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Significant reinforcement of poly(propylene carbonate): Nanostructured polymer composites of poly(propylene carbonate)/poly(methyl methacrylate) via a supercritical carbon dioxide route

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ABSTRACT

Biodegradable poly(propylene carbonate) (PPC) matrix composite with a significant improvement in yield strength was successfully prepared by incorporating a low content of poly(methyl methacrylate) (PMMA) via a supercritical carbon dioxide route. Atomic force microscopy measurement shows that the size of the dispersed PMMA phase in the PPC substrate is in the range from 50 nm to 200 nm, which is much smaller than the smallest ones that can be obtained by conventional melt blending method. Tensile tests demonstrate the excellent mechanical properties of the composites prepared in this study. By incorporating only 5 wt% PMMA, the obtained composites show approximately 4 times higher yield strength than pure PPC and the elongation at break of the composites is well remained. By comparing with the reported works, this method shows the highest enhancement efficiency of PPC. The significant reinforcement of PPC is ascribed to the nano size phase-separated domains of rigid PMMA. These findings show an effective modification method of PPC for the potential alternative to the non-biodegradable polymers.

1. Introduction

Since it was synthesized via the copolymerization of carbon dioxide and propylene oxide at the end of the 1960s by Inoue et al. [1,2], poly(propylene carbonate) (PPC) has attracted a lot of attentions with its advanced properties. The use of CO_2 as one of the monomers in the synthesis of PPC can not only overcome the shortage of petroleum resources but also contribute to reducing carbon dioxide pollution which has been considered to be the main factor causing the greenhouse effect in the world [3–5]. On the other hand, PPC is biodegradable and biocompatible in favor of reducing the white pollution as an ordinary plastic in daily life and is potential to be used as a biomedical material in the field of tissue engineering [6,7]. However, PPC as an amorphous polymer shows very low yield strength. Therefore, the as-synthesized PPC is still far from practical application, and it should be reinforced to extend its applications [8]. A lot of works, including chemical and physical attempts [9–20], have been done to modify the material profile of pure PPC by blending with polymers or fillers. However, they all show a very limited improvement for the investigated compounds using PPC as the dominant component (e.g., yield stress ratio of composite and matrix is less than 2 when the content of additives is less than or equal to 5 wt%). Besides, even though a yield stress ratio greater than 2 can be achieved at high additives contents, these kinds of composites usually show a dramatic degradation in elongation at break, which will restrict its application in the fields of food and packing.

As we all known that the blending of two or more polymers with different characteristics is one of the most important techniques used to prepare new materials with novel features not found in any current constituent polymer [21]. In particular, polymer blends with controlled structures and distributions of phase-separated domains on the nanometer scale often have desirable or tunable physical properties [22]. Unfortunately, duo to the limited miscibility between PPC and other polymers, to date, this type of PPC polymer blends with high performance has not been successfully prepared by the conventional solution casting or melt processing methods.

A synthetic method for producing new polymer composites using supercritical carbon dioxide ($scCO_2$) has been developed by Watkins and McCarthy [23]. In their method, both the monomer and initiator were dissolved in $scCO_2$ and then impregnated into the polymer substrate and subsequently polymerized. Fortunately, some immiscible polymers were successfully blended at

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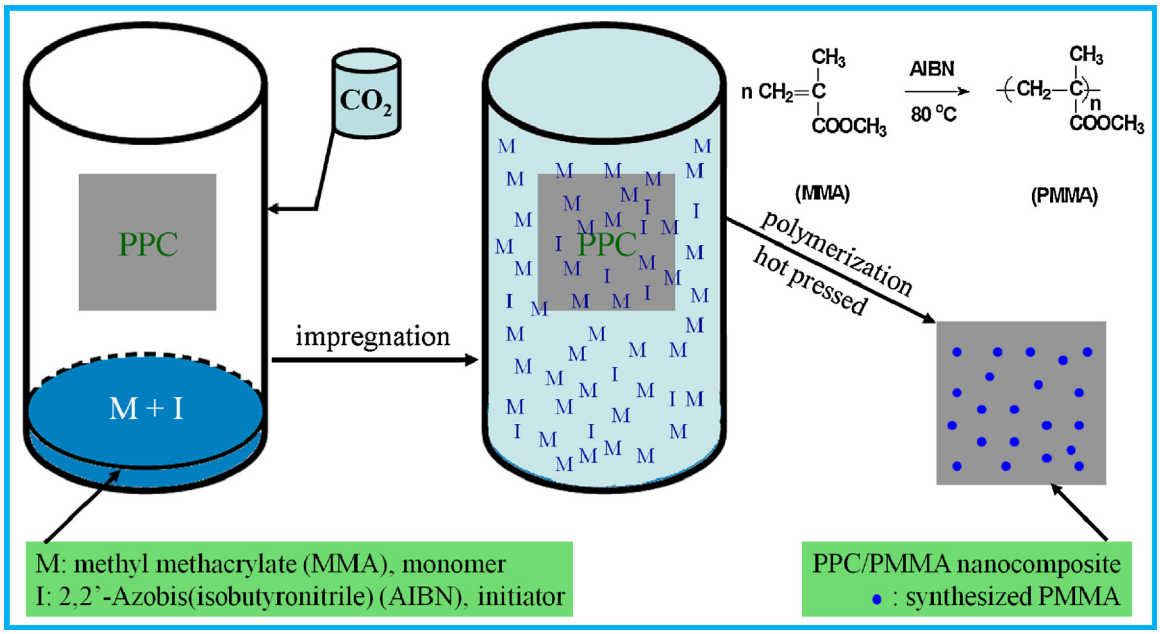

Fig. 1. Schematic illustration of the synthesis procedure of composites. Briefly, three pieces of poly(propylene carbonate) (PPC) substrates (1 g each) and a mixture of 3 g methyl methacrylate and 0.03 g initiator were placed in a stainless steel high-pressure vessel. Then the vessel was kept at a desired CO_2 pressure for 8 h (40 °C). After that, the impregnated PPC substrates were placed in a conical flask and heated at 80 °C for 7 h to ensure complete polymerization of methyl methacrylate. Finally, the samples were hot pressed at 140 °C to obtain composites.

the nanometer level by using this method [22–26]. Moreover, the mechanical properties of polymer composites prepared using this $scCO_2$ method can be controlled by using a combination of the substrate and monomer, and thus, these polymer composites show favorable mechanical properties which are superior to the blends prepared by the conventional methods. However, to the best of our knowledge, although there are extensive works in the area of polymer blends prepared in $scCO_2$, no studies of blending polymers into a biodegradable polymer substrate (such as PPC) via a supercritical fluid route are reported. On the other hand, it is well known that PPC and many other biodegradable polymers are thermal and solvent unstable. Thus, the traditional melt-blending and solvent-blending methods used to modify these polymers usually lead to a serious degradation, which has negative effects on the material properties. Besides, extensive use of organic solvents is not only bad for biological applications but also bad for environment. Fortunately, $scCO_2$ is non-toxic, nonflammable and inexpensive. Furthermore, the rather low $scCO_2$ temperature (31.1 °C) and pressure (7.37 MPa), in combination with the non-toxic properties of CO_2, may offer the possibility to process biodegradable and heat labile polymers at body temperature. This technological feature is extremely important in the pharmaceutical and biomedical fields, because of the need to retain chemical and bioactive properties of the formed biomaterials [6].

In this study, we blended a small amount of poly(methyl methacrylate) (PMMA) into biodegradable PPC by this $scCO_2$ route, and thus a new biodegradable PPC composites (PPC/PMMA) with PMMA dispersed on a nanometer scale in the PPC substrate were obtained for the first time. Thanks to the incorporated nano size phase-separated rigid PMMA, these PPC/PMMA composites showed excellent overall mechanical properties.

2. Experiment

2.1. Materials

Poly(propylene carbonate) (PPC) powders were supplied by Changchun Institute of Applied Chemistry, Chinese Academy of Science (Jilin, China). Its weight-average molecular weight (M_w) was 2.48×10^5 g/mol and M_w/M_n was 3.2. PPC substrates were prepared from powders by compression molding at 140 °C under a pressure of 10 MPa for 10 min, and then they were cut into pieces with dimensions of 20 mm × 20 mm × 0.5 mm. Methyl methacrylate (MMA) was purchased from Tianjin bodi chemical Co. Ltd. (Tianjin, China) and used as received. 2,2′-Azobis(isobutyronitrile) (AIBN) supplied by Tianjin bodi chemical Co. Ltd. was recrystallized from acetone twice prior to use. CO_2 with a purity of 99.9% was obtained from Chengdu Taiyu Gas Co. (Sichuan, China) and used as received.

2.2. Methods

2.2.1. Synthesis procedure

Fig. 1 shows a simple schematic illustration of the synthesis procedure. For all synthetic experiments, three pieces of PPC substrates (1 g each) were suspended in stainless steel high-pressure vessels by means of a wire mesh in order to ensure that no part of the substrate was in contact with the wall of the vessel or the mixture of monomer and initiator. MMA monomer (3 g) and AIBN initiator (0.03 g) were placed in the bottom of the vessel, which was then sealed. The vessel was then flushed by CO_2 at atmospheric pressure for 3 min. After the system reached thermal equilibrium (40 °C), the vessel was pressurized up to a desired CO_2 pressure using a CO_2 delivery pump. After soaking under the specific conditions for 8 h, the vessel was allowed to cool to 10 °C, and then the fluid in the system was released as quickly as possible and the PPC substrates were taken out for blend synthesis. Here we note that the impregnated PPC shows foamed features duo to its easy CO_2 foaming property [6]. Detailed impregnation conditions and the corresponding sample label are summarized in Table 1.

The substrates impregnated with MMA and AIBN obtained by the above procedures were placed in a conical flask of 500 mL. The flask was evacuated to remove the air, charged with N_2, and heated at 80 °C for 7 h to ensure that the polymerization of MMA was complete. Then the flask was cooled to room temperature and the samples were taken out. After that, the samples were hot