

Supercritical CO₂-Enhanced Clay Dispersion in Melt-mixing of Poly (ethylene-co-vinyl alcohol) Nanocomposite

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ABSTRACT

The poly (ethylene-co-vinyl alcohol) (EVOH)/clay nanocomposite (ECN) were prepared using a twin screw extruder with the aid of the supercritical carbon dioxide (Sc-CO₂). X-ray diffraction (XRD) and transmission electron microscopy (TEM) were used to characterize the dispersion of clay in the EVOH matrix. The XRD results demonstrated that for the ECN sample prepared with Sc-CO₂, there is a decrease in intensity and a broadening of the characteristic (001) diffraction peak to a certain extent. The TEM micrographs clearly show that better clay dispersion and thinner silicate layers can be observed in the ECN sample prepared with Sc-CO₂.

Keywords: polymer nanocomposite, poly (ethylene-co-vinyl alcohol), supercritical carbon dioxide, melt-mixing

1 INTRODUCTION

The poly (ethylene-co-vinyl alcohol) copolymers are widely used in the food-packaging industry due to their excellent barrier properties to oxygen and organic compounds (solvents and food aromas) as well as considerable chemical resistance and high transparency [1]. The major drawback of EVOH copolymers is their moisture sensitivity that causes a significant decrease in their barrier properties at high relative humidities. It has already been proved that the EVOH/nanoclay nanocomposites (ECNs) can present enhanced barrier properties mainly due to a tortuosity driven decreased in molecular diffusion of gases and vapors and in increased thermal resistance [2]. But the degree of barrier property improvement is strongly dependent on the clay content, especially its dispersion in the EVOH matrix. Appropriately higher clay content with good clay dispersion is commonly preferred. However, aggregated nanolayer tactoids normally exist in higher clay content EVOH nanocomposites [3].

Supercritical carbon dioxide (Sc-CO₂) has characteristics such as gas-like diffusivity and viscosity, liquid-like density, and lower critical point (critical temperature of 31.8°C, critical pressure of 7.38 MPa). Sc-CO₂ as a kind of green solvent offers many advantages compared with other solvents. So, great deal of attention has been given to the polymer processing with the aid of Sc-CO₂, such as the melt-mixing of polymer blends [4,5]

and polymer-based nanocomposites [6–10]. Direct injection of Sc-CO₂ into a molten polymer nanocomposite during melt-mixing was proved to be useful for the expansion of the clay intergallery and the promotion of polymer intercalation. Garcia-Leiner et al. [6,7] prepared polyethylene (PE)/clay nanocomposites in a single screw extruder with a modified hopper equipped with a Sc-CO₂ injection pump. Their results showed a 40–100% increase in basal spacing of clay with the aid of Sc-CO₂. Han et al. [8] employed two time extrusion process to prepare the polypropylene (PP)/clay nanocomposites with the aid of Sc-CO₂, and found that 2 wt% is the best concentration for Sc-CO₂ to promote the dispersion of clay. Nguyen et al. [9] used Sc-CO₂ to assist the extrusion of high density PE/clay nanocomposites, and found that the Young module and tensile strength of nanocomposites prepared with the aid of Sc-CO₂ are increased. Very recently, the authors [10] prepared PP/clay nanocomposites using a twin screw extruder with the aid of Sc-CO₂. It was demonstrated that the Sc-CO₂ with a concentration not higher than 4 wt% is helpful to promote the degree of dispersion of the nanoclay in PP matrix, but overloading of Sc-CO₂ would have a negative effect on the clay dispersion. To the best knowledge of the authors, no research paper has ever reported the Sc-CO₂-assisted melt-mixing of ECNs.

For the aforementioned reasons, in this work, the preparation of ECNs was conducted on an industrial twin screw extruder with the aid of Sc-CO₂ to improve the clay dispersion.

2 EXPERIMENTAL

2.1 Materials and equipment

The EVOH used was grade EVAL F101A manufactured by Kuraray (Japan). It consisted of 32 mol% ethylene and had a melt index of 3.8 g/10 min (210°C, 2.16 kg). The organically treated clay, Cloisite 30B, was supplied by Southern Clay Products (USA). The nanoclay had the basal spacing of 1.85 nm. Industrial carbon dioxide was used with purity of 99.5%.

The experimental equipment is schematically shown in Fig. 1. The equipment mainly included a co-rotating twin screw extruder (35 mm diameter, 40 length-to-diameter ratio) and a CO₂ injection system. The metered CO₂

injection system had a cylinder, a positive displacement syringe pump (500D, ISCO), and back pressure regulators.

The extruder screw was arranged with conveying, kneading, mixing, and reverse conveying elements. The polymer/CO₂ solution can only be obtained at pressures above the solubility pressure of CO₂, so the screw configuration was arranged to generate the required pressure. There were 6 reverse conveying elements inserted to elevate the pressure in the barrel. Between the CO₂ injection port and the CO₂ vent port, kneading and mixing elements were added to improve the mixing efficiency. At the same time, these kneading and reverse conveying elements helped to generate melt seal and prevent CO₂ from leaking. During the experiments, the pressure in the cylinder was kept above 8 MPa.

2.2 Experimental Procedure and Sample Preparation

The EVOH and clay were dried under vacuum at 100°C for 12 h before use. A mixture of 95 wt% EVOH and 5 wt% clay was fed to the hopper. The mixing was carried out at a feed rate of 5.5 kg/h, a screw speed of 100 rpm, and the temperature profiles of 30-80-160-180-180-160-180-180-180°C from the hopper to the pelletizing die. The Sc-CO₂ was injected into the extruder at a position about 22 times the screw diameter (D) from the hopper. The CO₂ in the syringe pump was compressed to 20 MPa. At a position of about 34D from the hopper, CO₂ in the molten nanocomposite was vented by a vacuum pump. The extruded nanocomposite strand was then pelletized after solidification in a water bath. Finally, the pellets were dried overnight at 80°C prior to preparing samples for rheological tests and microstructure characterization.

2.3 Characterization

X-ray diffractometer was used to measure the basal spacing between silicate layers in nanocomposites. The X-ray Diffraction (XRD) was performed using a Japan Rigaku D/max-III A diffractometer at room temperature. The samples were scanned in 2θ ranges of 2 to 10° at a rate of 1°/min. The generator was operated at 40 kV and 30 mA. The samples with the thickness of about 0.15 mm were prepared by compression molding the ECN pellets.

Ultra-thin films with about 100 nm in thickness were cut from the samples by an ultramicrotome. The ultra-thin films were then examined by transmission electron microscopy (TEM, Jeol JEM-100CX II) operated at an accelerating voltage of 100 kV to observe the dispersion of the nanoclay in the EVOH matrix.

3 RESULTS AND DISCUSSION

The XRD patterns for the prepared ECNs are shown in Fig. 2, where ECN0 and ECN3 represent the samples prepared at a CO₂ concentration of 0 and 3 wt% of the feed rate of the EVOH/clay mixture, respectively. The XRD curve of ECN0 sample exhibits an obvious characteristic (001) diffraction peak with the corresponding 2θ angle at 2.8°, and the basal spacing of clay calculated by Bragg equation is 3.15 nm. Whereas for ECN3 sample, there is a decrease in intensity and a broadening of the characteristic (001) diffraction peak to a certain extent.

The TEM micrographs of ECNs prepared without and with 3 wt% CO₂ are presented in Fig. 3(a) and (b), respectively. The dark lines in the micrographs represent the stacked silicate layers in the EVOH matrix. Fig. 3 demonstrates that the clay in ECN3 sample is more randomly dispersed in the matrix than that in ECN0 sample. Thinner silicate layers can be seen in ECN3 sample, whereas the clay in ECN0 sample exists as large aggregates and is unable to undergo exfoliation. The above observation is consistent with that observed from the XRD patterns shown in Fig. 2.

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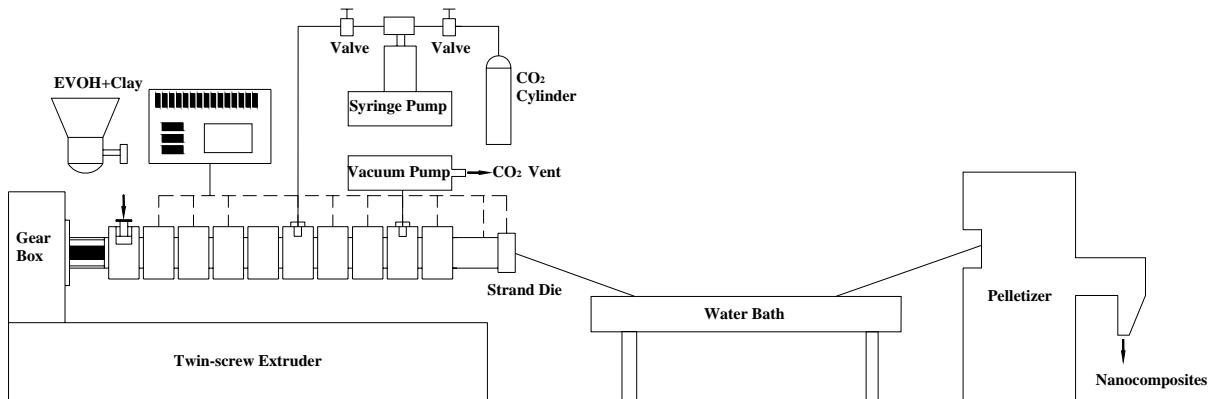


Figure 1: Schematic of Sc-CO₂ assisted extrusion setup for preparing the ECNs.

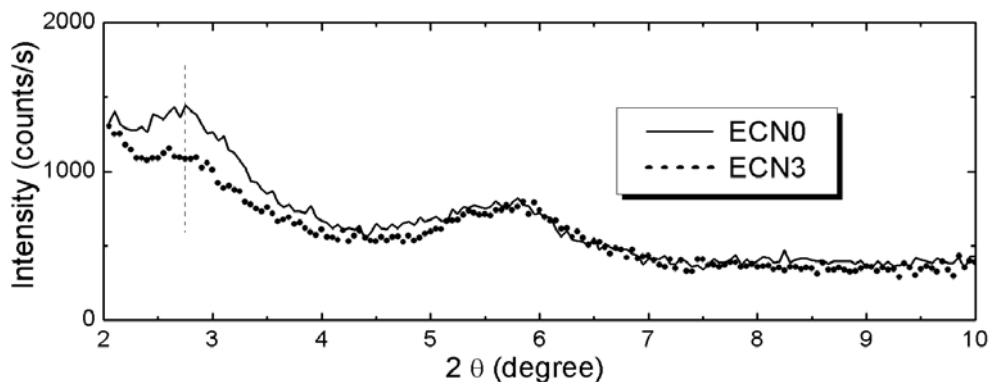


Figure 2: XRD patterns for ECNs prepared without and with 3 wt% Sc-CO₂.

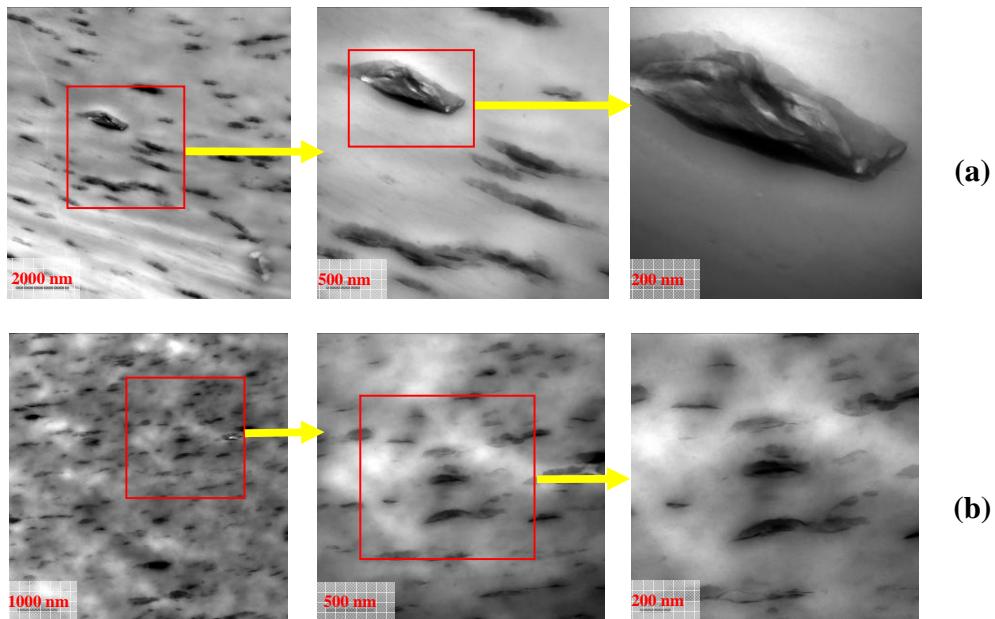


Figure 3: TEM images for ECNs prepared (a) without and (b) with 3 wt% Sc-CO₂ with different magnifications.