Incorporating Functionalized Cellulose to Increase the Toughness of Covalent Adaptable Networks

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Supplementary Information

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Materials and Instrumentation

Materials. All reagents were purchased from Sigma-Aldrich or Fisher Scientific. All reagents were used without further purification unless otherwise specified. Dimethylformamide (DMF) was purchased from Fisher Scientific and purified using a custom-built alumina-column based solvent purification system. Other solvents were purchased from Fisher Scientific and used without further purification.

Instrumentation. Infrared spectra were recorded on a Thermo Nicolet iS10 equipped with a ZnSe ATR attachment. Spectra were uncorrected.

Solution-phase NMR spectra were recorded on a Varian 400 MHz or an Agilent DD MR-400 400 MHz spectrometer using a standard 1H/X Z-PFG probe at ambient temperature.

Differential scanning calorimetry (DSC) was performed on a TA instruments Q1000 Differential Scanning Calorimeter. Samples were heated at a rate of 10 °C/min to at least 90 °C to erase thermal history, cooled to −30 °C at 10 °C/min, and then heated to at least 120 °C. All data shown are taken from the second heating ramp. The glass transition temperature ($T_g$) was calculated from the maximum value of the derivative of heat flow with respect to temperature.

Dynamic mechanical thermal analysis (DMTA) was performed on a TA Instruments RSA-G2 analyzer (New Castle, DE) using rectangular films (ca. 1.0 mm (T) × 3 mm (W) × 6 mm (L)). The transducer was set to spring mode. The axial force was adjusted to 20 g (sensitivity 1.0 g) before the test to ensure the sample was in tension and not buckling. The minimum axial force was set to 5 g, and a force tracking mode was set such that the axial force was twice the magnitude of the oscillation force during the test. A strain adjust of 30% was set with a minimum strain of 0.05%, a maximum strain of 10%, a minimum force of 1 g and a maximum force of 20 g in order to prevent the sample from going out of the specified strain. A temperature ramp was then performed from −30 °C to 120 °C at a rate of 5 °C/min, with an oscillating strain of 0.05% and an angular frequency of 6.28 rad s$^{-1}$ (1 Hz). The glass transition temperature ($T_g$) was calculated from the maximum value of the loss modulus ($\mathcal{E}''$).

Uniaxial tensile testing was conducted using dog bone shaped tensile bars (ASTM D-1708 1.0 mm (T) × 5 mm (W) × 25 mm (L) and a gauge length of 16 mm). The samples were aged for at least 48 h at ambient temperatures in a desiccator prior to testing. Tensile measurements were performed on a Sintech 20G tensile tester with 250 gram capacity load cell at ambient temperatures at a uniaxial extension rate of 5 mm/min. Young’s modulus ($E$) values were calculated using the TestWorks software by taking the slope of the stress-strain curve from 0 to 1 N of force applied. Reported values are the averages and standard deviations of at least three replicates.

Stress relaxation analysis (SRA) was performed on a TA Instruments RSA-III analyzer (New Castle, DE) using rectangular films (ca. 1.0 mm (T) × 3 mm (W) × 20 mm (L) and a Gauge length of 6 mm). The SRA experiments were performed with strain control at specified temperature (150 to 180 °C). The samples were allowed to equilibrate at this temperature for approximately 10 minutes, after which the axial force was then adjusted to 0 N with a sensitivity of ±0.002 N. Each sample was then subjected to an instantaneous 5% strain. The stress decay was monitored, while maintaining a constant strain (5%), until the stress relaxation modulus had relaxed to at least 37%
(1/e) of its initial value. This was performed three consecutive times for each sample.

To reprocess the materials, the polymer was ground into small pieces using a Cuisinart Grind Central coffee grinder and placed between two aluminum plates with a 1.0 mm thick aluminum spacer. This assembly was placed in a preheated PHI 30-ton manual compression hot press with 8-10 tons of force. All samples were reprocessed for 8 hours. The samples were then removed from the molds and placed in a vacuum oven for 2 days at 120 °C to further cure the materials. The samples were subjected to uniaxial tensile testing and dynamic mechanical thermal analysis to determine their recovery in mechanical properties.
**Experimental Section**

**Scheme S1.** Synthesis of bis(6-membered cyclic carbonate) (4) (bCC)

To a flame-dried round bottom flask under nitrogen, di(trimethylolpropane) (30.0 g, 120 mmol, 1 equiv.) in 700 mL of THF were added. While stirring at 0 °C, ethyl chloroformate (58.4 mL, 726 mmol, 6 equiv.) was added via syringe. Then, triethylamine (101.1 mL, 726 mmol, 6 equiv.) was added dropwise giving a white precipitate. The reaction mixture was allowed to warm to room temperature while stirring over 3 hours. The white precipitate was vacuum filtered and the filtrate was concentrated. The resulting oil was placed in the freezer to solidify. The resulting solid was recrystallized from THF (30 mL) to yield a white solid (21.5 g, 66% yield).

\[ ^1H \text{ NMR} (500 \text{ MHz, } d_6-\text{DMSO}) \delta 4.27 (d, J = 10 \text{ Hz}, 4H, -CH_aH_bOCOOC_H_aH_b-), 4.22 (d, J = 10 \text{ Hz}, 4H, -CH_aH_bOCOOC'H_bH_a-, 3.41 (s, 4H, -CHCH}_2OCH}_2-, 1.39 (q, J = 7.6 \text{ Hz}, 4H, -CH}_2CH}_3), 0.83 (t, J = 7.6 \text{ Hz}, 6H, -CCH}_2CH}_3) \text{ ppm.} \]

\[ ^{13}C \text{ NMR} (125 \text{ MHz, } d_6-\text{DMSO}): \delta 148.4, 72.8, 70.6, 35.2, 23.2, 7.65 \text{ ppm.} \]

**FT-IR** (solid, ATR): 2972, 2881, 1732, 1539, 1463, 1412, 1388, 1306, 1253, 1184, 1152, 1106, 1060, 1016, 988, 961, 868, 797, 762, 702 cm$^{-1}$

**Scheme S2.** Benzyl-protection of 2,2-bis(hydroxymethyl)propionic acid (S1)

To a flame-dried round bottom flask under nitrogen, 2,2-bis(hydroxymethyl)propionic acid (65.2 g, 486 mmol, 1 equiv.) was added and dissolved in DMF (360 mL). To this, potassium hydroxide (27.5 g, 491 mmol, 1.01 equiv.) was added. The reaction was allowed to stir at 100 °C for 3 h. After 3 h, benzyl bromide (69.5 mL, 585 mmol, 1.2 equiv.) was added via syringe to give a white precipitate. This crude reaction solution was allowed to stir at 100 °C for 14 h. The precipitate was removed by vacuum filtration. The solvent was removed from the filtrate by vacuum distillation at 100 °C to yield a white solid. The solid was recrystallized from toluene (75 mL) to yield the product as a white solid (63 g, 57.8 % yield).

\[ ^1H \text{ NMR} (500 \text{ MHz, } d_6-\text{DMSO}) \delta 7.34 (m, 5H, C_6H}_5CH}_2-), 5.10 (s, 2H, C_6H}_5CH}_2OOC-), 4.74 (t, J = 5.4 \text{ Hz}, 2H, [CH}_2OH}_2C-), 3.56 (dd, J = 10.4, 5.5 \text{ Hz}, 2H, [OHCH}_2H_bH_b-), 3.47 (dd, J = 10.4, 5.4 \text{ Hz}, 2H, [OHCH}_2H_bC-), 1.10 (s, 3H, CH}_2C[CH}_2OH}_2) \text{ ppm.} \]

\[ ^{13}C \text{ NMR} (125 \text{ MHz, } d_6-\text{DMSO}): \delta 174.5, 136.5, 128.3, 127.6, 127.1, 65.0, 63.9, 50.3, 16.9 \text{ ppm.} \]

**FT-IR** (solid, ATR): 3508, 3358, 3091, 3063, 3038, 2981, 2943, 2885, 1702, 1607, 1585, 1549, 1498, 1465, 1456, 1406, 1377, 1366, 1322, 1315, 1300, 1223, 1180, 1153, 1114, 1039, 1030, 1001, 976, 946, 910, 749, 699 cm$^{-1}$
Scheme S3. Synthesis of benzyl-protected carboxylate-containing 6-membered cyclic carbonate (S2)

To a flame dried round bottom flask under nitrogen, 1 (30 g, 133.8 mmol, 1 equiv.) was added with THF (300 mL). The solution was cooled to 0 ºC. To this, ethyl chloroformate (38.4 mL, 401.3 mmol, 3 equiv.) and triethylamine (65.8 mL, 468.2 mmol, 3.5 equiv.) were added to yield a white precipitate. The reaction was allowed to stir for 3 h and was brought to room temperature. After 3 h, the precipitate was removed via vacuum filtration. The filtrate was concentrated to yield an off-white solid. The crude solid was recrystallized from toluene to yield a white solid (25.5 g, 75 % yield).

\[ ^1H \text{ NMR (500 MHz, } d_6\text{-DMSO)}: \delta 7.38 \text{ (m, 5H, } C_6H_5CH_2\text{-)}, 5.22 \text{ (s, 2H, } C_6H_5C\text{H}_2OCO\text{-)}, 4.60 \text{ (d, } J = 10.6 \text{ Hz, 2H, } -CH_2H_5OCOOCH_2H_5\text{-)}, 4.39 \text{ (d, } J = 10.5 \text{ Hz, 2H, } -CH_2H_5OCOOCH_2H_5\text{-)}, 1.21 \text{ (s, 3H, } C\text{H}_3C\text{OO-}) \text{ ppm.} \]

\[ ^{13}C \text{ NMR (125 MHz, } d_6\text{-DMSO): } \delta 172.0, 147.6, 136.0, 129.0, 128.6, 128.1, 72.9, 67.2, 39.7, 16.8 \text{ ppm.} \]

FTIR (solid, ATR): 3034, 2982, 2948, 2913, 2883, 1733, 1608, 1586, 1536, 1499, 1474, 1466, 1458, 1406, 1378, 1334, 1314, 1286, 1228, 1171, 1130, 1096, 1035, 1011, 992, 932, 767, 738, 696 cm\(^{-1}\)

Scheme S4. Synthesis of carboxylic acid-containing 6-membered cyclic carbonate (S3)

A solution of 2 (20 g, 79.9 mmol) and ethyl acetate (267 mL) was made in a round bottom flask and mixed until homogeneous. To a Parr reactor, palladium on carbon (10 wt% loading, 1.32 g) was added with a stir bar. The solution of 2 and ethyl acetate was added to the Parr reactor. The reactor was sealed and filled with H\(_2\) (10 bar). The reaction was stirred at rt for 4 h at which the reactor was vented and refilled with H\(_2\) (10 bar). The reaction was allowed to stir at rt for 16 h. The Parr reactor was then vented and the palladium on carbon was removed via vacuum filtration on celite. The celite was washed thoroughly with ethyl acetate to remove all of the product, the solutions were combined and concentrated to yield 3 as a tan powder (11.9 g, 93.3% yield).

\[ ^1H \text{ NMR (500 MHz, } d_6\text{-DMSO): } \delta 13.4 \text{ (br s, 1H, } -\text{COOH}) \text{, 4.54 (d, } J = 10.1 \text{ Hz, 2H, } -CH_2H_5OCOOCH_2H_5\text{-), 4.31 (d, } J = 10.1 \text{ Hz, 2H, } -CH_2H_5OCOOCH_2H_5\text{-), 1.17 (s, 3H, } -CH_2C\text{COOH) ppm.} \]

\[ ^{13}C \text{ NMR (125 MHz, } d_6\text{-DMSO): } \delta 173.8, 147.8, 73.2, 39.8, 16.9 \text{ ppm.} \]
FT-IR (solid, ATR): 2988, 2624, 1744, 1537, 1464, 1418, 1372, 1311, 1282, 1241, 1199, 1176, 1138, 1102, 969, 936, 814, 799, 767, 748, 720 cm$^{-1}$

Scheme S5. Synthesis of acid chloride-containing 6-membered cyclic carbonate (1)

To a flame-dried round bottom flask under nitrogen, 3 (2.0 g, 12.4 mmol, 1 equiv.) was added and dissolved in anhydrous THF (62 mL). To this, oxalyl chloride (1.2 mL, 13.8 mmol, 1.1 equiv.) and DMF (20 drops) were added to the solution. The reaction was allowed to stir at room temperature for 5 h. Then the reaction mixture was concentrated and diluted with DCM and again was concentrated, resulting in a yellow oil. This oil was dried in vacuo to remove the excess oxalyl chloride to yield a yellow solid (4).

$^1$H NMR (500 MHz, $d_6$-DMSO): $\delta$ 4.54 (d, $J = 10.5$ Hz, 2H, -CH$_2$OCOOC$_2$H$_3$), 4.32 (d, $J = 10.4$ Hz, -CH$_2$OCOOC$_2$H$_3$), 1.17 (s, 3H, CH$_3$CCOCl) ppm.

$^{13}$C NMR (125 MHz, $d_6$-DMSO): $\delta$ 173.2, 147.3, 72.6, 39.3, 16.3 ppm

FT-IR (solid, ATR): 2978, 1728, 1525, 1464, 1416, 1400, 1268, 1230, 1200, 1179, 1144, 1103, 1028, 982, 931, 888, 804, 763, 736, 686 cm$^{-1}$

Scheme S6. Functionalization of cellulose with cyclic carbonate (2):

To a round bottom flask under nitrogen, 1-allyl-3-methylimidazolium chloride ([Amim]Cl, 8.0 g) was added with a magnetic stir bar. The flask is heated to 50 °C to melt the ionic liquid. To this, acid chloride 4 (2.21 g, 12.4 mmol, 2 equiv.) was added using DCM (7 mL) to transfer. To the solution, microcrystalline cellulose (2.14 g, 6.25 mmol, 1 equiv.) and triethylamine (1.82 mL, 13.1 mmol, 2.1 equiv.) were added. The reaction was allowed to stir at 55 °C for 16 h. Then the reaction solution was diluted with water and vacuum filtered to remove the ionic liquid. The reaction solution was washed with water 5x and then crushed using a mortar and pestle and washed another 3x with water to fully remove the ionic liquid. The solid was collected and dried in a vacuum oven at 120 °C for 5 h to yield a white powder, 5 (2.04 g).
FT-IR (solid, ATR): 3333, 2897, 1732, 1427, 1370, 1334, 1316, 1236, 1161, 1055, 1032, 896, 664 cm\(^{-1}\)

**Scheme S7.** Acylation of Functionalized Cellulose (3):

![Scheme S7](image)

To a round bottom flask under nitrogen, 1-allyl-3-methylimidazolium chloride (8 g) was added at 50 °C and stirred. Once the ionic liquid was melted, 5 (2 g, 4.13 mmol, 1 equiv.) was added to the flask. To the solution, acetic anhydride (3.91 mL, 41.28 mmol, 10 equiv.) and N,N-dimethylaminopyridine (100.9 mg, 0.826 mmol, 0.2 equiv.) were added and the reaction was stirred under nitrogen at 50 °C for 16 h. The solution was washed with water (2x) and vacuum filtered. The solution was then washed with saturated sodium bicarbonate and then washed with water (2x). The resulting solid was then dried in the vacuum oven at 120 °C overnight to give acylated functionalized cellulose (6) as an orange solid (3.0 g yield).

\(^1\)H NMR (500 MHz, \(d_6\)-DMSO): \(\delta\) 5.08, 4.88, 4.68, 4.55, 4.24, 4.01, 3.83, 3.68, 2.08, 1.95, 1.88, 1.37, 1.30, 1.24 ppm

FT-IR (solid, ATR): 2945, 1739, 1645, 1580, 1432, 1367, 1323, 1216, 1167, 1036, 901 cm\(^{-1}\)

**Scheme S8.** Synthesis of 0 mol% cellulose polycarbonate film (S4):

![Scheme S8](image)

To a scintillation vial, a solution of bCC (6.8 g, 22.4 mmol, 1 equiv.) in DMF (20 mL) was added. To this solution, 2-hydroxyethyl disulfide (2.745 mL, 22.4 mmol, 1 equiv.) is added and the solution was sonicated until homogenous. Titanium isopropoxide (67.5 µL, 0.224 mmol, 1 mol\%) was added to the solution resulting in a small amount of white precipitate, which is subsequently filtered. The resulting filtrate is poured into an aluminum mold (96 mm diameter) on the hot plate at 140 °C for two hours to remove solvent. After two hours, the film is placed in a vacuum oven at 120 °C for 8 days. The film is then removed from the pan and tensile bars and films for DMTA were cut.

FT-IR (solid, ATR): 3382, 2964, 2916, 2881, 2849, 1742, 1633, 1575, 1539, 1463, 1398, 1240, 1109, 1042, 953, 786 cm\(^{-1}\)
**Scheme S9. Incorporation of Functionalized Cellulose into Polycarbonate Films (6)**

Acylated functionalized cellulose (3) was dispersed using sonication in DMF (20 mL) in a scintillation vial. To this, bCC, 2-hydroxyethyl disulfide (2.745 mL, 22.4 mmol, 1 equiv.), and titanium isopropoxide (67.5 µL, 0.224 mmol, 1 mol%) were added. The solids were filtered off and the resulting filtrate was cast into an aluminum mold (96 mm diameter) on a hot plate at 140 °C for two hours to remove the solvent. The film was then cured in a vacuum oven for 8 days at 120 °C. The film was then removed from the pan and films were cut for testing.

**FT-IR (solid, ATR):** 3410, 2965, 2918, 2882, 1741, 1651, 1463, 1397, 1235, 1110, 1046, 950, 786 cm⁻¹

| Cellulose content in sample | Amount of cellulose monomer added (mg) | mmol of cellulose monomer added | bCC amount added (g) | mmol of bCC added |
|-----------------------------|---------------------------------------|---------------------------------|----------------------|--------------------|
| 1 mol%                      | 139.9                                  | 0.224                           | 6.71                 | 22.2               |
| 2 mol%                      | 281.0                                  | 0.450                           | 6.63                 | 22.0               |
| 3 mol%                      | 419.5                                  | 0.672                           | 6.57                 | 21.7               |
| 4 mol%                      | 559.5                                  | 0.896                           | 6.50                 | 21.5               |
| 5 mol%                      | 702.5                                  | 1.125                           | 6.46                 | 21.4               |

**Scheme S10. Incorporation of cellulose monomer into polyurethane film (9)**

Pentaerythritol ethoxylate (15/4 EO/OH, 0.1 equiv.), polyethylene glycol ($M_n \sim 400$ g/mol, 0.8 equiv.), and functionalized acylated cellulose (3, 3 mol%) were dispersed in acetone (5 mL) via sonication for 1 hour at 35 °C. To this, hexamethylene diisocyanate (97 mol%) and dibutyltin dilaurate (2 mol%) were added and the resulting solution was cast into an aluminum mold at room temperature. The solution was allowed to stir in the aluminum mold at room temperature for 45 min. The stir bar was then removed and the solution was placed in an oven at 70 degrees for 1 d. To further cure the material, the film was placed in a vacuum oven at 120 degrees for 1 d, resulting in a yellow film. The film was removed from the aluminum pan and tensile bars and DMTA films were cut for testing.

**FT-IR (solid, ATR):** 3330, 2919, 2866, 1702, 1536, 1456, 1349, 1249, 1098, 945, 846, 778 cm⁻¹
Figure S1. FTIR spectrum of 2 showing functionalization of the cellulose by cyclic carbonate 1 through the appearance of the C=O stretch at 1732 cm$^{-1}$.

Figure S2. FTIR spectrum of 3 showing complete acylation of the hydroxyl groups on the cellulose through the loss of the O-H stretch at 3333 cm$^{-1}$. 
Figure S3. $^1$H NMR quantification of the functionalization of cellulose with the cyclic carbonate moiety using tribromobenzene as the internal standard. Integration of the resonance at 1.23 ppm for the methyl group on the cyclic carbonate and comparing that to the integration of the peaks at 3.67-4.24 ppm for the cellulose protons labeled gives the ratio of 3 sugar monomer rings per cyclic carbonate.

Figure S4. DSC experiment to show when control film is cured fully due to the $T_g$ being the same after 8 days of heating at 120 °C.
Figure S5. DSC experiment to show when 5 mol% film is cured fully due to the $T_g$ being the same after 8 days of heating at 120 °C.

Table S1. Glass-transition temperatures ($T_g$s) and gel fractions for the control and cellulose-incorporated films. Glass-transition temperatures were determined by both differential scanning calorimetry (DSC) and dynamic mechanical thermal analysis (DMTA).

| Cellulose Content in sample | $T_g$DSC (°C) | $T_g$DMTA (°C) | Gel Fraction (%) |
|---------------------------|---------------|----------------|-----------------|
| 0 mol%                    | 12            | 14             | 83.5            |
| 1 mol%                    | 12            | 16             | 82.5            |
| 2 mol%                    | 17            | 22             | 74.4            |
| 3 mol%                    | 17            | 13             | 84.0            |
| 4 mol%                    | 8             | 25             | 88.7            |
| 5 mol%                    | 17            | 17             | 80.4            |
Figure S6. DSC plots of cellulose incorporated films and control showing the glass-transition temperature for each film.

Figure S7. Tan(delta) data for the polycarbonate films showing that all of the values are above 1, which denotes that the films are homogenous.
Table S2. Tensile data for as synthesized polycarbonate films.

| Sample | Tensile Stress (MPa) | Strain at Break (%) | Modulus (MPa) | Toughness (J/m³) |
|--------|----------------------|---------------------|---------------|------------------|
| 0 mol% | 2.3 ± 0.5            | 77.9 ± 19.4         | 8 ± 1         | 103 ± 34         |
| 1 mol% | 4.9 ± 0.9            | 60.8 ± 6.4          | 111 ± 50      | 168 ± 43         |
| 2 mol% | 5.6 ± 2.2            | 55.8 ± 2.3          | 50 ± 13       | 189 ± 71         |
| 3 mol% | 7.1 ± 1.4            | 65.2 ± 5.5          | 181 ± 29      | 258 ± 56         |
| 4 mol% | 9.5 ± 1.2            | 63.2 ± 13.3         | 148 ± 85      | 270 ± 56         |
| 5 mol% | 10.2 ± 0.8           | 50.2 ± 6.9          | 424 ± 91      | 331 ± 42         |

Figure S8. Plot of molecular weight between crosslinks (Mx) versus mol% cellulose incorporated. The molecular weight between crosslinks was determined from the storage modulus at 100 °C of the DMTA plot.
Figure S9. Plot of toughness versus mol% cellulose incorporated. The plot shows that with increasing functionalized cellulose amounts in the film, the toughness increases.

Figure S10. Plot of average tensile stress versus mol% cellulose added. The tensile stress was determined by the maximum stress of the stress-strain curve from tensile testing.
Table S3. Relaxation times ($\tau^*$) from 160-180 °C for the polycarbonate films.

| Cellulose Content in Sample (mol%) | Relaxation Times at Given Temperature (s) |
|-----------------------------------|-------------------------------------------|
|                                  | 180 °C | 170 °C | 160 °C |
| 0                                 | 50     | 235    | 393    |
|                                   | 60     | 225    | 449    |
|                                   | 80     | 182    | 493    |
| 1                                 | 90     | 165    | 425    |
|                                   | 100    | 200    | 479    |
|                                   | 70     | 273    | 436    |
| 2                                 | 151    | 501    | 1395   |
|                                   | 121    | 491    | 1676   |
|                                   | 154    | 582    | 1368   |
| 3                                 | 163    | 464    | 1738   |
|                                   | 138    | 626    | 1300   |
|                                   | 159    | 491    | 1705   |
| 4                                 | 321    | 760    | 3954   |
|                                   | 332    | 845    | 3562   |
|                                   | 341    | 966    | 2936   |
| 5                                 | 354    | 1586   | 5574   |
|                                   | 342    | 2070   | 4336   |
|                                   | 398    | 2002   | 5515   |

Table S5. Activation energies for the cellulose polycarbonate films and the $R^2$ for the linear fit of the log ($\tau^*$) versus 1000/T plot to determine the activation energy.

| Sample | Activation Energies ($E_a$, kJ/mol) | $R^2$ of linear fit for $E_a$ |
|--------|-------------------------------------|------------------------------|
| 0 mol% | 69 ± 3                              | 0.976                        |
| 1 mol% | 58 ± 1                              | 0.995                        |
| 2 mol% | 83 ± 2                              | 0.994                        |
| 3 mol% | 83 ± 1                              | 0.998                        |
| 4 mol% | 84 ± 2                              | 0.990                        |
| 5 mol% | 92 ± 4                              | 0.974                        |
Figure S11. FT-IR of the 2 mol% as synthesized and reprocessed films.

Figure S12. DMTA plot of 2 mol% as synthesized and reprocessed showing a similar T_g after reprocessing at 140 °C for 8 hours followed by a curing for 2 days at 120 °C, resulting in an 75% recovery in crosslink density in the reprocessed sample compared to as synthesized.
Table S6. Tensile data for the reprocessed films.

| Sample                  | Tensile Stress (MPa) | Strain at Break (%) | Modulus (MPa) | Toughness (J/m$^3$) |
|-------------------------|----------------------|---------------------|---------------|---------------------|
| 2 mol% 1$^{\text{st}}$ Reprocessed | 5.5 ± 0.6             | 49.4 ± 0.3           | 13.5 ± 2.1    | 164 ± 21            |
| 2 mol% 2$^{\text{nd}}$ Reprocessed | 4.5 ± 0.2             | 64.5 ± 7.3           | 27 ± 1        | 200 ± 2             |
| 5 mol% 1$^{\text{st}}$ Reprocessed | 8.5 ± 1.3             | 54.0 ± 6.8           | 30.7 ± 7.1    | 269 ± 62            |

Figure S13. FT-IR of the polyurethane films showing the lack of the isocyanate stretch around 2200 cm$^{-1}$ denoting that the films are fully cured.
**Figure S14.** DMTA plots of the polyurethane films with and without the cellulose monomer. The crosslinking density increases 2.5x with 3 mol% of the cellulose monomer added.

**Table S7.** Tensile data for the polyurethane films.

| Sample   | Tensile Stress (MPa) | Strain at Break (%) | Modulus (MPa) | Toughness (J/m³) |
|----------|-----------------------|---------------------|---------------|-----------------|
| 0 mol%   | 0.7 ± 0.3             | 90 ± 1              | 2 ± 1         | 61 ± 11         |
| 3 mol%   | 1.3 ± 0.4             | 107 ± 3             | 2 ± 1         | 143 ± 2         |

**Table S8.** Activation energies for the cellulose polyurethane films and the R² for the linear fit of the log (τ*) versus 1000/T plot to determine the activation energy.

| Sample   | Activation Energies (Eₐ, kJ/mol) | R² of linear fit for Eₐ |
|----------|----------------------------------|------------------------|
| 0 mol%   | 68 ± 3                           | 0.976                  |
| 3 mol%   | 71 ± 1                           | 0.997                  |
Figure S15. Stress relaxation curves for the 0 mol% film for 160 °C to 180 °C from left to right respectively.

Figure S16. Stress relaxation curves for the 1 mol% film for 160 °C to 180 °C from left to right respectively.
Figure S17. Stress relaxation curves for the 2 mol% film for 160 °C to 180 °C from left to right respectively.

Figure S18. Stress relaxation curves for the 3 mol% film for 160 °C to 180 °C from left to right respectively.
Figure S19. Stress relaxation curves for the 4 mol% film for 160 °C to 180 °C from left to right respectively.

Figure S20. Stress relaxation curves for the 5 mol% film for 160 °C to 180 °C from left to right respectively.
Polycarbonate Films-Reprocessing Data

Figure S21. DMTA plot of 5 mol% as synthesized and reprocessed showing a decrease in $T_g$ after reprocessing at 140 °C for 8 hours followed by curing for 2 days at 120 °C, resulting in a 75% recovery in crosslink density in the reprocessed sample compared to as synthesized.

Table S9. DMTA data for the reprocessed samples.

| Sample               | $E'$ at 100 °C (MPa) | $M_x$ (g/mol) | $T_{g,onset}$ (°C) |
|----------------------|----------------------|---------------|-------------------|
| 2 mol% 1st Reprocessed | 5.25                 | 709           | 15                |
| 2 mol% 2nd Reprocessed | 4.62                 | 805           | 19                |
| 5 mol% 1st Reprocessed | 9.90                 | 376           | 22                |
**Figure S22.** Tensile data of 5 mol% sample before and after reprocessing showing an 83% recovery in tensile stress compared to as synthesized.

**Polyurethane Films-SRA Plots and Data**

**Figure S23.** Stress relaxation curves for the 0 mol% film for 140 °C to 120 °C from left to right respectively.
Figure S24. Stress relaxation curves for the 3 mol% film for 140 °C to 120 °C from left to right respectively.

Table S10. Relaxation times ($\tau^*$) from 120-140 °C for the control and functionalized cellulose-incorporated polyurethane films.

| Cellulose Content in Sample (mol%) | 120 °C  | 130 °C  | 140 °C  |
|-----------------------------------|---------|---------|---------|
| 0                                 | 1327    | 400     | 116     |
|                                   | 1057    | 542     | 104     |
|                                   | 912     | 419     | 98      |
| 3                                 | 1911    | 455     | 190     |
|                                   | 1744    | 472     | 144     |
|                                   | 1670    | 440     | 136     |
FT-IR Data

Figure S25. FTIR of the polycarbonate films once fully cured.

Figure S26. FTIR spectrum of S1.
Figure S27. FTIR spectrum of S2.

Figure S28. FTIR spectrum of S3.
Figure S29. FTIR spectrum of 1.

NMR Spectra

Figure S30. $^1$H NMR (500 MHz, $d_6$-DMSO) of 4.
**Figure S31.** $^{13}$C NMR (125 MHz, $d_6$-DMSO) of 4.

**Figure S32.** $^1$H NMR (500 MHz, $d_6$-DMSO) of S1.
Figure S33. $^{13}$C NMR (125 MHz, $d_6$-DMSO) of S1.

Figure S34. $^1$H NMR (500 MHz, $d_6$-DMSO) of S2.
Figure S35. $^{13}$C NMR (125 MHz, $d_6$-DMSO) of S2.

Figure S36. $^1$H NMR (500 MHz, $d_6$-DMSO) of S3.
**Figure S37.** $^{13}$C NMR (125 MHz, $d_6$-DMSO) of S3.

**References**

(1) Snyder, R. L.; Fortman, D. J.; De Hoe, G. X.; Hillmyer, M. A.; Dichtel, W. R. *Macromolecules* **2018**, *51*, 389-397.