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"Nucleation density reduction" effect of biodegradable cellulose acetate butyrate on the crystallization of poly(lactic acid)

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ABSTRACT

Both poly(lactic acid) (PLA) and cellulose acetate butyrate (CAB) are bio-based and biodegradable. In this work, the effect of CAB on the cold and melt crystallization behavior of PLA was investigated by differential scanning calorimetry and polarized optical microscopy. Both the cold and melt crystallization of PLA was dramatically inhibited even at a very low loading of 0.5 wt% CAB. The isothermal crystallization kinetics was analyzed by the Avrami model. It was found that the Avrami exponent of PLA crystallization was not significantly influenced by the addition of CAB, indicating that the crystallization mechanism of PLA almost did not change in the blends. The crystallization half-time of the blends increased significantly with increasing CAB loading. The observation from optical microscopy further revealed that the presence of CAB reduced remarkably the nuclei density but had nearly no influence on the spherulite growth rate of PLA. These observations indicate that CAB has dramatic "nucleation density reduction" effect on PLA.

1. Introduction

Poly(lactic acid) (PLA) is a biodegradable semicrystalline polyester derived from renewable resources and widely used in biomedical and environmental applications [1–3]. PLA is generally synthesized by ring-opening polymerization of lactide, a lactic acid dimmer. Lactic acid has two optically active configurations known as L-lactic acid and D-lactic acid. The L-form is usually the main constituent of commercially available PLA. The introduction of D-lactic acid into PLA molecules induces the decrease in crystallinity and spherulite growth rates [4]. Judicious selection of appropriate PLA resin grade is important to match the conversion process conditions used. Usually, PLA resins of less than 1% D-isomer PLA articles would be more suitable for injection molding where higher crystallization rate is preferred [2,3]. Incorporating nucleating agent in PLA can further increase the crystallization rate of the material [3,5–9], which lowers the surface free energy barrier for nucleation and enables crystallization at higher temperature to take place upon cooling. In contrast, PLA resins with higher D-isomer contents (4–8%) would be more suitable for blow molded (e.g., injection molded preform for blow molding) products, since rapid crystallization of the polymer would hamper the stretching of the preform and optical clarity of the resulting bottle [2–10]. Note that incorporating an "nucleation density reduction" agent can also decrease the crystallization rate of polymers. It was reported that the addition of polystyrene or styrene-*co*-acrylonitrile could significantly reduce the crystallization rate of poly(ethylene terephthalate) [11,12]. However, to the best of our knowledge, "nucleation density reduction" effect on PLA has not been reported.

Cellulose acetate butyrate (CAB) is an abundant natural polymer derivative with environmentally friendly properties such as biodegradable [13]. Some researchers reported that CAB acted as a plasticizer for some polyesters [14,15]. And some researchers considered CAB as multifunctional additive for poly(butylene succinate) by melt blending [16], while others were interested in developing eco-friendly materials by blending CAB with other biodegradable polyesters [17].

In this work, the effect of CAB on the crystallization behavior of PLA was investigated using differential scanning calorimetry (DSC) and polarized optical microscopy. It will be shown that the presence of small amounts of CAB can dramatically reduce the nucleation density of PLA.

2. Experiment

Materials and sample preparation: The PLA comprising around 2% D-lactide comonomer was from Nature Works (Minnetonka,

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USA). The number- and weight-average molecular weights of this resin were 1.11×10^5 and 1.71×10^5, respectively. CAB was obtained from Eastman (Tennessee, USA). It was a cellulose ester with butyryl of 53 wt%, acetyl of 2 wt%, and hydroxyl of 1.5 wt%, and its number average molecular weight was 1.6×10^4. Neat PLA and PLA/CAB blends were prepared by solvent casting using dichloromethane. The solution of the blends (0.02 g/ml) was cast on a petri dish at room temperature, followed by evaporation in a controlled air stream until films were formed, and the films were further dried in vacuum at 40 °C for 16 h and then at 60 °C for 8 h. The weight fractions of CAB in PLA blends were 0, 0.5, 1, 2, 5, 10, 25, 50 and 100 wt%, and these blends were defined as PLA, CAB0.5, CAB1, CAB2, CAB5, CAB10, CAB25, CAB50 and CAB100.

Characterization: A DSC 2920 (TA Instruments) was used to study the crystallization behavior of PLA and its blends with CAB. The weight of sample was about 7 mg. Four groups of measurements

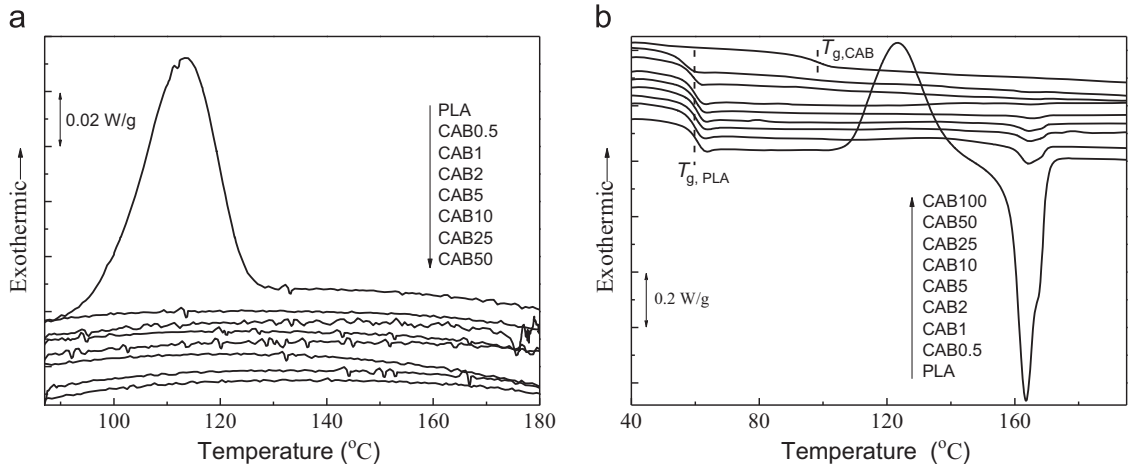

Fig. 1. DSC traces of PLA/CAB blends recorded (a) upon cooling from the melt at a rate of 2 °C/min and (b) during a heating process at 10 °C/min for melt-quenched samples.

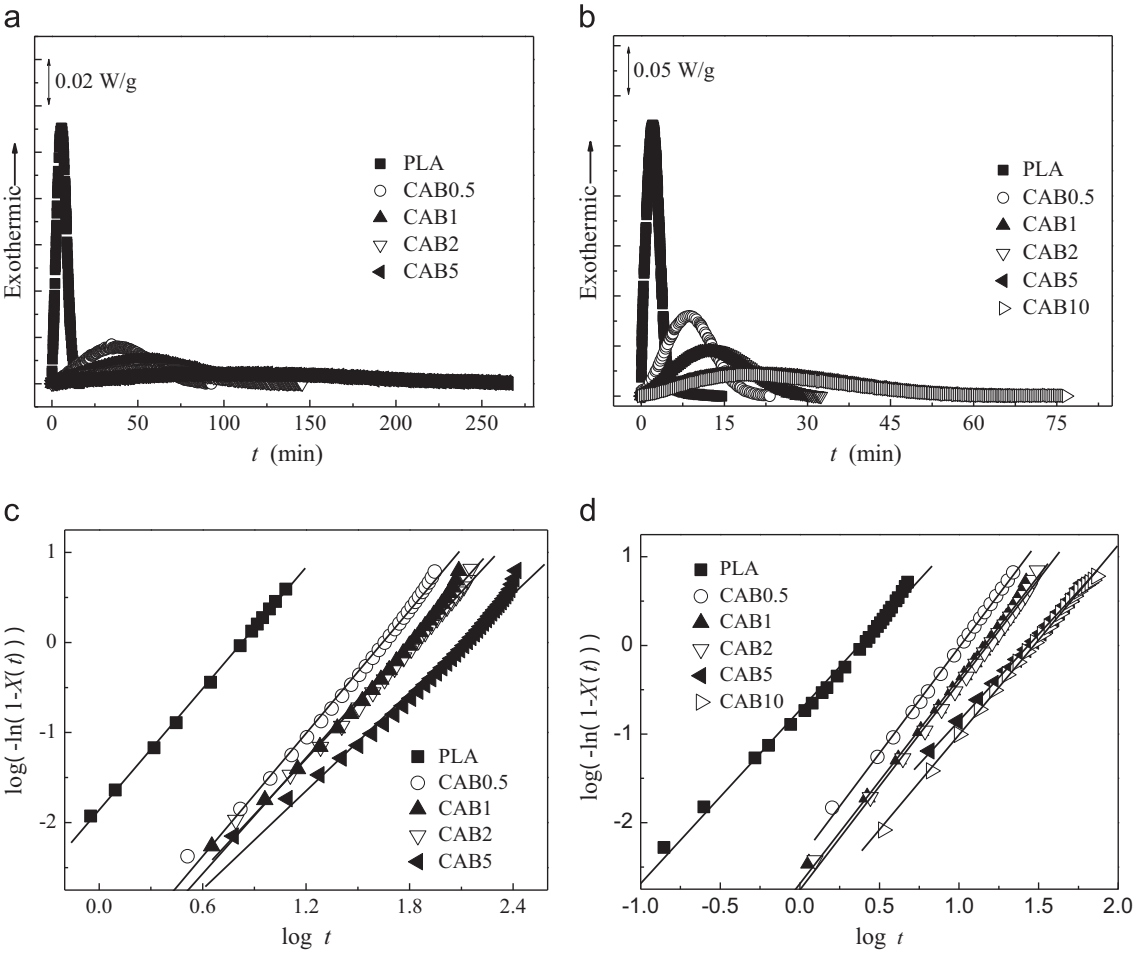

Fig. 2. DSC traces recorded in isothermal melt (a) and cold (b) crystallization at 125 °C for PLA/CAB blends; Plots of $\log(-\ln(1-X(t)))$ versus $\log t$ for isothermal melt (c) and cold (d) crystallization.