



Modification of biodegradable poly(butylene carbonate) with 1,4-cyclohexanedimethylene to enhance the thermal and mechanical properties

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ABSTRACT

Aiming to improve thermal stability of poly(butylene carbonate) (PBC), a series of poly(butylene-co-1,4-cyclohexanedimethylene carbonate) (PBCCs) random copolycarbonates with weight-average molecular weights (M_w) ranging from 1,09,000 to 1,74,000 g mol⁻¹ and yield of 82.4 to 88.4% were synthesized from Diphenyl carbonate (DPC), 1,4-butanediol (BD) and trans-1,4-cyclohexanedimethanol (CHDM) by a two-step melt polycondensation method. The structures and properties were characterized by ¹H NMR, ¹³C NMR, FT-IR, GPC, WAXD, DSC, TGA, mechanical testing as well as enzymatic degradation. The results manifested that the triad components were existed in the copolymers with a random sequential structure, and incorporation of cyclohexanedimethylene carbonate (CC) units into PBC could prominently impact the thermal transition behavior, crystallinity as well as thermal stability of PBCCs in a degree. In addition, T_g of PBCCs monotonously increased with the increasing CHDM content. WAXD results indicated that the CHDM introduction could obviously change the crystal structure and crystallinity of the copolymers. The thermal stability of PBCCs also expressed to be enhanced during the process of increasing CC unit content. Furthermore, the mechanical properties and biodegradability of copolymers can be easily adjusted by regulating the feed composition.

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1. Introduction

In order to solve the environmental pollution problems, a series of biodegradable polymers are attracting considerable attention as effective substitutes. Aliphatic polycarbonates (APCs) are noticeable for their unique properties, including superior biodegradability, no-toxicity and biocompatibility [1–4]. During the existing APCs, poly(butylene carbonates) (PBC) has become hotspot of the attention benefiting from its favorable synthetic and competitive features [5–9]. Lately, PBC has ever been selected to blend and block copolymerization with poly(butylene succinate) (PBS) and polylactide (PLA) to improve PLA and PBS's toughness but does not compromise its biodegradability and biocompatibility [10–13].

However, it is worth noting that the thermal stability of PBC is

still a major drawback due to the aliphatic chain structure of the diol, limiting its practical application. In order to broaden its application scope, a series of copolymers based on PBC have been synthesized, including poly(butylene carbonate-co-butylene succinate) (PBC-co-PBS) [14], poly(butylene carbonate-co- ω -pentadecalactone) (PBC-co-PPDL) [15] and poly(butylene-co-decamethylene carbonate) (PBDCs) [16]. Generally, copolymerization equipped with rigid cyclic comonomers has been widely verified to be a convenient and appealing approach to ameliorate the thermal property of polyesters. Take an example, aromatic composition incorporated into the PBC chain was already reported to enhance its T_g and improve stiffness of polymer backbone simultaneously. Unfortunately, the biocompatibility of the synthesized aliphatic-aromatic random copolymer acted as an obvious blemish on the other hand [17,18]. Another case is that biobased 2,5-furandicarboxylic acid (FDCA) and Glux monomer [19,20] had been tried to introduced into polyesters in large reports before, owing to these monomers are not industrially available, there were still a certain gap between the implementation of these

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measures and the intended purpose ultimately. As the only bio-based industrially available bicyclic carbohydrate-based monomer, isosorbide was regarded as the most prospective monomer on synthesizing of polymers thanks to its magnetic non-toxicity, rigidity and chirality [21,22]. Anyhow, we must bear in mind that isosorbide in fact had relatively poor activity owing to the 2- and 5-position hydroxyl groups which would hinder the production of polymers with high molecular weight to a certain extent. On account of a bulky stiff ringlike structure of the primary diol, the industrially available CHDM can be introduced easily into the backbone of polymer to strengthen the macromolecular chain's relative rigidity [23]. It was reported that Im et. al. had been tried to broaden its application by means of preparing a series of polyesters embodied CHDM unit considering remedy the decrement during the glass transition process [24,25]. Zhang' group and Tsai' group also reported a great deal of work about copolyesters based on CHDM monomer [26–29]. To summarize, there is no doubt that the introduction of CHDM could be a facile and effective way to ameliorate the features of PBC via random copolymerization.

Herein, a novel PBC based on copolycarbonates with improved thermal properties had been prepared from DPC, BD and CHDM via two-step melt polycondensation process in this study. The structure of the prepared copolycarbonates could be modulated via regulating the molar ratio of provided BD/CHDM and they had been tested by ^1H NMR, FT-IR and ^{13}C NMR. The CHDM unit content had an impact on the PBCCs thermal transition behavior, crystallinity as well as thermal stability were also investigated carefully. And we have found that the introduction of CHDM into PBC indicated copolycarbonates possessed with obviously increased T_g and T_m values, impelling PBC based polycarbonates workable on fabricating heatproof drinking bottles and food-bale materials.

2. Experimental

2.1. Materials

Commercial diphenyl carbonate (DPC) was purified via recrystallization in alcohol (absolute), 1,4-butanediol (BD) were obtained from Shanghai Aladdin Bio-Chem Technology Co., Ltd., China and of AR grade, trans-1,4-cyclohexanedime-ethanol (CHDM) with AR grade were purchased from Jiangsu Aikon Biopharmaceutical R&D Co., Ltd., China, The lipase from *Pseudomonas sp.* was purchased from Sigma-Aldrich. Other reagents were all of analytical scale and applied without any purification.

2.2. Synthesis of PBCCs

The PBCCs copolycarbonates were synthesized via two-step melt polycondensation procedure which was depicted in Scheme 1. A representative process for the preparation of copolycarbonate can be illustrated as following: In the step of transesterification, BD, CHDM, DPC (diol/DPC molar ratio 1:1) and CaO (0.1 mol % DPC) were placed into a 100 mL round-bottom flask, then the flask was stirring for a period of time under nitrogen atmosphere equipped with fractionating column. Then the temperature should be heated to 200 °C and the equipment should keep stirring for another 2.0 h. And we all know that in this step, we considered to remove volatile by-products. In the polycondensation process, in order to minimize oligomer sublimation and refrain from superfluous foaming, a high vacuum (about 100 Pa) should be applied over 0.5 h. And the state should be maintained for another 2 h. Finally, the polymer was acquired by dissolving the residue in CHCl_3 and precipitating with absolute methanol and drying under vacuum at 40 °C. PBC, PBCCx and PCC were prepared from BD and CHDM, the monomer molar ratio was ranging from 0 to 100 mol%; and x is the molar ratio of

CHDM molar content vs. total diol.

2.3. Characterization

Molecular weights of PBCCs were performed by GPC. And it was implemented at 30 °C on a Waters system of 515 HPLC (2410 refractive index and 2690D separation module was equipped). Tetrahydrofuran (THF) was employed as eluent, polystyrene were used as standards, and the flow rate was kept at 0.5 mL/min in this study.

^{13}C NMR spectra and ^1H NMR of the PBCCs were acquired with a Bruker spectrometer which was handling at 400 MHz for protons. The solvent were CDCl_3 and Tetramethylsilane (TMS) and the latter was used as internal standard.

FT-IR spectrum was recorded on a Fourier transform infrared spectrometer in a scope of 400–4000 cm^{-1} .

DSC analysis was carried out on the Instrument DSC-Q20, handling under nitrogen atmosphere. During this process, the samples were continuously heated to 160 at a rate of 20 °C/min, and this process should be maintained for 5–6 min to wipe off thermal history, cooling to –60 °C at –20 °C/min, and ultimately were re-warmed to 160 °C. The heat flow curves were also recorded as a function of temperature. The sample weight changed from 4 to 5 mg.

The thermal stability of the PBC, PBCCs and PCC was characterized using TGA under air on an installation of TGA-Q500. 3 mg samples were continuously recorded from 25 to 600 °C.

The tensile properties of PBCCs were measured on an Instron Tester (3010D, NFKK Instruments Co. Ltd.) at crosshead speed of 50 mm/min at room temperature. The dumbbell shaped samples were synthesized by melt pressing and cutting according to ISO 527. Every sample was measured for five times, and the final data was averaged to obtain a mean value.

The enzymatic degradation was tested as follow: PBCCs films with a dimension of 10 mm × 10 mm × 60 μm and weight of W_0 were attached to vial tubes containing phosphate buffer solution (pH = 6.86) and the lipase from *Pseudomonas sp.* (activity of 35 units per milligram) at 37 °C. The initial concentration of enzyme in the solution was 10 units per mL. The enzymatic concentration for the samples was 5 units per mL. After a predetermined degradation time, the samples were removed and washed with distilled water, and weighted until a constant weight was reached (W_1). The weight loss of the samples was calculated from the following equation:

$$W_{\text{loss}} = \frac{W_0 - W_1}{W_0} \times 100\%$$

3. Results and discussion

3.1. Synthesis and characterization of copolycarbonates

The PBCCs and corresponding homopolymers were synthesized via a melt polycondensation from DPC, BD and CHDM. The molar ratio of DPC/diols was 1:1. The synthesis route of PBCCs through two-step melt polycondensation can be depicted in Scheme 1.

In order to get an acquisition of the composition of copolycarbonates, ^1H NMR spectrum was applied by employing the proton peaks relative intensities appearing in butylene carbonate (BC) and cyclohexanedimethylene carbonate (CC) repetitive units. As shown in Fig. 1, the ^1H NMR spectra details of PBCC50 and the two homopolymers can be found, which can be seen that the peaks sites of copolymer are almost same to the homopolymers. For the spectrum of PBCC50, the multiple peaks appearing at 4.15 and

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