

Preparation of Polystyrene/Montmorillonite Nanocomposites in Supercritical Carbon Dioxide

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ABSTRACT: The preparation of polystyrene (PS)/montmorillonite (MMT) composites in supercritical carbon dioxide (SC-CO₂) was studied. Lipophilic organically modified MMT can be produced through an ion-exchange reaction between native hydrophilic MMT and an intercalating agent (alkyl ammonium). PS/clay composites were prepared by free-radical precipitation polymerization of styrene containing dispersed clay. X-ray diffraction and transmission electron microscopy indicated that intercalation of MMT was achieved. PS/clay composites have a higher thermal decom-

position temperature and lower glass-transition temperature than pure PS. The IR spectrum analysis showed that the solvent of SC-CO₂ did not change the structures of the PS molecules, but there were some chemical interactions between the PS and the clay in the composites. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 22–28, 2005

Key words: polystyrene; composites; montmorillonite; radical polymerization; supercritical carbon dioxide

INTRODUCTION

The number of applications of supercritical carbon dioxide (SC-CO₂) as a polymerization medium has increased rapidly over the last 10 years.^{1,2} There are many factors that make CO₂ a promising medium for polymerization reactions. From the industrial perspective, CO₂ is nontoxic, nonflammable, inexpensive, and abundant; it occurs naturally or is obtained as a by-product in chemical plants and thermoelectric power stations. In addition, the separation of CO₂ from a liquid or solid product can be realized simply by depressurizing. Based on this viewpoint, even water could be replaced by CO₂ with lower cost in drying procedures and wastewater treatments. From the chemical perspective, CO₂ is relatively inert; this allowed the synthesis of polymers by a wide variety of mechanisms, including free-radical chain growth, cationic chain growth, oxidative coupling, transition metal catalysis, and melt phase condensation polymerization.² Apart from a few cases where CO₂ was deliberately copolymerized (e.g., the synthesis of polycarbonates³), it has generally been found to be nonreactive in polymerization processes. In most of the research in free-radical polymerization, CO₂ has been found to be inert toward free radicals under common polymerization conditions.^{4,5}

Although CO₂ is a good solvent for many common industrial monomers, it is a very poor solvent for their corresponding polymers under readily achievable conditions (<100°C, <1000 bar). The only polymers shown to have good solubility in pure CO₂ under mild conditions are some kinds of amorphous fluoropolymers and silicones.⁷ The use of CO₂ as a polymerization medium was successfully realized in the research of DeSimone et al.,^{8,9} which opened up new areas of research not only in homogeneous polymerizations, but also in dispersion and emulsion polymerizations. Hu et al.¹⁰ also studied the precipitation polymerization of styrene in SC-CO₂. According to DeSimone and Hu's explanations, polymerization happened in two different places: the CO₂-rich phase and the styrene-rich phase. Under a certain range of CO₂ pressures, the gel permeation chromatography (GPC) sketch of the product showed double peaks. The polystyrene (PS) that caused the peak of the lower molecular weight in the GPC chromatogram was precipitated from the CO₂-rich phase. It was found that an increase in CO₂ pressure, a decrease in the concentration of styrene, and an increase in the initiator concentration decrease the molecular weight of the product.

The dispersion of montmorillonite (MMT) clay in a polymer optimizes the number of available reinforcing elements for carrying an applied load and deflecting cracks.¹¹ It is reported that the coupling between the huge surface area of the exfoliated clay (~760 m²/g) and the polymer matrix facilitates stress transfer to the reinforcement phase; and it has shown improvements in some aspects of their mechanical per-

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formance, such as rigidity, strength, elongation, and toughness.^{12–14} The impermeable clay layers make a tortuous pathway for a permeant to transverse the nanocomposite. The barrier characteristics, including the chemical resistance, reduced solvent uptake, and flame retardance of the clay–polymer nanocomposites, have been enhanced by the hindered diffusion pathways through the nanocomposite.

In this work, the preparation of PS/MMT clay–polymer nanocomposites in SC-CO₂ was studied. The thermal properties of the PS/MMT hybrids showed that the dispersion of clay made the hybrids quite different from pure PS.

EXPERIMENTAL

Materials

AIBN was purified by recrystallization from hot methanol. All other materials were used as received: CO₂ (99.9%), styrene (AR, Tianjin Chemical Plant), MMT (<200 mesh, cation exchange capacity = 90 mequiv/100 g), and cetyl trimethyl ammonium salt (AR, Beijing Chemical Plant).

The MMT clay was first exchanged by alkyl ammonium (cetyl trimethyl ammonium salt). A given amount of alkyl ammonium and 1000 mL of deionized water were added into a three-necked round-bottomed flask (2000 mL), which was equipped with a thermometer, a condenser tube with circumfluence, and a beater. The solution was heated with a heater. Fifty grams of MMT clay were added to the flask when the temperature reached 80°C. The reaction was stopped 2 h later. The solution of the product was filtrated and a proper amount of deionized water was used to wash the filter cake until there was no white precipitate appearing when the solution of 0.1 mol/L AgNO₃ was added into the eluate. The filter cake was dried and crushed to be able to pass a 200-mesh screen.

Procedure

Polymerizations were conducted in SC-CO₂ in a 200-mL supercritical reactor. Circulating water was heated to the desired reaction temperature to warm the rig. AIBN was employed as the free-radical initiator. Before being placed into the circulating water jacket, the reactor cell was charged with the desired amount of initiator, alkyl ammonium exchanged clay, and styrene monomer. Then, it was purged with a flow of CO₂. As the reaction vessel was heated, CO₂ was added to the system until the desired temperature and pressure were reached. The reaction proceeded for the desired time while being stirred. At the end of the reaction, the reactor was cooled. The CO₂ was

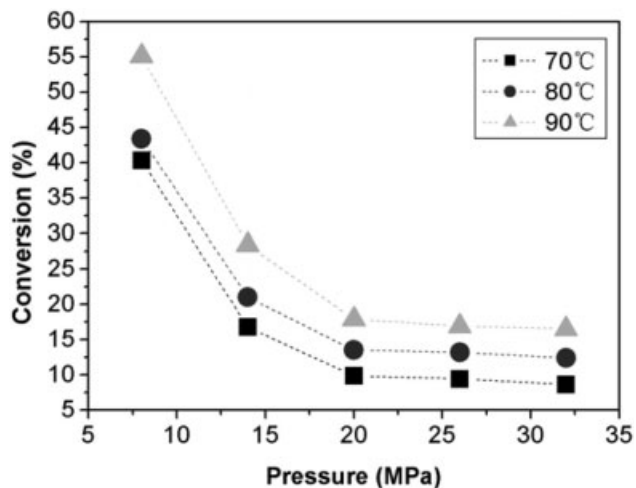


Figure 1 The conversion as a function of the CO₂ pressure. Styrene monomer (40 mL), AIBN (0.20 g), and organoclay (4.00 g) were added and the reaction was maintained for 8 h.

slowly vented from the vessel, and the polymer product was removed from the reactor and washed with water and methanol. Then, it was air dried and dried in a vacuum oven for 15–20 h at 80–100°C. The yield was calculated by weight.

Characterization

The IR spectra were obtained on a Nicolet 560 FTIR spectrometer at a resolution of 0.5 cm⁻¹. Differential scanning calorimetric (DSC) measurements were performed on a TA Instruments DSC 2910 in a dry nitrogen atmosphere. The glass-transition temperatures (*T_g*) were taken as the inflection point on the trace. Thermogravimetric analyses (TGA) were performed on a TA Instruments TGA 2910 thermal analyzer. The values of the weight loss for PS/MMT hybrid samples in nitrogen were determined at a heating rate of 20°C/min. The molecular weight data for the PS samples were determined using a Waters 150-CV GPC. X-ray diffraction (XRD) patterns were obtained by using a Rigaku Geiger Flex (D-max rB), two-circle powder diffractometer. The generator tension is 50 kV, and the generator current is 20 mA. Transmission electron microscopy (TEM) images of the composites were obtained at 60 kV with a Zeiss 10c electron microscope.

RESULTS AND DISCUSSION

Effect of pressure

With given amounts of styrene monomer, AIBN, and organoclay, the reactions were carried out at different

TABLE I
Molecular Weight of Polystyrene as Function of CO₂ Pressure

CO ₂ pressure (MPa)	8	14	20	26	32
M_w	84,541	38,003	40,916	57,309	51,212
M_n	23,170	7,517	7,060	7,570	7,843
M_w/M_n	3.649	5.055	5.795	7.570	6.530

Polymerization was carried out at 90°C for 8 h; 40 mL of styrene monomer, 0.20 g of AIBN, and 4.00 g of organoclay were added.

temperatures and pressures for 8 h. The results are shown in Figure 1 and Table I.

The results show that the conversion and average molecular weight decreased with increasing pressure, which was identical to the results in the literature.¹⁰ Particle product was not achieved in those experiments, because the PS that was produced would dissolve in styrene monomer under low conversion. Because PS cannot dissolve in high pressure CO₂, the free-radical polymerizations that were carried out were heterogeneous polymerizations. However, the processes in our system were slightly more complicated. According to the solubility data of styrene in high pressure CO₂,¹⁵ there should be two phases in the system. One is the continuous phase of SC-CO₂, and the other is the disperse phase of styrene. The organoclay dispersed into styrene and then generated a gel. Thus, it is assumed that the polymerization process was carried out in both the continuous phase and the disperse phase. The polymerization in the continuous phase was precipitation polymerization and that in the disperse phase was bulk polymerization. With the pressure increased, more PS was produced through precipitation polymerization in the continuous phase. Because of the gel effect, when PS is produced in the disperse phase, the gel that is formed slows down the termination rate of the reaction. Thus, the conversion and average molecular weight decreased as the pressure increased. Because the polymerization took place in both of the two phases, the polydispersity index (M_w/M_n) was very high. However, there was a single peak in the sketch of the GPC analysis.

TABLE II
Effect of Organoclay Granule Diameter on Conversion of Styrene, Weight- and Number-Average Molecular Weights and Polydispersity of Polystyrene

Granule diameter	Conversion (%)	M_w	M_n	M_w/M_n
<100 mesh	55.1	84,541	23,170	3.649
<200 mesh	59.2	272,738	29,696	9.184

The experiments were carried out under 8 MPa and 90°C for 8 h; 40 mL of styrene, 0.20 g of AIBN, and 4.00 g of organoclay were added into the autoclave.

Effect of organoclay granule diameter

It was shown that the conversion and average molecular weight could be improved by diminishing the granule diameter of the organoclay, which is indicated in Table II. The conversion and average molecular weight were increased by adding smaller organoclay (<200 mesh) under the same experimental conditions. It illuminated that the smaller organoclay, which has higher specific surface area, was more effective for the intercalation of styrene monomer into the layered clay and for the generation of styrene gel.

Effect of amount of organoclay added

The effect of the amount of organoclay on the resulting hybrid products was investigated. The results of those experiments are summarized in Table III. A comparison of polymerizations conducted with and without organoclay shows that the addition of organoclay was necessary to increase the conversion. For reactions conducted with organoclay, the conversions and molecular weights of the hybrid products changed significantly as the amount of the added organoclay was varied. Under the optimal conditions in Hu et al.'s¹⁰ research (80°C, 9.5 MPa), the number-average molecular weight was 14,430 and the M_w/M_n was 2.11. By adding organoclay in our research, the molecular weights of PS were greatly increased.

The concentration of stabilizer was very important for the formation of a stable gel system. Thus, the amount of organoclay added into the reaction system

TABLE III
Effect of Amount of Organoclay (<200 mesh) Added on Conversion, Weight- and Number-Average Molecular Weights, and Polydispersity of Resulting Hybrids

Organoclay added (g)	Conversion (%)	M_w	M_n	M_w/M_n
0.0	26.3 ± 0.5	—	—	—
2.0	60.7 ± 1.4	165,502	26,609	6.220
4.0	60.3 ± 1.1	272,738	29,696	9.184
6.0	54.8 ± 0.7	103,292	25,743	4.013

Reactions were conducted at 90°C and 8 MPa for 8 h with 40 mL of styrene and 0.20 g of AIBN.

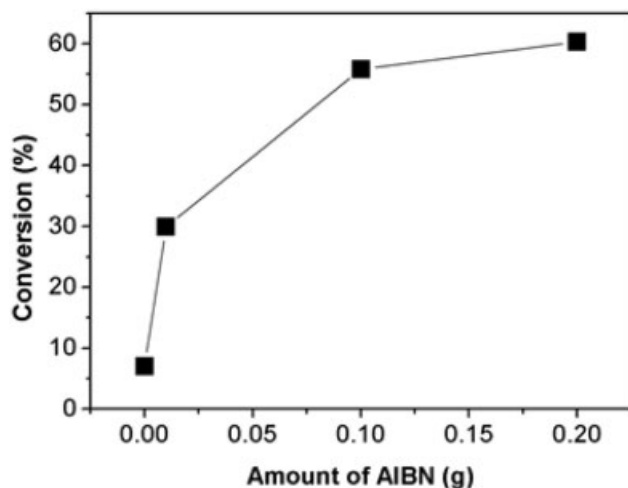


Figure 2 The effect of the amount of AIBN added on the conversion. Reactions were conducted at 90°C and 8 MPa for 8 h with 40 mL of styrene and 4.00 g of organoclay (<200 mesh).

had a great effect on the conversion of styrene and the molecular weight of PS. When the amount of organoclay in the system was insufficient, stable gel systems could not be formed. Thus, the PS particles that were produced were not sufficiently stable and tended to coagulate. They could cease the polymerization process and cause lower conversion and molecular weights. However, when excessive organoclay was added, the organoclay itself coagulated and the stable gel system was destroyed.

Effect of amount of AIBN added

The effect of the amount of AIBN on the resulting hybrid products was studied. The results of those experiments are shown in Figure 2.

The results show that the conversion could be increased by adding more AIBN. Because a high concentration of AIBN will decrease the molecular weight of the polymer product, 0.20 g of AIBN was enough to initiate the polymerization reaction.

XRD analysis

XRD was used to characterize the layer structure of polymer–clay hybrids, because the changes in 2θ indicate the changes in the gallery distance of the clay. The d -spacing of the galleries between the clay layers changed during the procedure. Chen et al.¹⁶ studied the exfoliated structure of PS/clay by XRD. In their research, exfoliated PS/clay was obtained by *in situ* emulsion polymerization in water at ambient pressure. The XRD peaks disappeared, which

TABLE IV
d-Spacing Changes of Organoclay after Dispensed in Styrene in Normal Condition

Original d -spacing of organoclay (Å)	19.1
2θ of organoclay in styrene (°)	2.24
d -Spacing of organoclay in styrene (Å)	39.4
Difference between d -spacing of original organoclay and organoclay in styrene (Å)	20.3

Organoclay/styrene = 4.00 g/40 mL.

indicated that there were no periodically stacked MMT layers. Compared with their results, the layer structure of polymer–clay hybrids formed in the experimental conditions was an intercalated PS/clay structure.

Table IV shows the 2θ decreases when the organoclay was dispensed into styrene under normal conditions (ambient pressure and temperature) to form a stable gel. The results suggest that the polarity of the organoclay matches the styrene monomer and the monomer intercalates into the clay galleries, spreading the clay layers further apart. An intercalated composite was formed.

It can be deduced from Tables IV and V that the styrene monomer intercalated into the clay galleries, further swelling the clay layers and producing PS by the initiation of AIBN diffusing into the galleries.

TEM analysis

Even though the XRD results noted above give useful information on the state of the hybrids, they do not provide a complete picture of the hybrids. To obtain actual images of the materials, TEM images were obtained for the polymer–clay hybrids by crushing the hybrids into fine powder and dispensing the powder in alcohol with the help of an ultrasonic wave. Figure 3 shows the TEM images of the MMT in the hybrid. The images indicate that the granule diameters of the clay particles in the hybrid are below 10 μm . In Figure 3(b) the opaque regions represent the clay layers and the translucent regions represent the PS. Figure 3(c) is

TABLE V
d-Spacing Changes of Organoclay after Polymerization Reaction

Original d -spacing of organoclay (Å)	19.1
2θ of organoclay in hybrids (°)	2.32
d -Spacing of organoclay in hybrids (Å)	38.0
Difference between d -spacing of original organoclay and organoclay in hybrids (Å)	18.9

The granule diameters of the original organoclay are less than 200 mesh. The reaction conditions are AIBN/organoclay*/styrene = 0.20 g/4.00 g/40 mL, CO₂ pressure = 8 MPa, temperature = 90°C, and reaction time = 8 h.

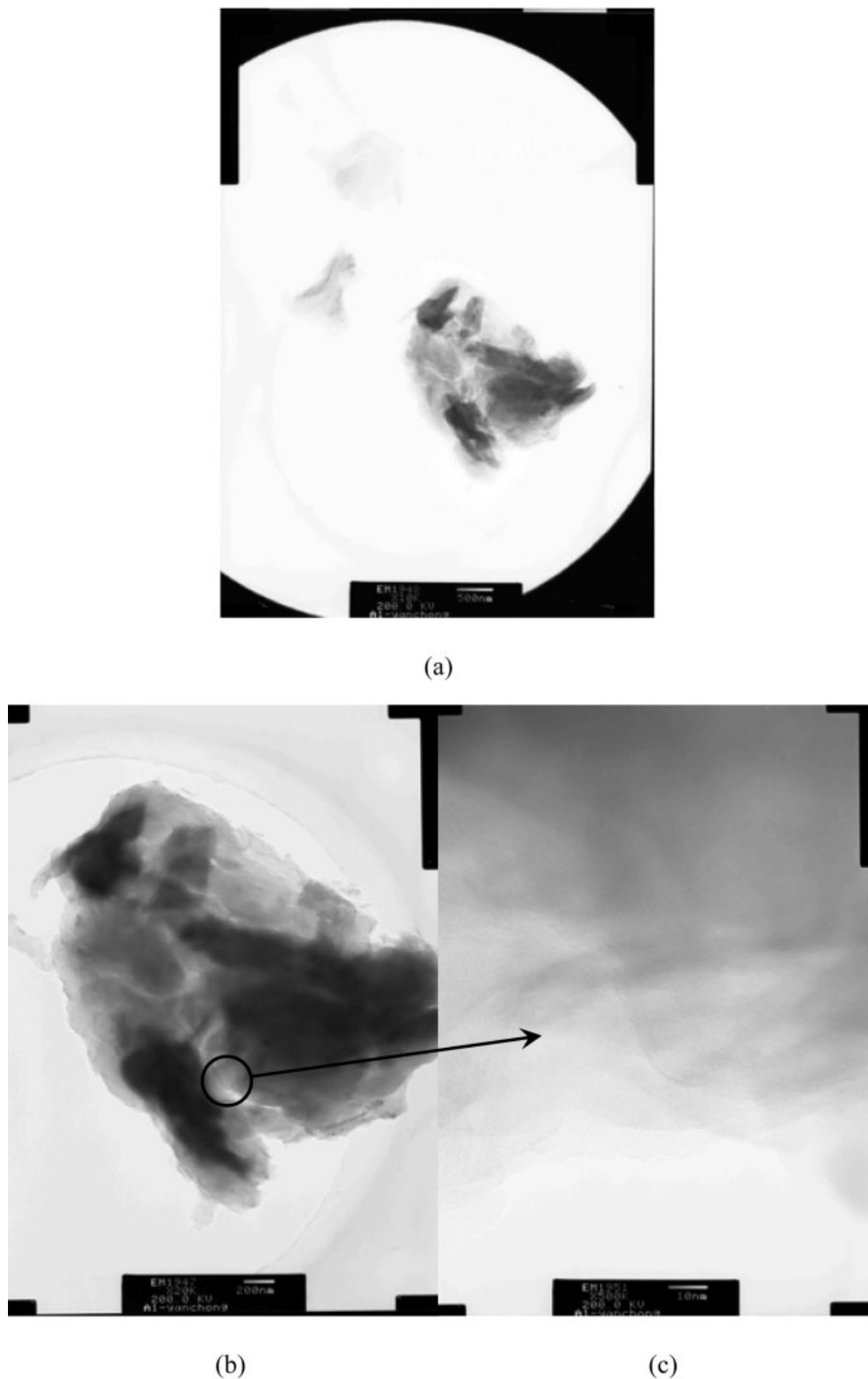


Figure 3 TEM images of montmorillonite in the polymer-clay hybrid with the following reaction conditions: AIBN/organoclay/styrene = 0.20 g/4.00 g/40 mL, CO₂ pressure = 8 MPa, temperature = 90°C, and reaction time = 8 h. (a) Original magnification $\times 10,000$, (b) original magnification $\times 20,000$, and (c) original magnification $\times 500,000$. The granule diameters of the original organoclay are < 200 mesh.

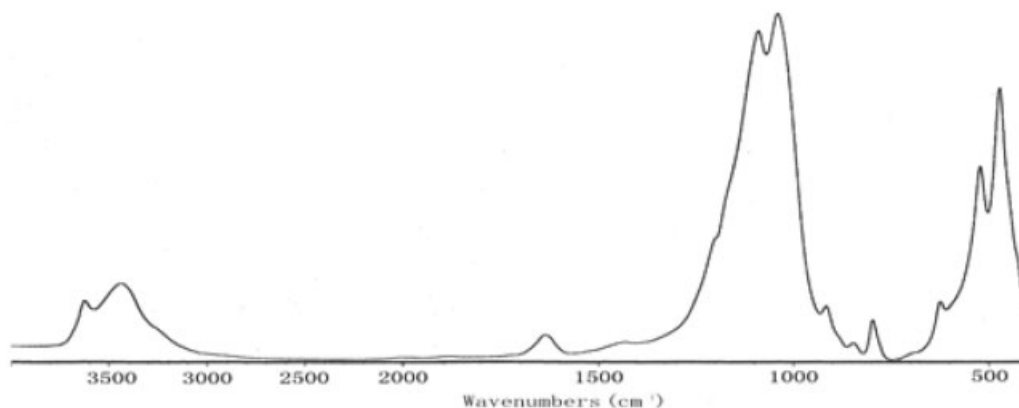


Figure 4 The FTIR spectrum of pristine sodium montmorillonite (Na-MMT).

a local amplification of a translucent region. The PS in the MMT clay layers can be seen under an original magnification of 500,000. Combined with the results of XRD, one can assert that the composites are intercalated hybrids with a nanolevel scale in the *d*-spacing dimension.

TGA and DSC analysis

Samples of the polymer–clay hybrid that had been sampled to carry out TEM analysis were used to carry out TGA and DSC analysis. The results show that the thermal decomposition temperature of the product was 395°C, and the T_g of the product was 58°C. Generally, the thermal decomposition temperature and the T_g of pure PS are 360 and 100°C, respectively. PS/MMT composites have a higher thermal decomposition temperature and a lower T_g than pure PS. The reason for the higher thermal decomposition temperature was the enhanced flame retardance by the hindered diffusion pathways through the nanocomposite. The decrease of the T_g for the PS/MMT composites was possibly caused by the movement of the polymer chains in the region between the polymer bulk and clay.

FTIR analysis

Figure 4 shows the FTIR spectrum of pristine sodium MMT (Na-MMT). The bands at 1090 and 1036 cm^{-1} are characteristic absorbance bands of Na-MMT. Figure 5 shows the FTIR spectrum of alkylammonium exchanged MMT. Compared with Figure 4, there is aliphatic C—H stretching at around 2920 and 2850 cm^{-1} .

Samples selected for IR analysis were obtained under the following conditions: the AIBN/organoclay/styrene ratio was 0.20 g/4.00 g/40 mL, the CO₂ pressure was 8 MPa, the temperature was 90°C, and the reaction time was 8 h. The sample was extracted in a Soxhlet apparatus for a minimum of 5 h using tetrahydrofuran (THF) as the solvent. The extract was the PS from the composites, and the remainder was the clay that could not dissolve in THF. After the extraction, the remainder (Fig. 6) and the extract (Fig. 7) were analyzed by FTIR and compared with the commercial PS (Fig. 8). The spectrum of the extract was nearly the same as the commercial PS, which means the SC-CO₂ did not affect the structure of the PS in the composites. However, as shown in Figure 6, the aromatic characteristic absorbance band at about 698 cm^{-1} still existed, which means some of the PS chains were intercalated into the clay galleries and the intercalated PS/MMT composite was achieved. There is

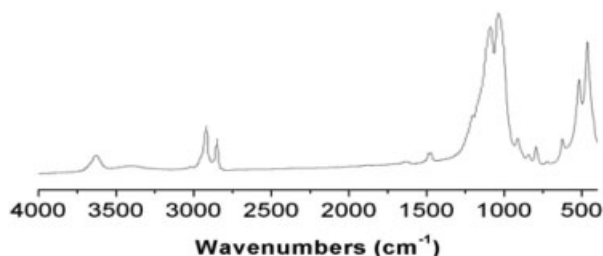


Figure 5 The FTIR spectrum of the organoclay.

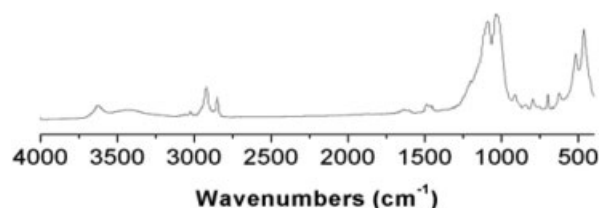


Figure 6 The FTIR spectrum of the remainder from Soxhlet extraction.

some kind of chemical interaction between the PS chain and the organoclay.

CONCLUSIONS

PS/MMT composites were synthesized by free-radical precipitation polymerization in SC-CO₂. The XRD and TEM results indicate that the hybrids were intercalated nanocomposites. The FTIR spectrum analysis showed there was some type of chemical interaction between the PS chain and the clay. It also indicated that the PS chain was intercalated into the clay galleries and an intercalated PS/MMT composite was achieved. The TGA and DSC test results showed that PS/MMT composites have a higher thermal decomposition temperature and a lower glass-transition temperature than pure PS.

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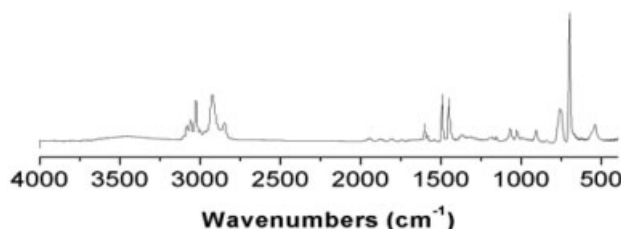


Figure 7 The FTIR spectrum of the extract from Soxhlet extraction.

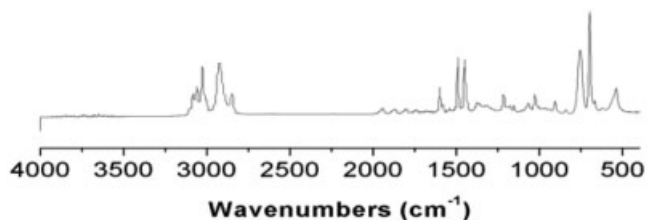


Figure 8 The FTIR spectrum of commercially pure polystyrene.

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