SHORT COMMUNICATION

Preparation and Rheological Characteristics of Poly(ε-caprolactone)/Organoclay Nanocomposites

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Received March 18, 2005; Accepted August 2, 2005

Abstract: Poly(ε-caprolactone) (PCL)/organoclay nanocomposites were prepared using a solvent casting method, and then the effects that the organoclay content has on nanoscopic internal structure and rheological properties of the PCL/organoclay nanocomposites were investigated. From an XRD diffractogram, we could confirm the increased interlayer spacing in OMMT that was due to insertion of the polymer chain. This intercalated structure was further analyzed using rheometry; the remarkable increases in the shear viscosity (η) and elasticity (G′) over a critical clay concentration suggest the formation of a solid-like structure. This solid-like structure was also verified by both the Cox-Merz rule and the Carreau model.

Keywords: poly(ε-caprolactone), organoclay, nanocomposite, rheology, solid-like structure

Introduction

Poly(ε-caprolactone) (PCL), a biodegradable polymer derived from the chemical synthesis of crude oil, is a linear aliphatic polyester possessing a low melting temperature (60 °C) and a relatively low shear viscosity, which makes it easy to process. Its hydrolytic and enzymatic degradation along polymer chains makes it of use in various fields, including the preparation of biodegradable packaging materials and mechanical applications. The resistance of PCL toward water, oil, solvent, and chlorine is also of merit [1]. However, the poor mechanical properties of PCL limit its potential applications. To resolve this drawback, PCL is used widely in nanostructured polymer/clay nanocomposite systems because polymer nanocomposites in general exhibit synergistic improvements in both of its components and display enhanced physical, electrical, and mechanical properties [2-11]. Accordingly, clay-reinforced PCL nanocomposites have been studied using various preparation methods, including solvent casting [12], in situ polymerization [13,14], and melt intercalation methods [15,16]. Because PCL readily forms homogeneous blends with various polymers, it has been found that a polymer lacking the tendency to exfoliate layered silicates can be blended with prepared PCL/clay nanocomposites [17]. A typical example is that of PCL/clay nanocomposite in styrene-acrylonitrile copolymer (SAN) [1].

In an effort to develop environmentally benign materials having superior mechanical properties, we applied the concept of preparing polymer/organoclay nanocomposites with PCL through solvent casting. We confirmed systematically the characteristics of the nanocomposites, such as their nanoscopic internal structures and rheological behaviors, utilizing wide-angle X-ray diffraction (WAXD) and a rotational rheometer, respectively. Specifically, from the rheological measurements, we found a remarkable increase in the shear viscosity and elasticity occurred over a critical clay concentration, which implies the formation of a physical network.

Experimental

PCL was purchased from Aldrich (Mw = 80000 g/mol; Tg = -55 °C; Tm = 60 °C). The clay used was a montmorillonite modified with quaternary ammonium ions (Cloisite 25A, Southern Clay Products). PCL/Clay nanocomposites were prepared through the solvent casting method...
using chloroform as a co-solvent and clay weight percentages of 0, 1.5, 3.0, and 4.5 wt%. Prior to use, both the PCL and clay samples were dried in a vacuum oven to remove moisture. The PCL and clay samples were dissolved and dispersed, separately, in chloroform (500 mL) at 25 °C using a magnetic stirrer for 1 day. After mixing the PCL solution and clay dispersion, the mixture was stirred for 2 days. The co-solvent was first evaporated in a hood and then the sample was dried in a vacuum oven for 1 day to complete the solvent removal. Disk-type pellets of these nanocomposites were prepared for rheological measurements using a hot press at 120 °C. The sample codes PCL, PCL1.5, PCL3.0, and PCL4.5 reflect the weight ratios of PCL and clay (100/0, 98.5/1.5, 97/3, and 95.5/4.5, respectively).

The intercalated state of the polymer chains in the nanocomposites was examined by means of WAXD. WAXD patterns were obtained using a Philips X-ray unit (PW-1847). The experiment was performed at 40 kV and 50 mA in the range of 2θ from 1.5° to 10° at a scan rate of 3°/min [18,19]. To measure the rheological properties, we used a rotational rheometer (Physica, MCR 300, Germany) equipped with a parallel plate (25-mm diameter) [20]. Rheological measurements were conducted in the gap distance of 1 mm in a melt state at 140 °C. The steady shear viscosity was measured in the range from 0.02 to 2 s⁻¹. Dynamic tests were examined in the region of angular frequency from 0.1 to 628 s⁻¹ at 1 % strain; they satisfied a linear viscoelasticity.

**Results and Discussion**

Figure 1 displays WAXD patterns of the PCL/clay nanocomposites. We estimated the variation of the (001) d-spacing, which was obtained from the observed peaks of the angular position (2θ) according to the Bragg formula (nλ = 2dsinθ) [21]. The d-spacings of clay were estimated to increase from 1.89 nm for Cloisite 25A to 2.69 nm for the PCL/clay nanocomposites. Such a change in d-spacing indicates that the PCL chains were intercalated into the clay interlayers. Maximum peak intensities of all the nanocomposites appeared at the same angular position. This result indicates that the d-spacings of the PCL/clay nanocomposites are independent of the clay loading. Similar behavior has been reported for other systems, i.e., variations only in the relative peak intensities [22,23].

The steady shear viscosities of the nanocomposites, measured using a rotational rheometer having a parallel plate geometry, increased with the clay content, following a shear thinning behavior. It is remarkable that a steep slope appeared for the viscosity at a clay content of 4.5 wt% [24]. Such a property can be quantified with the power law index, n, which is a parameter of the following Carreau model, where η is the zero shear viscosity and τ is the characteristic time [25]:

$$\eta = \frac{\eta_0}{[1 + (\dot{\gamma} \tau)^2]^{\frac{1-n}{2}}}$$  \hspace{1cm} (1)

With clay contents of 0, 1.5, 3.0, and 4.5 wt%, the power law index varied to be 0.95, 0.91, 0.89, and 0.78, respectively. As shown in Figure 2, the dramatic change in the value of n from 3.0 to 4.5 wt% is indicative of the formation of a solid-like structure over a critical clay content [26].

$$\eta(\dot{\gamma}) \approx \eta^*(\omega) \approx \sqrt{\eta''(\omega) + \eta''''(\omega)}$$  \hspace{1cm} (2)

In addition to the static mode, we measured the complex viscosity in the dynamic mode, we allowed us to predict the shear viscosity at a very high shear rate, even using a rotational rheometer [27]. This approach is based...
on an empirical relationship called the ‘Cox-Merz rule’ [Eq. (2)], which is very useful because the measurement of steady shear viscosity at high shear rates is rather difficult not only because of the instability of the sample but also the measurement limits of the rheometer. This relationship has been well adopted in various homogeneous systems. If nonhomogeneity occurs in the nanocomposite system upon the addition of clay, the two viscosity curves obtained from both steady shear and dynamic tests will deviate from each other. As shown in Figure 3, the deviation of the two curves increased upon the addition of clay. Specifically, the degree of deviation became significant at a clay content of 4.5 wt%, and seemed to be due to the formation of a solid-like structure, as mentioned above.

The storage moduli (G'), an index of elasticity, were also plotted as a function of angular frequency [28,29]. From these oscillatory measurements, we can confirm that a remarkable increase of storage modulus occurred at clay contents between 3.0 and 4.5 wt%. When compared with the value of G' of the pristine PCL, the value of G' of PCL4.5 exhibits a weak frequency dependence, indicating a dramatic change in the viscoelastic behavior from liquid-like to solid-like (see Figure 4). This dramatic solid-like transition can be explained in conjunction with the formation of a solid-like structure above any critical clay content.

Conclusions

We investigated the morphological and rheological properties of PCL/organoclay nanocomposites prepared using a solvent casting method. From XRD investigations, we confirmed that the increase in the interlayer spacing in OMMT was due to the insertion of the polymer chain. This intercalated structure was further analyzed using rheometry. Remarkable changes occurred in both static and dynamic modes at clay contents between 3.0 and 4.5 wt% in the rheological measurements, which were interpreted in conjunction with the formation of solid-like structures.

Acknowledgment

This work was supported by the Korea Science and Engineering Foundation (KOSEF) through the ARC at Korea University.

References