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The relationship between microstructure and mechanical properties of carbon nanotubes/polylactic acid nanocomposites prepared by twin-screw extrusion

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ABSTRACT

Twin-screw extrusion was applied to prepare the carbon nanotubes/polylactic acid (CNT/PLA) nanocomposites. Five different extruded plates were produced under variation of CNT concentrations. The internal microstructures were also observed by optical microscope to examine the distribution and dispersion of CNT in the PLA. Besides, the crystallinity of the CNT/PLA nanocomposites was investigated by differential scanning calorimetry (DSC) and density method. The effects of the CNT concentrations on the mechanical and electrical properties of the nanocomposites were investigated. Scanning electron microscope (SEM) was performed to observe the CNT dispersion in the nano-scale. These results suggested that the crystallinity was increased with the increase of CNT concentrations, demonstrating that CNT played a role as a nucleating agent in PLA. Moreover, the mechanical and electrical properties of PLA have been improved by a proper incorporation of CNTs due to a good distribution and dispersion of the CNTs.

1. Introduction

In recent years, conductive polymer composite (CPC) has been extensively used in the fields of electrostatic dissipation [1], electromagnetic interference-shielding [2–4], and electrically conductive materials for achieving enhanced mechanical properties, thermal stability, tribological properties, and reduced thermal expansion [5]. This makes researchers be more and more interested in the development of CPC. Different practical applications will require the CPC with different electrical properties, even mechanical properties. Therefore, for the preparation of CPCs, the selection of matrix, conductive filler and molding process is very crucial.

As for the matrix, owing to more and more serious impact of the petrochemical industries on the environment, it is strongly required to produce a potential CPC with environmental friendly. For this purpose, the biodegradable polymer has attracted more and more interests as an alternative matrix, such as polycaprolactone (PCL), polylactic acid (PLA), polybutylene succinate (PBS) and polyhydroxyalkanoates (PHA). Especially, polylactic acid (PLA) is one of the most promising biodegradable and thermoplastic polymer which can be derived from renewable resources such as starch and is a sustainable alternative to petrochemical-derived products. Also, PLA is a well-studied environmental friendly polymer because of its good strength and stiffness [6–8] and is being used in widespread applications, such as packaging materials, degradable plastic bags, water and milk bottles, as well as in automotive applications [9–13]. Therefore, it is considered that PLA as an environmentally friendly polymer could replace traditional polymers in potential industrial applications.

Shifting the attention to the filler, carbon nanotube (CNT) has been very maturely studied as an outstanding conductive filler. It has not only excellent thermal and electrical properties, but also good mechanical properties [14–16]. However, because of its some shortcomings, CNTs are easily agglomerated and non-uniformly distributed in the matrix, leading to the decline of composite mechanical and electrical properties, which also affect the application of CNT/polymer composites in industry. Thus the dispersion and distribution of CNTs, even their orientation, play an important role in determining the properties of CPCs, ranging from electrical to mechanical properties.

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In recent years, many researchers have interested in development of the CNT/PLA nanocomposites. However, most of them take advantage of the surface modification methods to prepare the nanocomposites [17,18]. Although their methods can improve the electrical properties of the CNT/PLA nanocomposites, the preparations of the nanocomposite commonly stay in laboratory-scale stage. Therefore, in order to achieve the industrialized produce, we choose the molding method to prepare the CNT/PLA nanocomposites.

As the molding methods, commonly injection molding, extrusion molding, blow molding and rolling molding are available. Some researchers attempted to take advantage of the molecular chain orientation of polymer during extending to improve the mechanical properties of degradable polymer through various molding processes [19–24]. In general, extrusion process is considered as an easy and continuous process, and there is not limit in process degree. Based on the strategy of the extrusion process, a novel CPC was expected to be created.

Additionally, literature reviews indicated that the matching between the solubility parameter (SP) of CNT and the polymer matrix is propitious to achieve higher electrical conductivity in CNT/polymer composites [25]. According to some literatures, the SP of CNT is about 17.8 $MPa^{1/2}$ [25–27], while the SP of PLA is approximately 18.5 $MPa^{1/2}$ [28,29]; their SP values are similar, which will result in continuous conductive pathways and good compatibility, leading to the achievement of a high electrical conductivity and good mechanical properties.

In view of the above, in this study, PLA was selected as the matrix polymer exemplarily, and CNT was employed as the conductive filler. The CNT/PLA conductive composites with various CNT concentrations (1–10 wt.%) were prepared by extrusion process. The relationship between the microstructures and the mechanical properties of the CNT/PLA nanocomposites were investigated for various CNT concentrations. Like most other aliphatic polyesters, PLA presents a slower crystallization rate and variations in crystal structure and crystallinity after the molding process [30,31], as well as its orientation which strongly affects mechanical properties [32]. Therefore, the variations of crystallization of the PLA nanocomposites were also investigated by DSC and density method. These characterizations confirmed that the reinforcement of the mechanical and electrical properties of the nanocomposites have been achieved by a proper incorporation of CNTs using an easy extrusion process. It offers an alternative green and easy solution to produce conductive CNT/PLA nanocomposites as an environmentally friendly CPC.

2. Experimental

2.1. Materials

Carbon nanotubes (CNTs) were vapor-grown carbon fibers and supplied by Shouwa Denko Company (VGCF-X, Tokyo, Japan). The CNTs were used without any purification process as the reinforced filler, having a diameter of 10–15 nm and an average length of 3 μm.

Polylactic acid (PLA) used in this study was purchased from Nature Works LLC (Ingeo 3001D, America). Its residual moisture content is less than 0.025% which was recommended to prevent viscosity degradation. The density is 1.24 g/cm^3 (ASTM D792) and the melt flow index is 22 g/(10 min) (ASTM D1238).

2.2. Specimen preparation

The compounding processes of CNT/PLA master batches were conducted using a twin screw extruder (KZX25TW-60MG-NH (-1200)-AKT, Technovel Co., Ltd, Japan), with a screw speed of 100 rpm and the temperature profile was varied from 150 °C at the feeding zone to 190 °C (TP1) or 210 °C (TP2) at the die, to ensure good fluidity of the molten state nanocomposites during the extrusion process. They were vacuum-dried at 50 °C for 8 h prior to this process whereby the PLA and its nanocomposites were compounded with 0, 1, 3, 5 and 10 wt.% CNT concentrations. All master batches were cooled down in a water bath and pelletized after the first extrusion process. The compounding process conditions are presented in Table 1.

Then the prepared master batches were dried at 50 °C for 8 h again prior to extrusion process and the nanocomposite plates were produced by the same extruder. Temperature profile 3 (TP3) was designed with a low temperature level to prepare the CNT/PLA master batches with 0, 1, 3 and 5 wt.% CNTs, whereas temperature profile 4 (TP4) was conceived to promote the fluidity of the master batches with high CNT concentration (i.e. 10 wt.%). The extrusion conditions refer to Table 2. In order to perform a smooth extrusion process, five different plates were produced under different processing conditions. A variation of CNT concentration, temperature profile, rotation speed and extrusion speed was executed (Table 3).

Finally, the extruded plates with dimensions of 2000 mm (length) × 100 mm (width) × 1.2 mm (thickness) were machined into standard dumbbell-shaped specimen with the size of 75 mm (length) × 10 mm (width) × 1.2 mm (thickness). The specimens were used for evaluating the internal microstructures and the mechanical properties, even the electrical properties.

2.3. Composite characterization

2.3.1. Morphology investigations

The state of micron-scale dispersion of CNTs within the PLA matrix was investigated by an optical microscope (Eclipse model ME600D, Nikon, Japan) on the middle of dumbbell-shaped specimens. The thin sections of the nanocomposites within 3 wt.% CNTs had a thickness of 10 μm. In order to achieve visibility of the composites with the CNT concentrations of 5 wt.% and 10 wt.%, the thickness of the thin section was reduced to 5 μm and 1 μm, respectively. The thin sections were cut by a microtome (RM2145, Leica Microsystems, Japan) at room temperature.

Moreover, the microstructures of fractured surfaces, including the state of micro dispersion and distribution of CNTs within the PLA matrix, were observed by scanning electron microscopy (Hitachi Ltd S-4300, Japan). The specimens were sputter-coated with gold using an ion sputtering apparatus (E-1030, Hitachi Science Systems Co., Ltd.) to avoid charging. The acceleration voltage was 3 kV.

Table 1
Mechanical blending process conditions.

	Heating zone (°C)						Rotation speed (rpm)
	C1	C2	C3	C4	H	SD/AD	
Temperature profiles 1 (TP1)	150	160	170	180	180	190	100
Temperature profiles 2 (TP2)	150	160	180	190	190	210	