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# Unexpected observation of highly thermostable transcrystallinity of poly(lactic acid) induced by aligned carbon nanotubes

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## ABSTRACT

Developing poly(lactic acid) (PLA) based biopolymers has long been perceived as a promising strategy for revitalizing the polymer technology and industry. Its poor crystallization ability caused by the inherent molecular characters, however, undesirably restricts the enhancement of physical properties of PLA products, and largely limits the potential applications. The melt-crystallization kinetics, in principle, is of paramount importance to alter the ultimate crystallization morphology of PLA submitted to normal polymer processing. Inspired by the extremely high specific surface energy and rich nucleation sites of carbon nanotubes (CNTs), we exploited PLA fibers containing highly oriented CNTs to enhance the nucleation kinetics of PLA, especially at ultrahigh crystallization temperatures. Furthermore, flexible poly(ethylene glycol) (PEG) chains were introduced to promote chain mobility of PLA and thus boost crystal growth rates. It was of great interest to observe that effective nucleation of PLA at temperatures up to 150 °C was established using aligned CNTs as the nucleating template, resulting in the formation of symmetrically developed transcrystallinity. A distinguished feature has been moreover revealed that the transcrystallinity developed at higher crystallization temperature presented higher thermal stability. Unexpectedly, the transcrystallinity fostered at 150 °C could be largely preserved even at the melting temperature of the bulk matrix.

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## 1. Introduction

Each year, more than 90 million tons of polymers are produced, yet most ending up in landfill [1]. The development of biodegradable polymeric materials has been critical, as this kind of materials enables a great balance between the increasing consumption of plastics and the limited availability of landfills [2–6]. Biodegradable

synthetic polyesters, especially poly(lactic acid) (PLA) derived from renewable natural resources, are among the most appealing candidates [7–12]. Inherently, PLA has remarkable mechanical properties with desirable biocompatibility and presents a great opportunity to substitute or complement conventional petroleum-based commodities in the packaging industry and biomedical applications [13,14], ranging from bone tissue engineering and wound sutures to biologically active controlled-release devices [15–19]. Recent industrial innovations have lowered the production costs of PLA, which further motivates its potential use in applications that require mechanical, biodegradable, and biocompatible properties [20–27].

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The mechanical and thermal performances of PLA profoundly rely on the supramolecular morphology, which is controlled by the crystallization process [28,29]. Unfortunately, the crystallization ability of PLA is generally poor and uncontrolled, presumably due to the semi-rigid backbone, relatively short chain length, and poor spatial regularity [30,31]. As a result, PLA-based products prepared by common processing methods are essentially amorphous and show unsatisfactory physical and mechanical performances [32–34]. To develop high-performance PLA-based materials, it is imperative to facilitate the crystallization kinetics of PLA, mainly through controlling nucleation of the melt during cooling because melt processing represents the typically involved method for the manufacture of PLA products. It appears from the existing literature that various fillers have been used in the PLA matrix to accelerate the nucleation. Two-dimensional (2D) fillers, such as polymeric fibers, carbon fibers, natural fibers, and carbon nanotubes (CNTs), have demonstrated excellent capability to anchor the small nucleus aggregates at the surfaces, rendering the formation of symmetrical transcrystallinity and thus enhancing the interfacial bonding of composites [35–38]. Among the candidates, CNTs, known for their unique geometrical structure and high strength properties [39–41], have long been attractive both as nucleation agents and as reinforcing elements for PLA [42–44].

On the other hand, since anchoring, ordering, and nucleation of PLA chains are successively induced by the CNTs surface, nucleation activity of CNTs is probably hindered by spherical impurities, entanglement and agglomeration of CNTs, especially at high CNT contents [45]. To properly exploit CNTs in PLA nanocomposites, uniform dispersion and full extension as well as strong interactions at the CNTs–PLA interfaces are essentially required. With their outstanding efficiency in maximizing the interfacial interactions and thereby the stress transfer efficiency, highly aligned CNTs with favorable dispersion are preferably desirable to induce polymer nucleation and reinforce the polymeric materials [46]. Up to date, it is still challenging to achieve these prerequisites for PLA/CNTs nanocomposites by the common processing, especially an industrially feasible approach.

It naturally stimulates us to obtain large-scale aligned CNT arrays to optimize the crystallization of PLA, especially for the nucleation under ultrahigh temperatures close to the melting point. Here, we report our recent progress in establishing uniformly dispersed, orderly aligned CNTs embedded in PLA fibers through the strong shearing/stretching force during the melt spinning of PLA/CNTs nanocomposites containing low CNT content (1 wt%). The nucleation activity of the nanohybrid fibers in PLA matrix was examined during the melt crystallization at ultrahigh temperatures, i.e., 140, 145, and 150 °C. Moreover, a small amount of poly(ethylene glycol) (PEG), a typical chain mobility accelerator for PLA, was introduced into the matrix, aiming at the combination of facilitated nucleation and enhanced crystal growth. The promotion of chain mobility of PLA presumably renders, at the same time, the enhancement of interfacial interactions, eventually boosting the formation of compact ordered nuclei at the nanohybrid fiber surfaces. Additionally, it is assumed that

the introduction of PEG significantly suppressed nucleation of spherulites in the bulk matrix and favored the exclusive development of interfacial crystalline superstructure. Integrating the heterogeneous nucleation activity of aligned CNTs with improved crystal growth rates, we observed some interesting results by direct morphological observation. Compact transcrystallinity closely wrapped the nanohybrid fibers at 150 °C (15 °C lower than the melting point of the PLA/PEG matrix), which was unexpectedly preserved during the subsequent annealing at 165 °C. This is the first-ever instance of forming compact, highly thermally stable transcrystallinity of PLA on the surfaces of aligned CNTs. Our proposed method, exploiting the effective tip structure of aligned CNTs, helps shape a simple approach to control the crystalline morphology and allows the mechanical performances and thermal stability of PLA-based materials to be customized to applications.

## 2. Experimental section

### 2.1. Materials

PLA ( $M_w = 230,000$ ,  $M_n = 110,000$ , 2% D-LA) was procured from Nature Works under the trade name of 4032D. Commercially available PEG (nominal weight-average molecular weight 3350, trade name Carbowax) was purchased from Dow Chemical Company. Multi-walled CNTs (1–2 nm thick, 0.5–2  $\mu\text{m}$  long, 20–30 nm outer diameter) powder was obtained from Sigma Aldrich and was used as received.

### 2.2. Preparation of nanohybrid PLA fibers

The PLA master batch containing 20 wt% CNTs was prepared by adding CNTs into a chloroform solution of PLA with continuous stirring and ultrasonic oscillation to obtain a homogeneous dispersion of CNTs. The CNT content was then diluted to 1 wt% in a co-rotating twin-screw extruder with a processing temperature of 180 °C. The PLA/CNT nanohybrid was spun into fibers at 160–180 °C using a custom-made melt-spinning device. Pure PLA fibers were subjected to the same processing conditions to prepare the counterparts. The thermal parameters of melt-spun fibers are shown in Figs. S1 and S2.

### 2.3. Polarized optical microscopy (POM) observation

An Olympus BX3 polarizing optical microscope (Olympus, Tokyo, Japan) equipped with a Canon camera was used to observe the fiber morphology and its evolution during isothermal crystallization. To explore the formation and growth of transcrystallinity, a nanohybrid PLA fiber was sandwiched between two pieces of thin PLA/PEG film, which was prepared by vacuum casting the chloroform solution of PLA containing 5 wt% PEG. The film was melted on a Linkam TS1500 hot stage at 190 °C for 3 min. The sample was then cooled rapidly to preset temperatures (i.e., 140, 145, and 150 °C), at which the isothermal crystallization proceeded for 30 min. All optical micrographs presented in this article were recorded under crossed

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