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



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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,

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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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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





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]. Bromoisobutyryl 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 CDCl₃ 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



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

spectrometer. The glass transition temperature (T_{σ}) 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 (Me₆TREN) (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-methycyclohexan-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.

3. Results & discussion

3.1. Synthesis of soybean polymers and epoxy resins

SMPs were synthesized in multiple steps. First, CNC-Br as an initiator was synthesized using a procedure reported earlier [43]. This reaction involves the esterification of hydroxyl groups on CNCs using bromoisobutyryl bromide (BIBr). The initiator was characterized by FTIR and XPS, which allowed the determination of grafted bromine sites on the surface of CNC (Fig. 1 and Table 1). The CNC-Br was determined to have ~1.3 wt% bromine from the bromoisobutyryl groups functionalized onto the surface (first reaction in Scheme 2).

Epoxidized soybean methacrylate monomer (ESBMA) was prepared using a reported method [42]. Soybean oil was transformed into a fatty alcohol, which was subsequently epoxidized using 3chloroperoxybenzoic acid (*m*-CPBA). The epoxidized soybean alcohol was reacted with methacrylic anhydride using a base catalyst to prepare the soybean epoxy monomer (Scheme S1). CNC*g*-PESBMA was subsequently synthesized by SI-ATRP, as shown in Scheme 2. The final grafted polymer was characterized by ¹H NMR and XPS (Fig. 1 and Table 1). XPS data confirmed the presence of bromine and nitrogen respectively on grafted CNC initiators and polymers. The absence of bromine in CNC-*g*-PESBMA could be due to Br content below the detection limit, given the dramatic decrease of bromine after polymers were grafted.

The weight content of cellulose in the grafted polymer was determined to be 3.9 wt% using conversion and ratio of initiator to monomer via ¹H NMR. Higher amount of cellulose resulted in poor dispersion of the CNC-Br initiators in the polymerization solvent system likely due to a lack of solubility. The number average molecular weight ($M_n = 49.5$ KDa) was determined theoretically using ¹H NMR (to obtain conversion, $[M]_o/[I]_o = 150$, $M_o = 424$ g/mol), and a T_g of 20 °C was determined by DSC. P(ESBMA-*co*-SBMA) copolymers were synthesized using free radical polymerization. The P(ESBMA-*co*-SBMA) copolymer used for blending has a M_n of 40.7 KDa and a T_g of 13 °C. CNC-g-PESBMA grafted polymer was blended with P(ESBMA-*co*-SBMA) copolymers. The control of composition between ESBMA and SBMA allowed for control of mechanical properties for tailored materials. Subsequent cross-linking can form epoxy resins.

Table 1

XPS data (atomic percentages) comparing the bare CNC, CNC-Br, and CNC-g-PESBMA.

	% O 1s	% C 1s	% Br 3 d	% N 1s	O/C
Bare CNC	44.3	55.7	_	_	0.79
CNC-Br	40.8	57.9	1.3	_	0.70
CNC-g-PESBMA	28.1	67.3	-	4.6	0.42

3.2. Mechanical properties of soy polymers and epoxy resins

To prepare epoxy resins, P(ESBMA-co-SBMA) and CNC-g-PESBMA were dispersed in THF. The mixture was crosslinked by 4methycyclohexan-1,2-dicarboxylic anhydride with DBU as a catalyst. Various ratios of epoxide to anhydride were used to optimize mechanical properties (Fig. 2A). A ratio of epoxide to anhydride at 2:1 produced the strongest and toughest films, while lower ratios resulted in poor mechanical properties and higher ratios reduced toughness. With the ratio of epoxide to anhydride at 2:1, four samples were synthesized with weight fraction of CNCs in the range of 0–1.8 wt% using a combination of grafted and copolymer (Fig. 2B). There was a marked decrease in toughness with introduction of CNCs. It is likely due to the increase in epoxide crosslinkers with increasing amount of CNC-g-PESBMA polymer. Grafted CNC composites were also compared with simple blends of CNCs and polymers (Fig. S1). The grafted materials showed a significant change in mechanical properties with a decrease in elasticity, likely due to an increase in crosslinking. While, the simple blends with cellulose lacked noticeable robustness in comparison. This is likely caused by the lack of good interactions between the CNC filler and polymer matrix in the blend.

Dynamic mechanical analysis (DMA) was performed on the epoxy resins to help determine their mechanical behavior (Fig. 3). Resins with three different fractions of CNCs (0.6 wt%, 1.2 wt%, and 1.8 wt%) displayed similar loss modulus and storage modulus above room temperature, with a clear plateau starting at $50 \degree \text{C}$ for the 0.6 wt% resins around 5000 MPa. The rubbery plateau for the 1.2 and 1.8 wt% resins begins later above $70 \degree \text{C}$ around 600 MPa. Unfortunately, the resins with 1.2 wt% and 1.8 wt% CNCs were quite brittle, with complete breakage of samples above $80 \degree \text{C}$, which did not occur for the 0.6 wt% sample. Thus, the resin with 0.6 wt% CNC



Fig. 1. (A) FTIR spectra of CNC, CNC-Br, and CNC-g-PESBMA; (B) ¹H NMR spectrum of CNC-g-PESBMA.



Scheme 2. Synthesis of CNC-g-PESBMA by SI-ATRP using CNC-Br as initiator.



Fig. 2. Tensile curves: (A) epoxy resins featuring various ratios of epoxide to anhydride of virgin polymer without cellulose; (B) epoxy resins featuring varying weight fractions of CNCs using a ratio of epoxide to anhydride of 2:1.



Fig. 3. (A) Loss modulus and (B) Storage modulus of the epoxy resins containing various wt% of CNC.

was chosen as the sample for the remainder of testing, as it maintained desirable flexibility, did not break before reaching a rubbery plateau, and maintained a higher storage modulus at increased temperature.

3.3. Thermal properties of soy polymers and epoxy resins

DSC and DMA were used to determine the T_g of polymers and corresponding epoxy resins. DSC provided comparison of T_g between virgin free copolymer, grafted polymer, and epoxy resin,

whereas DMA allowed for a more sensitive measurement of T_g for the epoxy resin (Fig. 3 and Fig. S2). Incorporation of CNCs into soybean polymers resulted in a slightly higher T_g , where P(ESBMA*co*-SBMA) has a T_g of 13 °C, versus 20 °C for CNC-*g*-PESBMA. The final epoxy resin containing 0.6 wt% cellulose has a T_g of 22 °C; however, DMA showed a T_g of 12 °C using the sigmoidal change in storage modulus. All polymers and epoxy resins showed high thermal stability, with 10 wt% loss at 315–318 °C (Table 2 and Fig. S3).

Table 2 Thermal properties of grafted copolymer, free soybean copolymer and the epoxy resin. T_g was measured using DSC.

Samples	$T_g(^{\circ}C)$	Temperature of 10% weight loss (T_{d10} , °C)
P(ESBMA- <i>co</i> -SBMA)	13	318
CNC-g-PESBMA	20	315
0.6 wt% CNC Epoxy Resin	22	315

3.4. Thermo- and chemo-responsive shape memory properties

These epoxy resins were expected to exhibit shape memory properties. The polymer matrix is made up of two separate networks. The permanent network involves crosslinking due to epoxide curing. The switchable network involves hydrogen bonding between hydroxyl groups on cellulose and secondary amides on the soybean polymers. Once heated above the T_g , the polymer chains could significantly reduce the hydrogen bonding network and enhance chain mobility, allowing deformation of polymers into a temporary shape. When polymers are cooled under stress, chains are locked with stressed conformation as the hydrogen bonding resumes. If polymers are heated again, the hydrogen bonding is again disrupted, and the polymer films quickly return to the thermodynamically favored permanent shape.

As shown in Fig. 4, stress- and temperature-programmed DMA was used to quantitatively analyze the shape memory properties of epoxy resins. The epoxy resin with 0.6 wt% CNC was heated to 80 °C and deformed under constant stress (0.07 MPa). A strain of 42% was obtained within 5 min. Following deformation, the film was cooled to 20 °C under the same stress (0.07 MPa). After cooling, the stress was released and the strain was tracked as the sample was reheated to 80 °C. Shape fixity was used to determine how well the polymer holds the stimulated temporary shape after removal of stress. According to equation (1),

$$R_f = \frac{\varepsilon_u}{\varepsilon_m} \times 100\%, \tag{1}$$

where \mathcal{E}_m is the strain after stretching and fixing for temporary shape and \mathcal{E}_u is the strain after removal of stress, the shape fixity ratio was calculated to be 96.7%. Shape recovery was used to determine how well the polymer recovers back to the original permanent shape. According to equation (2)

$$R_r = \left(1 - \frac{\varepsilon_r}{\varepsilon_m}\right) \times 100\%,\tag{2}$$

where ε r is the strain after recovery from temporary shape, the shape recovery ratio was calculated to be 85.4%.

Beyond thermo-responsive properties, other stimuli to the disruption of hydrogen bonds can also serve to stimulate the shape memory response of these composite materials [44]. Chemo-responsive behaviors were tested using solvents that could disrupt H-bonding, such as water and methanol. Methanol can easily be absorbed into the polymer matrix and interrupt hydrogen bonding within the polymer, leading to a return to the permanent shape in 35 min (Fig. 5). Water can also interrupt hydrogen bonds; however, water molecules exhibited slower diffusion into the polymer matrix than methanol, resulting in incomplete recovery while films were submersed at room temperature (Fig. S4). When heated to 40 °C, a combination of thermo- and chemo-response can accelerate shape recovery in just 45 min in water (Fig. 6).

Although THF is an aprotic polar solvent that cannot hydrogen bond itself, its vapor easily penetrated into the polymer matrix and caused quick return to the original shape in 6 min (Fig. S5). THF vapors serve to plasticize the polymer matrix, decreasing T_g and increasing flexibility and rubbery properties. When exposed to THF vapor, the polymer gained flexibility and caused faster recovery to the entropically favored original permanent shape.



Fig. 4. Dual (stress- and temperature-) programmed shape memory testing of epoxy resin with 0.6 wt% CNC; photos of films show time-dependent recovery.



Fig. 5. Time-dependent chemo-responsive shape memory testing in methanol at room temperature.



Fig. 6. Time-dependent chemo-responsive shape memory testing in water at 40 $^\circ\text{C}$

4. Conclusions

Epoxy resins were synthesized using soybean oil and cellulose nanocrystals via SI-ATRP. The resulting materials showed both thermo- and chemo-responsive shape memory. All synthesized polymers can be easily characterized to determine mechanical and thermal properties. These results indicate high thermal stability and excellent strength of the final epoxy resins. Overall, such results for these sustainable epoxy resins demonstrate promising utilization as smart materials.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.polymer.2018.04.047.

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