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Research Paper

Preparation of 3D printable micro/nanocellulose-polylactic acid (MNC/PLA) composite wire rods with high MNC constitution

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ABSTRACT

A method for the preparation of 3D printing wire rods of a micro/nanocellulose-polylactic acid (MNC/PLA) composite with up to 30% MNC constitution was developed. The micro/nanocellulose (MNC) obtained through a simple mechanical treatment of polyols swelled bleached softwood pulp possessed a mixture of micro-cellulose fibers (width was less than 2 μm) and nanocellulose fibers (width was at nanoscale). The results showed that the interfacial compatibility of MNC and PLA was improved by adding silane coupling agent (KH-550). The composition of MNC with PLA greatly decreased the melt flow rate, nevertheless, the addition of PEG increased the rate to some degree (0.568 g/10 min) to meet the printable demands for 3D printing with a FDM printer with a decomposition temperature of 250 °C–400 °C. The optimum ratio for the preparation of MNC/PLA composites for 3D printing was determined to be as follows: 30 wt% MNC modified with KH550, 5 wt% PEG6000, and 65 wt % PLA. At the optimum condition, the mechanical property of 3D products from MNC/PLA composites was maintained at a comparable level to that of neat PLA with elongation at break of 12%, tensile strength of 59.7 MPa and flexural strength of 50.7 MPa.

1. Introduction

In recent years, there has been great development in the field of 3D printing technology for the manufacturing of objects. Additive manufacturing (AM), also referred to as 3D printing, involves the manufacturing of objects by depositing material layer-by-layer, as opposed to conventional subtractive manufacturing processes such as milling, casting, forging or welding. The great advantage of 3D printing technology is the accurate control of the complex structure, and the waste from the manufacturing processes of 3D printing is very little. At present, various materials are available for FDM 3D printing ranging from polymers (such as polyamide, acrylonitrile butadiene styrene (ABS), polylactic acid (PLA), and polyvinyl alcohol (PVA)) to ceramic, gypsum, metals (stainless steel, gold and silver, titanium) and even concrete (Vatani et al., 2015). Among these materials, PLA has made great progress within the 3D printing field because of its biodegradability (Navarro et al., 2006; Rezwan et al., 2006). In particular, PLA is a currently used biodegradable polymer that has been approved by the FDA for various biomedical applications. At present, most of the reported PLA-based scaffolds fabricated by rapid prototyping require the molecular modification of the PLA matrix (Melchels et al., 2009; Zhuo et al., 2002). For the moment, PLA as a 3D printing material reveals some disadvantageous performance factors such as expense, higher hardness, poorer toughness, lack of flexibility and elasticity, and easily to bending deformation compared with polypropylene (PP) and polyvinyl chloride (PVC) plastics (Mukherjee and Kao, 2011).

Cellulose, the most abundant natural, renewable, bio-based polymer, largely derived from plants, demonstrates great potential for use in the plastic, automotive, and packaging industries because of their excellent characteristics such as low density, high specific stiffness, biodegradability, eco-friendliness, toxicological harmlessness, good thermal and acoustic insulation (Kalia et al., 2011; Klemm et al., 2005; Thakur et al., 2013). These cellulosic fibers can not only reduce the overall material costs from that of the pure polymer but can also act as

Abbreviations: PLA, Polylactic acid; MNC, Micro/nanocellulose; PEG, Polyethylene glycol; DCM, Dichloromethane; MNC_{-K}, Surface-modified MNC with KH-550; MNC/PLA, MNC composited with PLA; MNC_{-K}/PLA, MNC_{-K} composited with PLA; MNC/PLA_{-P}, MNC/PLA composites plasticized with PEG6000; MNC_{-K}/PLA_{-P}, MNC_{-K}/PLA composites plasticized with PEG6000

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reinforcements in composite materials. It has been intensively used to prepare (partially) bio-based and biodegradable composites. For example, the mechanical properties of plastics such as PLA (Fortunati et al., 2014), polycaprolactone and polyamide were modified using cellulosic fibers (Bai et al., 2013; Panaitescu et al., 2013). Comprehensive reviews have outlined the differences among natural fibers with regard to their mechanical properties and applications (He et al., 2015; Mohammed et al., 2015; Thakur and Thakur, 2014a; Thakur et al., 2014b). Susanne Christ et al. increased the wet strength of 3D printed products by using a fiber reinforcement approach and investigated fiber-modified gypsum powder (Christ et al., 2015). On the other hand, another more recent research project investigated the use of wood powder and adhesive as a mixture for 3D printing (Kariz et al., 2016). The researchers showed the principal feasibility on the use of wood-based material or natural cellulosic fibers in 3D printing processes. However, the mechanical strength of 3D printed products from wood powder or cellulosic fibers with adhesive mixtures was insufficient and needed to be improved. Many previous studies have shown the promising advantages by using a low amount of nanocellulose (about 1–5%) as reinforcement phase of the polymers such as PLA (Christ et al., 2015; Ma et al., 2015; Qu et al., 2012; Virtanen et al., 2014). Due to the complex process for the preparation of nanocellulose and their low addition amount in PLA, the application of such composites was still restricted due to the limited property improvement and high cost.

By our studies, a simple and feasible process for downsizing cellulose fiber to the micro- and nanolevel was established. Through the process, the micro/nanocellulose (MNC) containing a mixture of micro-cellulose fibers (width of less than 2 μm) and nanocellulose fibers was obtained, in which the micro-cellulose was the majority, as a result the MNCs exhibited different performances from pure micro-cellulose or nanocellulose fibers. The MNC can be used as reinforcing material to increase the mechanical properties of a large variety of polymer materials with low cost, low density, easy separation, renewability, sequestration of carbon dioxide, biodegradability, chemical or physical modification, etc (Bai et al., 2013; Bitinis et al., 2013a,b; Fortunati et al., 2014; Shim et al., 2008). These refined and downsized cellulose fibers were supposed to be one of the strategies to further improve the properties of 3D printing products. Nevertheless, micro- or nano-sized cellulose-based biodegradable composites for the development of 3D printing were barely reported. Especially, the size effects of cellulose fibers at the micro- or nanolevel on the reinforcement in the 3D printable composites were seldom investigated.

In another words, the simple preparation process of MNC was provided which make MNC a low-cost material compared to both PLA and nanocellulose and might exhibit distinctive performance. From the view of this point, in this study, our objective is to maximize MNC amount in PLA, at the same time, at least maintain the required properties for FDM 3D printing. To realize the objective, the optimum ratio between MNC and PLA, the effect of silane-coupling agent (KH-550) on the interface compatibility, and the function of PEG2000 on the plasticity and melt flow rate were studied and discussed. The goal was to achieve a composite with sufficient printability while simultaneously using as much MNC as possible.

Three important points in this study are: (1) The cellulose fiber was downsized to a mixture of micro- and nanosized cellulose fiber, i.e., MNC was first obtained by a simple mechanical process with PEG400 as dispersant. (2) MNC/PLA 3D printable composites were prepared in a dichloromethane medium with an improvement of the interfacial adhesion between the hydrophilic MNC and the hydrophobic PLA by the silane-coupling agent KH-550. (3) The plasticity and melt flow of the MNC/PLA was further improved by adding of PEG6000. Thereby, the mechanical strong and thermostable MNC/PLA composite wire rods with high MNC constitution were screwed. Finally, the redundant dichloromethane was recycled via a condensing unit accompanied by the extruding of the wire rods.

2. Experimental section

2.1. Materials

Bleached softwood pulpboard was supplied by Beijing Murun Technology Development Co. Ltd. Silane coupling agent KH-550 was purchased from Nanjing Chen Gong Organic Silicon Material Co. Ltd. Polylactic acid (PLA; Mw 100,000) was purchased from Dongguan Wen Liang plastic raw material Co. Ltd, China. Polyethylene glycol (PEG, Mw 400) and PEG (Mw 6000) was purchased from Shanghai Jiu Yi Chemical Reagent Co. Ltd. All other reagents were of analytical grade and used without further purification from NanJing Chemical Reagent Co. Ltd.

2.2. Preparation and modification of Micro/Nanocellulose (MNC)

The bleached softwood pulpboard as a cellulose sample was torn into small pieces and pretreated with PEG400 at 120 °C for 2 h under a solid to liquid ratio of 1:8. The swelled cellulose was extruded by mechanical extrusion using a spiral-squeezing device and repeated three times. Then, the cellulose PEG400 dispersion with 5% mass content (diluted by PEG400) was agitated by mechanical disintegration with a colloid mill (JIM-150, Wenzhou Kangding Machinery Co. Ltd., China) at room temperature with a rotor speed of 6000 rpm for 10 min, followed by thorough washing with dichloromethane (DCM) by filtration to remove the PEG400. Thereby, the MNC/DCM suspension was obtained. The silane coupling agent KH-550 was added in the MNC/DCM suspension with a final content of 0.5%, 1.0%, 3.0%, and 5.0% w/w based on MNC, respectively. The suspension was stirred for 20 min at room temperature to obtain the final surface-modified MNC with KH-550 (MNC_{-K}) to improve the interfacial compatibility of cellulose with PLA (as illustrated in Fig. 1).

2.3. Preparation of 3D printing wire rods of MNC/PLA composite

The PLA was dissolved in DCM with magnetic stirring at room temperature for 24 h to give clear 5% PLA/DCM solution. The MNC (or MNC_{-K}) in the MNC/DCM suspension was added into the PLA/DCM solution for a final content of 10%, 30% or 50% (w/w) based on the MNC/PLA composites, respectively. Polyethylene glycol (PEG, Mw 6000) was used as a plasticizer to lower the glass transition temperature and improve the ductility of the composites. The PEG6000/DCM solution was added into the MNC/PLA mixed suspension with final content of 5%, 10%, or 20% (w/w) based on the MNC/PLA composites. The mixed suspension was stirred on an electric mixer at room temperature for 10 min, and then on a magnetic stirrer at 50 °C for 30–50 min to recover DCM solvent by evaporating under the condensing unit. Thereby, MNC/PLA or MNC_{-K}/PLA_{-P} composites were obtained. Finally, the dried composites were crushed into particles. They were then extruded in a twin-screw extruder (HAAKE MiniCTW, Germany) at 190 °C. The speed of extrusion by the multiple screw extruder was set to 10 mm/s, and the diameter of the extruded 3D printing wire rod was 1.75 mm. The MNC/PLA composite 3D printing wire rods were used for printing products by a Fused Deposition Modeling (FDM) 3D printer (as illustrated in Fig. 1).

2.4. 3D printing

CATIA was used to model 3D specimens and generate STL data. The G-code was generated in CURA software. FDM Desktop 3D printer (Z603S, JGAURORA Ltd, China) was used for the manufacturing of the specimens. The printer has an interchangeable nozzle, for which 0.4 mm in diameter was chosen. The specimen was sliced into several layers with each layer bearing a height of 0.2 mm, and the shell thickness was set at 0.8 mm. The print speed was set to 50 mm/s, the printing temperature was 190 °C, the temperature of heated bed was