

# Synthesis of Montmorillonite/Polystyrene Nanocomposites in Supercritical Carbon Dioxide

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**ABSTRACT:** Monomer styrene and initiator *N,N'*-azobis(isobutyronitrile) were impregnated into montmorillonite (MMT) galleries using supercritical CO<sub>2</sub> at 35°C and 12.0 MPa, after thermal polymerization of monomer at 65°C, resulting in MMT/polystyrene nanocomposites. The morphology and structure of the products were characterized by FTIR, powder X-ray diffraction, transmission electron microscopy, differential scanning calorimetry, and thermogravimetric analysis. The results indicate that MMT is dis-

persed in the composite with intercalated and exfoliated structures, enhancing the thermal stability of nanocomposites. Changing the soaking time and the content of MMT in the supercritical solution during the impregnating process can control the exfoliated extent of MMT. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 1194–1197, 2004

**Key words:** montmorillonite; polystyrene; nanocomposites; supercritical CO<sub>2</sub>; morphology

## INTRODUCTION

Nanocomposites composed of clay or other layered silicate and polymer have attracted much attention in recent years. By using a small amount of nanoscale particles instead of conventional particulates to fill polymers, most properties of the polymers are substantially enhanced.<sup>1</sup> For instance, a clay/polyamide-6 composite has shown greatly improved tensile modulus, flexural strength, and flexural modulus.<sup>2</sup> Several methods, such as suspension polymerization in a solvent,<sup>3,4</sup> direct polymer melt intercalation,<sup>5</sup> interlayer polymerization,<sup>6</sup> sol-gel process,<sup>7</sup> and monomer/polymer grafting to clay layers,<sup>8</sup> have been used to prepare both intercalated and exfoliated nanostructures. Although several successful approaches have been demonstrated, new routes are still desired.

Recently, supercritical fluids (SCFs) have been used in material synthesis and processing<sup>9–11</sup> because of their special properties such as high diffusivity, low viscosity, and near-zero surface tension. Supercritical CO<sub>2</sub> (SCCO<sub>2</sub>) is the most attractive because it is non-toxic, nonflammable, chemically inert, and has moderate critical temperature and critical pressure. Moreover, SCCO<sub>2</sub> can dissolve many small organic molecules, and can also swell most polymers. Therefore, SCCO<sub>2</sub> can carry many organic molecules into fine spaces or any other spaces produced by swelling, thus offering the possibility of fabricating polymer/poly-

mer composites.<sup>11,12</sup> With the aid of SCCO<sub>2</sub>, poly-(methyl methacrylate) was intercalated into silicate layers, resulting in nanocomposites with a high level of layered silicates.<sup>13</sup>

In this article, we report a new route to prepare clay/polymer nanocomposites: *in situ* synthesis of nanocomposites with the aid of SCCO<sub>2</sub>. In this approach SCCO<sub>2</sub> was used to impregnate monomer and initiator molecules into montmorillonite (MMT) galleries. After thermal free-radical polymerization of monomer within the MMT interlayers, MMT/polymer composites were prepared.

## EXPERIMENTAL

### Materials

Pristine sodium montmorillonite (cation exchange capacity 90–100 mmol/g, particle size 40–70 μm) was supplied by Zhangjiakou Qinghe Chemical Plant (China). Before use, it was first modified with cetyltrimethylammonium chloride (CTAC), which was designated organic MMT. Monomer styrene (St, AR grade) used in this work was purchased from Beijing Chemical Reagent Center (China) and was distilled under vacuum before use. *N,N'*-Azobis(isobutyronitrile) (AIBN, Beijing Chemical Plant, China), used as an initiator, was recrystallized twice from acetone. CO<sub>2</sub> (purity of 99.95%) was provided by Beijing Analytical Instrument Factory (China) and used as received.

### Modification of MMT with CTAC

About 5 g of MMT was dispersed into 95 mL of deionized water, and the suspension was stirred at

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80°C until it became transparent. A 3 wt % CTAC aqueous solution (100 mL) was added dropwise. After the solution was stirred for 1 h at 80°C, the white precipitate was filtered and washed with deionized water until it was free of chloride ions, according to a test with an aqueous AgNO<sub>3</sub> solution. The resultant product was then dried in a vacuum oven overnight at room temperature. The final product had a *d*-spacing of 1.95 nm, and was kept in a dryer after grinding.

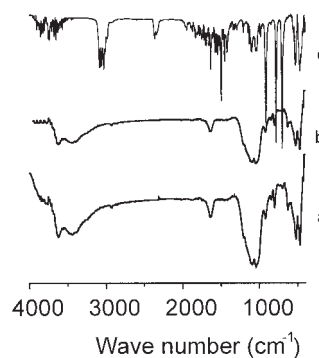
### Preparation of MMT/PS composites

In a typical experiment, the desired amounts of organic MMT, styrene, and AIBN (1 wt % in styrene solution), together with a magnetic stirrer, were placed in a high-pressure stainless steel vessel (22 mL). After the air in the vessel was replaced by CO<sub>2</sub>, the vessel was immersed in a water bath of 35.0°C, which was controlled by a Haake D3 temperature controller, (Haake, Bersdorff, Germany), with an accuracy of ±0.1°C. Then the vessel was charged with CO<sub>2</sub> up to 12 MPa, and the mixture was stirred at this temperature. After a desired soaking time, the cell was heated to 65°C for 24 h to initiate polymerization, after which the composite was obtained. For comparison, PS without MMT was also synthesized in supercritical CO<sub>2</sub> under the same conditions, designated pristine PS.

### Characterization

A Perkin–Elmer 180 FTIR spectrometer (Perkin Elmer Cetus Instruments, Norwalk, CT) was used for IR analysis. A transmission electron microscopy (TEM) image of the composite was obtained at 200 kV and low-dose condition by means of a JEOL 2010 electron microscope (JEOL, Tokyo, Japan). The sample was ground and then dispersed in ethanol by ultrasonication, and finally it was dropped onto carbon-coated Cu grids for TEM observation. The contrast between the layered silicate and the polymer phase was sufficient for imaging, so heavy metal staining was not required. Powder X-ray diffraction (XRD) patterns were obtained using a Rigaku (Tokyo, Japan) D/MAX.RB X-ray diffractometer, equipped with a Ni-filtered Cu–K<sub>α</sub> radiation source operated at 45 kV and 100 mA. The scanning speed used was 0.3°/min.

The thermal property of PS and MMT/PS composite was measured by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The PS or MMT/PS composite (4.8–5.2 mg) was sealed in an aluminum sample pan for DSC analysis, and the DSC curves were recorded under N<sub>2</sub> (50 mL/min) on a thermal analyzer (Netzsch STA 409 PC/PG; Netzsch-Gerätebau GmbH, Bavaria, Germany) at a heating rate of 10°C/min up to 150°C. TGA analysis was also carried out under N<sub>2</sub> protection on the thermal ana-



**Figure 1** FTIR spectra of organic MMT (a), CO<sub>2</sub>-processed organic MMT (b), and MMT/PS composite (c).

lyzer (Netzsch STA 409 PC/PG) at a heating rate of 10°C/min.

## RESULTS AND DISCUSSION

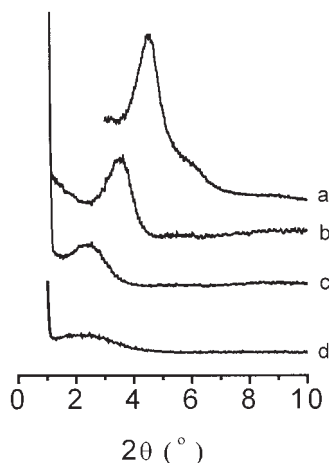
In this work, the impregnating experiments were conducted under conditions at which CO<sub>2</sub>, St, and AIBN existed as a single phase. MMT was suspended in the mixture by continuous stirring. The obtained MMT/PS composite was characterized with different techniques.

### Infrared spectroscopy analysis

The presence of MMT in the composites was confirmed by FTIR analysis. The FTIR spectra of organic MMT, SCCO<sub>2</sub>-treated organic MMT, and the MMT/PS composite are given in Figure 1. The peaks that appeared at 468, 521, 1042, 1090, 1637, 3440, and 3620 cm<sup>-1</sup> on spectrum a in Figure 1 are the characteristic bands of MMT. The IR spectrum of the CO<sub>2</sub>-treated organic MMT sample (spectrum b) is nearly the same as that of the original organic MMT sample, indicating that treatment of MMT using SCCO<sub>2</sub> cannot substantially change the properties of the MMT. For the composite (spectrum c), the characteristic bands of MMT at 1091, 1042, and 466 cm<sup>-1</sup> can also be observed, whereas other peaks disappear. The reason is that the content of MMT in the composite is small, and the bands with low intensity are not detectable.

### XRD analysis

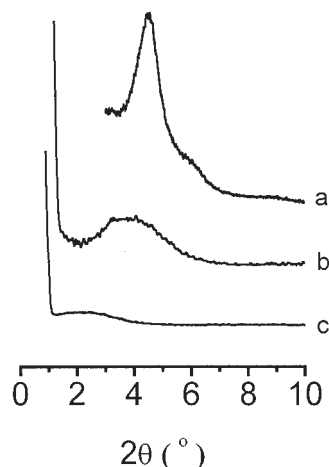
The microstructure of MMT in the composites was examined by XRD. Figure 2 illustrates the influence of impregnating time at 35°C and 12.0 MPa on the XRD patterns of the MMT in the composites. The weight ratio of organic MMT to PS in the composite was 1 : 100. The characteristic peak for the organic MMT appears at  $2\theta = 4.5^\circ$  (e.g.,  $d = 1.95$  nm), whereas the peaks for the composites are widened and shifted to  $2\theta = 2.3$ – $3.4^\circ$  ( $d = 3.84$ – $2.60$  nm) with different im-



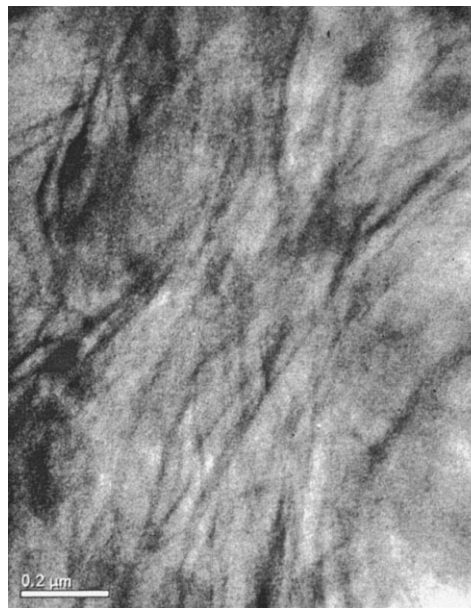
**Figure 2** XRD curves of organic MMT (a) and MMT/PS composites obtained with different impregnating times: (b) 5 h; (c) 10 h; (d) 15 h.

pregnating times, as observed from the figure. This indicates that the polymer chains have entered the clay galleries, thus enlarging the space of MMT layers. From the figure, it can also be observed that the intensity of the peaks of the composites decrease with increasing soaking time, suggesting that more MMT particles were exfoliated in the composites. This is reasonable because more styrene monomer molecules can infuse into the MMT layers with increasing impregnating time, and the polymerization of monomer leads to widening and/or exfoliating of the MMT layers.

We also changed the weight ratio of PS to MMT, from 100 : 1 to 10 : 1, to study its influence on the MMT structure in the composites. Figure 3 demonstrates that XRD peaks of composites monotonously shift to a lower degree as the PS to MMT ratio increases, indicating that the distance between the clay layers be-



**Figure 3** XRD curves of organic MMT (a) and MMT/PS composites with different MMT contents: (b) 10 wt %; (c) 1 wt %.

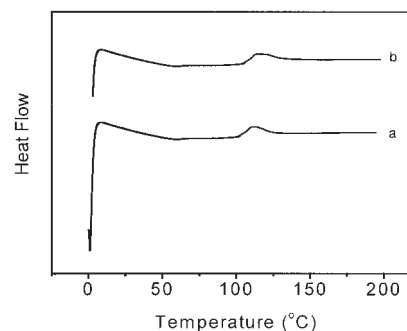


**Figure 4** TEM microphotograph of MMT/PS composite with MMT content of 3 wt %.

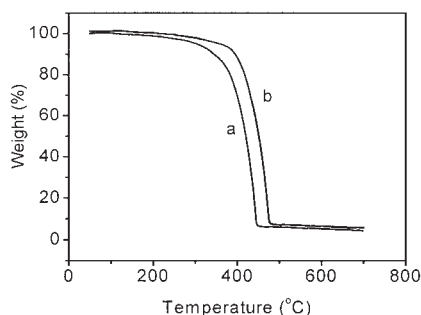
comes larger at higher monomer concentration in the impregnating process and larger exfoliating degree may be achieved.

#### TEM study

From XRD analysis, it is clear that there exists intercalated MMT in the composite. However, XRD analysis can detect only the periodically stacked MMT layers. There may be some exfoliated layers as well, which can be directly observed by TEM. Figure 4 shows a TEM micrograph of the composite with MMT content of 3 wt %. It is clear that intercalated layers and exfoliated layers coexist in the composite. It also can be observed that the thickness of most MMT particles (dark region) is less than 20 nm, indicating that the MMT particles (40–70  $\mu\text{m}$ ) have been exfoliated to primary particles. This is consistent with the XRD results discussed above, and it also can explain why the XRD peaks widen and weaken in the presence of the polymer.



**Figure 5** DSC trace of PS (a) and MMT/PS composite with MMT content of 3 wt % (b).



**Figure 6** TG curves of PS (a) and MMT/PS composite with MMT content of 3 wt % (b).

### Thermal property study

DSC traces of the pristine PS and the composite (3 wt % MMT) are shown in Figure 5. Both the pristine PS and nanocomposite show a large endotherm at approximately 115°C, corresponding to the glass-transition temperature of the two samples. The slightly higher glass-transition temperature of the polymer in the composite might be attributable to the confinement of the polymer chains in the intercrystalline regions between silicate particles.

The thermal stability of the nanocomposite is enhanced relative to that of virgin polystyrene, as shown in Figure 6. The onset decomposition temperature of the PS in the composite was about 40°C higher than that of pure PS. A similar phenomenon has been observed by other authors for the poly(dimethylsiloxane)/silicate nanocomposites prepared by melt processing.<sup>14</sup> The main reason may be that MMT layers in the composite can prevent the diffusion of the decomposed product in polymer, thus taking more time and energy in the decomposing process.

### CONCLUSIONS

The MMT/PS nanocomposite can be prepared by impregnating styrene and AIBN into MMT galleries with the aid of SCCO<sub>2</sub>, followed by free-radical polymerization of monomer within the swollen MMT layers. The original organic MMT particles were intercalated with polymer and partially exfoliated to primary particles, which resulted in the enhanced thermal stability of the nanocomposites. The composite structure can be controlled by changing the reaction condition, such as soaking time and the content of MMT in the reaction system.

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