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Strong synergetic effect of fibril-like nucleator and shear flow on the melt crystallization of poly(L-lactide)

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ABSTRACT

Bio-based and bio-degradable poly(L-lactide), PLLA, suffers from low crystallization rate. The synergetic effect of fibril-like nucleator (N^1,$N^{1'}$-(ethane-1,2-diyl)bis(N^2-phenyloxalamide)) (OXA) and shear flow on speeding up the melt crystallization of the PLLA is the first time reported in this work. The synergetic effect was investigated by using a rheometer. Neither fibril-like OXA nor shear flow showed obvious accelerating effect at 155 °C on the crystallization of PLLA leading to limited crystallinity (X_c) within 70–100 min. In contrast, a crystallinity of more than 40% and an onset crystallization time (t_{onset}) of less than 3 min were achieved by tailoring the shear conditions. The critical shear condition for the fast crystallization of the PLLA/OXA systems at 155 °C is 0.4 rad/s for 10–15 s. A lower shear temperature (e.g., 150 °C in comparison with 155 °C) would increase the crystallization rate much further. Mechanism study revealed that the OXA fibril network and a certain extent of PLLA chain orientation that induced by the shear flow while subsequently stabilized by the OXA fibrils are responsible for the significantly enhanced nucleation and overall melt crystallization kinetics. In addition, the shear flow and fibril-like OXA nucleators not only facilitated the crystallization of PLLA α-form crystals but also promoted the formation of α'- (or δ) and β-form crystals.

1. Introduction

The bio-based and bio-compostable semi-crystalline poly(L-lactide), PLLA, has gained increasing attention these years in view of the sustainability and environmental issues that associated with traditional polymers [1,2]. The excellent performances make PLLA promising as an alternative for traditional polymers [3–5]. However, the end-use of PLLA articles suffers from low heat distortion temperature (HDT) due to its relatively low glass transition temperature (~60 °C) and low crystallinity after practical processing such as injection molding. Consequently, the wide application of PLLA in both commodity and biomedical fields is restricted. It is thus of importance to achieve high crystallinity of PLLA by speeding up the crystallization.

Heterogeneous nucleating agent is widely used to enhance the crystallization kinetics of PLLA by promoting the polymer chain folding at high(er) temperatures. Inorganic nucleating agents such as talc, clay, carbon nanotubes and graphene have been introduced into PLLA matrix, whereas agglomeration was often obtained due to the poor compatibility and insolubility in the PLLA melt, leading to uncontrollable shape/size and nucleation efficiency [6–8]. On the other hand, organic additives

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such as N,N-ethylene-bis(12-hydroxylstearamide) (EBH), poly(vinylidene fluoride), orotic acid, nucleobases, substituted-aryl phosphate salts (TMP-5) and N,N′,N″-tricyclohexyl-1,3,5-benzene-tricarboxylamide (TMC-328), N,N'-bis(benzoyl) hexanedioic acid dihydrazide (TMC-306), N^1,$N^{1'}$-(ethane-1,2-diyl)bis(N^2-phenyloxalamide) (OXA) and PLA stereocomplex were also developed as nucleating agents for PLLA [9–24]. Among above nucleating agents, TMC-328, TMC-306 and OXA were proven with high reactivity which can self-organize into superstructures in PLLA melt to accelerate the crystallization of PLLA [18–21]. However, the previous study is mainly confined to the crystallization of PLLA under static conditions and very limited or even no crystallinity was obtained under high temperature conditions (e.g., 145 °C for 90 min) even in the presence of OXA [20–21,25].

In addition, shear flow is an effective approach to increase the rate of crystallization which exists inevitably in polymer processing, e.g., extrusion, injection and blowing molding. The flow-induced crystallization is evidenced to take place in various semi-crystalline polymers such as poly(ethylene) (PE) and poly(propylene) (PP) [26–28]. Apparently, in applied flow field, the high orientation of molecular chains is examined along the flow direction and shear flow brings a large amount of row nuclei and consequently enhance the crystallization kinetics [29,30]. PLLA, as one of environmentally friendly polymers commercialized recently, however, is less studied in terms of flow-induced crystallization compared with polyolefin [31,32]. Nucleators together with shear flow may further accelerate the crystallization of PLLA, whereas their synergetic effect is seldom reported [33].

Rheometry as a helpful technique providing shear-flow field to investigate the crystallization of polymeric materials possesses several important advantages[34,35]: (i) it is more convenient and easier than other measurement methods such as small-angle light scattering (SALS), small-angle X-ray scattering (SAXS), wide-angle X-ray scattering (WAXS), and optical microscopy to track the crystallization processes of polymers, (ii) it can produce a continuous shear-flow field to magnify the very small transformation of microstructure in the polymeric materials and (iii) it is applicable to the component where some other methods may not work, for instance, the colored system and/or the filled composite component [36–38].

In our previous works, the OXA was proven with high nucleation activity which can self-organize into needle-like templates in the PLLA melt to initiate the fast crystallization of PLLA. Consequently, the half-life crystallization time ($t_{0.5}$) is decreased from 38.6 to 2.6 min at 135 °C [20]. However, the effect of OXA on the PLLA's crystallization in a flow field has not been reported, and the synergetic effect of the needle-like OXA and the shear flow on the rapid crystallization of PLLA is not yet clear. In this work, it is confirmed by employing rheometer, DSC and SEM that the synergistic effect of the OXA and the shear flow on accelerating the crystallization of PLLA. The finding on the synergistic effect may create a new approach to make PLLA-based products with high(er) crystallinity and fast(er) shaping rate.

2. Experimental section

2.1. Materials

Poly(L-lactide) (PLLA, 4032D) ($M_n = 2.1 \times 10^5$ g mol^{-1}, PDI = 1.7) with 2 wt% of D-lactide was provided by NatureWorks LLC, U.S.A. N^1,$N^{1'}$-(ethane-1,2-diyl)bis(N^2-phenyloxalamide) with a purity of 98%, briefed as OXA, was synthesized in the lab-

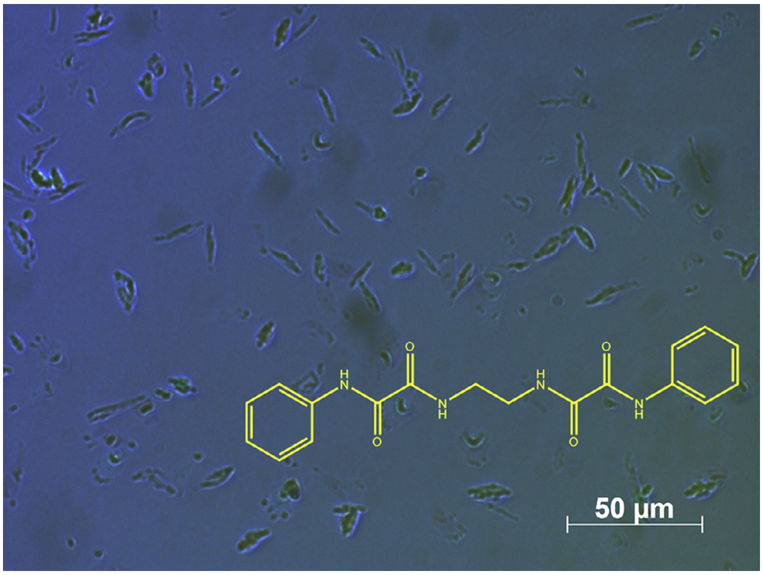

Fig. 1. The room temperature polarized optical microscopy (POM) image of the OXA with an inset of its chemical structure.