Contents lists available at ScienceDirect

European Polymer Journal

Macromolecular Nanotechnology

Non-isothermal crystallization behaviors of poly(lactic acid)/cellulose nanofiber composites in the presence of CO_2

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ARTICLE INFO

ABSTRACT

The effects of cellulose nanofiber (CNF) on the non-isothermal crystallization behaviors of poly(lactic acid) (PLA) at atmospheric pressure and at various CO_2 pressures were investigated using a regular differential scanning calorimeter (DSC) and a high-pressure DSC at different cooling rates of 1, 2, 3, and 5 °C/min. The POM images revealed that the CNFs acted as crystal nucleating agents, increasing the number of crystals and decreasing the crystal sizes. The non-isothermal crystallization showed that PLA's crystallization rate increased with cooling rates and the incorporation of CNFs accelerated the overall crystallization kinetics by providing more nuclei, thereby decreasing the crystallization half-time. The degree of crystallinity was not proportional to the CO_2 pressure. The highest crystallinity was obtained at a higher pressure with increased cooling rates. The activation energy analysis showed that the incorporation of CNFs restricted the movement of PLA molecular chains, thereby hindering crystallization. By comparing the Avrami analysis, Mo analysis, and activation energy results, it was speculated that heterogeneous crystal nucleation with the presence of CNFs might be the dominant factor in determining the overall non-isothermal crystallization rate of the PLA/CNF composites. Wide angle X-ray diffraction (WAXD) diffractograms showed that CNFs and CO_2 pressure had no influence on the crystalline structure of PLA. The effects of CNF content, CO_2 pressure, and cooling rate on T_c, T_m, and T_g were also investigated.

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1. Introduction

Each year, large amounts of petroleum-based plastic waste are produced worldwide, however, waste disposal has caused serious environmental problems. Poly(lactic acid) (PLA) is a bio-based, linear aliphatic polyester made entirely from annually renewable resources (e.g., corn and sugar beets) [1]. It consumes 50% less non-renewable energy during production than traditional petroleum-based plastics (e.g., polypropylene, low-density polyethylene, polystyrene, nylon, etc.) and is readily biodegradable for waste disposal purposes [2,3]. PLA has good physical and mechanical properties which are comparable to many petroleum-based plastics [1,2,4]. In addition, recent improvements in PLA manufacturing processes have made it a commercially available and large-volume plastic at competitive market prices [1,2,5]. Consequently, PLA is becoming one of the most promising sustainable alternatives to many petroleum-based counterparts. PLA is suitable for a

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wide-range of products including food packaging, nonwoven fabrics, and electronics [2,4,5]. It has also been widely used in biomedical applications due to its biodegradability and biocompatibility [4,6]. Nevertheless, the brittleness, slow crystallization rate, and low glass transition temperature of PLA limit its usages [1,2,7,8]. Enhancing the crystallization rate and developing higher crystallinity in PLA can improve its mechanical strength and service temperature, thereby broadening its applications [2,7–11].

Different strategies have been employed to enhance the crystallization kinetics of PLA including chain branching [12–15], iso-/non-iso- thermal treatment under plasticizing gas environments at elevated pressures [8,12,16,17], polymer blending [18–22], incorporation of inorganic/organic fillers or nucleating agents [8,21,23–30], and strain-induced crystallization [31–33]. Among these, adding inorganic/organic fillers or nucleating agents has been considered one of the most common and effective approaches. Inorganic particulates such as nanoclay [8], nanosilica [8,34], graphene [35], and carbon nanotubes [26,36] have been extensively studied. However, these nanoparticulates are inorganic and pose considerable health risks from their manufacturing process to their final disposal [37,38]. In contrast, organic natural cellulosic fillers have attracted great interest in recent years due to their sustainability and natural abundance [39–41]. Natural cellulosic fillers, produced from annually renewable resources, are lightweight, biodegradable, and biocompostable. The combination of cellulosic fillers and PLA offers the possibility of generating a new class of fully biorenewable resource-based and biodegradable composites. Several kinds of cellulosic fillers have been used as crystal nucleating agents for PLA and to tailor the thermal and mechanical properties of PLA for different end uses. These include wood flour (WF) [39], cellulose fiber (CF) [24,39], microcrystalline cellulose (MCC) [39], microfibrillated cellulose (MFC) [9,41], cellulose nanofiber (CNF) [40], and cellulose nanocrystal (CNC) [42,43].

Among these, CNFs have been highlighted recently as additives or reinforcement in various polymer systems to tailor the performance of the polymer matrix [9,11,44–49]. CNFs are long, flexible, and entangled cellulose fibrils of 20–90 nm in diameter and several micrometers in length [50,51]. CNFs possess a Young's modulus of 115–150 GPa in the longitudinal direction and tensile strength of up to 2 GPa [47,52–54]. These mechanical properties are comparable to or even higher than those of high strength glass fibers. The reinforcing ability of CNFs in PLA has been theoretically modeled [55,56]. The incorporation of CNFs could increase the tensile strength of PLA by over 2 times at 20 wt% [55] and increase the tensile modulus around 3 times at 5 wt% fiber content [56]. The predicted values could be even higher if a 3D CNF percolated network structure was taken into consideration [55]. CNF also has a very low coefficient of thermal expansion at $1 \times 10^{-7}\,\mathrm{K}^{-1}$ along the longitudinal direction [57]. Additionally, CNFs have huge potential in biomedical applications due to their low cytotoxicity and genotoxicity [37,58,59]. These intriguing properties make CNFs an attractive component for high performance polymer nanocomposites.

The effect of CNFs on PLA's crystallization behavior has been recently investigated [40,41,60,61]. However, the dependence of crystallization behaviors on the CNFs was not studied systematically. A few of these studies concluded that CNFs, acting as heterogeneous crystal nucleating agents, increased PLA's nucleus density, its crystallization rate, and its degree of crystallinity [40,41,60]. Conversely, another study found well-dispersed CNFs decreased PLA's chain mobility, and hindered the crystallization process [61]. Thus, our work to understand the effect of CNFs on PLA crystallization kinetics is greatly needed.

Although CNFs have excellent reinforcing ability, it is practically challenging to achieve an acceptable dispersion level because of the hydrophilic nature of CNFs and the hydrophobic characteristic of PLA [51,56,62–64]. CNFs tend to aggregate rather than disperse in PLA. Also, upon drying, the agglomeration of CNFs is irreversible due to the strong hydrogen bonds established through a large number of hydroxyl groups on the fiber surfaces [62–64]. During composite processing, especially during melt compounding, a sufficient shearing force is required to distribute and disperse the CNFs. However, the shear stress exerted on the fiber could lead to significant fiber breakage and would reduce the fiber length and the aspect ratio. As a result, the experimental values from mechanical tests were much lower than the theoretical ones. Many researchers have reported that the addition of 5–20 wt% CNFs improved PLA's tensile strength and modulus by only 8.6–33% and 10–73%, respectively [9,56,65,66]. The low percentage gain was attributed to the non-uniform fiber dispersion and to the decreased fiber aspect ratio [9,56,65,66].

To overcome some of the aforementioned issues during composite preparation, one option is to use CO_2-assisted polymer processing [67–75]. There are several advantages to this. First, dissolved CO_2 can significantly prevent particulate aggregation and improve dispersion [67,69–73,75]. At a high pressure, supercritical CO_2 enters the space between the particulates [67,69,76,77]. When the pressure decreases below a critical point, CO_2 changes from its supercritical to gaseous state. The volume expansion due to CO_2 phase change forces the stacked particulates to separate, which improves the particulate dispersion [67,69]. At the same time, this also facilitates the polymer chain intercalation into the inter-particulate space [67,69]. In addition, fiber breakage can be reduced by the decreased melt viscosity from the plasticizing effect of dissolved CO_2 [71,74]. The use of CO_2 also allows for polymer processing, especially for biodegradable polymers, at lower temperatures, due to the depressed melting temperature [8,12,68,78]. This minimizes their thermal degradation and maximizes the processing window. Moreover, the presence of CO_2 can also enhance the polymer's crystallization [8,12,79–81]. All these benefits from a CO_2-assisted polymer process would enable to produce PLA composite with superior mechanical properties [9,67,69,70].

The crystallization kinetics of PLA influences most regular polymer processes, especially for injection molding and extrusion. During these processes, it is a challenge to achieve high PLA crystallinity within a very short residence time for obtaining final products with desirable properties. In injection molding process, the slow crystallization rate of PLA leads