EFFECT OF SUPERCRITICAL CO_2 ON MORPHOLOGY AND RHEOLOGY OF POLYMER NANOCOMPOSITES PREPARED BY MELT COMPOUNDING*

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Abstract

Well dispersion or intercalation/exfoliation of nanoscale fillers (such as nano-$CaCO_3$ and nano-clay) in polymer matrix is currently not easy to be achieved. Supercritical carbon dioxide ($ScCO_2$) has been reported to have great potential for facilitating the dispersion or intercalation/exfoliation of the nanoscale fillers in polymer matrix. So, in this paper, the effects of dissolved $ScCO_2$ on the morphology of nano-$CaCO_3$ and nano-clay were investigated in the polymer nanocomposites prepared using a twin-screw extruder. X-ray diffraction (XRD) and transmission electron microscopy (TEM) were used to characterize the morphology of extruded nanocomposites. The dynamic rheological properties were measured using a dynamic rheometer in the oscillatory mode. Compared to the nanocomposites prepared without the aid of $ScCO_2$, the nanocomposites with $ScCO_2$ addition appear to have higher degree of nano-filler dispersion or intercalation/exfoliation.

Keywords: nanocomposites, supercritical carbon dioxide, melt compounding

Introduction

The polymer nanocomposites can be prepared by melt intercalation method. However, well dispersion or intercalation/exfoliation of nanoscale fillers in polymer matrix can not be easily obtained, because it requires strong interfacial interaction between the polymer matrix and the nano-fillers in order to generate enough shear forces [1]. Huang et al. [2–4] analyzed the effects of processing conditions and flow fields on the microstructure of polypropylene (PP)/clay and PP/nano-$CaCO_3$ nanocomposites using an industrial-scale twin screw extruder. Artzi et al. [5–7] improved the intercalation and exfoliation of nano-clay in EVOH matrix by dynamic melt mixing [5], and investigated the effect of extrusion processing conditions on the morphology and thermal and mechanical properties of the EVOH/clay nanocomposites [6], and they also concluded that compatibilizer could help the clay exfoliate [7].

Supercritical carbon dioxide ($ScCO_2$) has characteristics such as gas-like diffusivity and viscosity, and liquid-like density, better flow performance, dissolution, mass and heat transfer. In particular, it is used in a wide range of applications due to environmentally benign and lower critical point (31.1℃, 7.38 MPa), relatively low cost, nontoxic, and nonflammablity compared to other supercritical fluids [8]. Several works were reported that $ScCO_2$ has a positive effect on the dispersion or intercalation/exfoliation of nano-fillers in polymer matrix which includes PP [8], high-density polyethylene (HDPE) [9]. But little work has been reported on the EVOH/clay nanocomposites prepared with CO_2.

In this study, an industrial-scale twin screw extruder was used for the development of continuous manufacturing process of PP/nano-$CaCO_3$ and EVOH/clay nanocomposites. $ScCO_2$ was introduced to enhance the dispersion or intercalation/exfoliation of nano-fillers in polymer matrix. The effect of

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$ScCO_2$ at different concentration on the microstructure of the nanocomposites was investigated.

Experimental

Materials

In this work, the PP used was grade J501 (Sinopec Group Guangzhou Co.) with a melt index of 2.7 g $(10min)^{-1}$ at 230℃. This PP is a fiber extrusion grade resin. The EVOH (consisting of 32 mol% ethylene), grade EVAL F101A was supplied by Kuraray America. The nano-$CaCO_3$ was manufactured and pretreated by Inner Mongolia Mengxi High-Tech Materials Co. Ltd. Organically treated clay, Cloisite 30B (Southern Clay Products, Inc), was treated with a surfactant (MT2EtOH) to result in a $d_{(001)}$ of 1.85 nm. Industrial carbon dioxide was used with purity of 99.5%. The materials except PP were dried under vacuum at 100℃ for 12 hours before use.

Experimental Equipment and Sample Preparation

The experimental equipment is schematically shown in Figure 1. The equipment mainly included a co-rotating twin screw extruder (TSE 35, 35 mm diameter) and a CO_2 injection system.

The screw configuration is shown in Figure 2. The screw was arranged in a combination of conveying, shearing, mixing, and reversing elements. The polymer/CO_2 solutions can only be obtained at pressures above the solubility pressure. Therefore, the screw configurations were combined to generate the required pressure. There were four reverse conveying elements inserted to elevate the pressure in the barrel and to increase the residence time of melts. From the injection port to the vent port, kneading and mixing elements were added to improve the mixing efficiency. At the same time, these kneading and reversing elements would help to generate melt seals and prevent CO_2 from leaking.

The CO_2 injection system consisted of a CO_2 cylinder, syringe pump (model 500D from ISCO, Inc), and back pressure regulator.

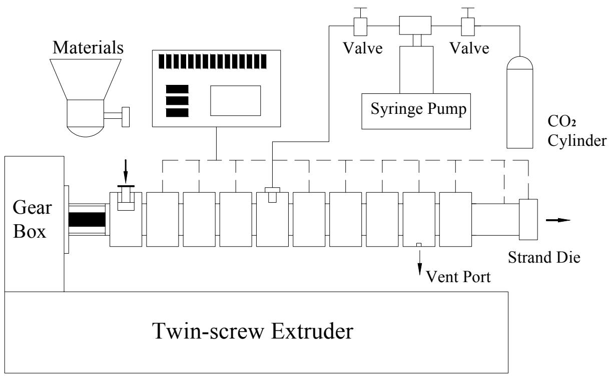

Figure 1. Schematic of Twin-screw Extruder and High Pressure Syringe Pump

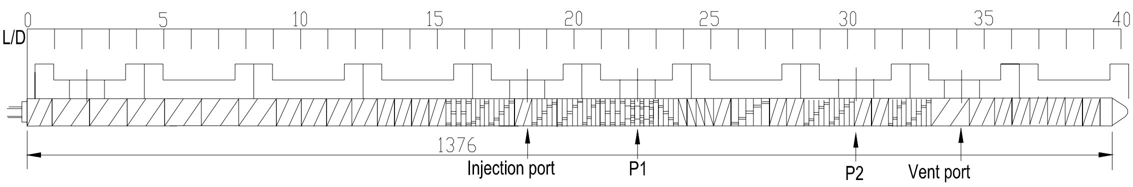

Figure 2. Schematic of Screw Configuration

The temperature profile of ten zones increased from 190℃ at the feed zone to 200℃ at the strand die. The screw speed was set at 100 rpm. The feed rate was set at 10 kg/h. Syringe pump was set to have CO_2 gas flow with a constant flow rate. Using the screw configuration shown in Figure 2 and setting the flow rate of CO_2 at 20 mL/min or 40 mL/min, the injection pressure of gas could be kept with the range of 7.5 MPa to 10MPa.

Extruded strands were pelletized for characterization.

Characterization

Rheological Properties

Bohlin Gemini 200 Rheometer with a parallel-plate fixture (25 mm diameter) was used in an oscillatory mode to conduct dynamic frequency sweep measurements of the nanocomposites. Dynamic complex viscosity (η^*) and the storage and loss moduli (G' and G'') as functions of angular frequency ω ranging from 0.01 to 100 rad/s were measured at 200°C.

X-ray Diffraction (XRD)

X-ray diffractometer (XRD) was used to analyze the intercalation/exfoliation of nano-clay in nanocomposites. The X-ray diffraction were performed using Japan Rigaku D/max-IIIA at room temperature. In order to measure the $d_{(001)}$-spacing between silicate layers, samples were scanned in 2θ ranges of 1.0 to 10^o at a rate of 1^o/min. The radiation was operated at 40kV and 40mA.

Transmission Electron Microscope (TEM)

Microstructure images of nanocomposites at high magnifications were taken on a Philips CM300 TEM for the study of the nano-fillers distribution.

Results and Discussion

Figure 3 shows the XRD patterns for EVOH/clay nanocomposites prepared with 3 wt% CO_2 and without CO_2. The (001) peak of nanocomposites prepared without CO_2 was observed at $2\theta \approx 2.60^o$ ($d_{(001)}$=3.4 nm), while the peak of the nanocomposites prepared with 3 wt% CO_2 was observed at $2\theta \approx 2.45^o$ ($d_{(001)}$=3.6 nm).

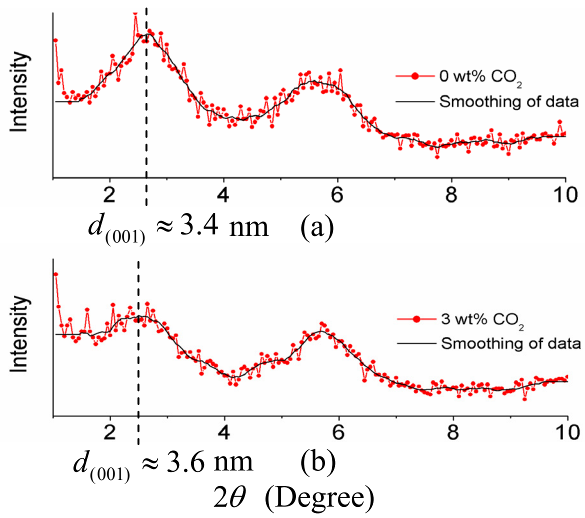

Figure 3. XRD Patterns for EVOH/clay Nanocomposites Prepared (a) without and (b) with 3 wt% CO_2

The increase in *d*-spacing for the EVOH/clay nanocomposites compared to pure clay ($d_{(001)}$=1.85 nm) shows that the clay layers have expanded because of intercalation of EVOH chains into the gallery spaces. The (001) peak of nanocomposites prepared with 3 wt% CO_2 is wider and lower than that without CO_2, which suggests that the layered silicates became more disordered [10] and more ilicate layers were exfoliated from the clay stacks [11].

The other results about the morphologies and rheological properties of PP/nano-$CaCO_3$ and EVOH/clay nanocomposites will be presented at the podium presentation.

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