Insight into the annealing peak and microstructural changes of poly(L-lactic acid) by annealing at elevated temperatures

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ABSTRACT

An endothermic annealing peak appears in DSC heating scans of cold-crystallized poly(L-lactic acid) after annealing above the cold-crystallization temperature. The annealing peak shifts to higher temperature and its magnitude increase with increasing annealing temperature or time. Furthermore, the origin of the annealing peak and microstructural changes of poly(L-lactic acid) were investigated by temperature-modulated differential scanning calorimetry (TMDSC), Wide-angle X-ray diffraction (WAXD), small-angle X-ray scattering (SAXS) and dynamic mechanical analysis (DMA). During TMDSC scan, the observed annealing peak on the total heat flow (THF) is separated into an endothermic peak of enthalpy relaxation on the nonreversible heat flow (NHF) and a glass transition (devitrification) step on the reversible heat flow (RHF). SAXS results showed that the significant increase in long period mainly arises from the increase in the amorphous layer after annealing. The storage modulus is enhanced with increasing annealing temperature, accompany with glass transition temperature shifts to lower temperature, and the softening is also observed above annealing temperature in DMA measurements. It is showed that the annealing at elevated temperature promotes the chain mobility of the constraint amorphous phase and divides them into more orderly rigid amorphous fraction (RAF) and more disorderly mobile amorphous fraction (MAF). The above results indicate that the annealing peak is attributed to the nonreversible enthalpy relaxation of RAF, which formed by annealing process, rather than the melting of thin lamellae or imperfect crystals formed by secondary crystallization.

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1. Introduction

Annealing a semicrystalline polymer at elevated temperature between the glass transition temperature and the melting point is an effective approach to promote chain relaxation toward a more stable thermodynamically state and induce significant changes in microstructure and physical properties [1–3]. Depending on the annealing temperature, secondary crystallization, lamellar perfection/thickening, (partial) melting-recrystallization, polymorphic phase transition, and rearrangement of molecular chain in constrained amorphous phase are thought to be common occurrences [4–6]. In the past decades, extensive efforts have been dedicated to trace the changes in microstructure and physical properties during annealing process [3–12]. Demonstrated in differential scanning calorimetry (DSC) measurements, a shoulder endotherm (usually termed an "annealing peak") is observed just about several degrees above the corresponding annealing temperatures. However, the origin of the annealing-induced endotherm, commonly observed for many semicrystalline polymers [2–26], is still under debate.

There are three major mechanisms proposed to explain this phenomenon, namely, melt- recrystallization, dual lamellae stack, and physical aging and/or relaxation [10,15–17]. The melt-recrystallization mechanism suggests that the low-temperature endotherm is attributed to the melting of the initial lamellae. The (partially) melted material then undergoes a continuous process of recrystallization into thicker and more perfect lamellae, which melt at higher temperature during DSC heating scans [10,27]. The dual lamellae stack model associates the double melting with two different morphologies formed prior to the heating scan, for example, from the primary and secondary crystallization. It is widely believed in many earlier studies that the annealing peak is associated with the melting of secondary (thinner or less perfect) lamellae formed in constrained

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amorphous phase between primary (thicker or more perfect) lamellae [13,15]. The physical aging and/or relaxation model prefers that the low endotherm is the enthalpic recovery of a physically aged intermediate phase between the crystalline and the amorphous chain segments, which is called the "rigid amorphous fraction" (RAF) [18–22,28]. Due to the physical constraints imposed by the conjoint lamellae, the devitrification of RAF is significantly higher than that of the mobile amorphous fraction (MAF) and can even reach the range of melting temperature of the coupled crystals. Since the formation and existence of RAF is evidenced for most of the semicrystalline polymers [18–22,29–36], it is essential to understand the role of RAF in the changes of microstructure induced by annealing. It should be noted that none of the models fit with all the experimental results.

Poly(L-lactic acid) (PLLA) is one of the most promising fully bio-based and biodegradable polymer with excellent mechanical properties, easy processability and reasonable price [37–39]. Because of its bioresorbable and biocompatible features, PLLA is widely used in biomedical applications, such as surgical sutures, scaffolds, bone fixation, and controlled drug release matrices. Furthermore, concerning its favorable biodegradability, renewability, good mechanical properties and processability, PLLA has excellent potential for substitution of petroleum-based polymers and serves as engineering plastics, such as packaging, agricultural films, office utensils, electric appliance bodies, and automobile components [40–42]. As for the polymorphic biodegradable polymers, a broad range of properties, for instance, thermal, mechanical properties, and biodegradation, greatly depend on the crystalline structure as well as morphology. In addition, it is difficult for PLLA molecular chains to arrive at their equilibrium state as they are rapidly cooled down from melt state because of its intrinsic low rate of crystallization [40]. As a result, the PLLA products are usually amorphous, thus, heat treatment is required to enhance the strength and dimensional stability [42–44].

Although the effects of annealing on the microstructures (including crystalline structure, crystal morphologies and modifications) and mechanical properties (modulus, tensile and impact strength) of poly(lactic acid) have been investigated extensively [44–49]. However, to our best knowledge, the analogous annealing peak induced by annealing has not been mentioned for PLLA during annealing at elevated temperature [50,51]. Shen and Wang [52] showed DSC curves for isothermally cold-crystallized samples with different crystallization temperatures (T_c). A weak endothermic peak becomes visible at a few degrees above T_cs, but they did not remark on it as "annealing peak" and suggested that it is probably from the thinner lamellae formed in the excluded regions. Until now, the assignment and origin of the low temperature peak for PLLA is still ambiguous, and its correlation between the microstructural or morphological changes and mechanical properties during annealing is not well established yet.

In this work, we performed standard DSC and temperature-modulated DSC (TMDSC), small-angle X-ray scattering (SAXS), as well as dynamic mechanical analysis (DMA) to focus on the origin of the low temperature endothermic annealing peak and provide a new insight into the relationship between the microstructural changes and physical properties of PLLA after annealing above the cold-crystallization temperature.

2. Experimental

2.1. Materials and sample preparation

An injection grade poly(L-lactic acid) (PLLA, Biopla 305D) resin used in this work was purchased from Biopla Products Factory (China). The content of D-isomer units is 4%, according to 92% of optical purity measured by a Jasco P-1010 polarimeter. The number-averaged and weight-averaged molecular weights are M_n = 71 kDa and M_w = 118 kDa, respectively, determined by gel permeation chromatography (GPC) using polystyrene as standard and tetrahydrofuran as solvent.

Amorphous films were compression-molded in a hydraulic press unit equipped with heating plates. Dried resin was sandwiched between a layer of PET film and then a layer of stainless steel platen on each side. This sandwich was first held at 185 °C for 5min to ensure the completion of melting and the equilibrium of temperature. Then, a load of 1.5 tons was applied for another 5min before immediately removing from the press and quenching into ice−water for preventing crystallization. The transparent films of approximately 0.3 mm thick were stored in a desiccator prior to further measurements.

2.2. Wide-angle X-ray diffraction (WAXD)

The as-molded amorphous films were isothermally crystallized at 90 °C for 2 h with/without subsequent annealing at 120 °C for 2 h, followed by quenching to room temperature for wide-angle X-ray diffraction (WAXD) measurements. WAXD analysis was performed on a D/max-Ultima+ X-ray diffractometer (Rigaku, Japan) with Ni-filtered Cu Kα radiation (λ = 0.15418 nm) at room temperature (ca. 20 °C). The operating target voltage was 40 kV and the tube current was 100 mA. Scans were made from 10° to 30° at a rate of 1.2°/min.

2.3. Standard DSC

DSC experiments were performed in a DSC1 (Mettler-Toledo, Switzerland) differential scanning calorimeter. The instrument was calibrated using high purity indium and zinc standards. The weights of all the samples were in the range of 5 ± 0.1 mg. The amorphous samples were isothermally crystallized and/or sequentially annealed at different temperatures for different times as indicated. After the completion of isothermal crystallization or annealing treatments, the samples were immediately heated to melt state at 10 °C/min. All crystallization and annealing treatments were performed in DSC cell under nitrogen atmosphere in order to diminish oxidation.

2.4. Temperature modulated DSC (TMDSC)

Temperature-modulated differential scanning calorimetry (TMDSC) studies were carried out with a TA Instruments temperature modulated DSC Q2000 (TA, USA). The amorphous samples were isothermally crystallized at different temperatures (90 °C or 120 °C) for 2 h with/without sequentially annealed at different annealing temperatures (120 °C or 90 °C) for 2 h, followed by quenching to room temperature for TMDSC measurements. All TMDSC measurements were performed under nitrogen atmosphere at a heating rate of 3 °C/min with temperature modulation amplitude of 0.5 °C and temperature modulation period of 60 s.

2.5. Small angle X-ray scattering (SAXS)

The as-molded amorphous films were isothermally crystallized at 90 °C for 2 h with/without sequentially annealed at 120 °C for 2 h, followed by quenching to room temperature for small-angle X-ray scattering (SAXS) measurements. SAXS measurements were carried out at room temperature with a NanoStar U SAXS instrument (Bruker AXS Inc., USA) with a wavelength of 0.154 nm using Cu Kα radiation at 40 kV and 650 µA. The 3-pinhole collimation system provides a precisely parallel X-ray beam with high intensity.