



Full Length Article

Mechanically strong plant oil-derived thermoplastic polymers prepared via cellulose graft strategy



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ABSTRACT

The design of polymers from renewable plant oils is gaining more attention within sustainable development. Most plant oils based thermoplastic polymers exhibit poor mechanical properties. In this paper, we reported the mechanically strong cellulose-graft-soybean oil copolymers, which combined two natural biomasses in one. The soybean oil-based monomers with secondary amide groups (SOM1) and tertiary amide groups (SOM2) were prepared and copolymerized. The mechanical properties of the P(SOM1-co-SOM2) copolymers were investigated. Cellulose-g-P(SOM1-co-SOM2) copolymers with 0.5 wt% cellulose were prepared via atom radical transfer polymerization. FT-IR, ¹H NMR, and TGA measurements demonstrated that the Cellulose-g-P(SOM1-co-SOM2) copolymers were successfully prepared. Tensile test results demonstrated that the mechanical properties of the as-prepared Cellulose-g-P(SOM1-co-SOM2) copolymers were superior to the linear P(SOM1-co-SOM2) copolymers.

1. Introduction

Natural resources, such as wood, bamboo, rattan, and fibers have been used within human society for thousands of years [1]. The emergence of synthetic polymers from fossil fuels has virtually replaced these natural materials [2–4]. However, non-degradable synthetic polymers from fossil fuels cause server environmental pollution [5]. Thus, the development of novel polymeric materials from natural resources that compete with synthetic polymers is important for sustainable development. Recently, renewable biomasses such as cellulose, lignin, hemicelluloses, starch, proteins, and plant oils have been commonly used in the design of polymeric materials for plastic, elastomers, adhesive, and coating applications [6–8]. Although promising, the design and application of polymers from renewable biomasses remain within the initial stages. There is a trend towards developing sustainable science and technology with environmental friendly materials.

Plant oils have been used as feedstock for preparing oleochemicals on an industrial scale [9–11]. The production of polymeric materials from plant oils and their derivatives have been intensively studied [12–14], although a majority are limited to thermoset materials, such as, alkyd resins, epoxy resins, and polyurethanes [15–17]. The design of mono-functional monomers and linear thermoplastic polymers derived

from plant oils could provide new opportunities for sustainable development [18]. The transformation of plant oils to mono-functional compounds, such as fatty acids, fatty alcohols, fatty amides, and fatty esters have been developed [19,20]. Plant oil derived (meth)acrylate monomer have been prepared by reactions with (meth)acrylate anhydride or (meth)acryloyl chloride [21,22]. Norbornene monomers, 2-oxazoline monomers, and vinyl ether monomers derived from plant oils have also been prepared. Depending on the incorporated functional groups in these monomers, polymerization strategies, such as free radical polymerization, living/controlled radical polymerization, ring-opening polymerization, group transfer polymerization, ionic polymerization, and cationic polymerization are used to prepared thermoplastic polymers from plant oils [23–25]. Our group developed a high efficient strategy for converting plant oils into N-hydroxyalkyl fatty amides with virtually quantitative yields. These N-hydroxyalkyl fatty amides were then converted into monomers and thermoplastic polymers. Sixteen polymers with glass transition temperatures ranging between –50 °C and ~60 °C were obtained. These polymers with the glass transition temperature (T_g) values higher than room temperature exhibit relative good mechanical properties and are treated as plastics [26,27]. The mechanical strength of our plant oil derived plastic (2 MPa) is not high enough for real applications [28]. Thus, the design of plant oil based polymers with higher architecture complex, such as

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random copolymers, block copolymers, and graft copolymers are required [29–33].

Cellulose is gaining additional attention due to its sustainable, renewable, biocompatible, and biodegradable characters. The application of cellulose in materials, particularly for functional materials design has been studied intensively [34,35]. The grafting of various polymers from cellulose macromolecular backbone provides various opportunities for a wide range of applications [36]. Grafting from polymerization techniques, such as free radical polymerization, atom transfer radical polymerization (ATRP), reversible addition-fragmentation polymerization (RAFT), and ring opening polymerization (ROP) have been introduced to prepare the cellulose graft copolymers [37,38]. Cellulose graft copolymers are typically used for preparing micelles in aqueous systems for biomedical applications [39]. Zhiqun Lin and coworkers used cellulose graft block copolymers in the preparation of 1D nanocrystals with strictly controlled dimensions, compositions, and architectures [40]. Our group used activators regenerates by electron transfer atom transfer radical polymerization (ARGET ATRP) technique to prepare cellulose-graft-poly(*n*-butyl acrylate-co-methyl methacrylate) copolymers. The cellulose rigid backbone reinforces the rubbery matrix. These cellulose graft copolymers with novel architectures are defined as third-generation thermoplastic elastomers [41,42].

We predict that the cellulose graft strategy could provide opportunity for designing mechanically strong thermoplastic polymers from plant oils. In this work, two soybean oil-based monomers, SOM1 and SOM2, were prepared according to our previous work (Scheme 1). A series of linear copolymers, P(SOM1-co-SOM2), with varied SOM1 contents and physical mechanical properties were prepared and defined as P1, P2, P3, P4, P5, and P6. The chemical and physical properties of these P(SOM1-co-SOM2) copolymers were characterized. In order to pursue the mechanically strong soybean oil derived thermoplastic polymers, Cell-g-P(SOM1-co-SOM2) copolymers were synthesized via ATRP using 2-bromoisobutyl bromide modified cellulose (Cell-Br) as the macroinitiator. In order to better understand the effect that the cellulose graft strategy had on the mechanical properties of the soybean oil-based polymers, a series of Cell-g-P(SOM1-co-SOM2) copolymers with varied SOM1 monomer contents and cellulose weight percentages were prepared. The glass transition temperatures (T_g s) were characterized by differential scanning calorimetry (DSC) and the mechanical properties were characterized with a tensile test. The mechanism that the cellulose graft strategy had on improving the mechanical strength of soybean oil derived polymers was investigated.

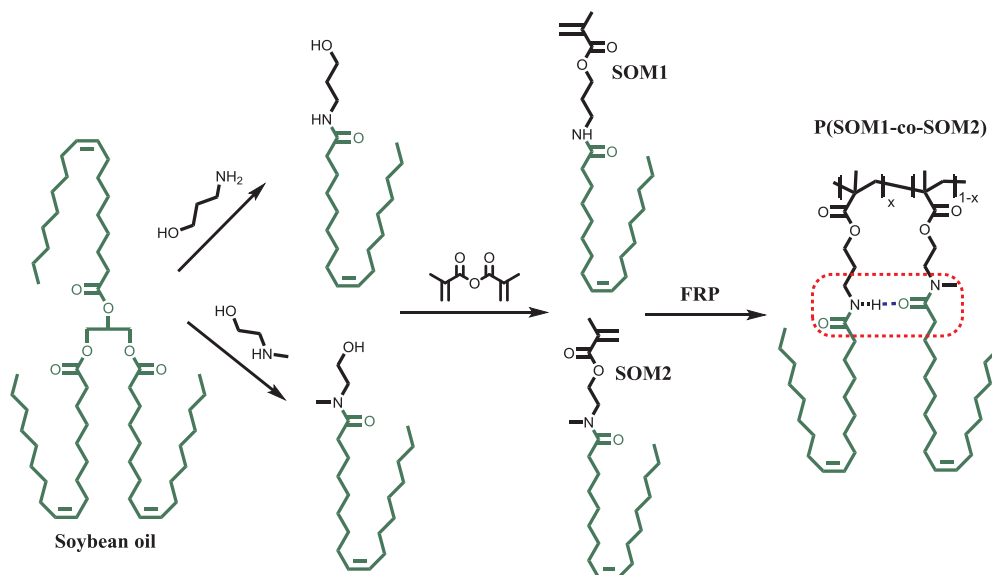
2. Experimental

2.1. Materials

Microcrystalline cellulose (Aldrich) was used as the starting cellulose material. Ionic liquid, 1-allyl-3-methylimidazolium chloride (AMIMCl) was used as the green cellulose solvent (Lanzhou Greenchem ILS, LICP, CAS, China). Cellulose macroinitiator (Cell-Br) and soybean oil based monomers, SOM1 and SOM2, were prepared in accordance with our previous work [41]. High oleic soybean oil was purchased from the super market. Azobis(isobutyronitrile) (AIBN, 98%, Aldrich) was recrystallized from methanol prior to use. 2-Bromoisobutyl bromide (98%, Aldrich), *N,N,N',N''*-pentamethyldiethylenetriamine (PMDETA, 98%, TCI), CuBr (99.9%, Aldrich), 3-amino-1-propanol (99%, Aldrich), *N*-methyl ethanolamine (98%, Aldrich), methacrylic anhydride (94%, Aldrich), 4-dimethylaminopyridine (99%, Aldrich), sodium methoxide (5.4 M solution in methanol, Acros Organics), and all other reagent were used as received.

2.2. Characterization

FT-IR characterizations of cellulose, Cell-Br, and Cell-g-P(SOM1-co-SOM2) were performed on a Bruker Tensor 27 FT-IR spectrophotometer. ^1H NMR spectra of P(SOM1-co-SOM2) and Cell-g-P(SOM1-co-SOM2) copolymers were recorded on a Varian Mercury 300 spectrometer using CDCl_3 as a solvent. The spectra were internally referenced with tetramethylsilane (TMS). The molecular mass and the molecular mass distribution of the prepared polymers were determined with size exclusion chromatography (SEC) on a Waters system equipped with three Styragel columns (HR1, HR3, and HR5E in the effective molecular weight range between 100–5000 g/mol, 500–30,000 g/mol, and 5000–500,000 g/mol). HPLC grade THF was used as the eluent at a flow rate of 1.0 mL/min. The glass transition temperature (T_g) was measured by DSC on a DSC 200 F3 Maia[®] instrument (METZSCH Instruments) under a nitrogen atmosphere. The sample was heated from room temperature to 150 °C and cooled to –50 °C at a rate of 10 °C/min. A second heating and cooling cycle was repeated at a rate of 10 °C/min. The thermal stability of the polymers was measured with a TG 209 F3 Tarsus[®] thermogravimetric analyzer (TGA, METZSCH Instruments) under a nitrogen atmosphere. The heating rate was set at 10 °C/min. Tensile tests were performed on an Instron 5500 tensile tester with 100 N load cell at a speed of 20 mm/min, at room temperature.



Scheme 1. Schematic illustration of the synthesis of the soybean oil-based monomers (SOM1 and SOM2) and the P(SOM1-co-SOM2) copolymers.

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