

# Miscibility and crystallization behavior of biodegradable poly(butylene succinate-co-butylene carbonate) and tannic acid blends



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## ABSTRACT

Biodegradable poly(butylene succinate-co-butylene carbonate) (PBSC) and tannic acid (TA) blends were prepared via a solution and casting method in this work. Miscibility and crystallization behavior of PBSC/TA blends were investigated with various techniques. PBSC is miscible with TA as evidenced by both a single composition dependent glass transition temperature and the depression of equilibrium melting point of PBSC in the blends. Relative to neat PBSC, blending with TA does not modify the crystal structure of PBSC in the blends. The nonisothermal melt crystallization of PBSC was retarded by TA in the blends. Both the overall isothermal melt crystallization rates and spherulitic growth rates of PBSC/TA blends show the similar variation trends, which become slower with increasing crystallization temperature and the TA composition. The crystallization mechanism of PBSC does not change, regardless of crystallization temperature and the TA composition in the blends.

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## 1. Introduction

As a relatively novel chemosynthetic biodegradable polymer, poly(butylene succinate-co-butylene carbonate) (PBSC) is a crystalline thermoplastic, which has recently been developed by Mitsubishi Gas Chemical Company, Japan [1–6]. PBSC is a random copolymer, which is related to biodegradable poly(butylene succinate) (PBS) and poly(butylene carbonate) (PBC); therefore, the thermal and mechanical properties as well as biodegradability of PBSC can be controlled by changing the butylene carbonate unit ratio of the random polymer. PBSC has attracted some commercial interests, because it possesses physical properties similar to common thermoplastics, such as polypropylene and polyethylene. Pranamuda et al. found that PBSC degraded completely and rapidly with a high yield of cell growth [1]. In our previous work, we once investigated the crystal structure, melting behavior, and morphology of PBSC by means of wide angle X-ray diffraction, differential scanning calorimetry, temperature modulated differential scanning calorimetry, and optical microscopy [2]. Ikehara et al. studied the miscibility and the spherulitic morphology of PBSC/poly(L-lactic acid) (PLLA) blends [3,4]. They found that PBSC and PLLA were miscible crystalline/crystalline polymer blends; moreover, the two

components could form interpenetrated spherulites under certain crystallization conditions [3,4]. Lee et al. prepared blends of cellulose acetate butyrate (CAB) and PBSC by thermal compounding and studied their mechanical, thermal and rheological properties, and crystallization behavior [5,6]. The experiments revealed that PBSC was partially miscible with CAB; moreover, the overall crystallization rates of PBSC were reduced with increasing the CAB component in the PBSC/CAB blends [5,6].

As a high molecular weight polyphenolic compound mostly extracted from plants and microorganisms, tannic acid (TA) is fully biodegradable [7]. Recently, Woo et al. have reported the miscibility and crystallization behavior of a series of the TA-based polymer blends [7–10]. They found that TA was miscible with some biodegradable polyesters, such as poly( $\epsilon$ -caprolactone) (PCL), poly(ethylene adipate) (PEA), and poly(butylene adipate) (PBA), respectively, over the entire blend compositions range, as evidenced by the single composition dependent glass transition temperature, because the phenolic hydroxyl groups of TA may form specific intermolecular hydrogen bonding interactions with the carbonyl groups of polyesters [7]. Woo et al. also reported that TA and poly(ethylene oxide) (PEO) were miscible polymer blends and studied the effect of TA on the crystalline morphology of PEO [8]. Similarly, TA was found to be miscible with poly(ethylene succinate) (PES); moreover, a single-crystal-like dendrites morphology induced by TA was observed in the blends [9,10]. However, in the case of TA/poly(hexamethylene sebacate) (PHS) polymer blends, TA

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was found to be immiscible with PHS without the specific interactions [9].

To our knowledge, the study on the miscibility and crystallization behavior of PBSC and TA blends has not been reported so far in the literature. In this work, we chose the PBSC/TA blends as the model system to study the miscibility and crystallization behavior of polymer blends for the following three reasons. First, both components are biodegradable; therefore, the PBSC/TA polymer blends are fully biodegradable without losing biodegradability. Second, it is very likely that PBSC form miscible polymer blends with TA because of their specific intermolecular hydrogen bonding interactions; therefore, PBSC and TA will form novel miscible crystalline/amorphous polymer blends. Third, blending with TA may not only enhance the glass transition temperature but also affect the crystalline morphology, crystallization rate, and degree of crystallinity of PBSC in the blends, which will further influence the final properties and biodegradation behavior of PBSC/TA blends. The research reported herein will be interesting and helpful for a better understanding of the miscibility and crystallization behavior study of biodegradable polymer blends from both academic and industrial viewpoints.

## 2. Experimental details

PBSC ( $M_w = 2.0 \times 10^5$  g/mol) used in this study has a butylene carbonate unit of 10 mol%, which was kindly provided by Mitsubishi Gas Chemical Company, Japan. TA ( $M_w = 1721$  g/mol) was purchased from Sigma–Aldrich (Shanghai) Trading Co., Ltd. Both samples were used as received.

PBSC/TA blends were prepared with 1,4-dioxane as mutual solvent at around 50 °C. The solution of both polymers (0.0125 g/mL) was cast on glass plates at 50 °C. The solvent was allowed to evaporate in a controlled air stream for 1 day, and the resulting films were further dried in vacuum at 50 °C for 3 days to remove the solvent completely. In this way, PBSC/TA blends were prepared with various compositions ranging from 100/0, 90/10, 80/20, 60/40, 40/60, 20/80, and 0/100 in weight ratio, the first number referring to PBSC.

Glass transition temperature ( $T_g$ ) and melting point ( $T_m$ ) of the melt-quenched PBSC/TA blends were measured with a TA Instruments differential scanning calorimeter (DSC) Q100 with a Universal Analysis 2000 at a heating rate of 20 °C/min. The samples were first annealed at 150 °C for 3 min to erase any thermal history and then quenched quickly to –70 °C. Both the nonisothermal melt crystallization behavior and overall isothermal melt crystallization kinetics of neat PBSC and the PBSC/TA blends were also studied with DSC under different crystallization conditions. For the nonisothermal melt crystallization behavior study, the samples were first annealed at 150 °C for 3 min to erase any thermal history and then cooled to 20 °C at a cooling rate of 5 °C/min. For the overall isothermal melt crystallization kinetics study, the samples were first annealed at 150 °C for 3 min to erase any thermal history, cooled to the crystallization temperature ( $T_c$ ) at 60 °C/min, and then maintained at  $T_c$  for a period of time until the crystallization was complete. After isothermal melt crystallization, the samples were heated to the melt again at 20 °C/min to study the subsequent melting behavior for the estimation of equilibrium melting point temperatures of neat PBSC and the PBSC/TA blends. In the present work, only three samples, i.e., neat PBSC, 90/10, and 80/20, were used to investigate the nonisothermal and isothermal melt crystallization behaviors, because PBSC did not crystallize or crystallized very slowly when the TA content was 40 wt% and above in the PBSC/TA blends.

Wide-angle X-ray diffraction (WAXD) experiments were performed with a Rigaku X-ray diffractometer RINT2100 at 40 kV and

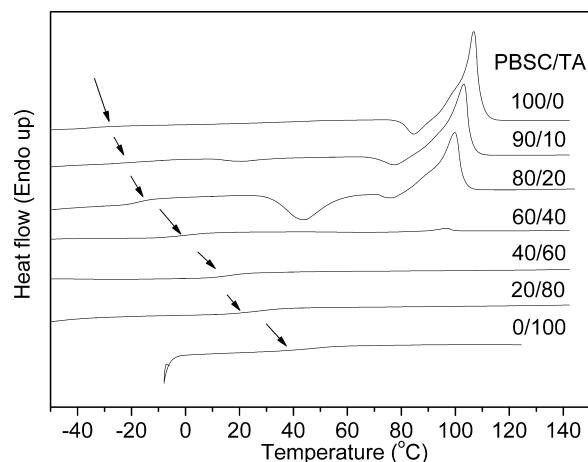


Fig. 1. DSC traces of neat PBSC, neat TA, and their blends from the melt-quenched samples at a heating rate of 20 °C/min.

200 mA at 5 °/min. The samples for the WAXD experiments were prepared as follows. They were first pressed into films with thickness of around 1 mm on a hot stage at 150 °C and then transferred into a vacuum oven at 79 °C for 3 days.

A polarized optical microscope (POM) (Olympus BX51) equipped with a first-order retardation plate and a temperature controller (Linkam THMS 600) was used to observe the spherulitic morphology and growth of neat PBSC and the PBSC/TA blends. The samples were first annealed at 150 °C for 3 min to erase any thermal history and then cooled to the crystallization temperature at 60 °C/min. The spherulitic growth rate ( $G$ ) was calculated by measuring radius ( $R$ ) against crystallization time ( $t$ ), i.e.,  $G = dR/dt$ .

## 3. Results and discussion

### 3.1. Miscibility and crystal structure of PBSC/TA blends

The miscibility study is of great importance for biodegradable polymer blends, because it not only affects the crystallization behavior but also the physical properties and biodegradation of polymer blends [11–16]. Therefore, the miscibility of PBSC/TA blends was investigated first with DSC. Fig. 1 shows the DSC traces of neat PBSC, neat TA, and their blends for the melt-quenched samples. As shown in Fig. 1, for neat PBSC, it has a  $T_g$  of –35.4 °C and a  $T_m$  of 106.9 °C with a  $\Delta H_m$  of 66.7 J/g, while for neat TA, it has only a  $T_g$  of around 42 °C, showing its amorphous feature. For the PBSC/TA blends, they present a single composition dependent  $T_g$  between those of neat PBSC and neat TA; moreover, the  $T_g$  values increase with the TA content in the blends, indicating that PBSC is miscible with TA over the entire blend compositions. It is also interesting to find a depression of  $T_m$  of PBSC in the PBSC/TA blends, relative to neat PBSC. In the case of a 90/10 sample, it has a  $T_m$  of 103.1 °C with a  $\Delta H_m$  of 58.1 J/g, and in the case of an 80/20 sample, it has a  $T_m$  of 99.8 °C with a  $\Delta H_m$  of 56.6 J/g. Especially, a cold crystallization exotherm is found for the 80/20 sample with a peak temperature of 43.7 °C and a cold crystallization enthalpy of around 38 J/g. With increasing the TA content to 40 wt% and above,  $T_m$  of PBSC can hardly be observed in the PBSC/TA blends. Such depression of  $T_m$  indicates not only the restricted crystallization of PBSC in the blends but also the miscibility of the PBSC/TA blends.

Fig. 2 summarizes the variation of  $T_g$  with the TA composition for the PBSC/TA blends. In the present work, the well-known Kwei equation was used to fit the measured  $T_g$  values against the TA

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