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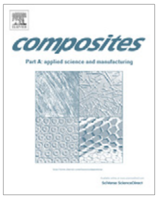

Isothermal crystallization behavior and mechanical properties of polylactide/carbon nanotube nanocomposites

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ABSTRACT

Carbon nanotube (CNT)–reinforced polylactide (PLA) nanocomposites were prepared using a melt compounding process employing a twin-screw extruder. The isothermal crystallization kinetics of PLA/CNT nanocomposites according to Avrami's theory were analyzed using differential scanning calorimetry in the temperature range 90–120 °C. There was a significant dependence of CNT on the crystallization behavior of the PLA matrix. The incorporation of CNT improved effectively the crystallization rate of PLA/CNT nanocomposites through heterogeneous nucleation. The nucleating effect of CNTs which increased the number of nucleation sites and decreased the average spherulite size was confirmed using polarized optical microscopy. The rheological properties of the PLA/CNT nanocomposites were also investigated. Changes in the microstructure of the PLA/CNT nanocomposites occurred by incorporating CNT. Furthermore, the tensile strength/modulus and thermal stability of PLA/CNT nanocomposites were enhanced when a very small quantity of CNT was added. This research accounts for the effect of CNTs, which significantly influenced the isothermal behavior, thermal stability, mechanical, and rheological properties of the PLA/CNT nanocomposites, providing a design guide for PLA/CNT nanocomposites in industrial fields.

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1. Introduction

Biomass-derived polylactide (PLA) has received much attention and is expected to replace petroleum-based commodity polymers, because it is biodegradable [1,2] and biocompatible [3,4]. PLA produced by the ring-opening polymerization of lactide is linear aliphatic thermoplastic polyester and shows outstanding performance, such as in its mechanical and molding properties. Although PLA is a very promising material in the field of eco-friendly biocomposites, it has an extremely slow crystallization rate and this presents a drawback for its application as a biomedical and packing material. This problem provides a shortcoming for the industrialization of PLA composites, where thermoplastics are employed [2,5]. In this research, nanofillers were incorporated into a PLA matrix to improve the crystallization rate and mechanical properties.

Among the various nanofillers available, such as silica, talc, clay, and carbon nanotubes (CNTs), CNTs are regarded as promising nanofiller in polymer nanocomposites owing to their excellent properties, such as high mechanical strength and electrical and thermal conductivity, along with a high aspect ratio and small size [6–9]. As a consequence, there has been considerable effort to develop advanced performance polymer nanocomposites based on CNTs for application in a wide range of industrial fields [10]. However, because of their high cost, there have been only a few applications of CNTs in industrial fields. Therefore, the fabrication of polymer nanocomposites reinforced by CNTs requires a cheap manufacturing process. There are some processing techniques in common use that can be used to incorporate inorganic nanoparticles into a polymeric matrix to fabricate polymer nanocomposites, such as solution mixing or film casting, *in situ* polymerization, and melt compounding [11–13]. Of these processing techniques, melt compounding is accepted as the most simple and effective technique, because it is economic from an industrial perspective to fabricate advanced nanocomposites at low cost. Furthermore, the incorporation of CNTs into a polymer matrix using a melt compounding process may improve the mechanical properties and thermal stability of the polymer nanocomposites with a low manufacturing cost [14]. Despite these advantages, few reports of PLA/CNT nanocomposites prepared by the melt compounding process are available in the literature. The rheological behavior of polymer nanocomposites is very important for the analysis and design of processing operations as a function of processing conditions, as well as helping to gain an understanding of the structure–property relationships of nanocomposites. Therefore, the rheological properties of CNT-reinforced biodegradable

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polymer nanocomposites should be investigated to optimize the processing conditions to obtain high-performance polymer nanocomposites. However, the rheological behavior of CNT-reinforced biocomposites has not been widely studied.

In this research, PLA nanocomposites reinforced by a small quantity of CNTs were prepared by a melt compounding as a low cost method for possible application in industry. The isothermal crystallization analysis of the PLA/CNT nanocomposites was investigated, and the effect of the CNTs on the thermal stability, the mechanical properties, and rheological properties of the PLA/CNT nanocomposites is discussed.

2. Experimental

2.1. Materials and preparation

The PLA used was purchased from Cargill-Dow Inc. (Natureworks PLA 4032D grade). The number-average molecular weight and density of the PLA were 52,000 g/mol and 1.25 g/cm^3, respectively. The CNTs used as a reinforcement were MWCNT (degree of purity >95%) and synthesized using a thermal chemical vapor deposition process, and were purchased from Iljin Nanotech, Korea. The diameter of MWCNT was 10–40 nm and length was 10–50 μm, implying that aspect ratio of MWCNT was 1000. All the materials were dried at 40 °C *in vacuo* for at least 8 h before use to minimize the effect of moisture. The PLA/CNT nanocomposites were prepared using a melt compounding process employing a Haake rheometer (Haake Technik GmbH, Germany) equipped with a twin-screw extruder. The temperature of the heated zone from the hopper to the die was set to 185, 190, 195, and 185 °C with a constant rotation speed of 20 rpm. To fabricate the PLA/CNT nanocomposites, PLA was melt compounded with the addition of various CNT contents, specified as 0.02, 0.05, 0.1, and 0.2 wt.% in the polymer matrix.

2.2. Characterization

The thermal behavior of the PLA/CNT nanocomposites was measured using a PerkinElmer DSC7 over the temperature range 30–200 °C at a heating rate of 10 °C/min and maintained at 200 °C for 10 min to eliminate any previous thermal history. In the isothermal crystallization experiments, the PLA/CNT nanocomposites were quenched to a controlled isothermal crystallization temperature, T_c (from 90 to 120 °C), and maintained for 60 min. The samples were then heated to 200 °C at a heating rate of 10 °C/min. The rheological properties of the PLA/CNT nanocomposites were measured using an Advanced Rheometric Expansion System (Rheometric Scientific Co.) in the oscillation mode with a parallel-plate geometry using a plate diameter of 25 mm and a gap setting of 1 mm at 190 °C, applying a time-dependent strain, $\gamma(t) = \gamma_0 \sin(\omega t)$, and a measuring resultant shear stress, $\gamma(t) = \gamma_0 [G' \sin(\omega t) + G' \cos(\omega t)]$, where G' and G'' are the storage and loss moduli, respectively. The frequency range varied between 0.05 and 500 rad/s. The morphology of the PLA/CNT nanocomposites was investigated using a Jeol 2000FX transmission electron microscope (TEM), and thermogravimetric analysis (TGA) of the PLA/CNT nanocomposites was performed using a PerkinElmer Pyris 1 thermogravimetric analyzer over the temperature range 30–800 °C under a nitrogen atmosphere at a heating rate of 10 °C/min. The PLA/CNT nanocomposites films were prepared by using compression molding machine from pellet-type samples after melt compound process. After film preparation, amorphous films were quenched in ice water and then held in compression molding machine at 110 °C for 20 min. After these treatments, the mechanical properties of the PLA/CNT nanocomposites were measured using an Instron 4465 testing machine at room temperature, according to the procedures in the ASTM D 638 standard. The width and thickness of specimen for mechanical testing were 10 mm and 0.4 ± 0.03 mm, respectively. The grip distance for mechanical testing was 25 mm. The gauge length was set to 20 mm and the crosshead speed was set to 5 mm/min. The spherulite morphologies were observed using a polarized optical microscope (POM, Olympus BX-51 TX) equipped with a CCD camera to investigate the morphology of the nucleation density and spherulite size with both time and temperature. Before observation of spherulite morphologies, about 3 mg samples were placed between two glass coverslips and melted on a hot plate at 200 °C for 2 min and then the samples were quickly transferred to FP82HT hot stage (Mettler-Toledo, Columbus, OH) and held at 110 °C for 10 min.

Table 1
Thermal behavior of PLA/CNT nanocomposites with various CNT content.

Material	T_g (°C)	T_{cc} [a] (°C)	T_m (°C)	T_{mc} [b] (°C)	ΔT [c]
PLA	67.2	109.6	168.8	115.4	53.4
PLA/CNT 0.02	67.1	99.2	169.1	121.1	48.0
PLA/CNT 0.05	67.1	98.3	168.7	121.4	47.3
PLA/CNT 0.1	67.4	97.5	168.9	122.1	46.8
PLA/CNT 0.2	67.3	96.3	168.7	123.6	45.1

[a] Cold crystallization temperature measured from DSC heating traces at 10 °C/min.

[b] Melt crystallization temperature measured from DSC cooling traces at 10 °C/min.

[c] Degree of supercooling, $\Delta T = T_m - T_{mc}$.

3. Results and discussion

3.1. Thermal behavior

The thermal behavior of the PLA/CNT nanocomposites for various CNT content is shown in Table 1. There was a low effect of CNTs on the glass transition temperature (T_g) and the melting temperature (T_m) of the PLA/CNT nanocomposites. The cold crystallization temperature (T_{cc}) of the PLA/CNT nanocomposites measured from the heating traces decreased, and the melt crystallization temperature (T_{mc}) increased with increasing CNT content. From these results, the degree of supercooling ($\Delta T = T_m - T_{mc}$) was investigated, and the value of ΔT of the PLA/CNT nanocomposites decreased with increasing CNT content, suggesting that CNT as a nucleating agents in the PLA/CNT nanocomposites had an influence on these properties. The inducement of a heterogeneous nucleation was caused by the CNTs, and lower energy consumption was required to reach the critical stability value for crystal growth [15].

3.2. Morphology

The effect of the CNTs on the spherulitic growth behavior of the PLA matrix was investigated using POM after all the samples had been held at 110 °C for 10 min. The POM images of PLA/CNT nanocomposites were shown in Fig. 1 and these photographs were obtained using a tint-color[1] plate with the optical retardation of 530 nm. As shown in Fig. 1, the neat PLA matrix exhibited morphology with large spherulites, whereas the size of the PLA spherulites decreased significantly with increasing CNT content in the PLA/CNT nanocomposites. In addition, the number of crystallization sites increased with CNT content. This observation indicates that CNTs acted as heterogeneous nucleating agents, assisting the crystallization of the PLA matrix [16]. This observation is very

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[1] For interpretation of color in Fig. 1, the reader is referred to the web version of this article.

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