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Effect of reinforcing particles on hydrolytic degradation behavior of poly (lactic acid) composites

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ABSTRACT

In this study, degradation behavior of polylactic acid (PLA) composite reinforced with different types of particles (titanium dioxide, multi-walled carbon nanotubes, surface-treated multi-walled carbon nanotubes, and graphene nanoplatelets) were investigated. Samples were prepared by extrusion and injection molding. Hydrolytic degradation was induced by immersing the specimen in a sodium hydroxide solution. Particles can affect the crystallization kinetics of PLA matrix which may affect the degradation behavior. In order to examine the crystallization kinetics and crystallinity of PLA matrix, differential scanning calorimetry and X-ray diffraction measurements were employed. Annealing was done for different durations of time in order to control the crystallinity of the matrix. The results show that the crystallization rate was remarkably increased due to the addition of particles and that there was an optimal concentration of particles. The degradation rate of most of the PLA composites was faster than that of neat PLA, indicating that the interface between the particle and the PLA matrix was not perfect. Meanwhile, the degradation rate of PLA reinforced with multi-walled carbon nanotubes became slower due to increased crystallinity.

1. Introduction

Recently, there has been an increasing interest in biodegradable composites based on polylactic acid (PLA) [1–4], polyhydroxybutyrate (PHB) [5–7], cellulose [8–10], and other materials, which are derived from renewable resources in order to reduce what has become known as 'white pollution' and to protect the environment [11,12]. Among many different sorts of biodegradable polymers, PLA is considered as the most promising candidates for further development due to its excellent mechanical properties [11,12]. Additionally, compared to conventional plastics, PLA is biodegradable and its hydrolysates are carbon dioxide and water, which are not harmful to the human body or to the environment [13]. If PLA and such biodegradable polymers were to replace conventional plastics, which require 500–1000 years to degrade, environmental pollution would be significantly reduced [14]. However, a major problem with PLA is low thermal resistance and slow degradation rate, both of which limit its wider use [13]. Research works have been done on how PLA degrades in different environments, such as in alkali solution, in saturated water vapor, in an acid solution, and in other environments [15–18].

In order to improve the thermal stability of PLA, particles such as $CaCO_3$, TiO_2, CNT, $BaSO_4$, or silicate have been added to the polymer [19–23]. It was found that the resulting composites can not only improve the mechanical and thermal properties but also affect the crystallization rate. Different degrees of crystallinity, along with particles, may affect the degradation rate and hence the product life may be controlled. Several studies on the crystallization and degradation kinetics of PLA composites have been undertaken, but the data remain insufficient.

The aim of this investigation was to study the degradation behavior of PLA composite reinforced with different types of particles. Particles considered in this study include titanium dioxide, multi-walled carbon nanotubes, surface-treated multi-walled carbon nanotubes, and graphene nanoplatelets. The effect of reinforcing particles on the crystallization kinetics was also investigated in an effort to control degradation rate of PLA composites.

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2. Experimental

2.1. Materials

The polylactic acid (PLA) polymer pellets (4032D) used in this study were supplied by Nature Works LLC. PLA has a density of 1.24 g/cm^3, a glass transition temperature of 60 °C, and a melting temperature of 165 °C. Four different types of particles were used as fillers: multi-walled carbon nanotubes (MWNTs), graphene nanoplatelets (GNPs), titanium dioxide (TiO_2), and surface-treated multi-walled carbon nanotubes (MWNT-OH). The properties of these particles are listed in Table 1.

Table 1
Properties of particles used in this study.

Property	Size	Density or specific surface area	Total surface area per gram (cm^2)	Manufacturer
MWNT	Diameter: 10–15 nm Length: 10–20 μm	200 (m^2/g)	2.0×10^6	Iljin Nanotech., Korea
TiO_2	Diameter: 1–2 μm	4.23 (g/cm^3)	$(1.4–2.4) \times 10^4$	Alfa Aesar, USA
GNP	Diameter: 1–20 μm Thickness: 5–15 nm	40–60 (m^2/g)	$(4.0–6.0) \times 10^5$	Knano Graphene Tech., China
MWNT–OH	Diameter: 20–30 nm Length: 5–20 μm	110 (m^2/g)	1.10×10^6	Nanostructured & Amorphous Materials, Inc., USA

2.2. Preparation of PLA composites

The PLA pellets were dried at 40 °C for 24 h to remove moisture. PLA composite compounds were prepared using a twin screw extruder (BA-19, Bautek, Korea) with 0, 0.03, 0.05, 0.1, and 0.15 wt% of MWNT. Furthermore, PLA/TiO_2 (0.1 wt%), PLA/GNP (0.1 wt%), and PLA/MWNT–OH (0.1 wt%) compounds were prepared via the same extrusion process. These compounded PLA composites were dried again at 40 °C for 24 h and were then injection-molded into dumbbell-shaped tensile specimens following the ASTM D638 standard using an injection molding machine (JinHua 170 ton, Korea). The specimens were 165 mm long, 13 mm wide, 3.0 mm thick, and the gage length was 50 mm. In order to investigate the relationship between the crystallinity of PLA and its hydrolytic degradation behavior, an annealing process was undertaken using a convection oven (FC-1D-2, Universal scientific, Korea) for different time durations.

2.3. Characterization and measurements

Differential scanning calorimetry (DSC-Q 1000, TA Instrument, UK) measurements were performed for each type of sample in order to examine the crystallization kinetics and the crystallinity. The samples taken from the extruded compounds were heated from room temperature to 200 °C at 20 °C/min and then held at this temperature for 5 min to erase the previous thermal history. The samples were then cooled down to 110 °C immediately and an isothermal scanning process was performed at this temperature for 20 min. The samples were subsequently cooled to room temperature as fast as possible. Finally, they were heated again from room temperature to 200 °C at a heating rate of 10 °C/min.

In order to confirm the relationship between the crystallinity and the annealing time, X-ray diffractometry (XRD) measurements were performed (D5005 X-ray diffractometry, Bruker Corporation, Germany). Measurement conditions were set at 40 kV and 45 mA with Cu Kα radiation (1.5406 Å), and the scanning range was from 0° to 40°.

Table 2
Thermal characteristics of PLA/MWNT composites evaluated as determined by DSC.

Weight percent	T_c (°C)	T_g (°C)	T_m (°C)	t_c (s)
0 wt%	110	61	169	983
0.03 wt%	110	61	170	597
0.05 wt%	110	61	170	125
0.1 wt%	110	61	170	339
0.15 wt%	110	61	170	445

Hydrolytic degradation tests were carried out in a sodium hydroxide (NaOH) solution (PH = 13) at 37 °C. After predetermined periods of time, the specimens were taken out and rinsed with distilled water until the pH approached 7. Samples then were dried in a vacuum oven at 70 °C for 48 h. The weight loss (W_{loss}) was estimated using the following equation:

$$W_{loss}(\%) = 100\% \times (W_0 - W_t)/W_0 \quad (1)$$

Here, W_0 is the initial weight of a specimen, W_t is the weight of the specimen dried in a vacuum oven at 70 °C for 48 h, and W_{loss} is the weight loss of the specimen [24].

The tensile properties of each specimen were measured by a universal testing machine (LR 50 K, Lloyd, UK) at a crosshead speed of 3.75 mm/min. For each data point, at least five test results were averaged, and the fracture of the tensile specimen was observed using a Hitachi S-4800 scanning electron microscope (SEM).

3. Results and discussion

3.1. DSC analysis

Effect of particles on the crystallization kinetics of PLA was examined from the DSC analysis data. Fig. 1(a) shows overall heating–cooling–heating cycles for the crystallization behavior of PLA/MWNT composites. Fig. 1(b) and (c) shows the first and the second heating processes of PLA/MWNT composites respectively. The first heating process was carried out in order to erase the previous thermal history of samples, and the second heating process was conducted in order to evaluate the crystallization behavior of PLA/MWNT samples. As shown in Table 2, the glass transition temperature and melting temperature remained almost the same after being fully crystallized at 110 °C for 20 min.

In Fig. 2, result of isothermal scanning at 110 °C is presented. The exothermic peak in the isothermal thermogram (Fig. 2) and Table 2 indicates that it takes about 983 s to fully crystallize neat PLA. However, with an addition of 0.03 wt% MWNT, the crystallization rate increased nearly twice as fast as that of neat PLA. The crystallization rate increased with the MWNT concentration up to 0.05–0.1 wt%. After that point, the crystallization rate declined by 339 s and 445 s with 0.1wt% MWNT and 0.15wt% MWNT, respectively.