

Influences of Catalysis and Dispersion of Organically Modified Montmorillonite on Flame Retardancy of Polypropylene Nanocomposites

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ABSTRACT: The degradation and flame retardancy of polypropylene/organically modified montmorillonite (PP/OMMT) nanocomposite were studied by means of gas chromatography-mass spectrometry and cone calorimeter. The catalysis of hydrogen proton containing montmorillonite (H-MMT) derived from thermal decomposition of (alkyl) ammonium in the OMMT on degradation of PP strongly influence carbonization behavior of PP and then flame retardancy. Brønsted acid sites on the H-MMT could catalyze degradation reaction of PP via cationic mechanism,

which leads to the formation of char during combustion of PP via hydride transfer reaction. A continuous carbonaceous MMT-rich char on the surface of the burned residues, which work as a protective barrier to heat and mass transfer, results from the homogeneous dispersion of OMMT in the PP matrix and appropriate char produced. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 3488–3494, 2007

Key words: polypropylene; montmorillonite; flame retardance; nanocomposites

INTRODUCTION

There are various methods of improving flame retardancy of polymers. These methods have been developed to offer fire safety of products in a wide variety of applications. However, to some degree, these methods are limited due to environmental requirements and may negatively impact polymer mechanical properties. Polymer/clay nanocomposites are believed to be a new promising approach in flame retardancy¹ as a result of its great potential in forced flaming conditions, for instance, the reduction of the flame spread and fire propagation.² In addition, it does not have the usual drawbacks associated with other flame retardant additives. Moreover, polymer/clay nanocomposites increase physical, thermal, and mechanical properties dramatically.^{3,4} Therefore, this technique has been responsible for the development of new flame retardant polymeric products, and has been recognized as a revolutionary new approach for flame retardancy.

Generally it is believed that the reason for the flame retardancy of polymer/clay nanocomposites is

formation of a carbonaceous silicate layer on the surface during burning.^{5,6} This structure creates a protective barrier to heat and mass transfer. Although reduced flammability has been demonstrated for a lot of polymer nanocomposites, many issues are unresolved as to how the barrier was formed, for example, how the char is created and in what condition the continuous carbonaceous MMT-rich surface can be formed. A chemical mechanism for this charring was proposed in poly(ethylene-co-vinyl acetate)/organically modified montmorillonite (EVA/OMMT) nanocomposite, in which a protective charred ceramic surface layer was formed as a result of reassembly of the clay layers and catalyzed charring of the polymer.⁷ It was believed that the larger surface area for clay-polymer contact in the nanocomposite comparing with microcomposite favored to catalyze dehydrogenation and oxidative dehydrogenation of the polymer to a conjugated polyene, which prevented volatilization of combustible volatiles by aromatization and charring. Protonic acid sites formed on the silicate layers by Hoffman decomposition of the organic modifier might enhance the catalysis. Very recently, Yang and coworkers⁸ have investigated the relationship of acid sites on the clay with the flame retardancy of polypropylene (PP)/clay nanocomposites, and found that the acid sites could induce the formation of char, which was a main reason for flame retardancy of

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PP/clay nanocomposites. Comparatively, the barrier effect of clay layers for volatiles offered a minor contribution on the decrease of heat release rate (HRR) in the nanocomposite. Wilkie and coworkers found that the change in the degradation pathway of a polymer by incorporation of clay had a significant effect on the decrease range in the HRR of polymer/clay nanocomposites.⁹ Furthermore, the authors concluded that the stability of radical produced upon degradation is closely related to the fire retardancy of polymer/clay nanocomposites.

These previous results are very important to understand deeply the essence of organoclay in the combustion of polymer nanocomposites. However, some fundamental issues need to be clarified further. For example, how does the acid site induce char formation during combustion of polymer nanocomposites? On the other hand, what are the effects of char content in the residue and the dispersion of clay in polymer matrix on flame retardancy of nanocomposites? The presence of clay may have different effects on degradation of polymers due to various chemical compositions. In some case, the clay not only has physical barrier effect and but also may have chemical effect on fire retardancy of polymers. It is well known that clay minerals can catalyze many organic reaction,¹⁰ however, what is the catalysis of organoclay during combustion of polymers (such as PP)? Which needs to be further investigated in the earlier system.

In this report, we will investigate the mechanisms of the flame retardancy of PP/OMMT nanocomposite, especially chemical catalysis of OMMT. Meanwhile effects of char formation, dispersion of MMT layers, and formation of carbonaceous MMT-rich surface on fire retardancy of PP will also be studied.

EXPERIMENTAL

Materials and preparation of samples

Polypropylene (PP), F401, was purchased from Panjin Petrochemical, with melt flow index of 0.8 g/min. Maleic anhydride-grafted-polypropylene copolymer (PP-MA) with acid values of 52 mg KOH/g are purchased from Sanyo Corp. Na⁺-montmorillonite (Na-MMT) with a cation exchange capacity of 119 mequiv/100 g used in this work is from Kunimine. Octadecylamine is from Wako Pure Chemical Industries. H-Beta zeolite (H-β) with Si/Al ratio of 70 was purchased from catalyst factory of Nankai University.

Octadecylammonium modified montmorillonite (OMMT) was synthesized as described in our previous articles.¹¹ Under the same conditions, the loading of octadecylammonium chloride with 80% and 150% cation exchange capacity (CEC) of Na-MMT was added into Na-MMT suspension, respectively,

maintained at 80°C in the process of modifying montmorillonite. The obtained OMMTs are named as OMMT-80 and OMMT-150, respectively. The factual adsorption levels of the modifier are 51 %CEC and 122 %CEC, respectively (estimated by TGA¹¹). According to our previous report,¹² the excess surfactants could enter and reside inside the interlayer, but not physisorbed to the exterior of the crystallites or contained in voids within the OMMT aggregates. Through extractions of OMMT with tetrahydrofuran, it also confirmed that below the CEC, surfactant cations were tightly attracted to the MMT surface by electrical neutralization between surfactant cations and anionic sites on the MMT platelets. After the anionic sites are completely occupied with surfactant cations at the CEC, excess surfactant cations enter the interlayer with counterions.

The above OMMTs and H-β were melt-mixed with PP, PP-MA, respectively, to fabricate PP composites in a Brabender mixer with a rotating speed of 100 rpm at 180°C for 10 min.

Characterization

OMMT-80 and OMMT-150 were extracted with tetrahydrofuran for 48 h in a Soxhlet apparatus then the extraction was precipitated by excess AgNO₃ solution (0.1N), a white precipitate appeared for OMMT-150. However, the white precipitate was not quite obvious for OMMT-80. After calculating, the results showed that almost no chloride existed in the OMMT-80, about 0.6 wt % chloride in OMMT-150.

For testing the residual char, 5 g sample was placed in a crucible and burned at 700°C until the flame disappeared, the residues were collected and weighed by analytical balance. The amount of residual char was obtained by subtracting amount of MMT in the OMMT from that of the residue. The yield of char was calculated by amount of the residual char divided by amount of the mixture.

The quartz tube, mounted in an electrical tube furnace, was heated to 700°C close to the temperature measured by cone calorimeter at heat flux of 35 kW/m² in a N₂ atmosphere. Subsequently, ~ 10 g of a sample was put into a quartz boat and pyrolyzed at 700°C. The condensable evolved products are collected using a cold trap, which were then analyzed by gas chromatography-mass spectrometry (GC-MS, AGILENT 5975 MSD).

Wide angle X-ray diffraction was carried out with a Rigaku model Dmax 2500 with a Cu Kα radiation and the interlayer distances (d_{001}) were estimated from the (001) peaks in the X-ray diffraction (XRD) patterns with Bragg formula. The morphology of the composites was observed by transmission electron microscope (TEM, JEOL2010) on microtome sections of the composites.

TABLE I
Composition of PP Composites and the Char Content in the Burned Residues

Samples	Solid acids	Content of solid acid (wt %)	PPMA (wt %)	Yield of char (wt %)
PR0	Na-MMT	2.50	12	0
PR1	OMMT-80	3.14 ^a	0	0.50
PR2	OMMT-80	3.14	12	0.51
PR3	OMMT-150	3.70 ^b	0	0.91
PR4	OMMT-150	3.70	12	0.87
PR5	Octadecylammonium chloride	2.50	0	0
PR6	OMMT-150	10.00	0	1.80
PR7	OMMT-150	10.00	12	1.72
PR8	H-β	10.00	12	3.80

^a 3.14 g of OMMT-80 consists of 2.50 g of MMT and 0.64 g of the modifier.

^b 3.70 g of OMMT-150 consists of 2.50 g of MMT and 1.20 g of the modifier.

Cone calorimeter 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 for cone calorimeter were prepared by the compression molding of the sample into 6 × 100 × 100 mm³ square plaques.

RESULTS AND DISCUSSION

Catalysis of OMMT on formation of residual char

PP/MMT composites with different composition were prepared (Table I) and all the composites were combusted at 700°C that is close to the temperature measured by cone calorimeter at heat flux of 35 kw/m². From Table I, adding PPMA does not affect the char content in the residues of PP/PPMA/OMMT nanocomposites, although it can effectively improve the dispersion of OMMT in the PP matrix.¹³ Higher amount of OMMT in the nanocomposites can result in higher yield of the residual char. In contrast, PP/PPMA/Na-MMT could not lead to formation of the residual char in spite of amount of Na-MMT. The difference in the formation of char between PP/PPMA/Na-MMT and PP/PPMA/OMMT composites should be attributed to formation of Brønsted acid sites on the surface of OMMT. FTIR measurements provide further evidence on formation of Brønsted acid sites after decomposition of organic modifiers on the OMMT (Fig. 1). It is known that the thermal decomposition of (alkyl)ammonium in the OMMT will leave hydrogen proton on the MMT layers to form hydrogen proton containing MMT (H-MMT).¹⁴ FTIR spectra for adsorbed pyridine after desorption at 150°C on Na-MMT and H-MMT from thermal decomposition of OMMT provide insights into the nature of the acid sites in these materials. Two bands at 1548 cm⁻¹ and 1441 cm⁻¹ can be assigned to the C—C bands of pyridine adsorbed, which are characteristic of Brønsted and Lewis acid sites, respectively,¹⁵ were observed for the H-MMT from

OMMT-80 and OMMT-150; however, no such band at 1548 cm⁻¹ was observed for the Na-MMT. This suggests that Brønsted acid sites on the H-MMT are a key factor to the formation of the residual char.

The influence of octadecylammonium on the char formation from PP/OMMT composites was investigated. Here we add 2.5 wt % octadecylammonium chloride into PP matrix. The char yield of PP/octadecylammonium chloride mixture was calculated after combustion at 700°C. The results in Table I (PR5) indicated that octadecylammonium did not affect the char content in the residues of PP/PPMA/OMMT nanocomposites despite excess addition of it in PP matrix comparing with the PR3 and PR4. Although some reports showed that halide could enhance the char yield during decomposition of polymer,¹⁶ here the chlorine contents in the OMMT-80 and OMMT-150 were too low to affect the formation of char from composites during combustion.

In general, the combustion of pure polymers includes two chemical reactions, that is, degradation of polymers and combustion of degradation prod-

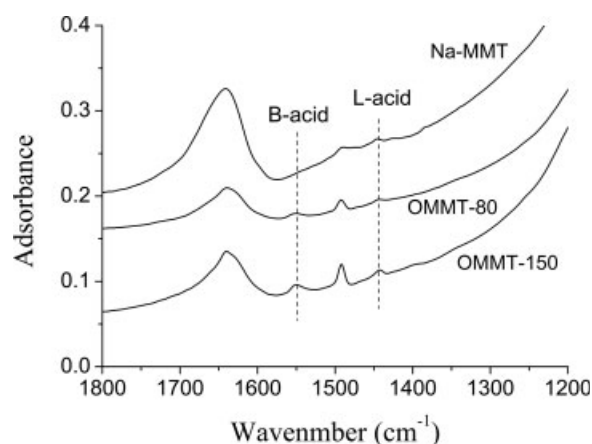
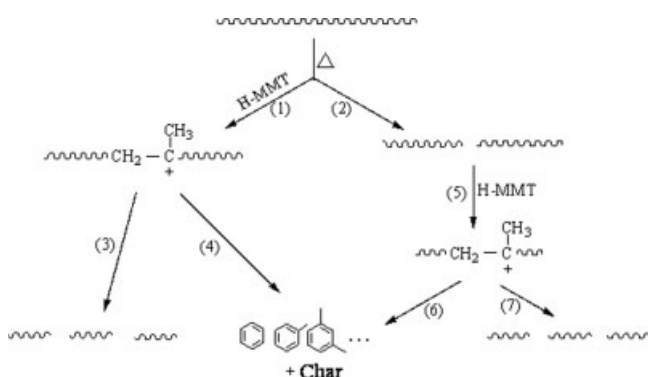


Figure 1 FTIR spectra of the adsorbed pyridine on Na-MMT and H-MMTs from OMMT-80 and OMMT-150 in the 1800–1200 cm⁻¹ range after pyridine adsorption and then desorption at 150°C.



Scheme 1 Possible chemical reaction for degradation and formation of char from PP catalyzed by solid acid.

ucts. The exterior polymer will undergo oxidative degradation due to existence of oxygen and the inside polymer will thermally degrade via radical mechanism due to absence of oxygen. However, thermal degradation of the inside polymers may be changed, for example, catalytic degradation of polymers may occur in the presence of acid catalyst (such as solid acids). It was believed that the nano-dispersed organoclay changes the EVA's thermal degradation reactions.⁷ Thermal decomposition of (alkyl)ammonium in the OMMT would take place via the Hoffman mechanism to evolve ammonia and corresponding olefin and leave proton acid sites on the MMT layers¹⁴ to form H-MMT. Although all catalytic active sites on the H-MMT were believed to accept single electrons from donor molecules and form free radicals at external heat flux, leading to the dehydrogenation and crosslinking of polymer chains,⁸ some other previous reports also showed that, as a solid acid catalyst, H-MMT catalyzed degradation of PP at high temperature via cationic mechanism.^{17–19} Carbenium can be formed by protonating alkanes via hydride transfer (Reaction (1) in Scheme 1), such as $C_nH_{2n+1}^+$, which serve as main reactive intermediates for the initiation and development of the degradation process.²⁰ Comparatively, it is difficult that thermal degradation occurs via free radical mechanism due to its high activation energy (Reaction (2) in Scheme 1).²¹ Even if primary thermal degradation occurs, its degradation products will be involved in secondary catalytic degradation in the presence of H-MMT (Reaction (5) in Scheme 1). Comparing with thermal degradation, the catalytic degradation of PP will afford more gas fractions and liquid fractions of lower molecular weight (Reaction (3) and (7) in Scheme 1), meanwhile the isomerization, cyclization, and aromatization would take place during catalytic degradation of PP (Reaction (4) and (6) in Scheme 1), which leads to the formation of alkene, cycloalkanes, cycloalkenes, aromatic hydrocarbons, and char in the degradation products.²²

To confirm the relationship between the formation of char and catalytic degradation of PP by H-MMT, we choose a common and widely used H-Beta zeolite (H- β) as a solid acid catalyst,^{23–25} which can effectively catalyze degradation of PP due to formation of carbenium. Indeed, upon burning PP/PPMA/H- β composites, the char was also formed in the residues, which can attribute hydrogen transfer reaction in catalytic degradation of PP by the Brønsted acid sites on the H- β . Hydrogen transfer reaction is one of the most important secondary reactions in catalytic cracking.^{26,27} During hydrogen transfer, olefin hydrocarbons are converted into paraffins without any external source of hydrogen. The hydrogen is supplied by converting a part of the alkene and cycloparaffin hydrocarbons into hydrocarbons containing less hydrogen, such as dienes, aromatics, and even coke (Reaction (4) and (6) in Scheme 1). The above process can be represented by the cationic mechanism in two steps.^{28,29} While the aromatics and coke are difficult to be formed during the thermal degradation of PP via free radical mechanism.²⁰ On the basis of this, catalytic degradation of PP via cationic mechanism can be demonstrated by the presence of aromatics in degradation products. Therefore GC-MS was used to analyze composition of the degradation products at 700°C under nitrogen atmosphere. There are a lot of aromatic components (C_7H_8 , C_8H_{10} , ...) in the degradation products of PP catalyzed by H-MMT and H- β [Fig. 2(b,c)]. While those from thermal degradation of PP are mainly composed of alkenes and dienes ($C_{12}H_{24}$, ...) with higher carbon number [Fig. 2(a)]. The GC-MS was recently used to measure the degradation products of pure PP and PP/OMMT nanocomposites.⁹ However, the results are different from those of this work, probably resulting from different degradation conditions.

Effect of content of the residual char on fire retardancy

The dispersion degree of OMMT in the PP composites was characterized by XRD and TEM measurements. Diffraction peaks of OMMTs in PR2 and PR4 have shifted to a lower angle ($2\theta = 2.9^\circ$), indicating that PR2 and PR4 are intercalated nanocomposites (Fig. 3). TEM images further confirm that there are almost the same dispersion states of OMMT in the PR2 and PR4 nanocomposites [Fig. 4(b,d)]. In this case, the char content becomes the only factor that affects flame retardancy of PP. Thus the effect of the char content in the residues on flame retardancy of PP could be investigated. From Table I, it can be seen that there is a higher content of the char in the residues of PR4 than PR2 after combustion at 700°C. The results from measurements of cone calorimeter

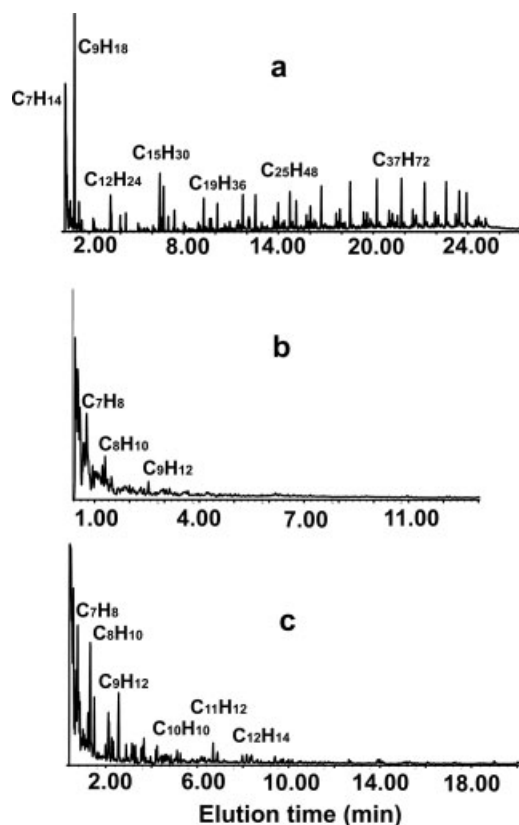


Figure 2 Gas chromatography-mass spectrometry (GC-MS) spectra of the degradation products. (a) PP/PPMA; (b) PP/PPMA/OMMT-150; (c) PP/PPMA/H- β .

showed that the PR4 nanocomposite had lower HRR than that of the PR2 [Fig. 5(a)], which demonstrate that a higher content of the char in the residue is profitable to flame retardancy of PP/OMMT nanocomposite under the same dispersion state of OMMT in the matrix. From Figure 5(b), it can be seen that mass lose rate of PR4 nanocomposite is lower than that of PR2 nanocomposite when the combusting time is from 150 s to 450 s. This means that less flammable volatiles diffuse into combustion area during burning the PR4 nanocomposite in this period. Probably, a better protective barrier was formed in the PR4 nanocomposite.

Effect of dispersion of OMMT on fire retardancy

The effect of dispersion of OMMT in PP matrix on fire retardancy of the composites was investigated. In previous literatures,^{5,8} there were two opposite views. One of them suggested that the dispersion state of the clay particles in the polymer matrix had an important influence on the flammability; the other suggested that the influence was a little. In this report, we compared the flammability of PR1 with PR2 and PR3 with PR4 (the dispersion state of the OMMT was apparent different), respectively.

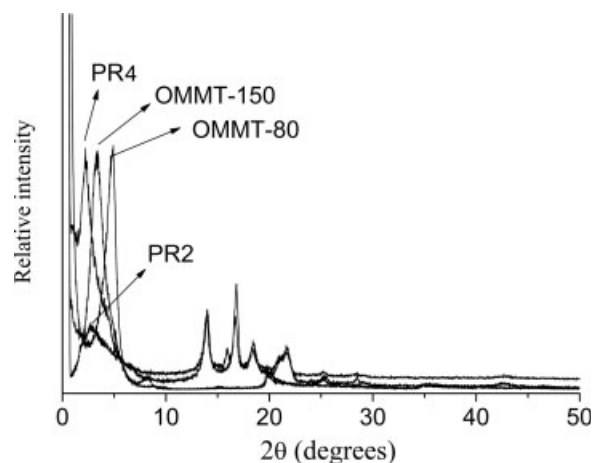


Figure 3 Comparison of XRD profiles of PR4 and PR2.

As we know, maleated PP (PPMA) used in PP/OMMT nanocomposites can effectively improve the dispersion of OMMT in the PP matrix,¹² therefore the dispersion states of OMMT in both PR2 and PR4 should be better than those of PR1 and PR3, respectively, which was confirmed by TEM observation (Fig. 4). PR1 and PR2 have the same content of the residual char after combustion (Table I), implying

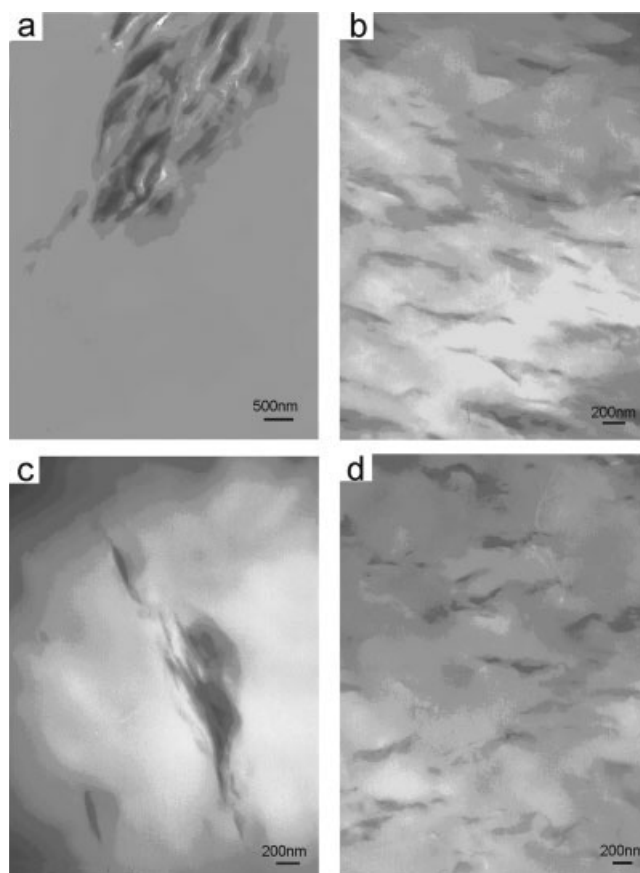


Figure 4 TEM images of PP/OMMT composites. (a) PR1; (b) PR2; (c) PR3; (d) PR4.

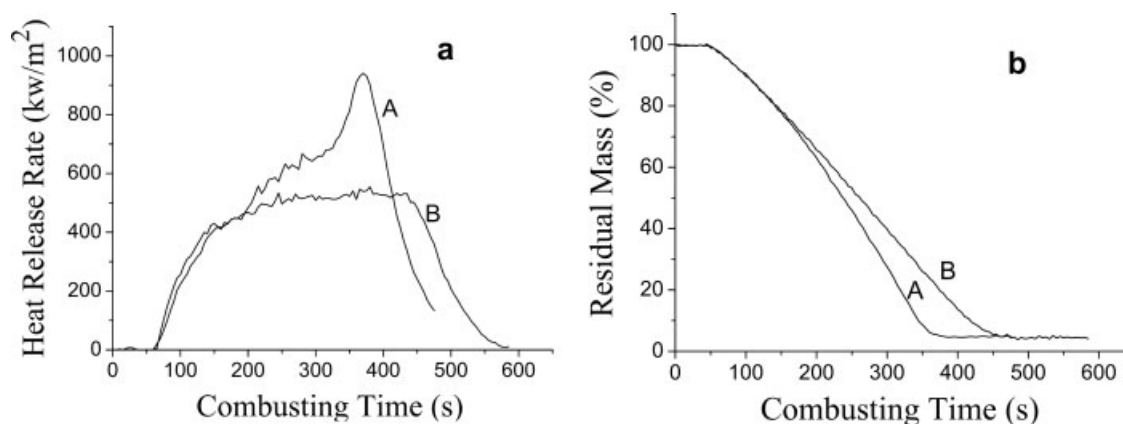


Figure 5 Comparison of heat release rates (a) and the residual mass (b) for PP/PPMA/OMMT-80 and PP/PPMA/OMMT-150 nanocomposites at 35 KW/m² heat flux. (A-PR2 and B-PR4).

that dispersion state of OMMT (as a precursor of solid acid catalyst) has no effect on the content of the residual char. The similar phenomenon was also observed in the PR3 and PR4. However, from Figure 6, it can be seen that the PR2 and PR4 are better than PR1 and PR3 in reducing HRR of PP during combustion, respectively, which demonstrate that the better dispersion of OMMT in the matrix is profitable to flame retardancy of PP/OMMT nanocomposite under the same content of the char in the residue.

The effect of dispersion of OMMT in PP matrix on the morphology of the burned residue was observed. Because of almost the same content of the residual char after combustion of PR1 and PR2, the difference in the morphologies of PR1 and PR2 residues could only be attributed to different dispersion state of OMMT in the matrix. From Figure 7(a,b), we found that the better dispersion of OMMT in the PP matrix could form a relative continuous carbonaceous MMT-rich surface after combustion. A similar phenomenon appeared in PR3 and PR4 nanocomposites

[Fig. 7(c,d)]. Furthermore, compared with the PR2, the residue of PR4 could form more perfect carbonaceous MMT-rich surface after combustion. Thus it can be confirmed that the better dispersion of OMMT and the appropriate char content in the residues can promote the formation of perfect carbonaceous MMT-rich surface in a burning material under forced flaming conditions, which can improve flame retardancy for PP/OMMT composite.

CONCLUSIONS

The results described in this article demonstrated that the Brønsted acid sites on the H-MMT layers formed via thermal decomposition of (alkyl)ammonium in the OMMT and the dispersion state of OMMT in the PP matrix are two important factors for flame retardancy of PP/OMMT composites. The Brønsted acid sites on the H-MMT layers catalyze degradation of PP via cationic mechanism, which lead to the formation of char via hydrogen transfer reaction during combustion of PP/OMMT nanocom-

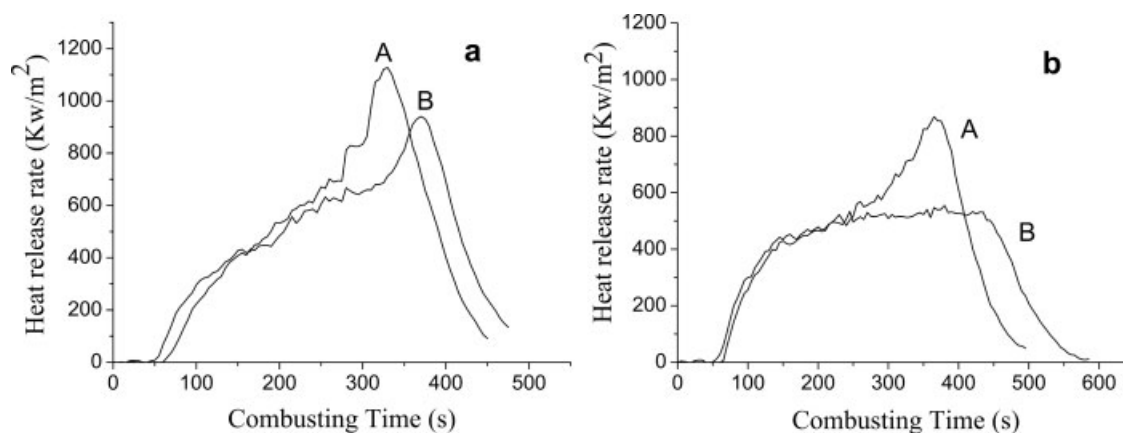


Figure 6 Comparison of heat release rates for PP/OMMT-80, PP/PPMA/OMMT-80, PP/OMMT-150 and PP/PPMA/OMMT-150 at 35 KW/m² heat flux. (a) A-PR1, B-PR2; (b) A-PR3, B-PR4.

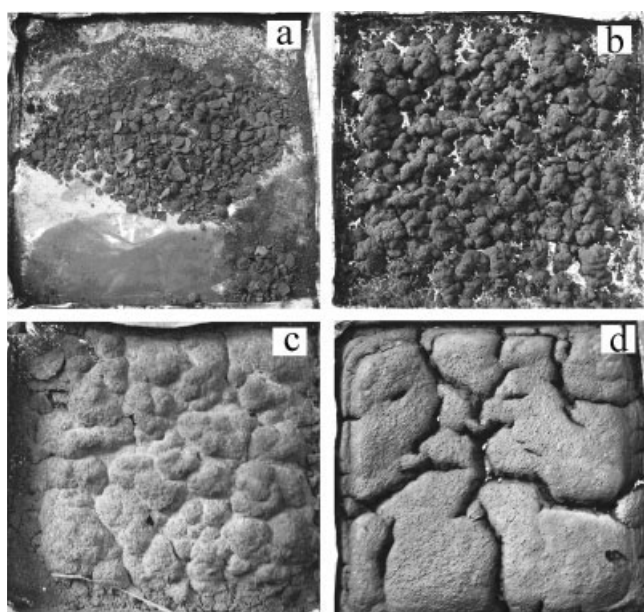


Figure 7 Photographs of the residues after combustion. (a) PR1; (b) PR2; (c) PR3; (d) PR4.

posites. Formation of carbonaceous MMT-rich surface in the residue depends on the better dispersion of OMMT in PP matrix and appropriate char content in the residue, which is profitable to fire retardancy.

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