

# Manufacturing Polymer/clay Nanocomposites Using a Supercritical Fluid Process

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*The increased interest in reducing the environmental effects caused by releasing organic compounds and aqueous waste has motivated the development of polymeric materials in supercritical fluids. Recently, supercritical fluids have been used in material synthesis and processing because of their special properties, such as high diffusivity, low viscosity, and low surface tension. Supercritical carbon dioxide is the most attractive because it is non-toxic, non-flammable, and has moderate critical temperature and critical pressure values. Supercritical carbon dioxide can also swell most polymers. In this study, we prepared polymer/clay nanocomposites using supercritical fluids. Cloisites 10A, 15A, 25A, and 30B used in this study are montmorillonites modified with a quaternary ammonium salt. The nanocomposites of polymer/clay were characterized by X-ray diffraction, thermogravimetric analysis, and differential scanning calorimetry.*

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## 1. Introduction

The application of supercritical fluids (SCFs) to composite material synthesis is of increasing interest in materials chemistry. SCF solvents are an attractive alternative to incompressible organic liquid solvents because they have a liquid-like dissolving power while exhibiting the transport properties of a gas. Supercritical carbon dioxide has attracted extensive interest as a polymerization and processing medium, primarily driven by the need to replace conventional solvents with those that are more environmentally benign, non-toxic, nonflammable, and inexpensive.<sup>1-3</sup> These unique properties of supercritical carbon dioxide have been exploited to prepare polymer blends.<sup>4-6</sup>

Supercritical carbon dioxide has been applied as a swelling agent to facilitate the diffusion of a guest monomer into a carbon dioxide swollen polymer matrix.<sup>7,8</sup> Recently, supercritical carbon dioxide and an *in-situ* polymerization method were used as a process to assist the achievement of a uniform reinforcement distribution in polymer/clay nanocomposites at high clay contents (~40wt%).<sup>9-11</sup>

In this study, we present a novel manufacturing technology for polymer/clay nanocomposites using supercritical carbon dioxide. The thermal properties of polymer/clay nanocomposites prepared using an SCF process were enhanced compared to those obtained using a melt intercalation method.

## 2. Experimental Details

### 2.1 Materials

Sodium montmorillonite (Na<sup>+</sup>-MMT) and Cloisites 10A, 15A, 20A, 25A, and 30B-MMT were obtained from Southern Clay

Products, Inc., and poly(ethylene oxide) (PEO) with an average molecular weight of  $1 \times 10^5$  was supplied by Aldrich Chemical Co., Inc.

### 2.2 Preparation of PEO/clay nanocomposites in supercritical CO<sub>2</sub>

PEO (0.6g) and Na<sup>+</sup>-MMT or organo clay (0.4g) were added to a cell. The cell was then filled with CO<sub>2</sub> until the pressure reached 70 bar, and heated to 70°C. After reaching this temperature, the pressure was increased to 250 bar, and the cell was allowed to proceed while stirring for 2 hr. After the cell was cooled, the CO<sub>2</sub> was slowly vented. The final product was taken out and dried at room temperature in a vacuum oven overnight.

### 2.3 Characterization

X-ray diffraction (XRD) data ( $2\theta = 2^\circ - 10^\circ$ ) were collected on a Rigaku multiflex diffractometer using Cu K $\alpha$  radiation (30 kv, 100 mA) at a scan rate of 4°/min. Differential scanning calorimetry (DSC) was used to measure the  $T_m$  of the nanocomposites at a heating rate of 10°C/min. Thermogravimetric analysis (TGA) was performed using a Perkin Elmer system in a nitrogen atmosphere at a heating rate of 20°C/min.

## 3. Results and Discussion

Polymer/clay nanocomposites were successfully prepared using an SCF process. Figure 1 shows the XRD patterns of PEO/MMT nanocomposites. The amount of Na<sup>+</sup>-MMT was increased from 10 wt% to 40 wt%. The d-spacing of the clay remained unchanged, regardless of the clay content. Only the intensity of the X-ray peak increased with the clay content.

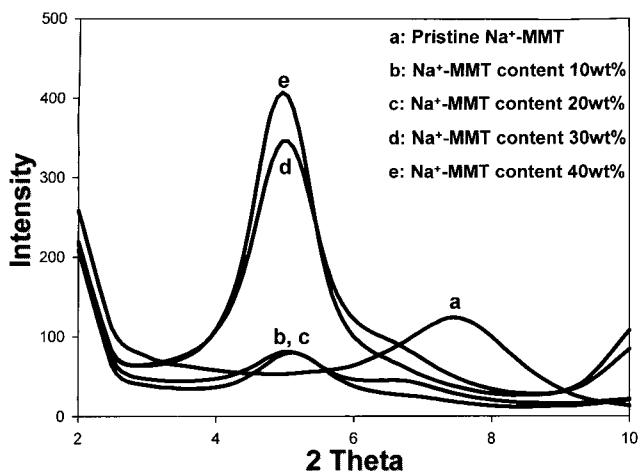


Fig. 1 XRD patterns of PEO/Na<sup>+</sup>-MMT nanocomposites made using an SCF process with differing Na<sup>+</sup>-MMT content

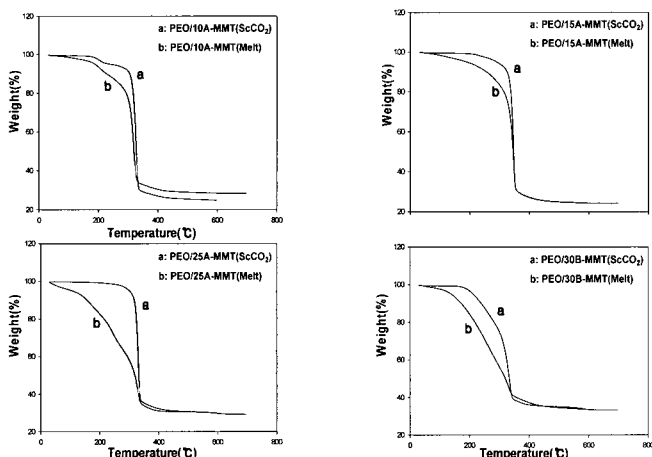


Fig. 2 TGA curves of PEO/organo-clay nanocomposites made using an SCF process and the melt intercalation method

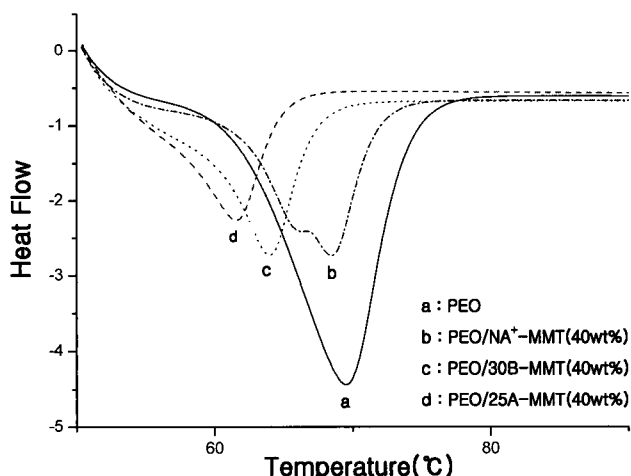


Fig. 3 DSC trace of PEO/clay nanocomposites made using an SCF process with clay content of 40 wt%

Table 1 D-spacing of clay and polymer/clay nanocomposites

	Na <sup>+</sup> - MMT	10A	15A	25A	30B
Clay	1.2 nm	1.9 nm	3.2 nm	1.9 nm	1.8 nm
Polymer/ clay	1.8 nm	2.8 nm	3.8 nm	2.8 nm	2.8 nm

Figure 2 shows that the thermal stability of nanocomposites prepared using an SCF process was enhanced compared to that obtained using the melt intercalation method. This was due to the powerful dissolving and diffusion ability of the SCF. There was also a decrease in melting temperature in the endothermic peak area, as shown in Fig. 3. This promotes intercalated PEO molecules.

### 3. Conclusions

PEO/clay nanocomposites were prepared using an SCF process. The nanocomposites were characterized by XRD, TGA, and DSC analyses. PEO intercalation was demonstrated by a shift of the XRD peaks, a decrease of the melting temperature, and the presence of endothermic peak areas. The thermal stability of nanocomposites prepared using an SCF process was enhanced compared to that obtained using the melt intercalation method. This was due to the powerful dissolving and diffusion ability of the SCF.

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