

STRUCTURAL EVOLUTION AND COMPOSITION CHANGE IN THE SURFACE REGION OF POLYPROPYLENE/CLAY NANOCOMPOSITES ANNEALED AT HIGH TEMPERATURES*

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Abstract A model experiment was done to clear the formation mechanism of protective layers during combustion of polypropylene (PP)/organically modified montmorillonite (OMMT) nanocomposites. The investigation was focused on the effects of annealing temperature on the structural changes and protective layer formation. The decomposition of OMMT and degradation of PP/OMMT nanocomposites were characterized by means of thermogravimetric analysis (TGA). The structural evolution and composition change in the surface region of PP/OMMT nanocomposites during heating were monitored by means of X-ray photoelectron spectroscopy (XPS), ATR-FTIR and field emission scanning electron microscopy (FESEM). The results showed that the formation of the carbonaceous silicate barrier in the surface region of PP/OMMT nanocomposites resulted from the following three processes: (1) The formation of strong acid sites on the MMT sheets, which could promote the degradation of PP and the carbonization of its degradation products; (2) The gases and gas bubbles formed by decomposition of the surfactant and degradation of PP, which pushed the molten sample to the surface; (3) The degradation of PP and the carbonization of the degradation products, which led to accumulation of MMT sheets tightly linked by the char in the surface region.

Keywords: Clay; Fire retardancy; Polypropylene.

INTRODUCTION

Since the Toyota research group reported nylon-6 (PA6)/montmorillonite (MMT) nanocomposites in 1990s, considerable interests have been paid in the application of polymer/clay nanocomposites (PCNs)^[1]. PCNs are a new class of composites that offer the possibility of developing the polymer materials with a desired set of properties, differing from macro- or micro-composites, 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.

PCNs have been believed as a revolutionary new and environmentally benign flame retardant approach. Heat release rate (HRR) of PCNs is significantly decreased in the presence of a small amount of clay particles. This effect has been attributed to the formation of a carbonaceous silicate char built up on the surface of the nanocomposites during combustion^[2–4]. Many researchers wondered how the initially well dispersed clay particles in polymer nanocomposites tended to accumulate and form a carbonaceous silicate char on the sample surface during burning. The accumulation of layered silicates on burning surface is considered due to three possible modes. First, it was believed that when the flame impinged on the nanocomposites, the polymer was

* This work was financially supported by the National Natural Science Foundation of China for the Outstanding Youth Fund (No. 50525311), general project (No. 50473029) and the Fund for Creative Research Groups (No. 50621302).

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Received October 17, 2008; Revised December 4, 2008; Accepted December 8, 2008

gasified and burned out, the clay was left and precipitated on the surface. According to this mode, Wang and Wilkie *et al.* examined polystyrene and poly(methyl methacrylate) nanocomposites by XPS, indicating that the clay content increased at the surface as the polymer underwent thermal degradation at 500°C^[5–7]. Secondly, 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 sample to the surface. This mode was suggested by Kashiwagi and coworkers to explain the accumulated clay particles outward the surface of polyamide (PA6)/clay nanocomposites^[4]. Recently, Lewin *et al.* brought forward an alternative hypothesis to explain the barrier effect of PCNs in the fire retardancy^[8, 9]. According to their hypothesis, the clay particles migrated to the surface before pyrolysis and combustion of polymer took place due to a difference in the surface free energy (SFE) between clay and polymer. Very recently, the same group also found an increase in the clay content of the surface during heating polypropylene (PP)/clay and PA6/clay nanocomposites below the decomposition temperature^[10–12]. In another previous report^[13], the clay migrated to the surface of PP/clay nanocomposites due to the addition of an organosiloxane elastomer, in which the low surface energy material around the clay particles promoted their migration to the surface region and the formation of a flexible barrier layer that led to better performance in fire retardancy.

According to the above previous results, it is disputable how a carbonaceous silicate char built up on the surface of the nanocomposites is formed. The origin for the above dispute is that different researchers focused on the different stage of structural evolution in different polymer nanocomposites and obtained their results. In fact, the char barrier formation undergoes different stages. The combustion is a quick and complicated process, in which several structural evolutions resulting from both physical and chemical factors took place in the nanocomposites, such as motion and degradation of polymer chains, migration of clay and decomposition of organically modified montmorillonite (OMMT)^[14–16]. Structural changes in PCNs during heating depended on the temperature and the nature of the atmosphere^[17]. Degradation and oxidation of polymers would take place during the combustion of polymer nanocomposites^[18]. Decomposition of the organic modifier in the OMMT would form acid sites on the MMT sheets and change the structure of OMMT in PCNs^[18, 19]. In addition, iron within the clay could work as free-radical scavengers^[20].

In order to further understand the mechanism for forming a carbonaceous silicate char, here PP/OMMT was used as a model. We annealed the samples at different temperatures as intermediate processes of structural evolution below the burning temperature of PP to investigate the structural evolution and composition change in the surface region of PP/OMMT nanocomposites. In this way, it was hoped to capture necessary and important information to understand the char barrier formation process and the mechanism of fire retardancy in polymer nanocomposites.

EXPERIMENTAL

Materials

Polypropylene (PP) with melt flow index of 0.8 g/min was purchased from Panjin Petrochemical Co. Ltd.. Maleic anhydride-grafted-polypropylene copolymer (PPMA) with acid values of 52 mg KOH/g was purchased from Sanyo Corp. Organically modified montmorillonite (Cloisite 20A, organic modifier: dimethyl dehydrogenated tallow ammonium, in which the hydrogenated tallow includes *ca.* 65% C18, *ca.* 30% C16 and 5% C14) was purchased from Southern Clay, USA.

Preparation of Samples and Annealing Treatments

The preparation of PP nanocomposites containing 5 wt% Cloisite 20A and 10 wt% PPMA was carried out in a Brabender mixer with a rotating speed of 100 r/min at 180°C for 10 min. Samples were hot pressed at 180°C to get 200 µm thick samples for measurements of morphology and composition, respectively. A polyester film was used to prevent the adhesion of the materials to the metallic mold. The above hot pressed samples were transferred in copper foil and put into the quartz tube, annealed at different conditions in the furnace under air or Ar. Table 1 collects specific annealing conditions of the samples.

Table 1. Annealing conditions for the samples

Samples	Annealing conditions
S1	Untreated
S2	190°C for 90 min in air
S3	250°C for 90 min in air
S4	190°C for 90 min in Ar
S5	250°C for 90 min in Ar
S6	300°C for 60 s in air
S7	350°C for 60 s in air
S8	400°C for 60 s in air
S9	450°C for 60 s in air
S10	500°C for 60 s in air
S11	500°C for 120 s in air
S12	300°C for 210 s in Ar
S13	350°C for 210 s in Ar
S14	400°C for 210 s in Ar
S15	450°C for 210 s in Ar
S16	500°C for 210 s in Ar

All samples contain 5% Cloisite 20A, 10% PPMA and 85% PP (by weight).

Characterization

Elemental composition of the various annealed nanocomposites was measured by X-ray photoelectron spectroscopy (XPS) on an ESCA 250 system under vacuum higher than 10^{-6} Pa. The binding energies were referred to that from adventitious carbon at 284.6 eV. Annealed samples were observed using an XL30ESEM FEG field emission scanning electron microscope (FESEM). All surfaces were coated with a thin layer of gold prior to FESEM examination. Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectrometry was performed using a Bio-Rad FTS-135. Spectrum signal was averaged over 128 scans at a resolution of 4 cm^{-1} . For each sample and annealing condition, multiple spectra were collected on the top surface of the specimens (directly contacting with the atmosphere during annealing). Thermogravimetric analysis (TGA) was carried out using a Perkin-Elmer instrument from ambient temperature to 800°C at a heating rate of 20 K/min in air or nitrogen. Isothermal TGA was carried out using the same instrument from ambient temperature to a designed temperature at a heating rate of 40 K/min and then isothermally equilibrated at this temperature for a specified time in air or nitrogen.

RESULTS AND DISCUSSION

There are two kinds of organic components in polypropylene/maleated polypropylene/OMMT (PP/PPMA/OMMT, 85/10/5 by weight) nanocomposites, one is the modifier and the other is a mixture of PP/PPMA. Generally, several processes will happen during heating polymer nanocomposites to burn, *i.e.* the motion of polymer chains after the temperature is higher than melting point or glass transition temperature, decomposition of modifier, and oxidation, degradation and even carbonization of polymers, which possibly influence the formation of a carbonaceous silicate char built up on the surface of polymer during combustion. The decomposition process of PP nanocomposites is shown in TGA curves (Fig. 1). In nitrogen, the degradation of the nanocomposites begins at about 300°C with the maximum rate at 451°C. In air, the degradation of the nanocomposites begins at about 230°C with the maximum rate at 443°C. There are 3.6 wt% residues at 700°C after degradation of the nanocomposites. In this work, the samples are annealed at different temperatures. Table 1 collects specific annealing conditions of the samples.

Annealing PP Nanocomposites below 250°C

At this region, two annealing temperatures are selected, one is 190°C at which the modifier in the OMMT will not degrade and PP chains has thermal motion, the other is 250°C at which the modifier in the OMMT degrades and PP chains has strong thermal motion. Isothermal TGA measurements show thermal behavior of OMMT (Fig. 2). When the sample is annealed under nitrogen at 190°C for 90 min, the weight loss is 2.9 wt%; when the

sample is annealed under air, the weight loss increases to 3.7 wt%. It is believed that at this temperature, the elimination of the free water and a little decomposition of modifier occur. However, the organic modifier is more stable in nitrogen. The decomposition of OMMT is accelerated at 250°C under nitrogen for 90 min, and the weight loss is 14.2 wt%, which is related to the decomposition of the surfactant bound to the OMMT. Also, 17.8 wt% of weight loss occurs when the OMMT is exposed to air for 90 min at 250°C.

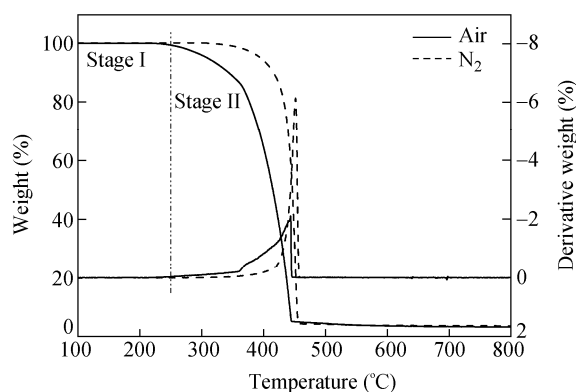


Fig. 1 TGA curves of PP/PPMA/OMMT (85/10/5 by weight) nanocomposites in air and nitrogen with a heating rate of 20 K/min

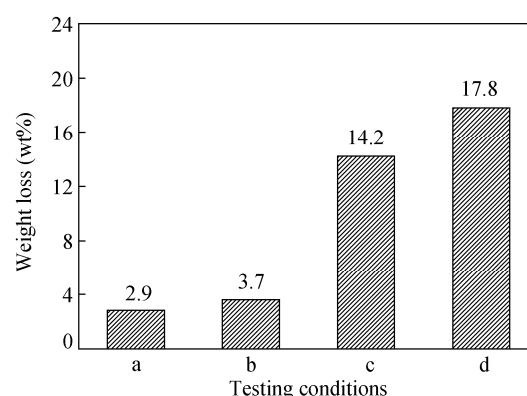


Fig. 2 Weight loss of Closite 20A during isothermal TGA measurements with different testing conditions
a) 190°C for 90 min in N₂; b) 190°C for 90 min in air;
c) 250°C for 90 min in N₂; d) 250°C for 90 min in air

Figure 3 provides the weight loss of PP nanocomposites during isothermal TGA tests under different conditions. When the sample is annealed at 190°C for 90 min under nitrogen, the weight loss reaches to 1.0 wt%, which is related to the elimination of the free water and a little decomposition of the modifier. When the sample is annealed at 190°C for 90 min under air, the weight loss increases to 7.9 wt%, which is corresponding to a low lever decomposition of PP in the nanocomposites. It is clear that PP degrades at 190°C under air and this reaction is accelerated at 250°C, the weight loss increases to 21.5 wt%. Generally PP degrades thermally by oxidative dehydrogenation and beta scission. In contrast, the sample annealed at 250°C under nitrogen for 90 min has 2.8 wt% of weight loss, resulting from the elimination of the free water and the decomposition of the modifier bound to the OMMT. When the sample is annealed at 250°C for 90 min under air, its weight loss increases to 7.9 wt%.

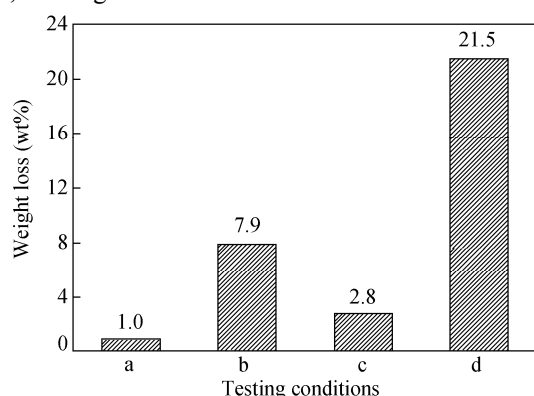


Fig. 3 Weight loss of PP/PPMA/OMMT (85/10/5 by weight) nanocomposite during isothermal TGA measurements with different testing conditions
a) 190°C for 90 min in N₂; b) 190°C for 90 min in air;
c) 250°C for 90 min in N₂; d) 250°C for 90 min in air

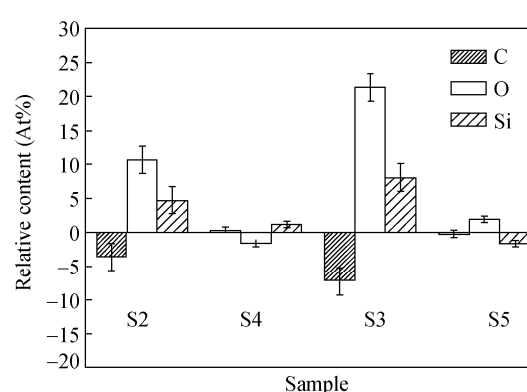


Fig. 4 The relative contents of carbon, oxygen and silicon atoms analyzed by XPS under different annealing conditions (PP/PPMA/OMMT nanocomposites, 85/10/5 by weight): S2, annealed at 190°C for 90 min in air; S4, annealed at 190°C for 90 min in Ar; S3, annealed at 250°C for 90 min in air; S5, annealed at 250°C for 90 min in Ar

The content of MMT on the surfaces of samples is monitored by XPS, as this technique can probe the surface of samples and detect subtle changes in the composition of the surface. There is some inherent error in the determination of the absolute content of an individual element, thus it is preferable to use the relative percentage content. The change of element contents in the surface region after annealing is obtained from $R = (E_{\text{(annealed)}}/E_{\text{(untreated)}} - 1) \times 100\%$, where E is the surface atom content, and R is the relative percentage content. It can be seen that the surface contents of carbon, oxygen and silicon atoms do not change when the sample is annealed at 190°C and 250°C for 90 min under Ar compared with the untreated sample (see S4 and S5 in Fig. 4). However, when the sample is exposed in air and annealed at 190°C for 90 min, the relative surface contents of oxygen and silicon increase to 10.6% and 4.7% accompanied by the decrease of carbon content, respectively; and those of oxygen and silicon increase to 21.4% and 8.1% at 250°C for 90 min, respectively (see S2 and S3 in Fig. 4). When the sample is exposed to air, the oxidation and degradation of PP result in the increase of relative contents of oxygen and silicon accompanied by slight decrease of the surface carbon contents. Compare with the sample annealed at 190°C for 90 min in air, there is more weight loss as the sample is annealed at 250°C for 90 min in air (Fig. 3), the more degradation of PP at surface results in the increase of silicon content at the surface of the sample.

The ATR-FTIR spectra clearly show that the carbonyl peak at 1712 cm^{-1} is obviously observed after the sample is annealed under air (Fig. 5). It coincides with the previous results in which the thermal oxidation in the samples results in the formation of carbonyl bonds^[10, 11, 18]. The oxygen atom results from the oxidation of the carbon atom created within the polymer chain by hydrogen abstraction. The intensities of the peaks in ATR-FTIR spectra are normalized by dividing by the intensities of the CH_3 symmetric deformation vibration at 1375 cm^{-1} . Table 2 shows the relative content of silicon based on the peak area ratio of Si—O band at 1037 cm^{-1} of the annealing sample to the untreated one. It is obvious that the silicon content on the surface of samples increases significantly after annealing in air; however, the annealing in Ar just leads to a little increase when the sample is annealed at 250°C. Lewin and coworkers has got the similar results in the previous reports^[10–12], in which they explained that the clay with lower surface energy was easier to accumulate at surface. However, their ATR-FTIR result showed that no obvious increase in the relative content of silicon occurred when the sample was annealed under Ar. Whether the surface energy of PP is lower than that of OMMT seems to need further investigation^[21, 22]. From the above XPS data (Fig. 4), there are almost no change of the silicon content in Ar and just a little increase in air, the latter is considered to be a slight decomposition of PP in the surface. In addition, in the PP/PPMA/OMMT nanocomposites, the CH_3 group is partly destroyed when the nanocomposites are annealed at 250°C for 90 min no matter in air or Ar, the decrease of CH_3 group peak results in the increase of the relative intensity of Si—O band comparing with the untreated sample and samples annealed at 190°C, the silicon content on the surface of samples increases after annealing in air and Ar from 190°C to 250°C. Based on the above results, it can be confirmed that the MMT sheets do not accumulate on the surface of PP/PPMA/OMMT nanocomposites annealed below 250°C (lower than the temperature of degradation of PP) in spite of a possible driving force by the surface energy difference. Recently, Lewin *et al.* have found migration of clay to the surface in the PA6/clay nanocomposites when the sample was annealed at 275°C and 300°C after 15 min^[12]. Our recent investigation shows that just 60 s annealing at 300°C can also obviously lead to the increase of the surface content of MMT in polyamide 12/OMMT nanocomposites no matter in air or Ar atmosphere. It can be speculated from the above results that the accumulation states of MMT in the surface region may vary in different polymer matrix under different environments.

Annealing PP Nanocomposites above 250°C

In order to investigate accumulation behavior of the MMT sheets during combustion, the annealing temperature is further raised to make PP chains degrade. A series of experiments are conducted to compare the surface contents of carbon, oxygen and silicon atoms by means of XPS. Figure 6 represents the change of the surface composition after the sample has been annealed in air. Up to 350°C, the relative content of oxygen atom increases with the decrease of carbon and silicon atoms. It is ascribed to the oxidation of PP above 300°C.

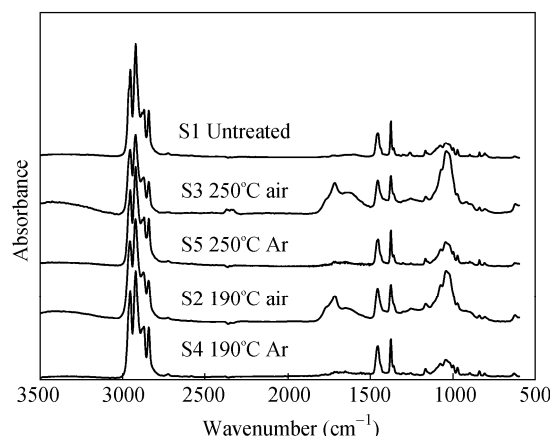


Fig. 5 ATR-FTIR spectra of the surface of the PP/PPMA/OMMT (85/10/5 by weight) nanocomposites: S1, untreated; S2, annealed at 190°C for 90 min in air; S4, annealed at 190°C for 90 min in Ar; S3, annealed at 250°C for 90 min in air; S5, annealed at 250°C for 90 min in Ar

Table 2. The relative content of Si—O band as determined by ATR-FTIR

Samples	Region by testing ^a	$I_{\text{Si}}(\sigma)^b$
S2	Surface	1.94 ± 0.18
S3	Surface	2.98 ± 0.29
S4	Surface	0.91 ± 0.05
S5	Surface	1.31 ± 0.09

^a Surface is the specimen in direct contact with the atmosphere during annealing;

^b The ATR-FTIR spectra were normalized by the intensities of the CH₃ symmetric deformation peak at 1375 cm⁻¹; R is the ratio of the peaks at 1037 cm⁻¹ and 1375 cm⁻¹ (A_{1037}/A_{1375}); $I_{\text{Si}}(\sigma) = R(\text{annealed})/R(\text{untreated})$; $I_{\text{Si}}(\sigma)$ represents the ratio of the area of Si—O band of the annealed sample to that of the untreated one.

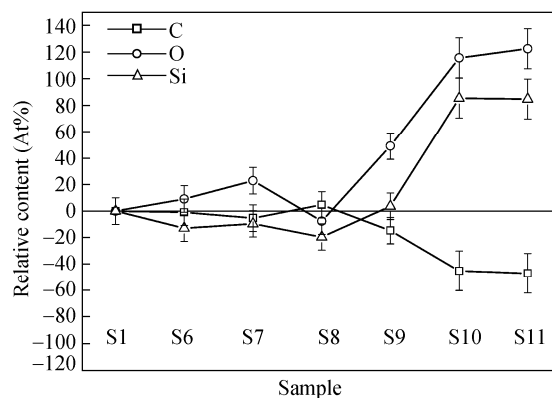


Fig. 6 The relative content of carbon, oxygen and silicon atoms measured by XPS at different annealing conditions (PP/PPMA/OMMT nanocomposites, 85/10/5 by weight): S1, untreated; S6, annealed at 300°C for 60 s in air; S7, annealed at 350°C for 60 s in air; S8, annealed at 400°C for 60 s in air; S9, annealed at 450°C for 60 s in air; S10, annealed at 500°C for 60 s in air; S11, annealed at 500°C for 120 s in air

When the temperature further rises, the hydrogen abstraction and oxidation become fast, which result in the degradation and the carbonization of PP. The rising bubbles formed in situ by the degradation products push the degraded PP to the surface region. The increase of PP content in the surface results in the decrease of content of oxygen and silicon atoms accompanied by the increase of carbon atom content to the peak at 400°C. As the

sample is heated at 500°C, the surface PP further degrades and burns out. At this time, the surface is mainly composed of the MMT left, and a carbonaceous silicate layer is formed on the surface. Meanwhile the relative content of oxygen and silicon atoms reach the maximum, therefore the more accumulation of the MMT sheets occurs when the sample is annealed at above 400°C.

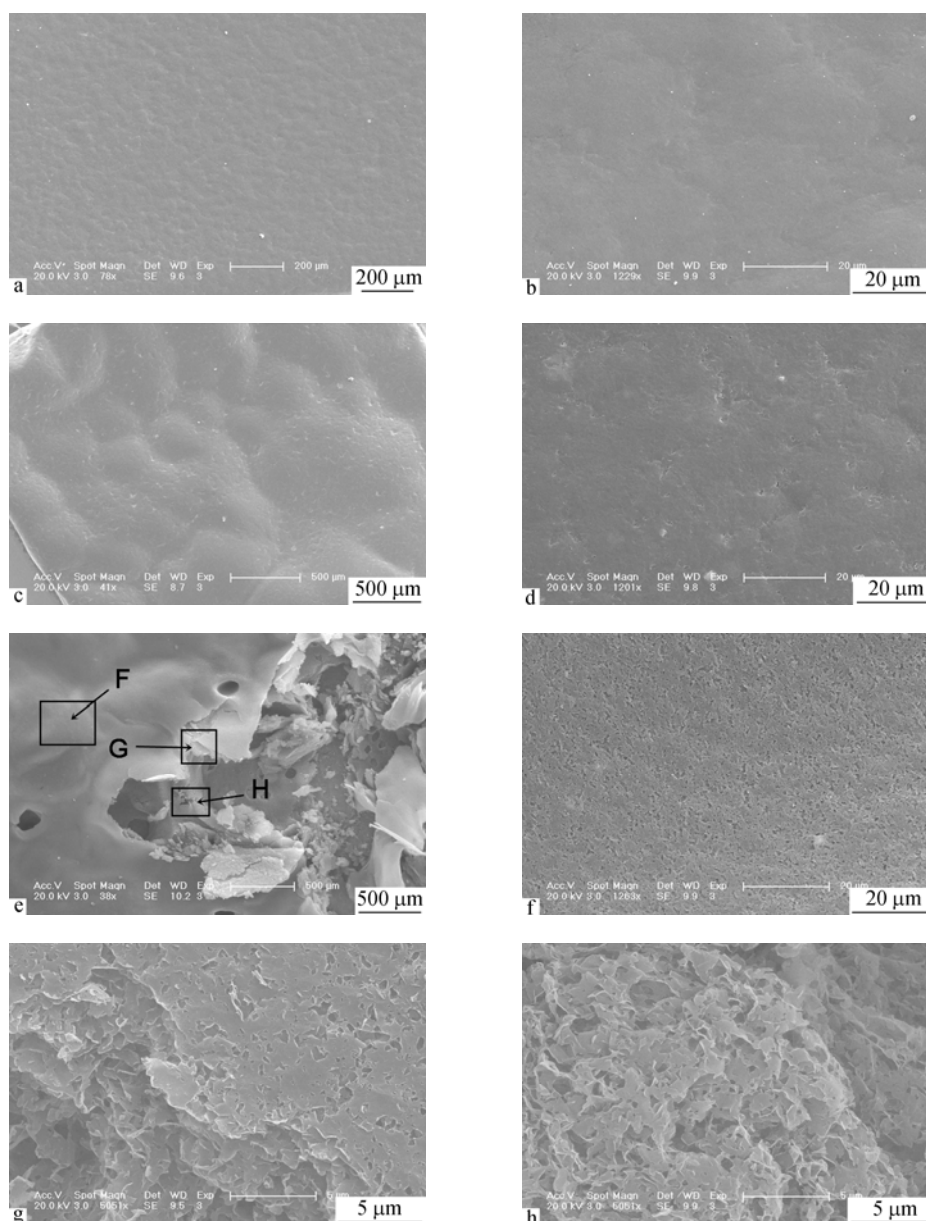


Fig. 7 SEM micrographs of the PP/PPMA/OMMT (85/10/5 by weight) nanocomposites annealed in air: (a) S6, heated at 300°C for 60 s in air; (b) high magnification of (a); (c) S8, heated at 400°C for 60 s in air; (d) high magnification of (c); (e) S10, heated at 500°C for 60 s in air (the destroyed area is a part of the surface protective char/silicate layer dug by needle.); (f), (g) and (h) micrographs of high magnification at different regions of (e)

FESEM micrographs of the sample annealed at 300–500°C (Fig. 7) further confirm the results of XPS. After annealed at 300°C for 60 s in air, the surface keeps flat (Figs. 7a and 7b). As the temperature rises to 400°C, the surface becomes rugged and a bubble-like shape could be observed (Figs. 7c and 7d). Figure 7(e)

represents the sample annealed at 500°C for 60 s in air. After digging a part of the surface protective layer with a needle, a lot of large holes appear below the protective layer. It is obvious that the rising bubbles push both MMT particles and PP (or the degraded PP) from the interior to the surface. Owing to the decomposition of the polymer and charring on the surface, the carbonaceous silicate protective layer is formed. Figures 7(f)–7(g) show the microstructure of the surface and the middle in the protective layer, respectively. It is obvious that the MMT sheets accumulate in the surface and the char link them together tightly. The degradation of PP leaves a lot of small holes on the surface. The MMT sheets in the middle of the sample form a netlike and porous structure (Fig. 7h).

Unlike the sample treated in air, no oxidation of PP occurs when PP/PPMA/OMMT nanocomposites are treated in Ar. It can be seen from Fig. 8 that the relative content of carbon atom increases with the decrease of oxygen and silicon atoms when the temperature rises. The rising bubbles formed by the degradation products push the degraded PP to the surface region. The surface is mainly composed of carbon and just a little oxygen and silicon left when the sample is heated at 400°C. From 400°C to 500°C, the relative content of carbon atom obviously decreases with the increase of oxygen and silicon atoms. A carbonaceous silicate layer is formed on the surface just like the sample treated in air.

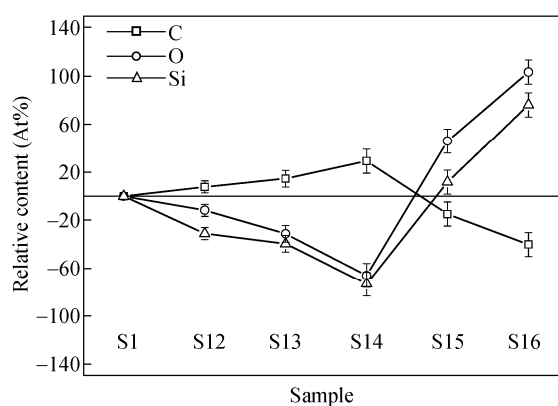


Fig. 8 The relative content of carbon, oxygen and silicate analyzed by XPS at different annealing conditions (PP/PPMA/OMMT nanocomposites, 85/10/5 by weight): S1, untreated; S12, annealed at 300°C for 210 s in Ar; S13, annealed at 350°C for 210 s in Ar; S14, annealed at 400°C for 210 s in Ar; S15, annealed at 450°C for 210 s in Ar; S16, annealed at 500°C for 210 s in Ar

FESEM micrographs in Fig. 9 show the microstructure evolution of the sample surface annealed under Ar. The phenomenon is just like the sample treated in air. The surface keeps flat in the sample annealed at 300°C (Figs. 9a and 9b). When the temperature rises to 400°C, the surface is rugged (Figs. 9c and 9d). The bubble-like structure can be detected when the sample is annealed at 500°C (Fig. 9f).

It is obvious that a surface protective layer has been formed, meanwhile a honeycomb like structure has been formed in the middle of the sample due to the formation of bubbles (Fig. 9e). The MMT sheets accumulate tightly in the surface region (Fig. 9g) and form a net-like and porous structure in the middle region (Fig. 9h).

Discussion on the Formation of Char Barrier

In comparing with the previous results, the detail information obtained from the model experiments in this work shows that the initially well dispersed clay sheets only tend to accumulate on the sample surface during the pyrolysis and gasification of PP. There are two routes to the accumulation of clay sheets on the sample surface, one is the recession of the polymer resin from the surface by pyrolysis to leave clay sheets behind, and the other is the transportation of clay sheets pushed by numerous rising bubbles of degradation products in the melt from the interior of the sample to the surface^[4]. The accumulation of clay sheets on the surface region is one of the necessary conditions for the formation of a carbonaceous silicate layer. The other is the strong catalytic effect of acid sites originated from the degraded OMMT^[23], which can promote the carbonization of the degradation

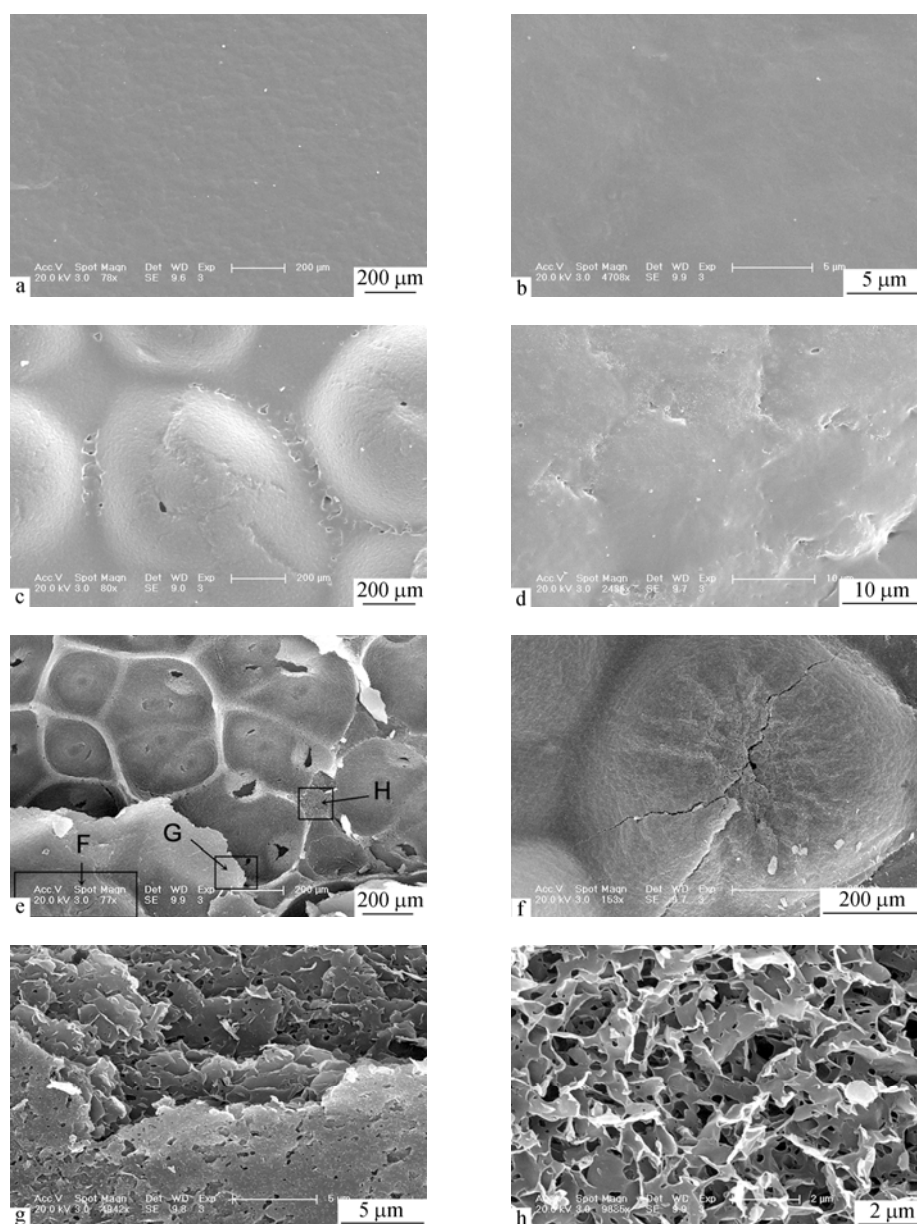


Fig. 9 FESEM micrographs of the PP/PPMA/OMMT (85/10/5 by weight) nanocomposites annealed in Ar: (a) S12, heated at 300°C for 210 s in Ar; (b) high magnification of (a); (c) S14, heated at 400°C for 210 s in Ar; (d) high magnification of (c); (e) S16, heated at 500°C for 210 s in Ar (the destroyed area of the surface protective char/silicate layer is formed by needle digging); (f), (g) and (h) micrographs of high magnification at different region of (e)

products, therefore the clay sheets on the surface aggregate together and are tightly linked by the char. The carbonaceous silicate layer built up on the surface can improve fire retardancy. In order to confirm catalytic effect of acid sites on the degraded OMMT, a contrast experiment has been done, in which we used sodium dodecylsulfonate (SDSo, an anionic surfactant) to modify MMT (a-OMMT) that could not form acid sites after decomposition of SDSo. A PP/PPMA/a-OMMT (85/10/5 by weight) mixture, prepared via melt mixing under the same conditions as those for preparing the nanocomposites containing cationic surfactant modified MMT (20A), was annealed at 500°C in air for 60 s. The surface absolutely collapsed and just had a little of ash left. Thus the nanocomposite can not form a good protective layer in the absence of the catalytic effect of acid sites

on the MMT sheets. In a previous report^[18], Zanetti *et al.* considered that a surface protective layer was formed due to the reassemble of the clay sheets and charring of the polymer catalyzed by acid sites. In our recent work^[23, 24], the catalytic effect of acid sites on the char formation of the degradation products of PP has been proved.

CONCLUSIONS

The structural evolution and composition change in the surface region of PP/clay nanocomposites depend on annealing conditions. When the nanocomposites are annealed at temperatures lower than the degradation temperature of PP, no obvious increase of MMT content is observed in the surface region. However, the accumulation of MMT sheets in the surface region occurs when the annealing temperature is higher than that of degradation of PP. According to the model experiments, the formation of the perfect carbonaceous silicate barrier in the surface region depends on the following three processes: (1) The decomposition of the cationic modifier leaves strong acid sites on the MMT sheets, which can promote the degradation of PP and the carbonization of its degradation products; (2) The gases and gas bubbles formed by decomposition of the surfactant and degradation of PP push the molten sample to the surface; (3) The degradation of PP and the carbonization of its degradation products lead to the accumulation of MMT sheets that are tightly linked by the char in the surface region. It is obvious that the existence of acid sites, which catalyze carbonization of the degradation products, is a key factor for the formation of a carbonaceous silicate barrier.

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