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Novel biorenewable composite of wood polysaccharide and polylactic acid for three dimensional printing

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ABSTRACT

Hemicelluloses, the second most abundant polysaccharide right after cellulose, are in practice still treated as a side-stream in biomass processing industries. In the present study, we report an approach to use a wood-derived and side-stream biopolymer, spruce wood hemicellulose (galactoglucomannan, GGM) to partially replace the synthetic PLA as feedstock material in 3D printing. A solvent blending approach was developed to ensure the even distribution of the formed binary biocomposites. The blends of hemicellulose and PLA with varied ratio up to 25% of hemicellulose were extruded into filaments by hot melt extrusion. 3D scaffold prototypes were successfully printed from the composite filaments by fused deposition modeling 3D printing. Combining with 3D printing technique, the biocompatible and biodegradable feature of spruce wood hemicellulose into the composite scaffolds would potentially boost this new composite material in various biomedical applications such as tissue engineering and drug-eluting scaffolds.

1. Introduction

Rapid prototyping (RP), also known as three-dimensional (3D) printing or additive manufacture (AM), has been well developed and adopted in many fields, such as construction, aerospace, healthcare, and so on. In the RP technique, a complex, high-resolution, and reproducible construct can be rapidly fabricated through a computer-aided design (CAD) model and computer controlled software. For the fabrication of biomedical devices, RP techniques offer attractive advantages, as customized implants or scaffolds for tissue engineering can be designed according to the patient's own 3D medical computed tomography (CT) scan and even very complex structures can be fabricated to meet the individual needs. (Hollister, 2005) Among the RP techniques, fused deposition modeling (FDM) has shown greatest versatility by nozzle-deposition-based extrusion with the utilization of biodegradable polymers, including acrylonitrile butadiene styrene (ABS), (Rocha et al., 2014) polylactic acid (PLA), (Almeida et al., 2014; Davidson, Appuhamillage, Thompson, Voit, & Smaldone, 2016; Matsuzaki et al., 2016; Sandler et al., 2014) poly(ε-caprolactone) (PCL), (Holländer et al., 2016; Seyednejad et al., 2011) polyvinyl alcohol (PVA), (Goyanes, Buanz, Basit, & Gaisford, 2014) and polyamides (Nylon). (Novakova-Marcincinova, Novak-Marcincin, Barna, & Torok, 2012) Currently, PLA is one of the main desktop 3D printer feedstock materials, owing to its favorable mechanical properties and thermoplastic processability, as well as the green feature of its synthesis routes from renewable resources.

PLA is a linear biopolyester, which is synthesized via ring-opening polymerization of lactide (cyclic di-ester of lactic acid) or polycondensation of lactic acid monomers. (Lee & Hong, 2013) In industry, lactic acid is predominantly produced via fermentation of sugars from agricultural products, mainly corn starch. PLA shows good biocompatibility in physiological conditions and is biodegradable through hydrolytic degradation, as well as bioresorbable with its end degradation product being metabolized through lactic acid cycles in vivo. (Maurus & Kaeding, 2004) Various applications has been found for PLA in fabricating biomedical devices, including surgical sutures, orthopedic fixation implants, drug delivery systems, and tissue engineering scaffolds. (Tanase & Spiridon, 2014)

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However, on one hand, the synthesis of PLA involves the use of catalyst and is also not simple to execute due to the rigorous control of reaction conditions, e.g., temperature, pressure, and pH, which also implies high energy consumption. (Lasprilla, Martinez, Lunelli, Jardini, & Maciel Filho, 2012) On the other hand, the popularity use of corn-based PLA has also raised the ethical concern on the global food crisis. To address this, a strategy to blend more economically feasible wood polysaccharides in PLA provides an alternatively sustainable approach to partially replace PLA in feedstock filaments for FDM 3D printing. (Willför, Rehn, Sundberg, Sundberg, & Holmbom, 2003; Willför, Sundberg, Tenkanen, & Holmbom, 2008; Xu, Willfor, Sundberg, Pettersson, & Holmbom, 2007)

Hemicelluloses are the second most abundant polysaccharide after cellulose. Galactoglucomannan (GGM) is the major hemicellulose type in softwoods. (Willför et al., 2003) It accounts for up to 25% in Norway spruce species. In the last two decades, different approaches have been developed to isolate GGM from pulping process as a waste stream where using softwoods as feedstock and from wood chips using hot water extraction. (Willför et al., 2003) A recent developed technology utilizes vacuum and a design that enables water-soluble and polymeric hemicelluloses to be extracted at almost 100% yield from commercial wood chips and at a lower temperature ($< 150\,^{\circ}C$) than conventional hot-water extractions or autohydrolysis processes.(Von, 2014) This makes hemicelluloses promising as cost-effective biomaterials. (Willför et al., 2003; Willför, Sundberg, Tenkanen, & Holmbom, 2008; Xu et al., 2007) Moreover, a wide range of modification routes have been developed ascribed to their copious hydroxyl groups. (Albertsson, Voepel, Edlund, Dahlman, & Soderqvist-Lindblad, 2010; Karaaslan, Tshabalala, Yelle, & Buschle-Diller, 2011; Kisonen et al., 2012; Söderqvist Lindblad, Ranucci, & Albertsson, 2001) GGM and other hemicelluloses can thus find a broad spectrum of applications as such or after modification, such as, in food and paint formulations, packaging and barrier materials, health care, and structural composites to replace oil-based products. (Liu, Willför, & Xu, 2015; Petzold-Welcke, Schwikal, Daus, & Heinze, 2014; Willför et al., 2008) GGM has also been found to have no cytotoxicity as a biomaterial in both cell culture and wound dressing applications. (Liu et al., 2016; Markstedt, Xu, Liu, Xu, & Gatenholm, 2017) Yet, due to the intrinsic structural features of not being thermoplasticizable and possessing complex structure, hemicelluloses cannot undergo the same fabrication processes as synthetic oil-based polymers and thus their commercialization potential is severely undermined. Previously, hemicelluloses, like xylan and xyloglucan, have been physically blended and chemically grafted with PLA as a component of thermoplastic. (Marais, Kochumalayil, Nilsson, Fogelström, & Gamstedt, 2012; Gårdebjer, Larsson, Löfgren, & Ström, 2015; Zhang, Wang, Liu, Zhang, & Ren, 2017) Other types of polysaccharides, such as chitosan and cellulose, have been blended with PLA as 3D printing materials to enhance the desired characteristics, e.g. antimicrobial property and mechanical strength. (Murphy & Collins, 2016; Wu, 2016) Still, studies on using hemicelluloses in feedstock materials for 3D printing are scarce. Hereby, within the concept of 3D printing feedstock material, we propose an approach to use a side-stream-derived biopolymer, GGM from Norway spruce wood, to partially replace the synthetic PLA in 3D printing constructs and investigate the RP feasibility. For the first time, the PLA/wood hemicellulose composites were prepared and directly used as the filament for 3D printing. In our study, a solvent blending approach was developed to ensure the even distribution of the formed binary biocomposites. The blends of GGM and PLA with varied ratio up to 25% of wood hemicellulose were extruded into filaments by hot melt extrusion (HME). Chemical, thermal and mechanical properties of the composites and macroscopic properties of the printed scaffolds were elaborately studied. The printability of the polysaccharide-containing feedstock materials was successfully demonstrated shown in Fig. 1. This study offers a new route to apply a wood biopolymer in bioplastics for versatile applications in, but not limited to, biomedical devices.

2. Experimental section

2.1. Materials

Polylactic acid (PLA, Ingeo™ biopolymer 4043D) pellets were purchased from NatureWorks, USA. Galactoglucomanan (GGM) with *Mw* of 30 kDa was isolated from Norway spruce (Picea abies) thermomechanical pulp (TMP) as previously reported. (Xu et al., 2007) Dichloromethane (DCM) and dimethyl sulfoxide (DMSO, technical grade) were purchased from VWR and Sigma-Aldrich, respectively. Ethanol (technical grade) was supplied from Altia Oy, Finland.

2.2. PLA and GGM composite preparation

In order to obtain an evenly distributed composite, a solvent blending method was developed. Different ratios between GGM and PLA were prepared as shown in Table 1. GGM was firstly dissolved in DMSO at 40 °C. DCM was added as co-solvent to dissolve the PLA and obtain an even solvent blend after the GGM had dissolved so that the DMSO:DCM ratio was 20:80. PLA pellets were then added. The concentration for all blends was 10 g of solid material per 100 mL solvent mixture. Ultrasonification for 15 min was applied with a VWR ultrasonic cleaner (600 W) to ensure homogeneous mixing. The blends in the solvent mixture of DMSO and DCM were stirred at 35 °C overnight. Afterwards, the blends were precipitated by dropwise adding them into cold ethanol (4 °C) so that the volume fraction between solvent and ethanol was 1:9. All the precipitates were collected and further dried in vacuum desiccator (D-6450 Hanau, Heraeus) at 40 °C overnight.

2.3. Hot melt extrusion (HME) and 3D printing with the FDM™ technique

Filaments were extruded by hot melt extrusion with NOZTEK pro extruder (UK) at 165 °C with a nozzle diameter of 1.7 mm after screening at different temperatures ranging from 150 °C to 185 °C.

The scaffold prototypes were designed and printed by the control of 'MatterControl' software as the stereolithography files (.stl). The screenshot of the prototype in MatterControl is shown in Fig. S1 (Supporting information). The dimensions of scaffold were 20 mm in length, 20 mm in width, and 2 mm in height (10 layers). A Me3D desktop printer (Australia), based on the FDM™, was used for 3D printing of the above-mentioned prototypes. The printing parameters are listed in Table S1.

2.4. Characterization

2.4.1. Attenuated total reflectance-infrared spectroscopy (ATR-FTIR)

The composites and HME filaments were analyzed by Thermo Scientific Nicolet iS™ 50 FTIR Spectrometer (USA). The spectra were collected with ATR in the absorbance mode from an accumulation of 64 scans at a 4 cm^{-1} resolution in the range of 4000–400 cm^{-1}. If not differently specified, the spectra were normalized to the peak at 1452 cm^{-1}.

2.4.2. Gel permeation chromatography (GPC)

GPC analyses were conducted using a Shimadzu setup. One percent of acetic acid in THF was used as eluent at flow rate of 0.8 mL/min with a column packed with X-stream H20 Mixed bed from JORDI, USA. One milligram of composites or filaments was dissolved in 10 mL of THF. Ultrasonic sound for less than 15 s was applied every 12 h to enhance the sample solubility. All the samples were shaken for one week. Each 0.5 mL dissolved samples was filtered with 0.2 μm nylon filters before injection. Molar mass analysis was conducted using a standard gel permeation chromatography (GPC) technique calibrated with polystyrene standard.