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Property reinforcement of poly(propylene carbonate) by simultaneous incorporation of poly(lactic acid) and multiwalled carbon nanotubes

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ABSTRACT

In this study, by directly melt-blending with 10 wt% poly(lactic acid) (PLA) and 1.5 wt% multiwalled carbon nanotubes (CNTs), yield strength of a biodegradable poly(propylene carbonate) (PPC) was increased more than one order of magnitude, and its Young's modulus was enhanced by 8 times. Meanwhile, the high elongation at break of PPC was maintained. This overall property reinforcement could not be observed by adding either PLA or CNTs separately. At room temperature, the obtained mechanical properties of the reinforced PPC are comparable to or even better than those of some traditional petroleum-based polymers such as low density polyethylene, high density polyethylene and polypropylene (PP). Together with good biodegradability and excellent conductivity, the PPC/PLA/CNT composites prepared in this work exhibit a potential to be used as a sustainable alternative to petroleum-based polymers such as PP around room temperature.

1. Introduction

Poly(propylene carbonate) (PPC), which has now been industrialized via the copolymerization of carbon dioxide and propylene oxide, has attracted much attention due to its good biocompatibility and biodegradability [1,2]. The use of CO_2 as one of the monomers in the synthesis of PPC cannot only overcome the shortage of petroleum resources but also contribute to reducing carbon dioxide pollution which has been considered as the main factor causing the greenhouse effect in the world [3–5]. The biodegradability of PPC will reduce the white pollution caused by traditional petro-based polymers in daily life, and its biocompatibility will make it potentially used as a biomedical material in the field of tissue engineering [6,7]. Unfortunately, PPC is an amorphous polymer with very low Young's modulus, tensile strength and glass transition temperature. Thus, the reinforcement of PPC is in urgent demand to extend its applications [8,9].

To improve the poor mechanical performances of PPC, much effort has been made on blending it with other biodegradable polymers such as starch [10,11], poly(3-hydroxybutyrate-co-3-hydroxyvalerate) [12,13], poly(3-hydroxybutyrate) [14], poly(butylene succinate) [15], ethyl cellulose [16] and other cellulose derivatives [2,17]. However, the improvement of overall performance is usually very limited because of low miscibility among the components. For example, in the study by Ma et al. [10], though a significant increase in yield strength of PPC can be realized by incorporating high content of starch, the elongation at break shows a dramatic degradation with the addition of starch. Xing et al. reported a similar elongation decrease in the system of PPC/cellulose acetate butyrate [16]. PPC could also be reinforced by inorganic or organic fillers, such as $CaCO_3$ [18], montmorillonite [19], graphite oxide [20,21], glass fiber [22] and lignocellulose [23]. These composites generally exhibit superior mechanical strength and stiffness compared to unreinforced polymers. However, because of the agglomeration of fillers during blending, these composites also show poor ductility at high concentrations of fillers. In summary, it is difficult to significantly strengthen PPC without degrading its ductility by adding either polymers or fillers separately. Nevertheless, it is interesting that most of the reported PPC composites exhibit moderate mechanical reinforcement and good ductility at a low content of fillers or polymers. Accordingly, some questions could be raised: what will happen if low contents of polymers and fillers are simultaneously incorporated into PPC? Can superior mechanical reinforcement of PPC be realized while its ductility is well maintained in this way?

In the present work, our attention is focused on the preparation of PPC composites with good overall performance by simultaneous incorporation of a low content of poly(lactic acid) (PLA) and multiwalled carbon nanotubes (CNTs). First of all, PLA is also a biodegradable polymer produced from biomass resources such as wheat, corn, and sugar beets [24,25]. The chemical structures of PLA and PPC are similar; they are consequently expected to be miscible and compatible to some extent [26]. Secondly, considering that PLA presents good mechanical strength and stiffness, it is expected as one of the most attractive choices to strengthen PPC

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[3,26]. Thirdly, numerous studies have confirmed that CNTs is a promising modifier for polymers. The obtained polymer/CNT composites usually show excellent mechanical properties because of the prominent physical and mechanical properties of CNTs, such as high aspect ratio, high Young's modulus and tensile strength [27,28]. Moreover, due to the excellent electrical conductivity of CNTs [29,30], polymer/CNT composites can be conductive and consequently have wider applications than nonconductive composites.

2. Materials and methods

2.1. Materials

Poly(propylene carbonate) (PPC) is obtained from State Key Polymer Physics and Chemistry Laboratory, Changchun Institute of Applied Chemistry, China. Its weight-average molecular weight is 2.48×10^5 g/mol, and $M_w/M_n = 3.2$. Poly(lactic acid) (PLA), with $M_w = 1.59 \times 10^5$ g/mol and $M_w/M_n = 2.75$, was purchased from Haizheng Biomaterial Co. (Zhejiang, China). Multiwalled carbon nanotubes (CNTs, Nanocyl 7000) were kindly provided by Nanocyl S.A. (Belgium). These CNTs have a diameter of 10 nm, length of 1.5 μm, and a surface area of 250–300 m^2/g according to the producer.

2.2. Composites preparation

Composites of 90PPC/10PLA/xCNT (in which the weight ratio of PPC, PLA and CNTs was 90/10/x) with various contents of CNTs were prepared by direct melt compounding in a HAAKE torque rheometer (Thermo Fisher Scientific, USA) at 50 rpm for 10 min. The compounding temperature was set at 150 °C, which ensured that PPC would not decompose. For comparison, PPC/PLA blends with different weight ratio and PPC/CNT composites with different contents of CNTs were also prepared in the same way. Before use, all materials were dried in a vacuum oven at 45 °C for 24 h. Then, the melt-compounded composites were ground into fine particles for further sample preparation. Specimens for mechanical and electrical measurements were compression molded at 150 °C for 6 min under a pressure of 10 MPa.

2.3. Characterization

Tensile testing was performed using an Instron 4302 universal tensile testing machine with a crosshead speed of 10 mm/min at room temperature (23 °C). The results reported were the average from at least five specimens for each testing.

The electric resistance was measured with a Keithley 6487 picoammeter. The samples were cut into specimens with the size of 60 mm × 10 mm × 4 mm and then coated with silver paint on both ends to eliminate contact resistance.

Dynamic mechanical properties (DMA) were conducted using a Q800 dynamic mechanical analyzer (TA Instruments, USA) in a tension mode at a frequency of 1 Hz. The temperature ranged from 0 to 70 °C at a heating rate of 3 °C/min.

The rheological measurements were performed on a controlled stress Gemini 200 rheometer (Malvern Instruments Ltd., UK) using 2.5 cm diameter parallel plate at 150 °C. A frequency sweep mode was adopted with a frequency range from 0.001 to 100 rad/s and under a constant stress of 10 Pa.

The morphologies of cryogenically fractured surfaces of the composites were characterized by using an Inspect field emission SEM (FEI Company, USA) with 5 kV accelerating voltage. To better determine the dispersion state of CNTs and PLA, the cryogenically fractured surface was etched in a mixed solution of anhydrous ethanol and acetone (1/1, v/v) at room temperature for 3 h to partially remove PPC. Before SEM characterization, all the surfaces were coated with a thin layer of gold.

3. Results and discussions

3.1. The effects of PLA and CNTs on mechanical properties of PPC

We firstly study the effects of PLA and CNTs on the mechanical properties of PPC, and the results are shown in Fig. 1. It is clear that the yield strength of PPC can be significantly improved by blending with PLA; however, there is a dramatic degradation in ductility with increasing the content of PLA. For example, by adding 10 wt% PLA, the yield strength increases from 2 MPa to 10 MPa and the elongation at break is almost unchanged. When the amount of PLA is 20 wt%, though the yield strength continues to increase, the elongation at break of PPC decreases dramatically from 690% to 370%, and it even drops to less than 100% with further addition of PLA. As for PPC/CNT, the yield strength is enhanced modestly from 2 MPa to 12 MPa with the increase of CNTs amount from 0 to 2 wt%. Meanwhile, the ductility of PPC is almost unaffected and the elongation at break is still above 500% with the addition of 2 wt% CNTs.

According to the above results, we carefully investigated the effects of CNTs on mechanical properties of composites with a high PPC/PLA weight ratio of 90/10 (90PPC/10PLA/CNT) in the following study, aiming to get PPC composites with superior mechanical strength and ductility.

3.2. Mechanical and electrical properties of 90PPC/10PLA/CNT composites

Fig. 2 shows the tensile behaviors of 90PPC/10PLA/CNT composites with various CNTs contents. For comparison, the tensile properties of PPC/1CNT composite and 90PPC/10PLA blend are also included in this figure. Upon simultaneously adding 10 wt% PLA and various contents of CNTs, not only evident reinforcement in both the strength and the modulus is observed but also the elongation at break of the reinforced PPC is well maintained. For instance, the yield strength and Young's modulus increase from 2 MPa and 200 MPa for neat PPC to 23 MPa and 1600 MPa for 90PPC/10PLA/1.5CNT composite, respectively. In addition, even with such a high strength and modulus, the elongation at break is still as high as around 600%, indicating a good tensile toughness after reinforcement. This excellent overall property reinforcement could not be observed by adding either PLA or CNTs separately (Fig. 2(c) and (d)). In other words, PPC composites with superior mechanical strength and ductility can be obtained by simultaneously adding 10 wt% PLA and various contents of CNTs. Moreover, it is worth to be noted that, at room temperature (23 °C), the mechanical properties of 90PPC/10PLA/CNT composites are completely comparable to or even better than those of some mainstream plastics such as petroleum-based low density polyethylene (LDPE), high density polyethylene (HDPE), polyethylene copolymers and polypropylene (PP) [4,31]. For better comparison, we characterized the tensile behaviors of PPC, 90PPC/10PLA/2CNT and PP at room temperature and the corresponding stress–strain curves are shown in Fig. 3. As shown in this figure, the yield strength of 90PPC/10PLA/2CNT is about 29 MPa, which is much close to that of PP (32 MPa). Meanwhile, the elongation at break of 90PPC/10PLA/2CNT is as high as 350% while it is only slightly above 100% for PP. Therefore, it is reasonable to conclude that PPC composites prepared in this study exhibit a potential to be used as a sustainable alternative to petroleum-based polymers such as PP around room temperature.