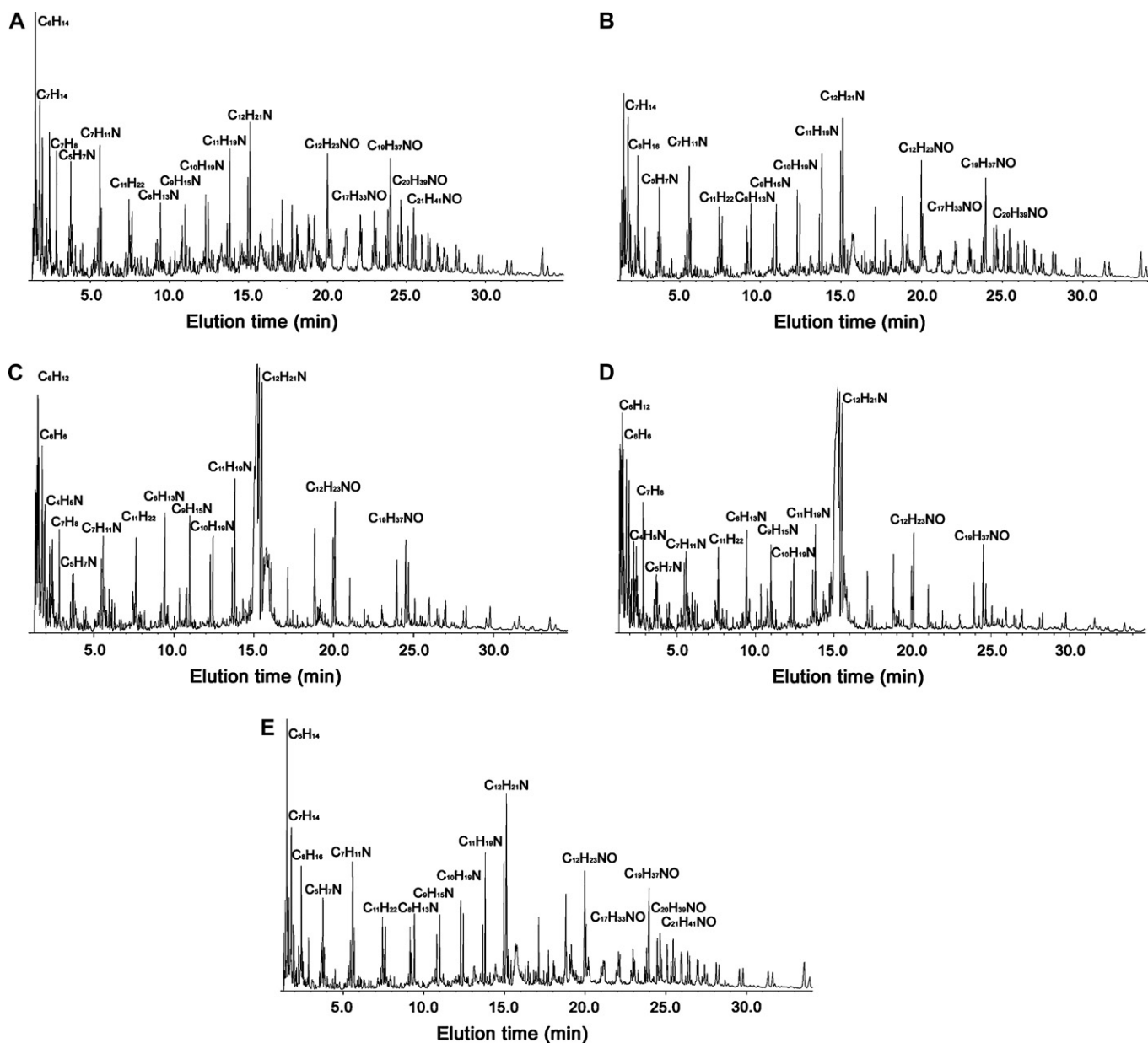


Fig. 4. Gas chromatography–mass spectrometry (GC–MS) profiles of the degradation products. (A) PA12; (B) PA12/Na-MMT; (C) PA12/c-60MMT; (D) PA12/c-150MMT; (E) PA12/a-MMT.

of the liquid fraction containing waxy solid in the degradation products from PA12 is very wide. The main products included lactams, unsaturated olefinic nitriles, unsaturated olefinic amide and some unsaturated olefins. However, in the cases of PA12/c-60MMT and PA12/c-150MMT nanocomposites, the degradation products in the liquid fractions showed some difference. Table 2 represents the weight percentage of main products at different elution time regions according to GC–MS measurements. As the elution time was over 17 min, the peak of large degradation products of PA12/c-60MMT and PA12/c-150MMT nanocomposites were almost disappeared. The main degradation products of PA12/c-60MMT and PA12/c-150MMT nanocomposites were unsaturated olefinic nitriles, and some unsaturated olefins. More importantly, the larger amount of

dodecene nitrile appeared in the degradation products from these nanocomposites at around 15 min of the elution time comparing with that from pure PA12, which showed catalytic

Table 2
Weight percentage of major degradation products at different elution time regions obtained by GC–MS measurements

Samples	Elution time (min)			
	<3	3–14	14–17	>17
PA12	38.1	19.6	10.5	31.8
PA12/Na-MMT	32.2	24.8	11.1	31.9
PA12/c-60MMT	31.2	17.4	37.1	14.3
PA12/c-150MMT	34.5	14.2	37.2	14.1
PA12/a-MMT	31.9	25.9	11.6	30.6

effect of the acid sites on degradation of PA12. In contrast, the main liquid fractions containing waxy solid in the degradation products of PA12/Na-MMT and PA12/a-MMT were almost the same as those of PA12. It is obvious that the addition of Na-MMT and anionic surfactant modified a-MMT in PA12 matrix does not strongly change the degradation process, but the addition of cationic surfactant modified MMT leads to the formation of more liquid fractions with lower molecular weight due to catalytic effect of the acid sites on degradation of PA12.

Combustion behaviour of the above-mentioned PA12, PA12/Na-MMT composites and PA12/OMMT nanocomposites was compared by means of cone calorimeter (Fig. 5). At the continuous heat flux of 35 kW/m^2 , all the samples turned soft and some of volatile gases were generated. Comparing with pure PA12, all peak values of heat release rate (HRR) of PA12/OMMT nanocomposites decreased in spite of existence of cationic surfactant modified MMT or anionic surfactant modified MMT. Meanwhile the ignition time for the nanocomposites becomes longer than that of pure PA12. Moreover, it can be seen that the peak value of HRR in PA12/c-150MMT nanocomposites is lower than that in PA12/c-60MMT nanocomposites. Although there are the same weight percentage (5 wt%) of OMMT in these two samples, the absolute content of MMT is higher in PA12/c-60MMT nanocomposites due to the lower content of surfactant in c-60MMT. As the decomposition of cationic surfactant results in the formation of acid sites, the presence of more acid sites in PA12/c-150MMT nanocomposites further improves fire retardancy. Dispersion of c-60MMT is almost the same with c-150MMT in PA12 matrix, which has been proved by TEM results. Therefore the difference in the HRR of these nanocomposites suggests that the dispersion state of MMT layers in polymer matrix just has assistant effect to reduce flammability. Comparing the HRR curve of PA12/c-60MMT with PA12/c-150MMT nanocomposites, the HRR of PA12/c-60MMT nanocomposites quickly increased after ignition, then the HRR was kept constant as the burning time increased. Owing to catalytic effect of more acid sites in

PA12/c-150MMT nanocomposites, the more carbonaceous silicate char residue was formed on the sample surface, and the HRR of PA12/c-150MMT nanocomposites was slightly lower. The similar phenomena were observed by other researchers [8,15]; the HRR of nanocomposites was almost the same or slightly lower as the burning time increases. In contrast, both Na-MMT and a-MMT could not form acid sites on the MMT layers. In the case of Na-MMT, the physical barrier of MMT layers was not effectively formed as a result of poor dispersion of Na-MMT in PA12 matrix, thus the HRR peak value of PA12/Na-MMT was almost the same as that of pure PA12. Comparatively, dispersion of a-MMT was much better than Na-MMT in PA12 matrix, which led to lower HRR in PA12/a-MMT nanocomposites than PA12/Na-MMT composites. However, the HRR of PA12/a-MMT was still higher than those of cationic surfactant modified MMT containing PA12 nanocomposites. The above results demonstrate that the chemical effect mainly controls fire retardancy of nanocomposites and the physical barrier effect has assistant effect.

The mass loss plots of the samples are shown in Fig. 6. Among all the samples, the mass loss of pure PA12 sample is the largest at the same burning time. PA12/Na-MMT almost shows the same process of mass loss as pure PA12. The mass loss of PA12/c-60MMT is larger than that of PA12/c-150MMT nanocomposites as burning time increases. There were more residues in PA12/c-150MMT nanocomposites. However, the mass loss of PA12/a-MMT nanocomposites is very slow at the beginning and fast at the final stage.

The observation for burning surface of the samples provided further evidence about effect of OMMT on combustion behaviour of PA12. For pure PA12 and PA12/Na-MMT, some black char floated on the boiling surface during combustion. In the cases of PA12/c-60MMT and PA12/c-150MMT nanocomposites, with the aid of MMT layers, a good carbonaceous silicate protective layer was formed. A similar phenomenon was observed in PA12/a-MMT nanocomposites. However, without the catalytic effect of acid sites, the protective layer still floated

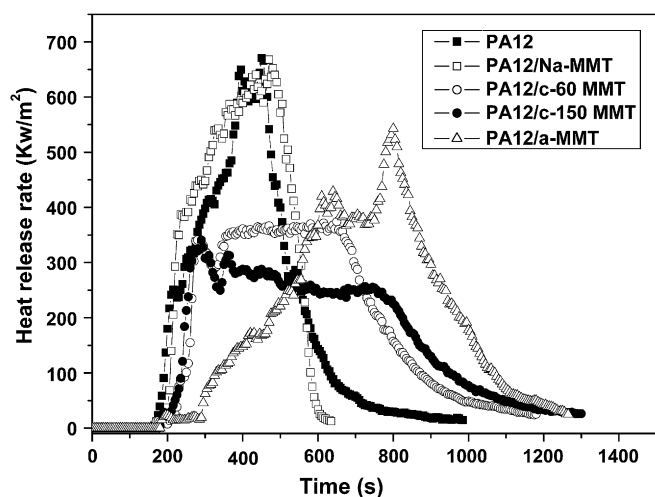


Fig. 5. Comparison of heat release rate (HRR) plots for PA12, PA12/Na-MMT composites and PA12/OMMT nanocomposites.

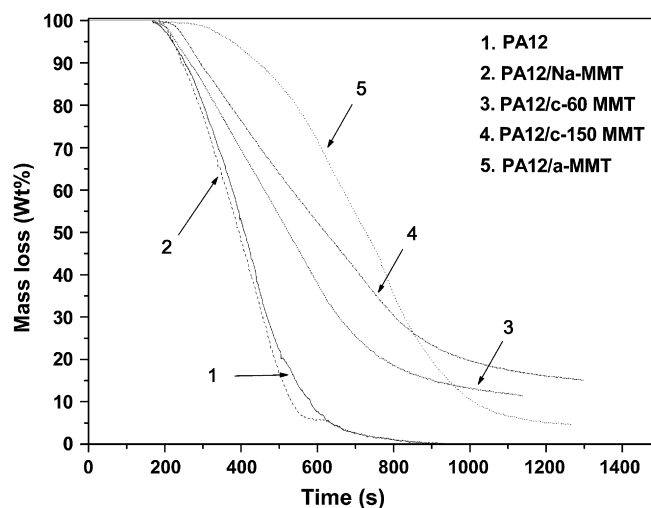


Fig. 6. Mass loss curves of PA12, PA12/Na-MMT composites and PA12/OMMT nanocomposites.

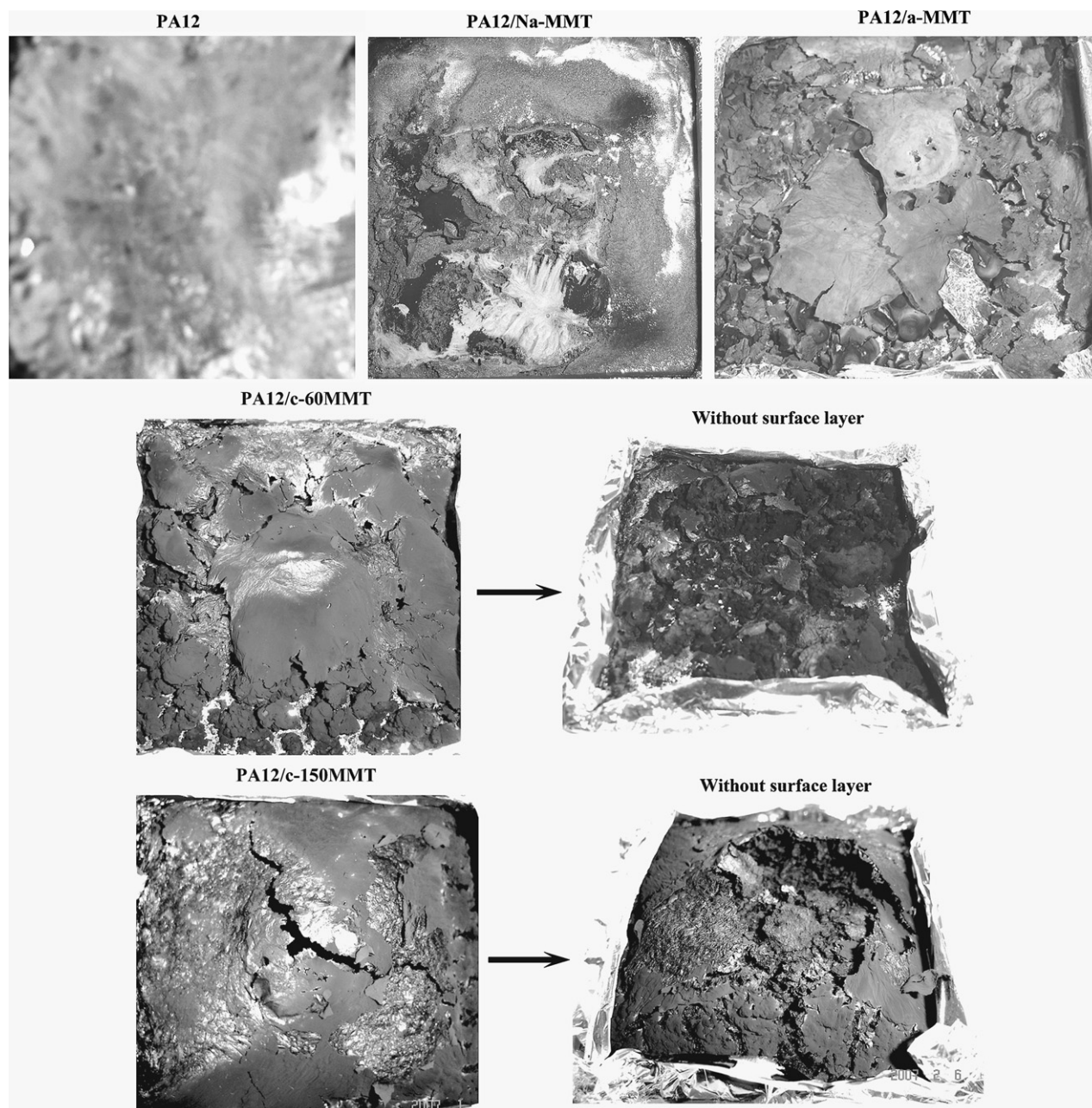


Fig. 7. Photographs of the residues after combustion.

on the boiling surface of this sample. When the burning time increased, there were more degradation products that broke the protective layer on the burning surface, thus the HRR of PA12/a-MMT nanocomposites increased again. Fig. 7 shows photographs of the residue surface at the end of combustion during the measurements of cone calorimeter. Pure PA12 burned out and there was nothing left on the sample pan. There was a carbonaceous protective layer in the residues of PA12/c-60MMT and PA12/c-150MMT nanocomposites. Removing the surface layer, some black block residues were left in PA12/c-60MMT nanocomposites; however, owing to catalytic effect of more acid sites in PA12/c-150MMT nanocomposites, the continuous char residues had been formed. In contrast, without

catalytic effect of acid sites, only gray ash was left in PA12/Na-MMT composites and PA12/a-MMT nanocomposites. This shows that the acid sites also have catalytic effect on carbonization of the degradation products of PA12, which is profitable for the formation of a carbonaceous protective layer on the burning surface.

4. Conclusion

Effects of the modifiers in OMMT on degradation and fire retardancy of PA12/OMMT nanocomposites have been studied in this work. The acid sites created by the decomposition of cationic surfactant could catalyze degradation of PA12 and

carbonization of the degradation products, which improve fire retardancy of the nanocomposites. The HRR of PA12/OMMT nanocomposites obviously decreased when more acid sites were introduced. The dispersion state of OMMT layers just played a minor role. In contrast, anionic surfactant modified MMT and Na-MMT could not form acid sites on the MMT layers at high temperature, which did not damage thermal stability of PA12 matrix. The poor dispersion of Na-MMT in PA12 matrix resulted in no effect of the physical barrier, thus the HRR peak value of PA12/Na-MMT was almost the same as that of pure PA12. Furthermore, the HRR of PA12/a-MMT was higher than those of cationic surfactant modified MMT containing PA12 nanocomposites. Therefore the chemical effect is a main factor to improve fire retardancy of PA12/OMMT nanocomposites; the physical barrier effect has assistant effect. It should be stressed that chemical effect of acid sites may be different in the polymer matrix with various chemical structures. More efforts need to be done to investigate chemical effect of the modified clay on degradation and performance (such as flame retardancy) of other polymers. Selecting a proper modifier for preparing OMMT depends on concerned properties of polymers and their specific application.

Acknowledgments

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