J. of Supercritical Fluids 49 (2009) 385–393

Contents lists available at ScienceDirect

The Journal of Supercritical Fluids

journal homepage: www.elsevier.com/locate/supflu

Supercritical CO_2 intercalation of polycaprolactone in layered silicates

Yeong-Tarng Shieh[a,*], Jhen-Gang Lai[b], Wei-Li Tang[b], Chien-Hsin Yang[a], Tzong-Liu Wang[a]

[a] Department of Chemical and Materials Engineering, National University of Kaohsiung, Kaohsiung 811, Taiwan
[b] Department of Chemical and Materials Engineering, National Yunlin University of Science and Technology, Douliou, Yunlin 640, Taiwan

ARTICLE INFO

Article history:
Received 20 January 2009
Received in revised form 23 February 2009
Accepted 24 February 2009

Keywords:
Polycaprolactone
Clay
Intercalation
Supercritical CO_2
WAXD
DSC

ABSTRACT

Supercritical carbon dioxide ($scCO_2$) intercalation of polycaprolactone (PCL) in layered silicates (clay) is studied. Wide angle X-ray diffraction patterns find that PCL is slightly intercalated in unmodified montmorillonite clay (NaMMT) but considerably intercalated in organic-modified montmorillonite clay (OMMT). The interlayer spacing in OMMT increases considerably from 1.94 nm in OMMT to 3.58 nm in the OMMT/PCL 10/90 sample. PCL8 having molecular weight of 80,000 is harder to intercalate into OMMT than PCL1 having molecular weight of 10,000. Higher $scCO_2$ pressures at a temperature allow larger intercalations of PCL in OMMT to exhibit larger interlayer spacings in OMMT. The interlayer spacings in OMMT, however, are not clearly found to relate with the CO_2 temperature at a given pressure. TGA data show that OMMT enhances the thermal stability of PCL1, with a higher content of OMMT giving a higher amount of PCL1 residue. DSC data find that the PCL1-intercalated OMMT expedites the melt-crystallization rate of PCL1 from the melt but suppresses the crystallinity of PCL1. Study of Avrami's rate constants k and exponent n finds that the PCL1-intercalated OMMT enhances the isothermal crystallization rate of PCL1 and that the crystal growth dimension is 3 for pure PCL1 but decreases with increasing OMMT content in the blends. Modulus data find that the PCL1-intercalated OMMT is an effective reinforcement for PCL8.

1. Introduction

Supercritical CO_2 fluids ($scCO_2$) have attracted much attention because the environmentally friendly, chemically inert, inexpensive, and nonflammable carbon dioxide has potential to be an alternative to substitute for organic solvents to reduce environmental pollutions. The $scCO_2$ used as a medium to prepare clay nanocomposites drew attention recently [1–7]. Polymer/clay nanocomposites have been reportedly prepared by a variety of methods including melt intercalation, in-situ polymerization, and solution intercalation. The latter method is limited to certain polymer/solvent pairs, in which the polymer is soluble and the silicate layers are swellable [4,8]. Monomers are mostly soluble in common solvents, conventional solution intercalation of the monomer in clay is easily obtained and the polymer-intercalated clay can be easily prepared via in-situ polymerization of the intercalated monomer. Via this method, poly(methyl methacrylate) or polystyrene/clay nanocomposites could be prepared in $scCO_2$ in the presence of a fluorinated surfactant-modified [1] or a poly(dimethylsiloxane) surfactant-modified [2] or organic-modified [3,5,7,9] clays.

Because of very low solubility of polymers in $scCO_2$, due to lack of strong interactions between CO_2 and polymers and low entropy driving force for mixing CO_2 and polymers, the $scCO_2$ intercalation of polymer in clay is qualitatively different from the conventional solution intercalation. Although very few polymers were reportedly soluble in $scCO_2$, some polymers with carbonyl groups [10–14], ether linkages [15], or C–F linkages [16–20] have specific interactions with CO_2 that could cause depression of melting temperatures of polymers in CO_2. Without being soluble in the $scCO_2$, poly(ethylene oxide) (PEO) having ether linkages was reportedly [4] intercalated in the Na-montmorillonite clay via a meltlike intercalation at a temperature (48 °C) lower than its normal melting temperature near 60 °C, with the spacing in the clay slightly increasing from 1.20 to 1.71 nm.

Poly(ε-caprolactone) (PCL) having carbonyl groups is a semicrystalline and biodegradable aliphatic polyester having a glass transition temperature of about −60 °C and a melting temperature (T_m) of about 60 °C. PCL/clay nanocomposites could be prepared by melt intercalation of PCL [21] or by in-situ polymerization of ε-caprolactone [22,23]. By the melt intercalation, the nanocomposites were prepared by mechanical kneading in a two-roll mill at 130 °C [21]. Following the melt intercalation, the interlayer spacing in the natural sodium montmorillonite (MMT) remained unchanged whereas that in the organic-modified MMT increased from 1.86 nm in the MMT modified by dimethyl 2-ethylhexyl (HTA) ammonium cation to 2.77 nm or from 1.85 nm in the MMT modified by methyl bis(2-hydroxyethyl) (HTA) ammonium cation to about 3 nm, both intercalated composites containing 10 wt% of clay [21]. In a previous study, we investigated [24] the effects of high-pressure CO_2 treat-

* Corresponding author. Fax: +886 7 5919277.
E-mail address: yts@nuk.edu.tw (Y.-T. Shieh).

0896-8446/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.supflu.2009.02.005

ments on morphology of PCL. We found that PCL could melt at 8.5 and 30.8 MPa of CO_2 at 35 °C, a much lower temperature than T_m of PCL. These high pressures of CO_2 could assist melting of PCL because of the presence of CO_2-carbonyl groups interactions [10–14]. In this study, we investigate whether $scCO_2$ intercalation of this carbonyl groups-containing PCL in montmorillonite clays, both unmodified and organic-modified, can be obtained.

2. Experimental

2.1. Materials

The unmodified sodium montmorillonite (Na^+-MMT) clay (denoted by NaMMT) with a cationic exchange capacity (CEC) of 92.6 meq/100 g was supplied by Southern Clay Products, Inc. The organically modified montmorrillonite clay (denoted by OMMT), supplied by Pai Kong Nanotechnology Company, was modified by stearyltrimethylammonium chloride $CH_3(CH_2)_{17}N^+(Cl^-)(CH_3)_3$. NaMMT and OMMT are both powders. Poly(ε-caprolactones) having number average molecular weights of 10,000 (denoted by PCL1) and 80,000 (denoted by PCL8) were supplied by Aldrich. PCL1 was used for the intercalation in the clays while PCL8 was used as the matrix for preparations of the PCL1-intercalated clay nanocomposites for investigation of mechanical properties.

2.2. Intercalation experiments

The NaMMT powders were dried at 130 °C for 24 h before blending with a certain amount of PCL1 which was previously pulverized into powders of about 1 mm in diameter. The compositions of the NaMMT/PCL1 blends included 10/90, 20/80, and 30/70 in weight ratios. Each blend was then put in a preheated high-pressure cylindrical chamber into which CO_2 was filled to pressurize to a desired pressure to conduct the intercalation for 1 h. The cylindrical chamber has 6 cm in diameter and 200 cm^3 in volume. Following intercalation experiments, the chamber was depressurized in 1 min to ambient pressure at a controlled constant volumetric rate and evacuated. The so-prepared sample was pulverized into powders and vacuumed to remove all dissolved CO_2 before characterizations. The intercalation experiments of OMMT were similar to those of NaMMT except that OMMT did not pre-dry at 130 °C for 24 h. The compositions of the OMMT/PCL1 blends included 10/90, 20/80, 30/70, and 60/40 in weight ratios. The total weight of each blend of NaMMT/PCL1 and OMMT/PCL1 was 4 g.

2.3. Characterizations

Wide angle X-ray diffraction (WAXD) patterns of the pulverized samples were analyzed to investigate the interlayer spacings in the clays. The WAXD analysis was conducted at 2°/min between 2° and 30° on an X-ray diffractometer, supplied by Mac Science with a model MXP18. The wavelength of the X-ray source is 1.54 Å. Thermal gravimetric analyzer (TGA) was used to analyze the thermal stability of PCL1 in the clay/PCL1 nanocomposites. TGA analysis was conducted at a heating rate of 20 °C/min in air from room temperature to 900 °C.

The melt-crystallization temperatures (T_c) and enthalpies (ΔH) of samples during cooling from the melt were measured on a differential scanning calorimeter (DSC) with a model Q100 supplied by TA Instruments. The sample was heated on the DSC at 10 °C /min to 100 °C at which temperature was held for 10 min, followed by cooling at −10, −5, −3, or −1 °C /min to 0 °C. During cooling, T_c and ΔH of the melt-crystallized sample were obtained.

In the isothermal crystallization experiments, the samples were held in melt at 100 °C for 10 min in an oven in order to erase all previous crystalline history of PCL and then quickly moved to DSC cell preliminarily set at 42 °C (the crystallization temperature, T_c) at which the isothermal DSC scan was recorded. The moving of the melt from the oven to the DSC cell was quick enough to ensure that the samples did not crystallize before the isothermal crystallization in DSC. If any crystallization occurred during the quick cooling to a T_c, the isothermal experiment was not performed at that T_c. In the isothermal crystallization experiments at 42 °C in DSC, the crystallization onset times were 0.64, 0.70, 0.47, and 0.64 min after starting the isothermal DSC scan for pure PCL1, OMMT/PCL1 10/90, 20/80, and 30/70 blends, respectively, ensuring that the samples did not crystallize before the isothermal crystallization in DSC. The isothermal crystallization kinetics of samples can be analyzed using the Avrami equation as in Eq. (1):

$$1 - X_t = \exp(-kt^n) \tag{1}$$

where X_t is the relative crystallinity at crystallization time t, n is the Avrami exponent, and k is the rate constant. The relative crystallinity X_t at time t can be obtained by calculation using Eq. (2):

$$X_t = \frac{\int_0^t (dH_c/dt)dt}{\int_0^{t_\infty} (dH_c/dt)dt} \tag{2}$$

where dH_c/dt is the rate of heat evolution and t_∞ is the end time of the crystallization. The crystallization rate constant k and Avrami exponent n can be determined, respectively, from the intercept and slope in the plot of $\ln[-\ln(1 - X_t)]$ versus $\ln(t)$. The crystallization rate can be estimated by determining the crystallization half-time ($t_{1/2}$) as in Eq. (3):

$$t_{1/2} = \left(\frac{\ln 2}{k}\right)^{1/n} \tag{3}$$

The storage modulus, modulus and tensile strength at break of samples were measured on a dynamic mechanical analyzer DMA (DMA 2980, TA Instruments) through a tensile mode. For the storage modulus, the measurements were conducted at a heating rate of 3 °C/min from −100 to 50 °C and at an oscillation frequency of 2 Hz with oscillation amplitude of 10 μm. The storage modulus data presented in this report were the average of three tests for every sample. For modulus and tensile strength at break, the measurements were conducted at a constant strain rate and room temperature. The modulus and tensile strength at break data presented in this report were the average of at least five tests for every sample. The samples for all DMA measurements, dynamic and static, were prepared by dissolving the PCL1-intercalated clay prepared by $scCO_2$ intercalation at 50 °C and 34.5 MPa for 1 h and a certain amount of PCL8 as a matrix in chloroform, followed by casting into films and drying for 24 h in a hood and 2 h in a room temperature vacuum oven. The chloroform solution used to cast films was not found to affect the interlayer spacings in the clays as determined by WAXD analysis. All the cast films had 0.05 mm in thickness and were cut into rectangular specimens each with 5 mm in width and 30 mm in length for all the DMA measurements. For the sample denotation, the (OMMT/PCL1 x/y)/PCL8 20/80, for example, stands for the sample in which 20 parts in weight of (OMMT/PCL1 x/y) was blended with 80 parts in weight of PCL8. The (OMMT/PCL1 x/y) refers to the sample in which x parts in weight of OMMT and y parts in weight of PCL1 were blended for the $scCO_2$ intercalation experiment.

3. Results and discussion

Fig. 1 shows wide angle X-ray diffraction patterns for NaMMT and NaMMT/PCL1 blends following $scCO_2$ intercalation experiments at 34.5 MPa and 50 °C for 1 h. Table 1 tabulates WAXD angles obtained from Fig. 1 and the calculated (using the Bragg equation)