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Bio-based composite of stereocomplex polylactide and cellulose nanowhiskers

Purba Purnama [a,b], Soo Hyun Kim [a,c,*]

[a] Biomaterials Research Center, Korea Institute of Science and Technology, Seoul 136-791, Republic of Korea
[b] Center for Biomaterials and Supercritical Fluid, Surya University, Tangerang 15810, Banten, Indonesia
[c] KU-KIST Graduate School of Converging Science and Technology, Korea University, Seoul 136-701, Republic of Korea

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ABSTRACT

The advanced bio-based composite of stereocomplex polylactide containing cellulose nanowhiskers was successfully prepared by supercritical fluid technology. This bio-stereocomplex–nanocomposite material was produced by stereocomplexation of polylactide-graftcellulose nanowhishkers through supercritical carbon dioxide–dichloromethane at 65 °C and 350 bar. The bio-stereocomplex–nanocomposite polylactide was obtained in high stereocomplex degree (100%). The bio-stereocomplex–nanocomposite polylactide exhibits excellent stereocomplex memory which is the main limitation of linear stereocomplex polylactide. It also shows improvement in mechanical properties up to 2.70 GPa (Young's modulus) and thermal degradation temperature. The combination of stereocomplex and nanocomposite approaches offers simultaneous improvement on physical properties. The bio-stereocomplex–nanocomposite polylactide is promising material in the future to replace petroleum-based polymer as eco-friendly materials.

1. Introduction

Non-degradable waste is the main problem caused by the use of fossil-based polymers. The high consumption of those traditional polymers in various fields causes tremendous environmental problems. Environmental protection drives attention in order to increase recycling of non-degradable polymer and focus on development of bio-based polymer to replace fossil-based polymers.

Polylactide (PLA) is economically bio-based polymer which accomplishes large scale production since 2001 [1,2]. It is potential polymer for replacing fossil-based polymer due to its biodegradability and biocompatibility [3,4]. However, comparing to petroleum-based polymer, PLA exhibits limitation in mechanical and thermal properties.

Stereocomplexation [5–7] and nanocomposite [8–10] are proper approaches to improve PLA properties. Stereocomplexation of PLA is an approach to improve PLA physical properties by combining stereospecific PLA (poly (L-lactide) (PLLA) and poly (D-lactide) (PDLA)) [5]. Stereocomplex PLA (s-PLA) can be formed through solution [5,11], melt [12,13], supercritical fluid [7,14], and also microwave irradiation process [15]. In other hand, nanocomposite is an approach to enhance thermal stability, mechanical, and barrier properties of polymer by adding nano-scale inorganic material [8–10,16–18]. PLA nanocomposite can be also generated through solution [19], melt [18], and supercritical fluid [20].

In the nanocomposites fields, the selection of nanoparticle should consider environmental and sustainability aspect for future applications. Cellulose nanowhiskers (CNW) are one of the promising candidates which have excellent mechanical properties [21]. It was generated from bioresources with diameter of whiskers-like regions polysaccharide chain between 5 and 30 nm [22]. In the polymer CNW nanocomposites, the hydrophilic nature of CNW can be solved by surface functionalization [23,24] and polymer grafting [25–27]. The surface-modification of improved the CNW dispersion in organic solvents [23,24]. The silanized CNW enhanced the crystallinity and thermomechanical properties of PLA materials [24]. The grafted PLA onto CNW surface enhanced the compatibility of CNW in the polymer matrix [25]. Furthermore, the partial functionalization of CNW enhanced CNW dispersion in organic solvent and support PLLA polymerization which affect to their properties improvement [27].

Regarding PLA properties enhancement, combination of stereocomplexation and nanocomposite is expected to bring both unique characteristics. In this work, we studied about stereocomplexation of PLA containing CNW through supercritical fluid

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* Corresponding author. Biomaterials Research Center, Korea Institute of Science and Technology, Seoul 136-791, Republic of Korea. Tel.: +82 2 958 5343; fax: +82 2 958 5308.
E-mail address: soohkim@kist.re.kr (S.H. Kim).

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media and evaluated the properties of generated stereocomplex materials: stereocomplex memory, thermal, and mechanical properties.

2. Experimental sections

2.1. Materials

L-Lactide (Biomedichem, Korea, high-purity > 99.0%) and D-lactide (Purac Biochem bv, Netherlands, high-purity > 99.5%) were stored in oven at 55 °C for 30 min before used. Stannous octoate (Sigma–Aldrich, USA, purity > 95%) was used after purification. Microcrystalline cellulose (Sigma–Aldrich, USA, powder, 20 μm), acetic acid (Sigma–Aldrich, glacial, ≥99.85%), hydrochloric acid (Sigma–Aldrich, ACS reagent, 37%), carbon dioxide (CO_2) (Shin Yang Oxygen Industry Co. Ltd., minimum purity 99.9%), and all solvents (toluene (Sigma–Aldrich, HPLC grade), chloroform, methanol (Daejung Chemicals & Metal Co., Ltd., with a purity >99.5%), dichloromethane (JT Baker, HPLC grade)) were used as received.

2.2. Preparation of nanocomposite materials

The nanocomposite materials of polylactide-graft-CNW (PLA–CNW) were prepared through in situ bulk polymerization. The acetylated-CNW (a-CNW) was used to produce PLA–CNW. The a-CNW was prepared through hydrolysis of microcrystalline cellulose by glacial acetic acid and hydrochloric acid [27]. The freeze-dried a-CNW, stannous octoate, and toluene (1 mL) were putted into round bottom flask (ampoule) equipped with magnetic stirrer under nitrogen atmosphere. The mixture was stirred around 5 min. The lactide monomer (D-lactide or L-lactide) was added into the mixture. The monomer to a-CNW composition is 95:5 weight ratio. The monomer to initiator was varied to obtain various level molecular weights of PLA chains. The mixture is then purged with nitrogen gas and vacuum cycle for 3 times and followed by vacuum for 6 h. The ampoule was sealed and submersed in an oil bath at 130 °C with continuous stirring for 24 h. The polymer product was dissolved in chloroform and purified by pouring the solution into excess of methanol. Then, the product was dried in oven for 24 h.

2.3. Stereocomplexation of PLA–CNW

The stereocomplexation of PLA–CNW was proceeded through supercritical CO_2–dichloromethane (sc-CO_2–DCM) as describe in previous work [7]. Briefly, PLLA–CNW and PDLA–CNW with 1:1 weight ratio (1.030 g for each PLLA–CNW or PDLA–CNW) were stereocomplexed in sc-CO_2–DCM at 65 °C and 350 bar for 5 h in the 50 mL stainless steel high-pressure reactor equipped with magnetic stirring and electrical heating mantle. The reactor was opened immediately after the reaction had finished. The s-PLA was collected and vacuumed at 40 °C for 1 night. The s-PLA–CNW1 corresponds to the starting material PLLA–CNW1 and PDLA–CNW1.

2.4. Characterizations

The appearance of a-CNW was examined in an atomic force microscopy (AFM). A very dilute suspension was dropped onto fresh mica surface and allowed to dry before analysis. The molecular weight of grafted PLA chains was estimated by evaluation the molecular weight of non-covalently bonded PLA using Gel Permeation Chromatography (GPC) (GPCmax 2001) at 40 °C with chloroform as a solvent (flow rate was 1.0 mL/min and polymer concentration was 0.1% (wt/vol)). The non-covalently bonded PLA chain was obtained by stirring the PLA–CNW/chloroform solution for 24 h and centrifugation at 8600× g for 40 min. The acetylation of a-CNW and the graft of PLA chain onto a-CNW were evaluated by Fourier transform infrared (FTIR) spectroscopy, Thermo Mattson model Infinity Gold FT-IR. Thermal properties of nanocomposites were measured by a differential scanning calorimeter (DSC) (Modulated DSC 2910, TA Instrument). The stereocomplexation was examined by DSC and re-confirmed by X-ray diffraction (XRD) (X-ray diffractometer Rigaku D/Max-2500 composed of Cu K_α ($\lambda = 1.54056$ Å, 30 kV, 100 mA) source) instrument. The

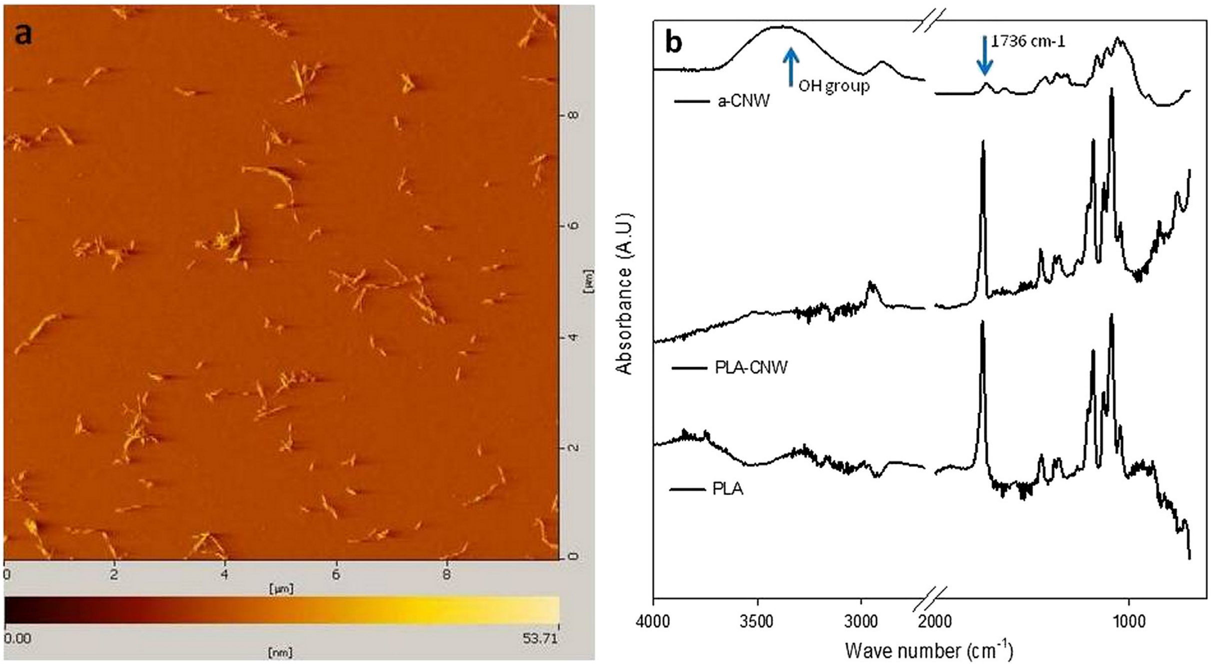

Fig. 1. a. AFM image of a-CNW; b. FTIR spectra of a-CNW, PLA–CNW, and PLA.

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