



Sustainable epoxy resins derived from plant oils with thermo- and chemo-responsive shape memory behavior

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ABSTRACT

Shape-memory epoxy resins were synthesized using plant oils and cellulose nanocrystals (CNCs). Epoxidized soybean homopolymers (PESBMA) were grafted from CNCs using surface-initiated atom transfer radical polymerization (SI-ATRP). The polymer grafted CNCs were combined with P(ESBMA-co-SBMA) copolymer and cured using anhydride to prepare epoxy resins. Controlling weight fractions of CNCs and ratios of epoxide to anhydride provided tunability over mechanical and thermal properties. The grafted polymer nanocomposites were also compared to simple blends to confirm better properties of the grafted system. Thermo- and chemo-responsive shape memory properties were obtained for these materials.

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1. Introduction

Shape memory polymers (SMPs) are a class of smart materials that can change functions upon exposure to external stimuli, such as temperature, pH, solvation, or electricity [1–4]. Most of these materials utilize petroleum-based chemicals for their components. Recent advances have focused on making sustainable SMPs from renewable resources for a variety of applications, including biomedical uses [5–11]. SMPs typically involve two separate networks: a permanent network and a temporary or switchable network. The permanent network is needed to maintain a permanent shape while the switchable network is responsible for allowing induction of a temporary shape resulting from a stimulus. In general, the easiest and most widely used switchable SMPs are thermo-responsive, in which the switching temperature, often the glass transition temperature (T_g) of the temporary network polymers, is just above room temperature.

The two networks in a SMP serve different functions and therefore require distinct chemistries. Specifically, the first,

permanent network serves to control and return the material to the primary permanent shape. This can be achieved using covalent bonding. The second network, the temporary or switchable network, utilizes dynamic interactions such as hydrogen bonding or other exploitable properties such as crystallization. Many systems have utilized nanocrystals or nanomaterials to achieve the response, such as graphene oxide, magnetite, silica, and polymers like polylactic acid (PLA) and polycaprolactone (PCL), which help strengthen the permanent network and provide a switchable network through crystallinity [12–22].

Cellulose, specifically cellulose nanocrystals (CNCs), possesses crystallinity and high mechanical strength, and shows potential for the preparation of entirely biobased shape memory polymers [23–31]. Similarly, plant oil based polymer materials have shown promise in the preparation of shape memory polymers [32–34]. Our group successfully synthesized SMPs using CNCs and soybean oil, where the permanent network was achieved through triazolinedione (TAD) crosslinking chemistry [5]. However, a more economical and industry-benign approach is epoxy curing chemistry [35]. We recently demonstrated the preparation of biobased epoxy resins from soybean polymers [36,37]. Herein we present thermo- and chemo-responsive shape memory composites using supramolecular soybean epoxy resins with CNCs, utilizing epoxy

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curing to form a permanent network while hydrogen-bonding and T_g induced a dynamic network (Scheme 1). The response of hydrogen bonding and T_g allows thermal and chemical triggers. CNCs were grafted with soybean polymers via surface-initiated atom transfer radical polymerization (SI-ATRP).

2. Materials

Plenish high oleic soybean oil (HOSO) was provided by DuPont Pioneer. Cellulose nanocrystals were provided by CelluForce (Canada). Azobisisobutyronitrile (AIBN, 98%, Aldrich) was recrystallized twice from methanol. Monomers were run through basic alumina to remove inhibitors. All other reagents were from commercial resources and used as received unless otherwise mentioned. Soybean methacrylate (SBMA) and epoxidized soybean methacrylate (ESBMA) were prepared according to our previous work (Scheme S1) [26,36,38–42]. Bromoisobutryl bromide-coated cellulose nanocrystal as initiators (CNC-Br) were synthesized according to literature [5,43].

2.1. Characterization

300 MHz ^1H NMR spectra were recorded on a Bruker Avance III HD 300 spectrometer using CDCl_3 as solvent with tetramethylsilane (TMS) as an internal reference. Molecular weight and molecular weight distribution of polymers were determined by gel permeation chromatography (GPC) on a Waters system equipped with a 515 HPLC pump, a 2410 refractive index detector, and three Styragel columns (HR1, HR3, HR5E in the effective molecular weight range of 100–5000 g/mol, 500–30,000 g/mol, and 5000–500,000 g/mol, respectively) with HPLC grade tetrahydrofuran (THF) as the eluent at 30 °C and a flow rate of 1.0 mL/min. THF and polymer solutions were filtered through microfilters with an average pore size of 0.2 μm . The columns were calibrated against polystyrene standards. Dynamic GPC samples were prepared by dissolving the sample in THF with a concentration of 5.0 mg/mL and passing through microfilters with average pore size of 0.2 μm . Fourier transform infrared spectrometry (FTIR) spectra were taken on a PerkinElmer spectrum 100 FTIR spectrometer. Zetasizer nano instrument, equipped with an 830 nm wavelength laser, was used to determine the hydrodynamic radius (R_h) of CNCs and CNC-g-PESBMA. X-ray photoelectron spectroscopy (XPS) measurements were carried out on a Thermo-VG Scientific ESCALAB 250 X-ray photoelectron

spectrometer. The glass transition temperature (T_g) of polymers was tested through differential scanning calorimetry (DSC) conducted on a DSC 2000 instrument (TA Instruments). Samples were first heated from -70 to $+200$ °C at a rate of 10 °C/min. After cooling down to -70 °C at the same rate, the data was collected from the second heating scan. About 8 mg of each sample was used for the DSC test with nitrogen gas at a flow rate of 50 mL/min. Dynamic thermomechanical analysis (DMA) was performed by using a Q800 DMA (TA Instruments). The DMA spectra were scanned with a frequency of 10 Hz and a heating rate of 3 °C/min. All the shape memory tests were carried out in a stress controlled thin film tension mode. Thermogravimetric analysis (TGA) was conducted on a Q5000 TGA system (TA Instruments), ramping from 25 to 600 °C with a rate of 10 °C/min. About 10 mg of sample was used per test. Tensile stress–strain testing was carried out with an Instron 5543 A testing instrument. The films were prepared by dissolving 1 g of polymers in 15 mL of solvent. The solution of polymers was poured in a PTFE mold. After the evaporation of solvent over 72 h, the film was put under vacuum for 4 h at room temperature followed by 4 h at 60 °C. Dog-bone shaped specimens were cut from the cast film with a length of 20 mm and width of 5.0 mm. The thickness was measured prior to each measurement. Testing was done at room temperature with a crosshead speed of 20 mm/min. Five replicate samples were used to obtain an average value for each.

2.2. Synthesis of CNC-g-PESBMA by SI-ATRP

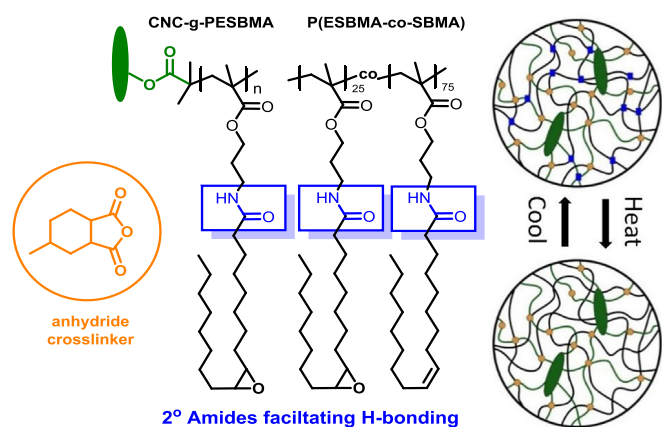
CNC-Br (104 mg, 0.0466 mmol of Br), ESBMA (3.00 g, 7.13 mmol), tris [2-(dimethylamino)ethyl]amine (Me_6TREN) (23 mg, 0.1 mmol), THF (1.0 mL) and dimethylformamide (DMF) (1.0 mL) were introduced to a 10 mL Schlenk flask. The solution was degassed by three freeze–pump–thaw cycles and sealed. Cu(I)Br (14.4 mg, 0.1 mmol) was added during the last cycle. The flask was sealed under nitrogen and placed into an oil bath set at 90 °C. After 36–72 h, the polymerization was stopped by opening the flask and exposing the reactive mixture to air. THF was added to the mixture, and the product was precipitated into cold methanol three times. The resulting polymer was dried under vacuum at 40 °C.

2.3. Synthesis of P(ESBMA-co-SBMA) copolymer

ESBMA (3.00 g, 7.13 mmol), SBMA (9.00 g, 21.4 mmol), AIBN (46.9 mg, 0.285 mmol) and dry toluene (12 mL) were introduced to a 50 mL round bottom flask. The flask was sealed, purged with nitrogen for 20 min and placed into an oil bath at 75 °C. After 7 h, the polymerization was stopped by opening the flask and exposing the reactive mixture to air. THF was added to the mixture, and the product was precipitated into cold methanol three times. The resulting polymer was dried under vacuum at 40 °C.

2.4. Synthesis of epoxy resins

A typical procedure was as follows: CNC-g-PESBMA (0.5 g) was dispersed in 1 mL DMF. To this solution was added P(ESBMA-co-SBMA) (0.5 g), 4-methylcyclohexan-1,2-dicarboxylic anhydride (39.2 mg, 0.675 mmol), 1,8-diazabicyclo [5.4.0] undec-7-ene (DBU) (10 mg), and 5 mL THF. The solutions were sonicated for 5 min, degassed, and poured into Teflon molds. Solvents were evaporated at room temperature over 72 h. The films were then placed into an oven under vacuum for 24 h and heated under vacuum at 50 °C for 24 h. Finally, the films were cured at 100 °C for 24 h.



Scheme 1. Shape memory polymers using soybean oil polymers and cellulose nanocrystals containing epoxy-curing networks and supramolecular hydrogen-bonding networks.

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