Effect of Alkylammonium Salt on the Dispersion and Properties of Poly(p-phenylene sulfide)/Clay Nanocomposites via Melt Intercalation

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ABSTRACT: To explore the possibility of making poly(p-phenylene sulfide) (PPS) nanocomposites via melt intercalation and improving the mechanical properties of PPS, in this study we first modified clay (montmorillonite) with alkylammonium salt by cation exchange and then mixed the modified clay together with the PPS matrix by twin-screw extrusion. Because the PPS/clay composites were made at a high temperature (300°C), thermogravimetric analysis experiments were carried out first to check the thermal stability of the alkylammonium salt treated clay and the obtained composites. Possible degradation of the alkylammonium salt during processing caused a decrease in the interlayer spacing of the clay. Scanning electron microscopy, transmission electron microscopy, and X-ray diffraction were used to investigate the dispersion of the clay sheet in the matrix. The clay layers were homogeneously dispersed in the PPS matrix with a nanometer scale, and an exfoliated structure was achieved at a low load of clay. The alkylammonium salt modifier enhanced the interaction between the PPS and clay on the one hand, but on the other hand, it also acted as a plasticizer and caused decreases in the glass-transition temperature and tensile properties. More work is needed to find a modifier and processing conditions by which the modifier can help the dispersion of clay and also be completely degraded after the formation of an exfoliated structure. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 99: 1724–1731, 2006

Key words: degradation; dispersions; melt; nanocomposites

INTRODUCTION

Poly(p-phenylene sulfide) (PPS) is a semicrystalline, aromatic polymer with outstanding high-temperature stability, inherent flame resistance, and good chemical resistance.[1–3] However, the applications of neat PPS have been somewhat limited because of its relatively low glass-transition temperature (T_g) compared to its high melting temperature (T_m) and its inclination toward brittleness. Therefore, commercial PPS grades are usually filled with glass fibers.[4–6]

Polymer/clay nanocomposites have been increasingly studied over the last decade due to their demonstrated enhancements in mechanical properties[7–9] compared with unmodified resins or microcomposites. These enhancements appear to be a general phenomenon related to the nanometer-scale dispersion of clay sheets, but the degree of property enhancement is not universal for all polymers. The dominant factors are (1) clay distribution and orientation and (2) the strength of interactions between the polymer and clay. There are two idealized morphologies for polymer/clay nanocomposites, namely, an intercalated morphology and an exfoliated morphology. In practice, however, many systems fall between these idealized morphologies. In other words, the polymer/clay nanocomposites usually possess a mixed dispersion with intercalated and exfoliated structures; sometimes, even some aggregated particles coexist in the system.[10,11] An intercalated structure is formed when there is a limited inclusion of the polymer chain between the clay layers with a corresponding small increase in the interlayer spacing of a few nanometers. On the other hand, an exfoliated structure is formed when the clay layers are well separated from one another and are individually dispersed in the continuous polymer matrix. Because exfoliated nanocomposites have a higher phase homogeneity than the intercalated counterpart, the exfoliated structure is more desirable in enhancing the properties of the nanocomposites.

Since the possibility of direct melt intercalation was first demonstrated by Viaia and Giannelis,[12,13] the

melt intercalation method has become a main method for the preparation of the intercalated polymer nanocomposites without *in situ* intercalative polymerization. Because it is not thermodynamically spontaneous, the formation of nanocomposites by melt intercalation needs to increase the interaction between the polymer and clay layers so that the melt intercalation process can occur. In general, the clay is modified with alkylammonium salt to facilitate its interaction with polymers. A lot of polymer nanocomposites have been made through melt intercalation. These include polystyrene,[14,15] nylon 6,[16] polypropylene,[17,18] polyethylene,[19] ethylene–vinyl acetate copolymers,[20,21] and poly(styrene-*b*-butadiene) copolymers,[22] and poly(ethylene oxide).[23] Also, some studies have been done on the theoretical analysis of thermodynamics[24,25] and the kinetics[26] involved in melt intercalation. The effect of melt-processing conditions on the extent of exfoliation was discussed recently, and the degree of dispersion was interpreted on the basis of the residence time distribution in the extruder and the intensity of shear.[27]

So far, most polymers that have been used for the preparation of polymer/clay nanocomposites via melt intercalation have had relatively low processing temperatures (<250°C), and the degradation of alkylammonium salt during processing has been negligible. In this study, to explore the possibility of making PPS nanocomposites via melt intercalation and improving the mechanical properties of PPS, we first modified clay [montmorillonite (MMT)] with alkylammonium salt by cation exchange and then mixed the modified clay together with the PPS matrix by twin-screw extrusion or via a mixer. The obtained nanocomposites were characterized with X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA). The tensile behaviors were also examined to test the enhancement of mechanical properties. Because PPS possesses a relatively high processing temperature (>300°C), special focus was given to the degradation of alkylammonium salt during processing and its effect on the dispersion of clay in the PPS matrix.

EXPERIMENTAL

Materials

PPS (weight-average molecular weight = 48,000) was purchased from Shichuan Deyang Science Tech Shareholding Co. (Deyang, China). Organically modified clay with a cation/charge capacity of 100 mequiv/100 g was prepared in our laboratory. The dioctadecyl dimethylammouium bromide (2C-18) was an alkylammonium salt used for cation exchange.

TABLE I
Composition of Various Blends Based on PPS, 2C-18 MMT, MMT, and 2C-18 Modifier

| Sample | Composition (wt %) | | | |
	PPS	2C-18 MMT	MMT	2C-18
PPSCN1	99	1	—	—
PPSCN3	97	3	—	—
PPSCN5	95	5	—	—
PPSCN10	90	10	—	—
PPSCN20	80	20	—	—
PPSM5	95	—	5	—
PPSM10	90	—	10	—
PPSO1	99	—	—	1
PPSO3	97	—	—	3

Preparation of the organically modified MMT

Sodium MMT (50 g) was dispersed into 1000 mL of hot water with a stirrer. 2C-18 (25 g) was dissolved into hot water (300 mL) and then poured into the MMT–water solution under vigorous stirring for 2 h. The product (termed *2C-18 MMT*) was washed three times, filtered, and then dried *in vacuo* at 100°C for several hours.

Preparation of the PPS/MMT nanocomposites

2C-18 MMT (powder form) and PPS (powder form) were first dry-mixed with a home mixer. The mixture was then melt-extruded with a twin-screw extruder (TSSJ-25, ChenGuang, Ltd., Chengdu, China) operated at 300°C. The screw speed was 120 rpm. Composites loaded with untreated MMT and 2C-18 were also individually prepared by melt extrusion in the same manner for comparison. The extruded strands were then pelletized and dried at 85°C. The samples are listed in Table I. Hereafter, we call the PPS/organically modified MMT samples *PPSCNs,* the PPS/untreated MMT samples *PPSMs,* and the PPS/2C-18 modifier samples *PPSOs.* The resulting pellets were injection-molded in PS40E5ASE (NISSEI, Tokyo, Japan) at 275–300°C for characterization and mechanical properties.

Characterization of the dispersion of MMT in the PPS matrix

The dispersion of the silicate layers in the composites was evaluated with XRD, SEM, and TEM. XRD analysis was performed with a Rigaku Denki RAD-B (Tokyo, Japan) with Cu Kα radiation (λ = 0.154 nm) at room temperature. The basal spacing of the MMT was estimated from the (001) peak in the XRD pattern. For SEM investigation, the samples were fractured in liquid nitrogen. The fractured surfaces were then gold-coated and investigated in a scanning electron micro-
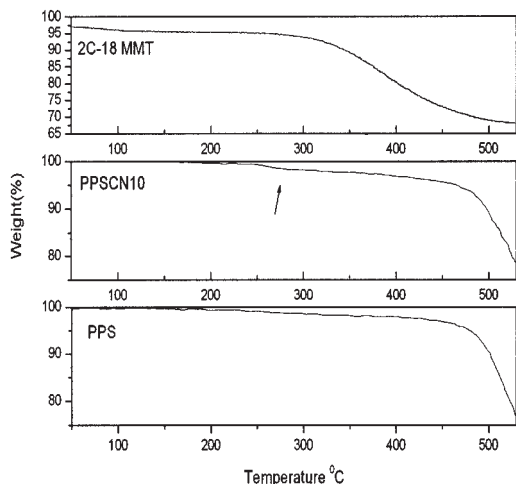
Figure 1 TGA of PPS, PPSCN10, and 2C-18 MMT. Rate = 20°C/min.

scope (Jeol JSM-5900LV, Tokyo, Japan) with an acceleration voltage of 20 kV. For TEM measurement, an ultrathin section with a thickness of 100 nm was prepared at −80°C with a diamond knife. The measurement was performed on a LEO 912 Omega Transmission electron microscope (Tokyo, Japan) at 120 kV.

TGA was performed with a DuPont thermogravimetric analyzer (DuPont 2100). The samples were heated to 550°C at a heating rate of 20°C/min under a nitrogen atmosphere.

The change in the T_g of PPS was measured by a PerkinElmer Pyris 1 (Boston, MA) differential scanning calorimeter. The samples were melted at 310°C for 5 min and then quenched into the liquid nitrogen. Then, the quenched samples were heated up in the differential scanning calorimeter at 20°C/min to examine the T_g and cooled to their crystallization temperatures (T_c's).

Mechanical properties

The tensile strength and tensile modulus were measured with a Shimadzu AG-10TA universal testing machine (Shimadzu, Japan) at a speed of 50 mm/min. Each mechanical test was repeated at least five times, and the results were averaged.

RESULTS AND DISCUSSION

Thermal stability of the alkylammonium salt modified clay and the PPS/clay composites

Because the PPS/clay composites were made at a high temperature (300°C), it was necessary to know the thermal stability of 2C-18 MMT. For this reason, the TGA experiment was carried out first for 2C-18 MMT and then for the PPS/clay composites. Figure 1 shows the TGA scans of PPS, 2C-18 MMT, and PPSCN10

recorded in a nitrogen atmosphere. PPS showed degradation onset at 513°C, whereas the weight loss at this temperature was 26.5 wt %. However, the degradation onset for 2C-18 MMT was seen at 275°C, which was much lower than that of PPS. The same reduced degradation onset was observed for PPS/2C-18 MMT (10 wt %), which occurred at about 275°C. This was due to the fact that PPS/2C-18 MMT (10 wt %) was subjected to a high temperature during the preparation of the composites; thus, a reduced thermal stability was expected. Therefore, it was not evitable that some degradation of alkylammonium salt would take place during processing. This certainly affected the final dispersion of clay in the PPS matrix. On the other hand, even the degradation onset occurred at less than 300°C, but a complete degradation of alkylammonium salt took quite a long time (more than 30 min), as shown in Figure 2. It was still possible to make PPS/clay nanocomposites by the control of the residence time in the extruder.

Dispersion of clay in the composites

To obtain the overall macroscopic view of the dispersion of the clay layers in the PPS matrix, SEM observation was done. Figure 3 shows the fractured specimens of the PPS/clay composites, including the composite of PPS with untreated clay for comparison. As shown in Figure 3(a), the untreated clay was totally immiscible with the PPS. The adhesion between the untreated clay and the PPS matrix was very poor. The clay particles aggregated together, and the exposed size was about 10 μm. In contrast, the organic-treated clay was dispersed in the PPS very well. None of the clay particles were observed at low contents. Only at high contents (20 wt %) could the organic-treated clay flakes be observed clearly [Fig. 3(d)]; these spread
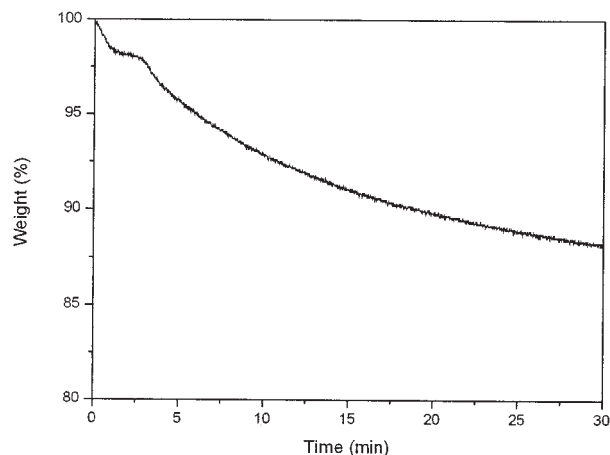

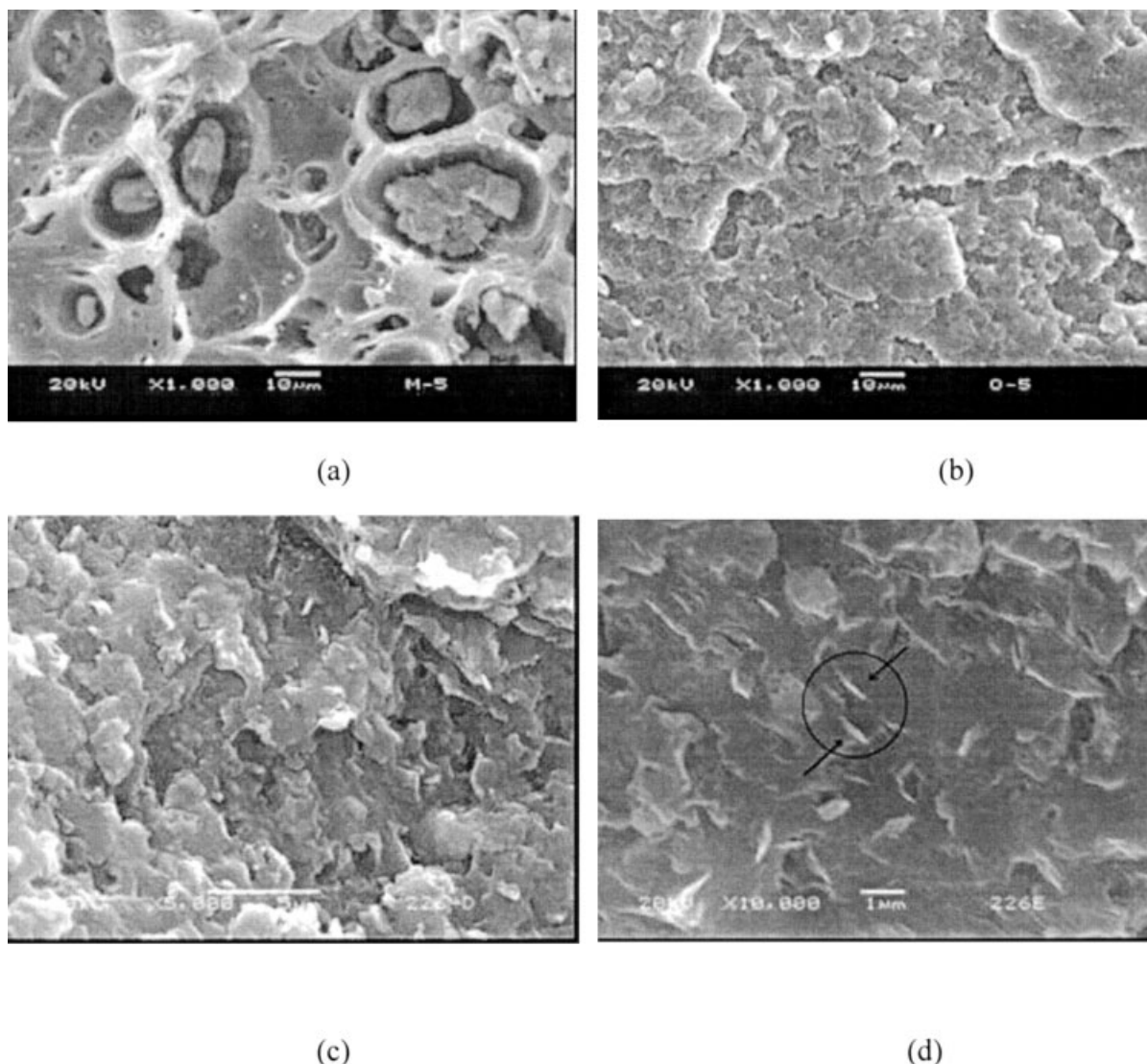**Figure 2** TGA of 2C-18 MMT at a constant temperature (300°C).

Figure 3 SEM photos of the fractured surfaces of the PPS/clay composites: (a) 5 wt % MMT, (b) 5 wt % 2C-18 MMT, (c) 10 wt % 2C-18 MMT, (d) 20 wt % 2C-18 MMT.

around uniformly in the PPS matrix. In this case, the size of the clay layer thickness was about 50–200 nm.

Because of the low resolution of SEM, we did not know whether the observed particles had an intercalated structure or an exfoliated structure in the composites. XRD is a powerful tool for characterizing the globe structure of polymer/clay nanocomposites. We used XRD to further characterize the dispersion of clay in the PPS matrix. Figure 4 shows the XRD profiles of the PPS/2C-18 MMT composites with different clay contents. The interlayer spacing was determined from the position of the diffraction peak in the XRD pattern. The basal spacing of the treated MMT (2C-18 MMT) was 3.5 nm The three peaks for 2C-18 MMT represented the first-order, second-order, and third-order diffractions of interlayer spacing of 2C-18 MMT, respectively. At a low content of 2C-18 MMT (1 wt %), we observed the disappearance of the low-angle dif-

fraction peaks ($2\theta = 2.5$ and $5°$) of 2C-18 MMT after it was mixed with PPS. However, when the load of 2C-18 MMT was higher than 1 wt %, a higher angle diffraction peak at $2\theta = 6.5°$ appeared, which was different from the diffraction peak of the 2C-18 MMT. How did the new diffraction peak ($2\theta = 6.5°$) form? There are two possibilities. First, it may have been due to the formation of a new ordered structure resulting from the strong interaction between the PPS chain and flakes of clay, just as in the case of polystyrene/clay.[28] The second possibility is that it may have been due to the degradation of alkylammonium salt in the gallery of clay during processing at the high temperature (300°C), which resulted in a decrease in the interlayer spacing of the clay. To rule out the first possibility, the XRD experiment of PPSCN3 was done at an increased temperature; this is shown in Figure 5. Peaks a and b (near $2\theta = 20°$) were the diffraction peaks of the PPS
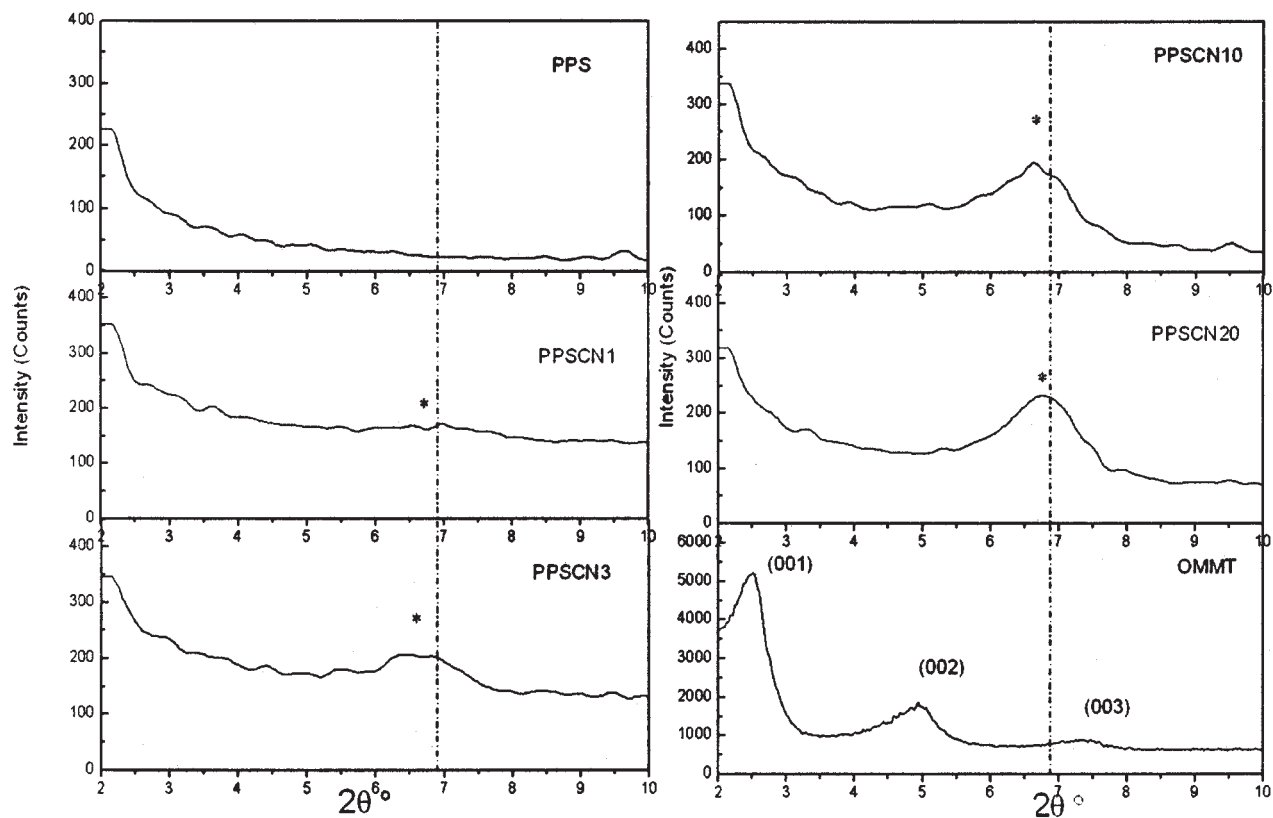
Figure 4 XRD profiles of different contents of 2C-18 MMT after the samples were melt-mixed with PPS.

crystal. They became more and more clear and shifted to lower angles with increasing temperature. This meant that the crystal of PPS became perfect due to the annealing effect during heating. At 310°C, peaks a and b decreased a little due to the melting of crystal. On the other hand, peak c ($2\theta = 6.5°$) had no any change in the temperature range studied, so it must have belonged to the structure of the inorganic clay rather than a new ordered structure of the PPS. Thus, the
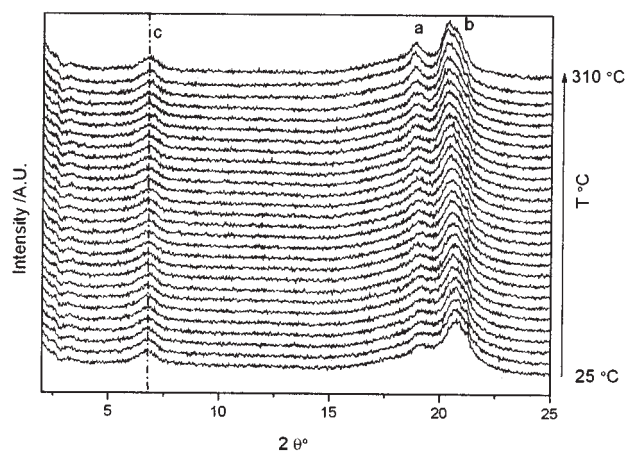
reduced interlayer spacing was most likely due to the degradation of the alkylammonium salt.

Detailed information of the clay dispersion was obtained via TEM. Figure 6 shows the results of TEM bright-field images of PPSCN1 and PPSCN3 corresponding to the XRD experiments as shown in Figure 4. The dark entities were the layers of the 2C-18 MMT stacked clay layers and were evident in PPSCN3 [Fig. 6(a,b)], whereas good dispersion was obvious in PP-SCN1 [Fig. 6(c,d)]. Combined with XRD data, the observed clay dispersion was well understood. The 2C-18 organic alkylammonium salt evidently improved the compatibility between MMT and PPS (from the SEM results). During processing, the big particles of MMT (ca. 5–10 μm) became small particles (ca. 50 nm) in PPSCN3, together with the exfoliated layers. So a broad peak was observed in the XRD pattern. Because of the degradation of the alkylammonium salt, the distance of the clay went back somewhat to the position of original MMT; thus, a stacked clay was observed. On the other hand, for the PP-SCN1, an exfoliated structure was most likely formed. It was not possible that an exfoliated structure could go back to a stacked layer structure, even with the degradation of the alkylammonium salt. Thus, no peak was seen in the range $2\theta = 2$–10° in the XRD pattern, and an individual layer was observed under TEM for PPSCN1.

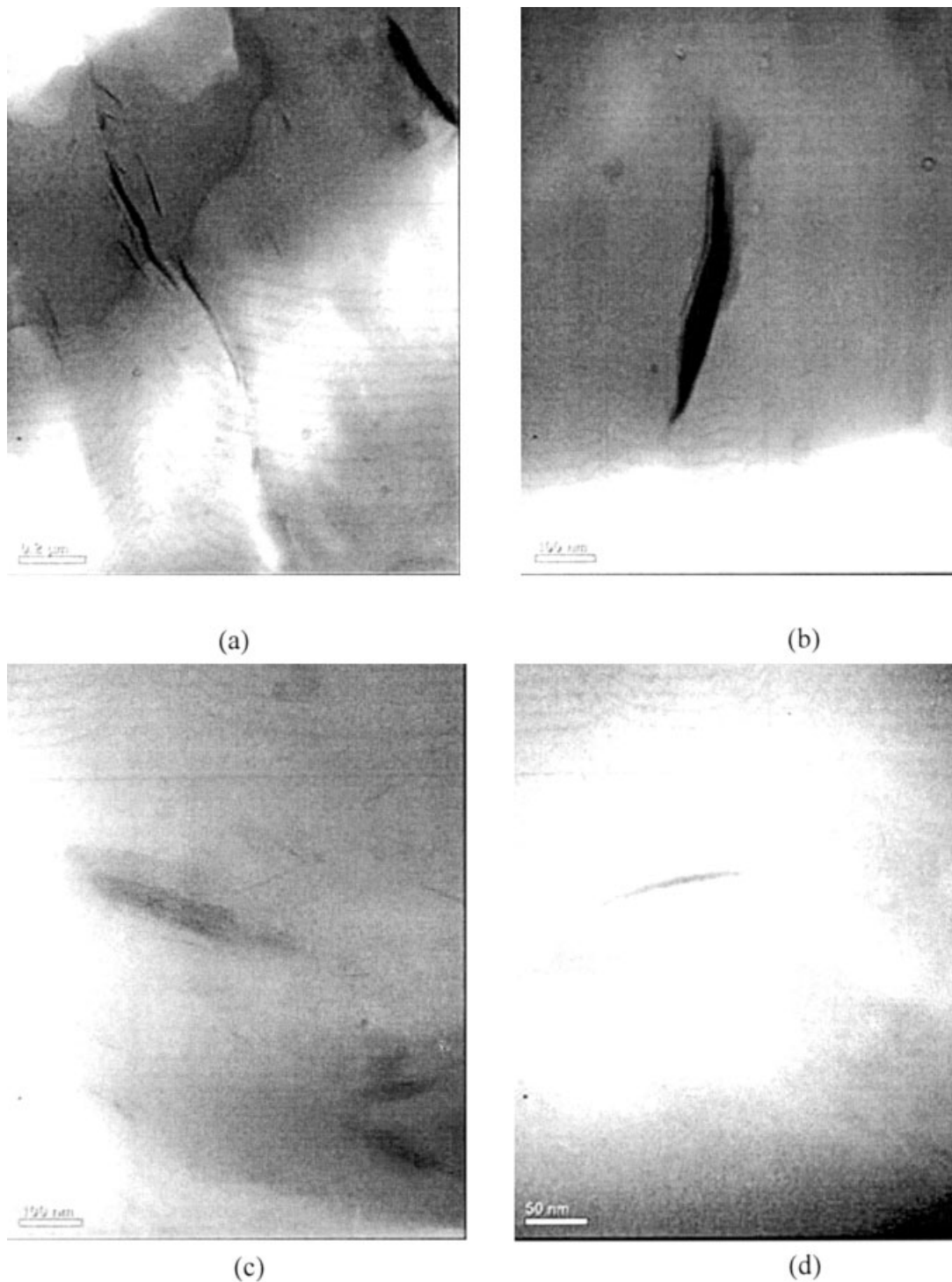**Figure 5** XRD profiles of 3 wt % 2C-18 MMT at elevated temperatures (20°C/min).

Figure 6   TEM photographs of the PPS/clay nanocomposites: (a,b) 3 and (c,d) 1 wt % 2C-18 MMT.

T_g

To check the effect of 2C-18 MMT on the T_g of PPS, the PPS/2C-18 MMT composites were first kept at 310°C for 5 min under the protection of nitrogen and were then quenched directly into liquid nitrogen. The DSC heating curves for the quenched samples are shown in Figure 7. A glass transition was observed around 90°C, and then, cooled crystallization was observed around 120°C for pure PPS. Decreases in T_g and cooled T_c were seen with the addition of 2C-18 MMT into PPS. Here, the decrease in T_g may raise an argument. It is an abnormal phenomenon compared with other result of polymer/clay nanocomposites. In
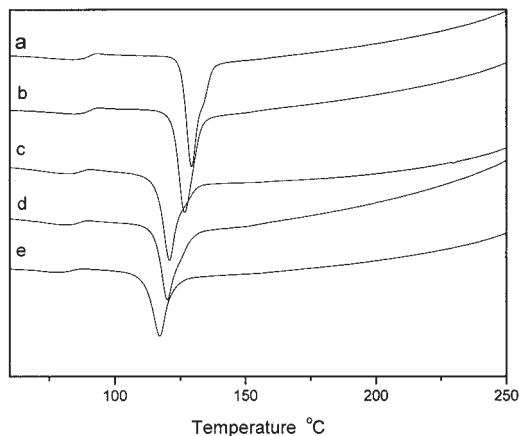
Figure 7 DSC heating curves of the PPS/clay composites after they were quenched in liquid nitrogen. Clay contents = (a) 0, (b) 1, (c) 3, (d) 10, and (e) 20 wt %.

Figure 8 Tensile strengths of the PPS/clay composites.

many cases, it has been reported that T_g has increased with the addition modified clay, which has been attributed to the restricted segmental motions at the organic–inorganic interface neighborhood of intercalated compositions.[29–31] There have been several cases in which T_g has been reported to decrease.[32,33] This has been thought to be caused by a decrease in the polymer crystallinity. However, in our case, no obvious change of PPS crystallinity was observed by DSC (the data is not shown here), so it should have been due to the existence of the 2C-18 small molecules, which acted as plasticizers and weakened the interaction between the PPS molecules. We did the same experiment with the PPSMs and PPSOs and measured their T_g values. The results are listed in Table II. The T_g of PPS increased 1–2°C with the addition of untreated MMT, and a decrease in the T_g of about 8°C in PPS was observed with the addition of the alkylammonium salt. This result clearly indicates that it was the alkylammonium salt modifiers that caused the decrease in T_g in the PPS/clay nanocomposites. To make
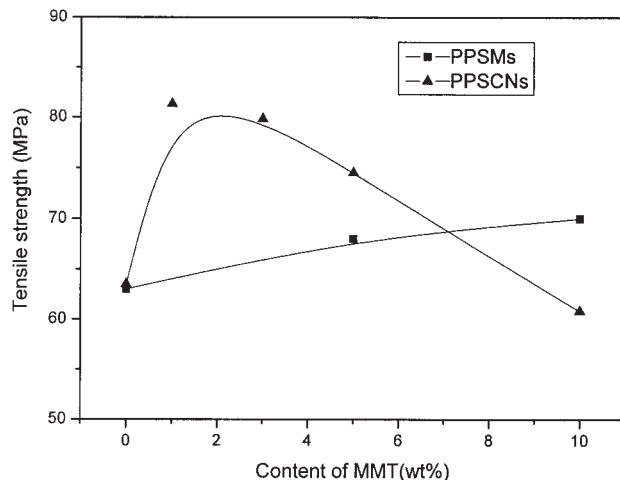
sure of this conclusion, another experiment was carried out. First, we put the samples at 350°C under the protection of N_2 for certain time to get rid of the alkylammonium salt. Then, the same method was used to measure T_g. T_g of PPS showed little change, which meant that there was no crosslinking during the treatment at the high temperature. However, the T_g values of PPSCNs increased a few degrees, especially for PPSCN3 (see Table II). So, the alkylammonium salt could enhance the interaction between the PPS and clay on the one hand, but on the other hand, it also acted as a plasticizer and caused a decrease in T_g. More work is needed to find a modifier and a processing condition by which the modifier can help the dispersion of clay and can also be completely degraded after the formation of an exfoliated structure.

Mechanical properties

Figure 8 shows the tensile strengths of the PPS/2C-18 MMT composites; the data for untreated MMT is also included for comparison.

The tensile strength increased first at low contents of 2C-18 MMT (1 and 3 wt %) and then decreased. The addition of 1 wt % 2C-18 MMT increased the tensile strength of PPS from 63 to 81 MPa. The remarkable increase may have been due to the exfoliated layer of clay. When the specimen was deformed during tensile stretching, the individual layer was oriented to act as the fiber to improve the tensile strength. With a high content of 2C-18 MMT, the proportion of the exfoliated layers decreased, and the proportion of the unexfoliated layers increased, as indicated by wide-angle XRD data. So the tensile strength decreased correspondingly. This result suggests that only the exfoliated structure dramatically enhanced the tensile strength. The tensile strength of PPS with 10 wt % 2C-18 MMT was lower than that with the correspond-

TABLE II
DSC Characteristic Parameters of Various Compositions

Sample	T_g (°C)	T_g AH* (°C)	T_m (°C)	T_c (°C)	ΔT_c** (°C)
PPS	89.6	89.5	278.1	228.2	50
PPSCN1	89.6	89.4	280.9	236.7	44.3
PPSCN3	86.8	88.2	280.2	238.2	42.0
PPSCN5	86.7	—	280.5	238.3	42.2
PPSCN10	85.1	—	280.7	238.0	42.7
PPSCN20	83.9	—	279.9	237.9	42.0
PPSM5	91.3	—	280.3	231.1	49.2
PPSM10	90.8	—	279.2	230.4	48.8
PPSO1	88.2	—	280.7	—	—
PPSO3	81.2	—	280.5	—	—

*AH = after heating to a constant weight under N_2; **ΔT_c = $T_m - T_c$.
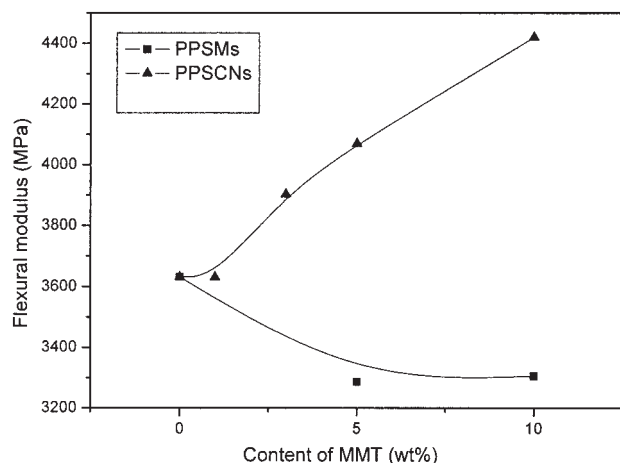
Figure 9 Flexural moduli of the PPS/clay composites.

ing untreated MMT. This may have been due to the additional effect of 2C-18, which acted as a plasticizer. For untreated MMT, there was only a slightly increase in the tensile strength, even with 10 wt % MMT.

The change in the flexural modulus of PPS after the clay was added is shown in Figure 9. There was a remarkable increase in the flexural modulus with increasing 2C-18 MMT content. For example, a modulus of 4413 MPa was obtained with 10 wt % 2C-18 MMT, compared to a modulus of 3600 MPa obtained with pure PPS. In contrast, there was always a decrease in the flexural modulus of PPS/MMT with increasing untreated MMT content.

CONCLUSIONS

PPS/clay nanocomposites were successfully prepared via direct melt intercalation. Exfoliated structures existed for PPS with low clay contents. However, stacked layers (size ≈ 50 nm) were evident for PPS with high clay contents (>3 wt %). The degradation of alkylammonium salt during processing played an important role in the determination of the final dispersion of clay in the PPS matrix, which caused a decrease in the interlayer spacing of the clay. A remarkable increase in the tensile strength was achieved for the PPS/clay nanocomposites with an exfoliated structure of 1 wt % clay. The alkylammonium salt modifier enhanced the interaction between PPS and clay on the one hand, but on the other hand, it also acted as a plasticizer and caused a decrease in T_g and the tensile

properties. More work is needed to find a modifier and a processing condition by which the modifier can help the dispersion of clay and also be completely degraded after the formation of an exfoliated structure. This idea is applicable not only to PPS but also to other polymers with low processing temperatures.

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