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Improvement of properties for biobased composites from modified soybean oil and hemp fibers: Dual role of diisocyanate

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ABSTRACT

An environmentally friendly composite was developed from hemp fibers (HFs) and a biobased thermosetting resin that was formulated from the copolymerization of acrylated epoxidized soybean oil (AESO) and *N*-vinyl-2-pyrrolidone. The properties of the composites were enhanced through the incorporation of isophorone diisocyanate (IPDI). The FTIR and ^{13}C NMR spectra reveal that the incorporated IPDI could react with the hydroxyl groups of both HFs and AESO by forming urethane connections; hence, IPDI plays two roles in composites, i.e., as a crosslinker and a coupling agent. The results show that both effects greatly contribute to increasing the tensile and flexural properties, storage modulus, and glass transition temperature of the resulting composites. However, the modification does not significantly influence the impact strength and slightly decreases the thermal stability of the composites. Further, the addition of IPDI into AESO resins results in resins with improved processability due to the lower viscosity and curing temperature.

1. Introduction

Thermosetting resins are of great importance in producing fiber-reinforced composites due to their good mechanical properties, thermal and chemical resistances, and durability. The currently used thermosets are mainly derived from petroleum resources and account worldwide for a sizable amount of all oil and gas used. In an era of increasing environmental concerns and continuous depletion of fossil oils, however, researchers are encouraged to exploit thermosetting polymers using renewable resources as starting materials [1]. Particularly, triglyceride-based vegetable oils, consisting of esters of glycerol with three long-chain fatty acids, are an important biobased resource that can achieve this objective through various modifications [2]. Among these, acrylated epoxidized soybean oil (AESO), derived from the epoxidation followed by the acrylation of soybean oil, is commercially available in industrial fields, such as coatings and adhesives. AESO contains two types of functional groups: double (C═C) bonds that can undergo self-polymerization and copolymerization with other components; and hydroxyl (—OH) groups and epoxy rings, both of which can react with some active chemicals, including amines, anhydrides and isocyanates [3]. For the formulation of AESO-based thermosetting polymers, a reactive diluent, typically styrene, is required to increase the mobility of AESO molecular chains such that a resin with low viscosity is obtained for processing needs and to facilitate the formation of rigid three-dimensional networks in the cured resins. However, styrene is a hazardous air pollutant and a volatile organic compound. Potential styrene alternatives for use in AESO resins have been obtained either from petroleum monomers, such as methyl methacrylate, vinyl toluene and divinylbenzene, or biobased feedstocks, including fatty acids, sucrose, and lignin [4–10]. The reaction between AESO and these monomers is the free-radical polymerization of the active C═C bonds of both components; thus, the epoxy and —OH groups in AESO are retained. These two groups give another route to alter AESO through introducing new functional structures. Wool and co-workers modified AESO with a series of acids or anhydrides to obtain AESO resins with high crosslinking density and hence superior thermal-mechanical properties [11–13]. The modification of AESO foams with a difunctional monomer carrying a C═C bond, phosphorus and biphenyl groups significantly increased the mechanical properties and flame resistance of the biofoams [14].

In addition, concerning the development of soybean oil-based polymer composites, the substitution of synthetic fibers with natural fibers has also drawn attention [15–19]. Similarly to the traditional natural fiber–polymer composites, the intrinsic challenge for these biobased composites is the poor interfacial

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adhesion between the hydrophilic fibers and the hydrophobic matrices. To overcome this issue, the chemical strategy has been utilized to modify the fiber surface characteristics and to introduce some functional groups that are able to react with the matrix [20]. This method usually involves the reactions of fibers with chemical reagents, in which a large amount of organic solvents is needed to dissolve the reagents for uniform and effective reactions because the reagents are normally a small portion of the fibers [21]. By contrast, the change of resin composition can prepare the resin matrix that has intrinsically good compatibility with fiber reinforcements, which can avoid the use of organic solvents. It was reported that the incorporation of maleic anhydride into linseed oil- or soybean oil-based resins significantly improved the fiber-resin interaction of the biobased composites reinforced by rice hull, wood flour and wood fibers, respectively [22,23]. Asolectin was developed from soybean and incorporated into tung oil-based polymer for use as a natural compatibilizer between the hydrophobic polymer and hydrophilic cellulose [24].

To formulate the AESO resins for hemp fiber (HF) composites, a highly reactive vinyl monomer, *N*-vinyl-2-pyrrolidone (NVP), as shown in Fig. 1, was used to replace styrene for copolymerizing with AESO in our previous study [25]. The results indicated that the NVP-resulting composites have superior processability and thermal-mechanical properties compared to the styrene-based composites. However, the HF/AESO composites still have two key limitations, i.e., the retained epoxy and —OH groups in the AESO molecules and the absence of chemical connections between the HFs and the AESO resins, leading to their high water absorption and relatively low mechanical properties. Therefore, the purpose of this work is to improve the overall properties of the HF/AESO composites by mixing directly the AESO resins with isophorone diisocyanate (IPDI), in which the IPDI is expected to serve two functions, i.e., improving the crosslinking capability of AESO resins and increasing the interfacial adhesion between the fibers and AESO matrix. The reinforcing effects of IPDI modification on the properties of the composites were investigated by mechanical property tests, dynamical mechanical analysis (DMA), thermogravimetric analysis (TGA), and scanning electron microscopy (SEM). The mechanism of IPDI in strengthening the composites can be understood through Fourier transform infrared spectroscopy (FTIR) and nuclear magnetic resonance (NMR). The effects of IPDI incorporation on the rheological and curing behavior of AESO resins were also investigated.

2. Experimental section

2.1. Materials

HFs with average length 3.86 cm and average fiber diameter 64.58 μm were obtained from Sanxing Hemp Industry (China). AESO (average molecular weight: 1200 g/mol) with 4000 ppm monomethyl ether hydroquinone as inhibitor and *tert*-butyl peroxybenzoate (TBPB, 98%) were purchased from Sigma-Aldrich. NVP (99%, stabilized with NaOH) and IPDI (99%) were purchased from Aladdin (China). All chemicals were used as received without further purification.

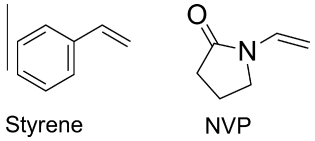

Fig. 1. Chemical structure of styrene and NVP.

2.2. Preparation

AESO was mixed with NVP at a weight ratio of 80:20 (AESO: NVP) in a beaker at 70 °C using a magnetic stirrer at 500 rpm for 10 min. After cooling to room temperature (r.t.), IPDI and TBPB were added to the mixture, which was further stirred for 5 min to form the final resins. TBPB was kept at 2 wt% based on the AESO-NVP mixture. The weight ratios of the IPDI to AESO-NVP mixture were 0:100, 5:95, 10:90, 15:85, and 20:80, and the resulting resins were denoted as control, IPDI-5, IPDI-10, IPDI-15, and IPDI-20, respectively. The reaction mechanism between IPDI and AESO is proposed in Fig. 2.

The obtained resins (20 g) were degassed under vacuum and were transferred into a silicon mold to prepare the cured resin samples. The curing reaction was performed at 120 °C for 2 h, followed by 160 °C for another 4 h in an oven. After being cooled to r.t., the samples were removed from the mold for characterization.

HFs were opened with a cotton opener to loose and separate the fibers and then to form randomly orientated fiber-mats ($20 \times 20 \times 0.5\ cm^3$). After being oven-dried at 103 °C for 24 h, the fiber-mats (75 g) were mixed with the prepared AESO resin solutions (75 g) to fabricate the HF/AESO composites with 50 wt% fiber fraction. The resin solutions were evenly coated on the fiber-mat surface by hand, and then the resulting resin-mixed fiber-mats were stacked in a steel mold ($20 \times 20 \times 0.3\ cm^3$) at r.t. The mold was successively pressed at r.t. for 5 min, at 70 °C for 5 min, and at 160 °C for 30 min under a pressure of 6 MPa. Finally, the mold was cooled to r.t., and the formed composite board was removed from the mold.

2.3. Characterization

Rheological analysis of uncured AESO resins was conducted on a HAAKE MARS III rotational rheometer (Thermo Electron, USA) using a PP35Ti parallel plate (gap: 0.105 mm) at a shear rate of 10 γ/s and a heating rate of 10 °C/min from 25 to 100 °C. The curing behavior of the resins was studied through differential scanning calorimetry (DSC) analysis on a STA 449 F3 Jupiter Simultaneous Thermal Analyzer (NETZSCH, Germany). The resin sample (5–10 mg) was placed in a standard porcelain crucible with a lid and was tested under N_2 (flow rate: 30 mL/min) from 25 to 250 °C with a heating rate of 10 °C/min.

The cured AESO resins (5 g) and composite samples (5 g) were ground into powders for the FTIR and NMR tests. The powders were mixed with KBr in a mass ratio of 1:100, and then the obtained mixtures were pressed at 15 MPa to form a pallet for FITR analysis. FTIR experiments were conducted using a Nicolet 5700 FTIR spectrometer (Thermo Fisher Scientific, USA) over a scanning range from 4000 to 400 cm^{-1} at a spectral resolution of 4 cm^{-1}. The collected spectra were normalized based on the carbonyl peak of ester groups at 1735 cm^{-1}. Solid-state ^{13}C NMR spectra were recorded on an Avance III 500 NMR spectrometer (Bruker, USA) equipped with a 4-mm, double-resonance, CP-MAS probe.

The tensile, flexural, and impact properties of the HF/AESO composites were evaluated according to ASTM D 638-10, ASTM D 790-10, and ISO 179-10, respectively. Dumbbell specimens with 50 mm gage length and 10 mm narrow section width were used for the tensile test. Rectangular specimens ($80 \times 10\ mm^2$) were prepared for the flexural and impact tests. The tensile and flexural tests were conducted on a CMT6104, microcomputer-controlled, electronic universal testing machine (MTS Systems, USA) at a crosshead rate of 10 mm/min. The impact test was performed on a ZBC-25B Charpy impact tester (MTS Systems, USA). Five replicates were measured for each type of composite. Rectangular samples ($55 \times 10\ mm^2$) of composites were prepared for the DMA tests. The tests were conducted on a DMA 242 (NETZSCH, Germany)