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Material Properties

Dynamic rheology and microstructure of polypropylene/clay nanocomposites prepared under Sc-CO_2 by melt compounding

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Abstract

Polypropylene (PP)/clay nanocomposites were prepared using a twin-screw extruder with the aid of supercritical carbon dioxide (Sc-CO_2). The dynamic rheological properties were measured using a rheometer in the oscillatory mode. X-ray diffraction and transmission electron microscopy were used to characterize the microstructure of extruded nanocomposites. Results showed that an optimized CO_2 concentration existed. When the CO_2 concentration increased up to the optimized level, the nanocomposites tended to be more viscous, especially at low frequency, whereas further increasing the CO_2 concentration resulted in a decrease in the complex viscosity and dynamic moduli. The presence of Sc-CO_2 with a concentration not higher than the optimized level was helpful to promote the degree of dispersion of the nanoclay in PP matrix, but overloading of CO_2 would have a negative effect on the clay dispersion.

Keywords: Polymer nanocomposite; Supercritical carbon dioxide; Melt compounding

1. Introduction

Polymer/clay nanocomposites (PCNs) have been the subject of intensive research in recent years. Typically, PCNs are prepared via in-situ intercalative, sol-gel methods or a direct melt-intercalation approach such as melt extrusion [1–4]. No matter which method is used, the extent of dispersion of clay in the polymer is mainly decided by the interfacial interaction between the polymer matrix and the clay.

In the preparation of polypropylene (PP)/clay nanocomposite (PPCN) by melt-intercalation, PP has an unfavorable interaction with the clay because PP does not include any polar group in its backbone, and silicate layers even modified by non-polar alkyl groups are incompatible with PP. So, some chemical methods such as using compatibilizers are frequently used to promote the nanoclay dispersion [5–7]. However, the addition of the compatibilizers results in lower mechanical properties of the final composite [7].

Recently, a great deal of attention has been given to the preparation of nanocomposites with the aid of supercritical carbon dioxide (Sc-CO_2) to expand the clay intergallery and promote polymer intercalation. Sc-CO_2 as a kind of green solvent offers many advantages compared with other solvents. Direct injection of Sc-CO_2 into a molten

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nanocomposite during melt blending was proved to be useful for the dispersion of clay. Treece et al. [8] used a single-screw extruder to prepare PPCNs and found that Sc-CO_2 was useful to improve the clay dispersion. Garcia-Leiner et al. [9,10] used polyethylene and clay to prepare nanocomposite in a single-screw extruder with a modified hopper equipped with a Sc-CO_2 injection pump. Their results showed a 40–100% increase in basal spacing of clay with the aid of Sc-CO_2. Han et al. [11] employed a two-time extrusion process to prepare the PP/clay nanocomposites with the aid of Sc-CO_2, and found that 2 wt% is the best concentration for Sc-CO_2 to promote the dispersion of clay.

However, some researchers found that using Sc-CO_2 did not improve the clay dispersion. Yang et al. [12] found a negative effect of Sc-CO_2 on the clay dispersion for nylon 6/clay nanocomposites. They thought that, with the addition of supercritical fluids, the free volume of polymer melt increased and the melt viscosity decreased, which meant that interaction between the molecule chains decreased. These factors did not contribute towards improving clay dispersion.

In consideration of the aforementioned contrary results, the objectives of this work are to demonstrate the effect of Sc-CO_2 on the clay dispersion and further investigate the relationship between the concentration of Sc-CO_2 and the final microstructure of PPCNs. An industrial-scale twin-screw extruder (TSE) was used for the continuous extrusion of PPCNs with the Sc-CO_2 injected into the barrel. The prepared PPCN pellets were then compression molded into samples to be used for characterization.

2. Experimental

2.1. Materials and equipment

The PP used was grade J501 (fiber extrusion grade) with a melt index of 2.7 g/10 min (230 °C, 2.16 kg), manufactured by Sinopec Group Guangzhou Co. The organically treated clay used was a commercial product of Nanocor USA, octadecyl amine modified Nanocor I30P, having particle size within a range 16–20 μm and basal spacing of 2.1 nm. Industrial carbon dioxide was used with purity of 99.5%. The clay was dried under vacuum at 80 °C for 12 h before use.

The experimental equipment is schematically shown in Fig. 1. The equipment mainly included a co-rotating TSE (35 mm diameter, 40 length-to-diameter ratio) and a CO_2 injection system. The metered CO_2 injection system had a cylinder, a positive displacement syringe pump (500D, ISCO) and back pressure regulators.

The melt and Sc-CO_2 were mixed using a screw configuration as shown in Fig. 2. The screw was arranged with conveying, kneading, mixing, and reverse conveying elements. The polymer/CO_2 solution can only be obtained at pressures above the solubility pressure of CO_2, so the screw configuration was arranged to generate the required pressure. There were six reverse conveying elements inserted to elevate the pressure in the barrel. Between the CO_2 injection port and the CO_2 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 CO_2 from leaking. During the

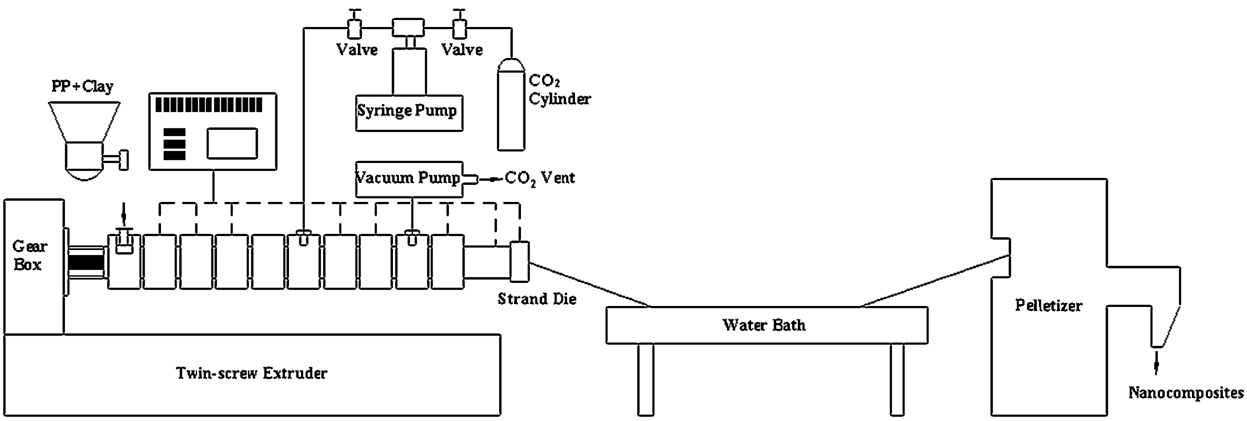

Fig. 1. Schematic of the extrusion process to prepare the PPCNs using Sc-CO_2.