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Synthesis, characterization and properties of novel linear poly(butylene fumarate) bearing reactive double bonds

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ABSTRACT

Poly(butylene fumarate) (PBF) bearing reactive double bonds on the polymer main chains has been designed and synthesized by coupling with hexamethylene diisocyanate (HDI) under very mild condition. The chemical structure, conformational structure, crystal structure and molecular weight of PBF were systematically characterized by ATR-FTIR, ^{1}H NMR, ^{13}C NMR, GPC and WARD. The thermal properties, mechanical properties and biodegradability of PBF were carefully studied by DSC, mechanical testing and enzymatic degradation. The results of ^{1}H NMR and ^{13}C NMR spectra indicate that no isomerization or Ordelt saturation reaction of trans C=C took place during the bulk polymerization and the reaction just proceeded in the way we designed. Linear PBF with high-molecular-weight has been successfully synthesized. This new type of uncrosslinked polyester is shown to have many merits such as relatively high melting point (T_m), satisfactory processability and good mechanical properties. The impact strength of PBF is higher than 200 J/m; tensile and flexural strength can reach to 41.0 and 26.7 MPa, respectively.

1. Introduction

Development of novel biodegradable materials is of increasing interest and urgent need due to the inferior properties or higher cost of the present biodegradable materials as compared with the traditional plastic. Poly(butylene succinate) (PBS) is known to be one of the most promising and most significant biodegradable aliphatic polyesters because of the excellent thermal stability and processing properties [1–3]. Unfortunately, the low thermal deformation temperature, insufficient impact strength, high price, high hydrophobicity, lack of desirable hydrophilicity and reactive sites for further modification or functionalization of PBS prevent its widespread utilization [4–7]. Therefore, development of functionalizable polyesters with desirable thermomechanical properties is one of the most challenging and valuable topics.

Since the chemical structure, conformational structure and volume of linear PBF are very similar to that of PBS, the physical properties of PBF are expected to be close to that of PBS. The presence of carbon–carbon double bonds is expected to increase the rigidity of PBF macromolecular chains and contribute to the enhancement of mechanical properties and thermal properties such as melting point and thermal deformation temperature. Moreover, due to the presence of sensitive ester bonds, PBF is potential to be biodegradable as PBS. The widely investigated poly(propylene fumarate) (PPF) has already been proved to be biodegradable and biocompatible [8,9]. In addition, the carbon–carbon double bonds on the polymer main chains offer various merits of being derived and post functionalized to endow the polyester with specific properties. They also have the potential for the further synthesis of comblike and brushlike polymers with advanced structures [10–13].

Furthermore, it should be mentioned that fumaric acid, as a raw material for the synthesis of PBF, is a naturally formed dicarboxylic acid during Krebs cycle and has already been used as a food-grade acidulant widely. Another major reason for the design and synthesis of PBF is that the price of fumaric acid is around 1000 $/ton in China, which is much cheaper than that of the corresponding saturated dicarboxylic acid, i.e., succinic acid. Therefore, the cost of the PBF is expected to be substantially lower than that of PBS.

Regretfully, it's very hard to obtain uncrosslinked and linear unsaturated polyesters with high-molecular-weight because C=C is very unstable under conventional polycondensation condition

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which always requires reaction temperature as high as 230 °C. Consequently, the great majority of work on unsaturated aliphatic polyesters has been concentrated on the synthesis and crosslinking of amorphous PPF [8,9], which is a promising candidate for medical applications. Unfortunately, thermoplastic processability of crosslinked polymers is usually much poorer as compared to that of uncrosslinked ones, which greatly restricts their application.

Therefore, linear and high-molecular-weight PBF was designed and synthesized. Because of the presence of instable carbon–carbon double bonds stemmed from fumaric acid, the reaction condition should be very mild (reaction temperature < 150 °C), and a radical crosslinking inhibitor should be adopted, for the prevention of crosslinking reaction from carbon–carbon double bonds. Though the crosslinking reaction of carbon–carbon double bonds can be successfully prevented, the polycondensation reaction proceeds very slowly as it is known that the reaction rate decreases sharply with decreasing temperature. Consequently, the molecular weight of synthesized PBF is very low. On the other hand, it's well-established that chain-extension of dihydroxyl-terminated aliphatic polyester with highly reactive diisocyanates, as an effective strategy to obtain aliphatic polyesters with high-molecular-weight and satisfactory mechanical properties, can take place at a much lower temperature [14,15]. Japan Showa Denko has commercialized PBS with brand name of 'Bionolle' *via* this technique [16]. Therefore, this technique was employed to synthesize linear and high-molecular-weight PBF by chain-extension of dihydroxyl-terminated PBF prepolymers, which can be synthesized by polycondensation under mind condition, with HDI as a chain extender in this work. Chemical structure, conformational structure, crystal structure, molecular weights, thermal properties, mechanical properties and biodegradation of PBF have been investigated by attenuated total reflectance Fourier transform infrared (ATR-FTIR), ^{1}H NMR, ^{13}C NMR, GPC, DSC, WAXD, mechanical testing and enzymatic degradation in detail. To the best of our knowledge, it is the first time to systematically report the synthesis, characterization and properties of this kind of unsaturated polyester in its uncrosslinked form.

2. Experimental

2.1. Materials

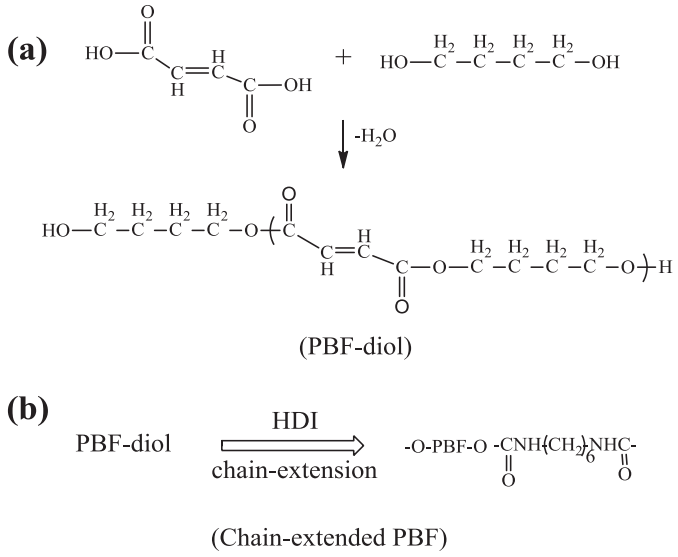
Fumaric acid (FA) and 1,4-butanediol (1,4-BD) were purchased from Alfa Aesar (USA) and BASF (German), respectively. HDI was bought from Bayer (German). Hydroquinone was obtained from Xilong Chemical Corp. (China). The lipase from *Pseudomonas cepacia* (activity: 37.8 unit/mg) used for enzymatic degradation was purchased from Sigma–Aldrich (USA). All the other reagents and solvents, analytical grade, were purchased from Beijing Chemical Reagents Corp. (China) and used without purification.

2.2. Synthesis of dihydroxyl-teminated PBF prepolymer (PBF-diol)

PBF-diol in Table 1 was synthesized from FA and 1,4-BD in bulk by a two-step process, i.e., esterification and polycondensation, according to Scheme 1a. Generally, FA, 1,4-BD, zinc chloride and hydroquinone were fed to a four-neck round-bottom flask in a 1:3:0.01:0.006 molar ratio. Zinc chloride was added as a catalyst while hydroquinone was introduced as a free radical crosslinking inhibitor. The esterification was carried out at 150 °C under nitrogen atmosphere until theoretical amount of water was separated. Subsequently, the pressure of the reaction system was gradually reduced to 5–15 Pa, and maintained for predetermined time to synthesize PBF-diol with different molecular weights. The chemical structures, conformational structures and molecular weight of PBF-diol were characterized by NMR spectra. All the prepolymers were purified by repeatedly reprecipitation from hot $CHCl_2CHCl_2$ solution by cold methanol, and dried for 12 h at 40 °C.

Table 1
Molecular weight of synthesized PBF-diol.

Sample	M_n
PBF1000	933
PBF3000	2853
PBF5500	5552



Scheme 1. Synthesis routes of PBF-diol (a) and high-molecular-weight PBF (b).

2.3. Synthesis of high-molecular-weight PBF by chain-extension

High-molecular-weight PBF was synthesized by chain-extension reaction of PBF-diol in bulk under nitrogen atmosphere. Typically, chain-extension reaction of PBF3000 (100 g) was carried out in a silicone oil bath at 150 °C under nitrogen atmosphere. After the PBF-diol was completely molten, HDI (6.48 g) was added to the reactor under mechanical stirring. The chain-extension reaction proceeded for 1 h under mechanical stirring with nitrogen protection. All the polymers were purified by dissolving in hot $CHCl_2CHCl_2$, then precipitating with cold methanol repeatedly, and dried for 12 h at 40 °C for measurements of ^{1}H NMR spectra and GPC. The synthesis routes of PBF-diol and PBF are schematically illustrated in Scheme 1.

2.4. Attenuated total reflectance Fourier transform infrared (ATR-FTIR)

The ATR-FTIR spectra of PBF-diol and PBF were recorded on a Thermo Nicolet Avatar 6700 FT-IR equipped with an attenuated total reflectance device (Smart Orbit). The samples were scanned 32 times with a resolution of 4 cm^{-1} from 400 to 4000 cm^{-1} at room temperature.

2.5. Nuclear magnetic resonance (NMR) spectroscopy

The chemical structures of PBF-diol and PBF were characterized by NMR spectrometer (Bruker DMX-400) at ambient temperature, using $CDCl_2CDCl_2$ as the solvent.