



Enhancing mechanical performance of polylactide by tailoring crystal morphology and lamellae orientation with the aid of nucleating agent



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ABSTRACT

The performance of semicrystalline polymers is significantly dependent on the crystal morphology and lamellae orientation. In this work, the crystal superstructure and mechanical properties of polylactide (PLA) with different amounts of nucleating agent (tetramethylene-dicarboxylic dibenzoyl-hydrazide, TMC-306) were investigated. It was found that TMC-306 can be dissolved in PLA melt and re-crystallize into fibrils upon cooling. These fibrils can serve as nucleation templates to induce the crystallization of PLA on their surface, resulting in a large enhancement in crystallization rate. More importantly, PLA lamellae can grow perpendicular to the long axis of TMC-306 fibrils, inducing the formation of shish-calabash, shish-kebab and needle-like structures, depending on the concentration of TMC-306 used. Taking advantage of shear flow experienced in injection molding, TMC-306 fibrils tend to align in PLA melt along the shear flow direction, inducing the formation of highly orientated PLA lamellae in injection-molded articles. In this way, a simultaneous improvement in impact toughness, tensile strength and elongation at break is achieved. This work provides a good example of using a fibrous nucleating agent as a template to tailor the crystal morphology and lamellae orientation, thus achieving greatly enhanced properties for PLA.

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1. Introduction

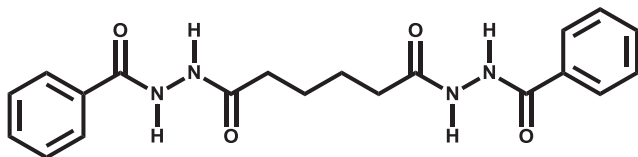
With the increasing environmental problems, much attention has been paid to the development of the eco-friendly polymers to replace petroleum-based ones during the last two decades [1,2]. Polylactide (PLA) has been regarded as one of the most promising candidates because of its renewability, excellent biodegradability, good processability, well biocompatibility, extraordinary transparency, and favorable mechanical strength [3,4]. It has been applied to industrial packaging materials, bio-medical devices, and commodity plastics [2,5,6]. However, although PLA is a crystallizable polymer, nearly fully amorphous articles are usually obtained through traditional processing methods due to its very low crystallization rate, which gives rise to a poor heat-resistance [4,7,8]. Both strength and modulus drop dramatically when the temperature is close to the glass transition temperature (T_g , about 55–60 °C) [9], thus the practical applications of PLA have been greatly limited in many fields where heat-resistance is required. Heat-resistant articles can be obtained by annealing to increase the crystallinity

of PLA, but it is time-consuming and difficult to realize in industrial production.

Adding a nucleating agent (NA) is one of the easiest and most efficient ways to accelerate the crystallization of PLA by providing a low energy barrier for nucleation and permitting crystallization at higher crystallization temperatures (T_c) [10]. Many kinds of NAs have been developed to effectively nucleate PLA crystallization, including inorganic NAs [9–15], macromolecular NAs [16–22], and small molecular organic NAs [23,24]. For example, with the addition of 1 wt% talc, half-crystallization time ($t_{1/2}$) of PLA at 115 °C is reduced from around 25 min to 0.4 min and the optimum T_c is increased by about 20 °C as compared to that of neat PLA [11]. Stereocomplex formed by equimolar mixtures of poly(L-lactide) (PLLA) and poly(D-lactide) (PDLA) is a recently developed NA for PLA. The stereocomplex has a strong nucleation effect on the crystallization of PLA, the $t_{1/2}$ at 140 °C is decreased from 17 min to no more than 1 min in the presence of 3 wt% stereocomplex [18,19]. In contrast with the use of inorganic NAs and stereocomplexes, incorporation of small molecular organic NAs is a more promising method for the modification of the crystallization behavior of PLA. Besides much higher nucleation efficiency, they have the ability to effectively control the crystal morphology of PLA [23,24]. It has been demonstrated that N,N',N''-tricyclohexyl-1,3,5-benzene-tricarboxylamide (TMC-328), a kind of small molecular organic NA,

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Scheme 1. Chemical structure of TMC-306.

can be dissolved in PLA melt and self-organize into fine fibrils upon cooling to induce the epitaxial growth of PLA lamellae on their surface, forming charming shish-kebab-like structure [24].

Crystal morphology is of great significance for the manipulation of final properties of semicrystalline polymers [25–30]. It is well-known that semicrystalline polymers including PLA can crystallize into two different crystal morphologies from the melt, i.e., spherulites and shish-kebab crystals. Compared with spherulites, the highly oriented shish-kebab crystals can impart polymer articles with significantly improved mechanical properties [27–29]. Unfortunately, exclusive formation of such highly oriented crystal structures in the articles can only be realized by using special processing technologies, such as shear-controlled orientation injection molding [27–29] and vibration-assisted injection molding [31], whereas only a very small amount of oriented crystal structures can be obtained in the articles prepared by traditional injection molding technology because of the absence of the oscillatory shear field allowing for the occurrence of flow-induced crystallization. On the other hand, very limited efforts have been devoted to the improvement in its mechanical properties of PLA by tuning the crystallization, probably because it is difficult to control the crystal morphology, especially lamellae orientation. Herein, an effort to enhance the performance of PLA by using an organic NA capable of self-organizing into fibrils to function as a robust template to tailor the crystal morphology and lamellae orientation is reported. A small molecular organic NA, i.e., tetramethylene-dicarboxylic dibenzoyl-hydrazide (TMC-306) with a much higher solubility than TMC-328 in the PLA melt and a similar self-organization behavior to that of TMC-328 was selected as an efficient NA for PLA. It was expected that TMC-306 fibrils would align along the flow direction during injection molding and the preorientation of these fibrils could transform into the orientation of PLA lamellae during subsequent isothermal crystallization in hot mold, thus imparting the injection molded PLA articles with greatly improved impact toughness and tensile strength. This strategy may provide a universal platform for optimizing the performance of PLA by controlling crystal morphology and lamellae orientation.

2. Experimental

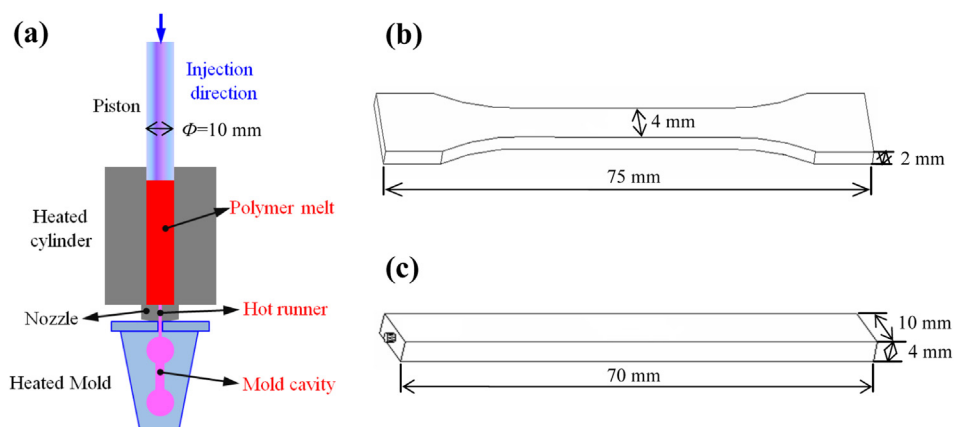
2.1. Materials and sample preparation

PLA (4032D) containing 1.2–1.6% D-LA were purchased from Natureworks, USA. It has a weight-average molecular weight (M_w) of 207 kDa and a polydispersity index of 1.74. Tetramethylenedicarboxylic dibenzoylhydrazide (TMC-306) was provided by Shanxi Provincial Institute of Chemical Industry, China. The chemical structure of TMC-306 is given in Scheme 1.

A HAAKE internal mixer (Thermo Scientific, USA) was used to prepare PLA containing various amounts of TMC-306. The melt-compounding was performed at a temperature of 190 °C and a rotation rate of 60 rpm for 6 min. Since small amounts of TMC-306 are difficult to disperse well in PLA matrix, a master-batch of PLA containing 5 wt% TMC-306 was first prepared and then diluted with neat PLA. Mixtures of PLA and TMC-306 were labeled as a code of PLA-x, in which x represents the weight percentage of TMC-306 in the mixture (i.e., 0.1 wt%, 0.2 wt%, 0.3 wt%, and 0.5 wt%). After melt-compounding, samples for mechanical testing were injection molded using a HAAKE MiniJet (Thermo Scientific, USA), the barrel temperature and the mold temperature were set at 200 °C and 130 °C, respectively. The schematic representation of the MiniJet injection molding system and the dimension of the mold cavities used for preparing mechanical testing bars are presented in Scheme 2. The system is designed as a piston injection machine. During injection molding, the polymer melt in the heated cylinder is injected into the hot mold under high pressure imposed by a piston. Specially, to achieve highly crystalline PLA, all injection molding samples were permitted to crystallize in the hot mold for 8 min. For comparison, neat PLA without nucleating agent was also prepared using the same method. PLA is known to undergo thermal-induced hydrolytic degradation during melt processing, leading to a drop in molecular weight. In order to minimize the molecular weight drop, besides choosing low process temperature (i.e., 190 °C), all materials were dried in vacuum oven at 60 °C for at least 12 h before compounding and injection-molding.

2.2. Differential scanning calorimetry (DSC)

Thermal analysis was performed using a Perkin–Elmer pyris-1 DSC (USA) in a nitrogen atmosphere. Specimens with a weight of about 5 mg were first heated to 200 °C and held for 5 min to eliminate the thermal history. The crystallization temperature (T_c) was determined from the cooling run at a rate of 2 °C/min. The melting temperature and melting enthalpy of each specimen were



Scheme 2. (a) Schematic representation of HAAKE MiniJet injection molding system; typical geometries of the mold cavities used for preparing (b) tensile testing bars, and (c) impact testing bars.

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