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Preparation, characterization, and biodegradation of poly(butylene succinate)/cellulose triacetate blends

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ABSTRACT

Poly(butylene succinate) (PBS) and cellulose triacetate (CT) were blended using chloroform as solvent. The solid-state properties of PBS/CT blends were confirmed by Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), X-ray diffraction (XRD), thermogravimetric analysis, scanning electron microscopy (SEM), and water contact angle measurements. FTIR results show that PBS and CT were physically blended. Tensile strength was not distinguished when the weight percent of CT was <15%, and Young's modulus increased gradually with increasing CT. DSC and XRD results show that the crystals were homogeneous, and crystallinity had no apparent decrease when <10% CT was added to the PBS matrix. However, the addition of more CT components could destroy the crystal behavior of PBS. SEM showed that no phase separation occurred between the two materials. The addition of CT increased the hydrophilicity of PBS/CT1–15 blends. The weight loss was nearly 90% after 16 h of degradation for PBS/CT10. The appropriate proportion of PBS to CT was 90:10.

1. Introduction

Poly(butylene succinate) (PBS) has attracted much interest as one of the biodegradable polymers on academic and industrial territories [1]. PBS has many excellent characteristics, including low cost, well processability, robust thermal stability, and chemical resistance [2–5]. Therefore, PBS is usually used in toys, food packaging, disposable tableware, and biomedical fields [6–9].

Cellulose and its derivatives are usually used to modify PBS-based polymer as one of the most abundant renewable materials [10]. PBS [11], polylactic acid [12], poly(butylene succinateco-butylene adipate) [13], and poly(butyleneadipate-co-terephthalate) [14] have been modified using cellulose and its derivatives. The composites have appealing properties after blending, including excellent mechanical properties, high aspect ratio, high surface area, good thermal resistance, free from harm, low energy consumption [15], and appropriate hydrophilic properties [16–20].

However, the major restraints to the properties of compositions are poor compatibility and interfacial adhesion between polymer and cellulose. Therefore, cellulose is always functionalized with other materials before using.

Cellulose triacetate (CT) is obtained by converting all hydroxyl groups to acetyl groups, which can enhance solubility in organic solvents and heat resistance [21,22]. CT has relatively high hydrophilicity, wide availability, good mechanical strength, and certain resistance to chlorine and other oxidants [23,24].

PBS/cellulose acetate, PBS/cellulose diacetate, and PBS/CT blends had been prepared and their structure and physical properties had been investigated [25–28]. Číhal et al. prepared PBS/CT blends containing 0–50 wt% of PBS and discussed the influence of the PBS content on the physical structure and thermal properties of the CT-rich blends [28]. In this study, PBS was modified with CT through melt blending. Some solid-state properties, including crystallization behavior, thermal stability, mechanical properties, and hydrophilic properties of the blends, were studied. The biodegradation behavior of PBS/CT blends was also investigated using the mixture of cutinase and cellulase.

2. Materials and methods

2.1. Materials

PBS was obtained from Anqing He Xing Chemical Corp. Ltd., China with number average molecular weight from 150,000 g/mol to

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210,000 g/mol. CT was obtained from Acros Organics (code number: 177822500), USA. Cutinase was purified from the zymotic fluid of recombinant *Pichia pastoris* containing a gene encoding cutinase from *Fusarium solani* [29]. Cellulase R-10 derived from *Trichoderma viride* was purchased from Yakult Pharmaceutical Industry Co., Ltd. (Japan). All of the chemicals were analytical grade reagents.

2.2. Synthesization of PBS/CT composites via melt blending

PBS and CT powders were dried in a vacuum at 50 °C for 8 h. They were mixed with ratios of 99/1, 95/5, 90/10, 85/15, 80/20, 75/25, and 70/30 in chloroform at 65 °C under condensing and stirring for 120 min. Neat PBS was processed under the same conditions. The obtained blends films (thickness of 0.5 mm) were hot-pressed at 160 °C and cold-pressed at 30 °C. Subsequently, dry the blends for 48 h in a fume hood and for 24 h in vacuum at 50 °C to remove chloroform. PBS/CT blends were named PBS/CT1–PBS/CT30, which corresponded to the weight fractions of 99/1–70/30, respectively.

2.3. Fourier transform infrared spectroscopy (FTIR)

ATR-FTIR analysis was carried out at an Agilent Cary 660 FTIR spectrometer (USA) with a resolution of 2 cm^{-1}. The wavenumber was from 4000 cm^{-1} to 400 cm^{-1} with 18 scan times.

2.4. Scanning electron microscopy (SEM)

The surface of the blends was observed using field emission SU8010 SEM (Japan) at an acceleration voltage of 5 kV. A thin gold layer was coated on the surface of the film prior to testing.

2.5. Differential scanning calorimetry (DSC)

The DSC experimental was performed using TA Q20 (USA) in nitrogen. Samples were heated from 40 °C to 150 °C at a rate of 10 °C/min, held for 5 min, and then cooling down to 40 °C at the same rate. The samples were scanned again at the same condition. The crystallinity (X_c) was calculated using Eq. (1):

$$X_c = \frac{\Delta H_m}{f_p \times \Delta H_m^0} \times 100\%, \quad (1)$$

where ΔH_m = the melting enthalpy, J/g), f_p = the mass fraction of PBS, and ΔH_m^0 = 110.3 J/g (the melting enthalpy of 100% crystallinity PBS) [30].

2.6. X-ray diffraction (XRD)

XRD experiments were completed on a Bruker D8 Advance XRD (Germany) employing a Cu Kα radiation. The acceleration voltage is 40 kV with 200 mA. The diffraction angles were from 5° to 50° at a scan rate of 5° min^{-1}.

2.7. Mechanical properties

Mechanical properties of the samples were finished by an Instron (Canton, MA) 5500R Universal Testing Machine (USA) with a crosshead speed of 10 mm/min. All films were cut into 60 mm × 25 mm × 0.5 mm in length, width, and thickness, respectively.

2.8. Thermal stability analysis

Thermogravimetric (TG) analysis of the samples was conducted using a Q600 TG analyzer (TA, USA). Heating was performed from 30 °C to 500 °C at a heating rate of 20 °C/min in nitrogen.

2.9. Water contact angle (WCA)

The hydrophilic properties were determined by WCA measurements (DSA100, KRUSS, Germany). The water was injected at a speed of 0.6 μL s^{-1}. All samples were measured five times at the round and center of every film. The final value was the average of the five numbers.

2.10. Enzymatic degradation

The blend films, 30 mm × 10 mm × 0.5 mm in length, width, and thickness, were incubated in K_2HPO_4/KH_2PO_4 buffer (0.1 M, pH 7.2) containing 0.15 U/mL cutinase and 0.2 U/mL cellulase at 45 °C. Collect the degraded films, wash with deionized water after incubating, and dry the cleaned films at 50 °C in vacuum. The weight loss rate before and after degradation was calculated according to Eq. (2):

$$W_{loss}(\%) = \frac{W_{before} - W_{after}}{W_{before}} \times 100\%, \quad (2)$$

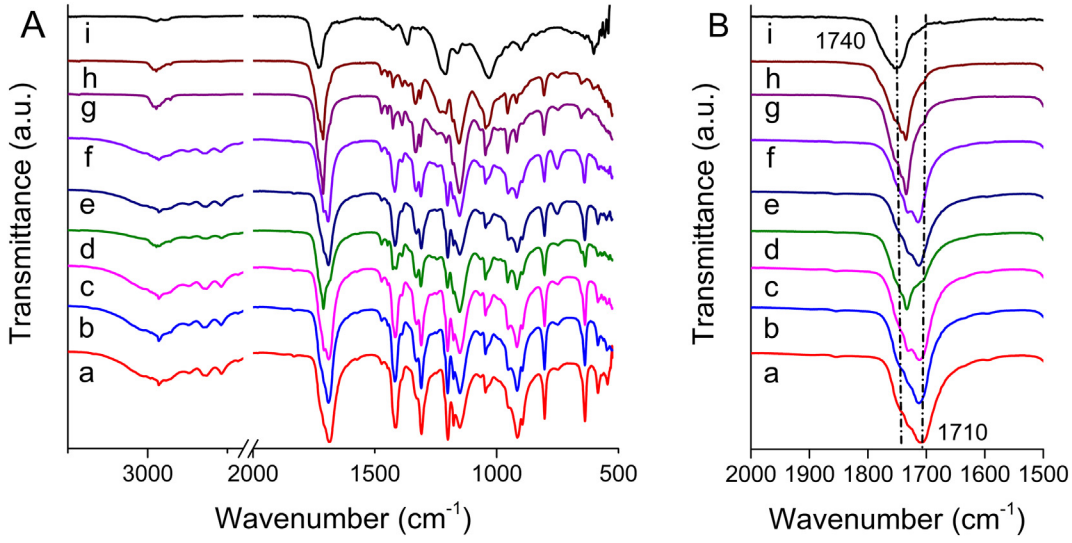

Fig. 1. FTIR spectra of (a) neat PBS, (b) PBS/CT1, (c) PBS/CT5, (d) PBS/CT10, (e) PBS/CT15, (f) PBS/CT20, (g) PBS/CT25, (h) PBS/CT30, and (i) neat CT. Spectra (A) is from 3500 cm^{-1} to 500 cm^{-1}, and (B) is from 2000 cm^{-1} to 1500 cm^{-1}.