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Incorporating Functionalized Cellulose to Increase the Toughness of Covalent Adaptable Networks

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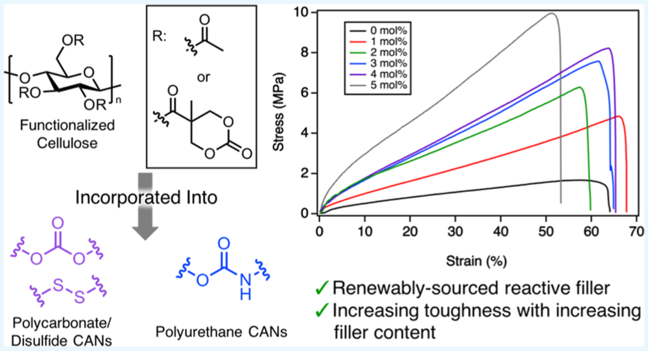

ABSTRACT: Covalent adaptable networks (CANs) are cross-linked polymers that have mechanical properties similar to thermosets at operating conditions yet can be reprocessed by cross-link exchange reactions that are activated by a stimulus. Although CAN exchange dynamics have been studied for many polymer compositions, the tensile properties of these demonstration systems are often inferior compared to those of commercial thermosets. In this study, we explore toughening CANs capable of forming covalent bonds with a reactive filler to characterize the trade-off between improved toughness and longer reprocessing times. Polycarbonate (PC) and polyurethane (PU) CANs were toughened by incorporating cellulose modified with cyclic carbonate groups as a reactive filler with loadings from 1.3 to 6.6 wt %. The addition of 6.6 wt % of the cellulose derivative resulted in a 3.2-fold increase in average toughness for the PC CANs, yet it only increased the characteristic relaxation time of stress relaxation (τ^*) via disulfide exchange at 180 °C from 63 to 365 s. The cellulose-containing samples also showed >80% recovery in crosslinking density and mechanical properties after reprocessing. The addition of 3.2 wt % of the functionalized cellulose into a polyethylene glycol-based PU CAN led to a 2.3-fold increase in toughness while increasing τ^* at 140 °C from 106 to 157 s. These findings demonstrate the promise of functionalized cellulose as an inexpensive, renewable, and sustainable filler that toughens CANs containing hydroxyl groups.

KEYWORDS: *cellulose, composites, covalent adaptable networks, polycarbonates, polyurethanes*

INTRODUCTION

Covalent adaptable networks (CANs) have attracted recent interest because they exhibit similar mechanical properties to thermosets at ambient temperatures yet are reprocessable under an external stimulus via dynamic cross-link exchange reactions.[1] Despite their robust mechanical properties, including high mechanical strength and thermal stability, thermoset polymers are not reprocessable due to their permanent chemical crosslinks, which preclude recycling and repair. The reprocessable nature of CANs might ultimately reduce the environmental impact of durable polymer networks. A variety of chemistries have proven useful in CANs,[2−4] many of which rely on free hydroxyl groups including transesterification,[5] transcarbamoylation,[6,7] transcarbonation,[8] silyl ether exchange,[9] and oxime-promoted transcarbamoylation[10] reactions. Unfortunately, many CANs used to demonstrate new exchange chemistries either exhibit inferior mechanical properties compared to commercial thermoset composites, or in many cases, the mechanical properties of these materials are not investigated. Commercial thermosets are often used as composites, which impart superior mechanical properties through the inclusion of fillers. In contrast, fillers have only been recently incorporated into CANs and are not well explored in these dynamic polymer networks.[11] Yang and coworkers enhanced the mechanical properties of polyester vitrimers through the addition of graphene as a nonreactive filler.[12] The incorporation of 1 wt % graphene into these materials increased the ultimate tensile stress from 12 to 23 MPa. Fillers have also been shown to influence dynamic exchange in CANs. The incorporation of amine- and hydroxyl-functionalized silica nanoparticles into a polyhydroxyurethane network exhibited a decreased activation energy compared to that of polyhydroxyurethane networks containing unfunctionalized silica nanoparticles or no filler.[13] Nevertheless, there have been few investigations into how reactive fillers influence the mechanical properties and reprocessing of CANs. Here, we use functionalized cellulose as a renewable and reactive filler to improve the mechanical properties of polycarbonate (PC) and

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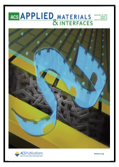


polyurethane (PU) CANs and evaluate their effect on the stress relaxation kinetics.

Cellulose has previously been incorporated into polymer matrices to enhance their mechanical properties[14−17] and is a greener and less expensive alternative filler. Crystalline forms of cellulose, such as cellulose nanocrystals, have been incorporated as nonreactive fillers. For example, Nakagaito and coworkers integrated cellulose nanofibrils into phenolic resins, which had higher strength/modulus ratios than other composites.[18,19] However, aggregation of cellulose, even at low loadings, precluded further enhancement.[20] One of the challenges of incorporating cellulose into polymer networks is its poor solubility, which is typically improved by functionalizing some or all of its hydroxyl groups.[21−27] Cellulose−CAN composites have only recently been explored,[28] and cellulose has not been covalently incorporated into a dynamic cross-linked polymer network.

Previously, we investigated the synthesis and properties of a PC vitrimer network that relaxed stress through a transcarbonation pathway catalyzed by a Ti(IV) metal complex.[8] We also determined that disulfide exchange decreased the characteristic relaxation time (τ^*) and activation energy of a polyhydroxyurethane CAN.[29] Here, PC vitrimers were modified with a disulfide comonomer to enable rapid exchange reactions and stress relaxation. Furthermore, we functionalized cellulose with reactive cyclic carbonate moieties to enable its incorporation as a reactive filler at relatively high loadings (1.3−6.6 wt %) into PC- and PU-based CANs. The cellulose-containing composites exhibited increased toughness and crosslinking density but with only modest slowing of the exchange dynamics for stress relaxation of the CANs. The cellulose prepolymer represents a green and renewable alternative to polymer additives that can be homogenously incorporated into a CAN to improve its mechanical properties while retaining its dynamic behavior.

■ EXPERIMENTAL SECTION

Functionalization of Cellulose with a Cyclic Carbonate. 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 (5×) and then crushed using a mortar and pestle and washed another (3×) 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, 2 (2.04 g).

Acylation of Functionalized Cellulose. 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 (2×) and vacuum filtered. The solution was then washed with saturated sodium bicarbonate and then washed with water (2×). The resulting solid was then dried in the vacuum oven at 120 °C overnight to give acylated functionalized cellulose (**3**) as an orange solid (3.0 g yield).

Synthesis of Unfilled Cellulose PC Film. To a scintillation vial, a solution of the bis(six-membered cyclic carbonate) (bCC, **4**, 6.8 g, 22.4 mmol, 1 equiv) in dimethylformamide (DMF) (20 mL) was added. To this solution, 2-hydroxyethyl disulfide (2.745 mL, 22.4 mmol, 1 equiv) was 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 was subsequently filtered. The resulting filtrate is poured into an aluminum mold (96 mm diameter) on the hot plate at 140 °C for 2 h to remove the solvent. After 2 hours, the film was placed in a vacuum oven at 120 °C for 8 days. The film was then removed from the pan, and films were cut for testing.

Incorporation of Functionalized-Cellulose Prepolymer into PC Films. Acylated functionalized cellulose (**3**) was dispersed using sonication in DMF (20 mL) in a scintillation vial (Table 1). 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 2 h 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.

Table 1. Amounts of Cellulose Prepolymer and bCC Added to PC CANs

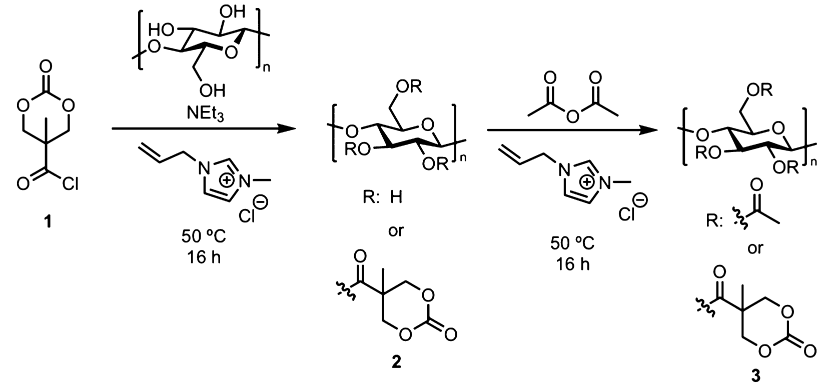
cellulose content in sample (wt %)	amount of cellulose prepolymer added (mg)	mmol of cellulose prepolymer added	bCC amount added (g)	mmol of bCC added
1.3	139.9	0.224	6.71	22.2
2.7	281.0	0.450	6.63	22.0
4.0	419.5	0.672	6.57	21.7
5.3	559.5	0.896	6.50	21.5
6.6	702.5	1.125	6.46	21.4

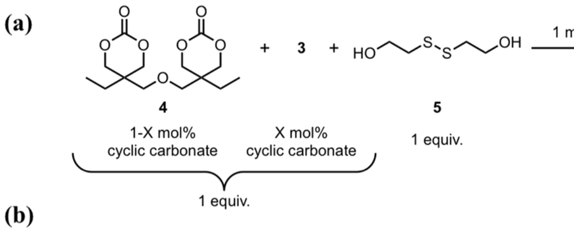
Incorporation of Cellulose Prepolymer into PU Film. Pentaerythritol ethoxylate (15/4 EO/OH, 0.1 equiv), polyethylene glycol (M_n ~ 400 g/mol, 0.8 equiv), and functionalized acylated cellulose (**3**, 3 mol %) were dispersed in acetone (5 mL) via sonication for 1 h at 35 °C. To this, hexamethylene diisocyanate (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 °C for 1 d. To further cure the material, the film was placed in a vacuum oven at 120 °C for 1 d, resulting in a yellow film. The film was removed from the aluminum pan and tensile bars, and dynamic mechanical thermal analysis (DMTA) films were cut for testing.

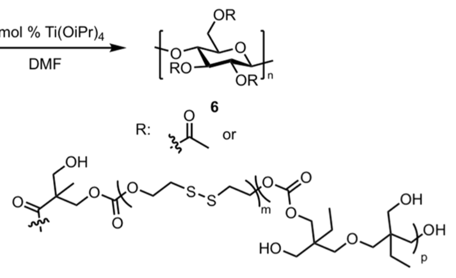
■ RESULTS AND DISCUSSION

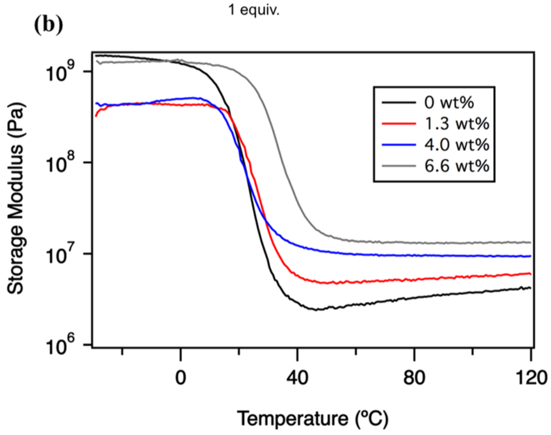
To incorporate cellulose into CANs homogenously at reasonable loadings, we first developed a functionalization strategy to ensure its dispersibility while also incorporating reactive groups capable of participating in the formation of PC and PU networks. Microcrystalline cellulose was functionalized with a six-membered cyclic carbonate derived from bis(hydroxymethyl)propionic acid (Scheme 1).[30] Cellulose was dissolved in an ionic liquid, 1-allyl-3-methylimidazolium chloride, at 50 °C. The presence of the cyclic carbonate on the modified cellulose was confirmed by the presence of a carbonyl stretch at 1732 cm^{-1} in the Fourier transform infrared (FTIR) spectrum (Figure S1); however, functionalized cellulose **2** displayed poor dispersibility in common organic solvents and was difficult to characterize in solution. Acetylation of the remaining hydroxyl groups provided cellulose derivative **3**, which was dispersible in polar organic solvents such as DMF and dimethyl sulfoxide (DMSO). The complete acylation of the cellulose hydroxyls was confirmed by

Scheme 1. Synthesis of Cellulose Functionalized with Cyclic Carbonates (2) and Subsequent Acetylation of Its Remaining Alcohols (3)









(c)

Wt % Cellulose Incorporated	E' at 100 °C (MPa)	M_X (g/mol)
0	3.73	992
1.3	5.70	653
2.7	6.97	534
4.0	9.44	394
5.3	11.3	329
6.6	13.3	280

Figure 1. (a) Synthesis of PC films containing a disulfide linkage and 3. (b) Storage modulus (E') obtained by DMTA of PC films at various loading levels of cellulose derivative 3. (c) E' and the corresponding molecular weight between crosslinks (M_x) as a function of the cellulose content of the films. M_x was calculated based on the E' at 100 °C.

the loss of the −OH stretch at 3333 cm^{-1} in the FTIR spectrum (Figure S2). The resulting cellulose powder was found to be ~3−5 μm in size by scanning electron microscopy (SEM) (Figure S3). **3** formed stable dispersions in DMSO and DMF to concentrations around 50 mg/mL. The structure of product **3** was characterized by ^{1}H NMR spectroscopy, and the average structure for **3** was determined to have one cyclic carbonate moiety per three glucose subunits, as determined by comparing the combined integration of four cellulose proton signals (3.67−4.24 ppm) to the methyl resonances of the cyclic carbonate (1.23 ppm, Figure S4). The cellulose proton resonances were found at similar chemical shifts as those reported for cellulose acetate in DMSO.[31]

A disulfide-linked PC network was synthesized by sonicating varying amounts of **3** (0−0.05 molar equivalents of carbonate in increments of 0.01 equiv, 0−6.6 wt % filler) and **4** (0.95−1 molar equivalents of carbonate) in DMF until the solution appeared homogenous and then adding 1 equiv of **5** and 1 mol % of Ti(OiPr)$_4$ as a catalyst. The solution was cast into an aluminum mold, and the solvent was removed by heating on a hot plate at 140 °C for 2 h before being placed in a vacuum oven at 120 °C for 8 days. Curing was monitored by differential scanning calorimetry (DSC) analysis of the glass-transition temperature (T_g) of the films after 6, 7, and 8 days of heating at 120 °C (Figures S5 and S6). The films were determined to be fully cured once the T_g stopped increasing. T_g was determined by both DSC and DMTA to be around 25 °C for all samples (Table S1 and Figure S7). The T_g values do not show a clear trend with increasing filler content due to the decrease in the amount of bCC monomer in the networks with increasing cellulose prepolymer. Films containing **3** exhibited sharp tan(δ) responses around 1 in magnitude, suggesting that the cellulose-containing films were homogenous (Figure S8). SEM images of the cross-section of both the unfilled and 6.6 wt % films also showed that the films were homogenous and that the filler did not aggregate during the film synthesis (Figures S9 and S10). The crosslinking density was also determined via DMTA analysis of the storage modulus (E') at 100 °C. With the addition of 6.6 wt % **3**, the storage modulus of the networks increased from 3.23 to 13.3 MPa, a 3.6-fold increase compared to the unfilled film (Figure 1). Furthermore, with the increasing cellulose content the molecular weight between crosslinks (M_x) decreased from 992 g/mol (0 wt %) to 653 g/mol (1.3 wt %), 534 g/mol (2.7 wt %), 394 g/mol (4.0 wt %), 329 g/mol (5.3 wt %), and 280 g/mol (6.6 wt %) (Figure S11). These dynamic thermomechanical responses demonstrate that **3** acts as a covalent crosslinking agent in these networks.

Films with higher cellulose loadings showed increased average toughness via tensile testing. These tests showed that the properties were enhanced continuously from 1.3 to 6.6 wt % of added **3**. All tensile tests were performed at room temperature which was above the T_g for these materials (Figures 2 and S12). These materials all demonstrated elastomeric properties with strains-at-break above 50%. The ultimate tensile stresses of these networks increased with increasing functionalized-cellulose loadings from 2.3 ± 0.5 MPa for unfilled films to 7.1 ± 1.4 MPa for 4.0 wt % and 10.2 ± 0.8 MPa for 6.6 wt % loading of **3**, correlating well with their increased crosslinking densities. The toughness of each network was determined by integrating its stress−strain curve for three samples at each cellulose-loading amount. The toughness of the materials increased from 103 ± 34 J/m^3 for 0 wt %, to 168 ± 43 J/m^3 for 1.3 wt %, 189 ± 71 J/m^3 for 2.7 wt %, 258 ± 56 J/m^3 for 4.0 wt %, 270 ± 56 J/m^3 for 5.3 wt %, and 331 ± 42 J/m^3 for 6.6 wt % (Table S2). Therefore, the toughness and tensile stress increased linearly for 1.3−6.6 wt % of **3** (Figures S13 and S14). When 6.6 wt % of the filler was added to the PC network, a 4.4-fold increase in tensile stress, a 3.2-fold increase in toughness, and no significant decrease in the strain at break were observed. Since there are no crystalline aggregates found in the SEM images of the filled materials, this increase in toughness of the materials is due to the covalent crosslinking through the cellulose filler. CANs with cellulose loadings of 10.4 wt % had inferior tensile properties than those with 6.6 wt % loading (Figure S15), which suggests that there is a cellulose content limit on the material's mechanical enhancement. At filler content loadings higher than 10.4 wt %, the filler is difficult to disperse in a reasonable amount of organic solvent prior to solvent casting. Overall, loading a cellulose-based reactive filler into these dynamic networks between 0 and 6.6 wt % content, which acts as a crosslinking agent, enhanced the tensile properties of the CAN.

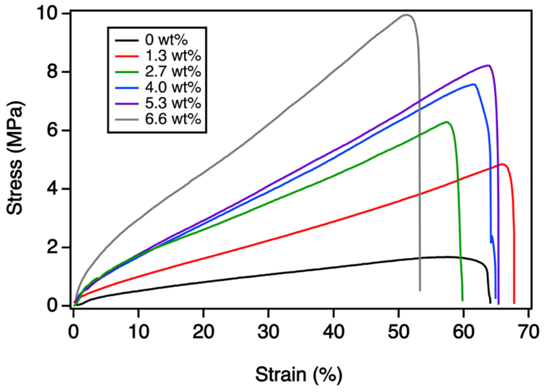


Figure 2. Stress−strain curves for the cellulose-incorporated and unfilled PC films. The tensile stress increases with the cellulose loading.

To demonstrate that the property enhancement by this functionalized cellulose filler, DMTA and tensile testing of a sample containing 4.0 wt % of cellulose acetate, a nonreactive analogue to the reactive cellulose filler, showed that the enhanced crosslinking density and increase in toughness in the reactive filler-containing films was due to the covalent bonds formed through the cyclic carbonate on the cellulose (Figures S16 and S17). The addition of 4.0 wt % of cellulose acetate does not increase the crosslinking density in the material compared to the unfilled PC CAN and is lower than the M_x of 4.0 wt % reactive filler sample. The mechanical properties of the sample with the nonreactive filler showed that the toughness of the material was not enhanced when compared to the unfilled network and was also inferior to the material containing 4.0 wt % of the reactive functionalized-cellulose filler. The incorporation of cellulose acetate instead of the cyclic carbonate-functionalized cellulose showed that the mechanical enhancement was due to the enhanced covalent crosslinking in the material.

Having established that the cellulose prepolymer increases the tensile properties of the networks, its impact on CAN reprocessing was also examined via stress relaxation analysis (SRA). SRA was performed at various temperatures by applying a 5% strain on the sample while measuring the resulting stress as a function of time. Unfilled films relaxed stress with a characteristic relaxation time (τ^*, time at which stress equals $1/e$ of its initial value) of 63 s at 180 °C. The film containing 6.6 wt % cellulose showed a modest increase in τ^* to 365 s at the same temperature (Figure 3a). The activation energies for the six samples were determined by plotting $\log(\tau^*)$ versus $1000/T$ (Table S3 and Figure 3b). As M_x increases in this system due to increasing cellulose incorporation, the activation energy increases stepwise from below 70 kJ/mol for the 0 and 1.3 wt % to 92 kJ/mol for the 6.6 wt % films (Table S4). Even at the upper end of this range (6.6 wt %), the τ^* at 180 °C of the composite is lower than that of

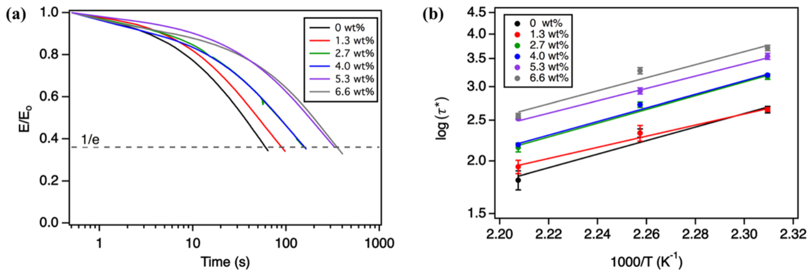


Figure 3. (a) Stress relaxation plots for all films at 180 °C showing an increase in τ^* ($1/e$, gray dashed line) with increasing cellulose incorporation. (b) Activation energy analysis for all films derived from stress relaxation analysis (SRA) at 180, 170, and 160 °C.

previous PC polymer networks.[8] The modest increase in τ^* with increasing cellulose content is offset by the 3-fold increase in toughness.

These networks were reprocessed by compression molding followed by curing, which recovered the majority of their mechanical toughness. Broken films were heated to 140 °C for 8 h under 8−10 MPa of pressure, once again yielding homogenous films (Figure 4a). In order to further recover the crosslink density during the reprocessing, the reprocessed film was further cured at 120 °C for 2 days in the vacuum oven. The reprocessed materials retained more than 80% of their tensile stress and toughness when compared to the as-synthesized materials for both the first reprocessed and second reprocessing cycles (Figure 4b). The change in plot shape, that is, presence of a yield point and higher modulus in the reprocessed films, can be attributed to the change in T_g compared to the as-synthesized (Figure S18). Cross-sectional SEM images show possible aggregation in the center of the sample after compression molding of the 6.6 wt % sample. This possible aggregation could result in the change in plot shape in the tensile plots (Figure S19). The chemical integrity of the reprocessed films was determined by FTIR spectroscopy. No change in the spectra were observed between the as-synthesized and reprocessed samples (Figure S20). DMTA analysis showed that 75% of the crosslinking density was recovered using this reprocessing procedure (Figure S16). This recovery is in contrast to the unfilled sample, which only saw a recovery of 33% of the crosslinking density by this reprocessing procedure (Figure S21). The characterization of the reprocessed samples showed that the reprocessing procedure yielded similar material quality as the as-synthesized samples (Table S5).

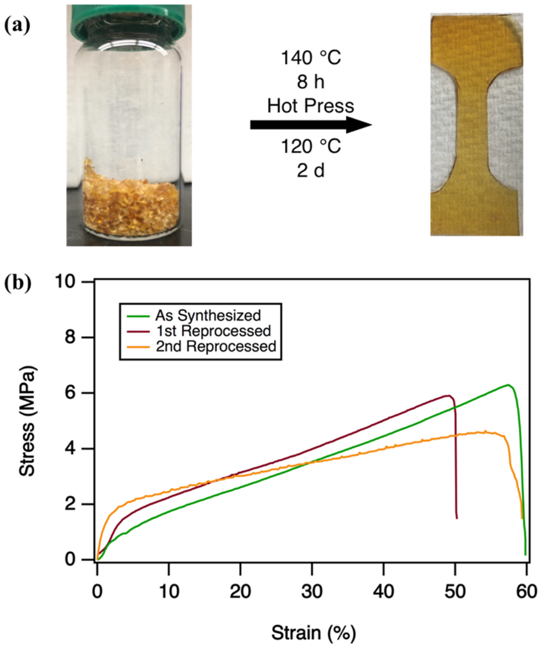


Figure 4. (a) Reprocessing scheme for the PC CANs. (b) Tensile data for the reprocessing of 2.7 wt % cellulose films showing an 86% recovery of average toughness of the material compared to the as-synthesized after the first reprocessing cycle and a 105% recovery of average toughness after the second reprocessing cycle.

We next evaluated the generality of using **3** as a reactive filler in CANs that relax stress via urethane exchange. PUs have previously been shown to have rapid stress relaxation in the presence of tin(IV) catalysts,[32,33] which was proposed to occur through the partial reversion of carbamates to isocyanates and alcohols. We designed a network comprised of hexamethylene diisocyanate, a short-chain PEG (M_n = 400 g/mol), along with a 4-arm polyethylene glycol (PEG) star (M_n = 800 g/mol) macromonomer and **3** as crosslinkers. In the absence of cellulose, the material is a PEG-based network crosslinked with urethane linkages. However, when **3** is incorporated, free hydroxyl groups can ring-open the cyclic carbonate, yielding a crosslinked network by both urethanes and a small number of carbonates. **3** (3.4 wt %, 0.03 molar equivalents of carbonyl) was dispersed in acetone along with **8** and **7**, followed by the addition of the aliphatic diisocyanate and dibutyltin dilaurate as a urethane exchange catalyst. The resulting solution was cast at room temperature into an aluminum mold and was cured at 70 °C for 24 h and at 120 °C for 24 h under reduced pressure to ensure removal of the solvent. The extent of curing of the materials was determined by FTIR through the absence of the isocyanate stretch around 2200 cm^{-1} (Figure S22).

After curing, the crosslinking density was determined, via DMTA, to be 2.5 times higher with 3.2 wt % cellulose incorporated (Figure S23), which is consistent with the PC/disulfide system. The tensile stress and toughness also were shown to increase from 0.7 MPa and 62 J/m^3 without cellulose incorporated, respectively, to 1.3 MPa and 143 J/m^3 with 3.2 wt % of **3** incorporated (Figure 5c and Table S6). The activation energy for urethane exchange, however, only slightly increased from 68 kJ/mol for the 0 wt % films to 71 kJ/mol, which was within error, for the 3.2 wt % materials (Figure 5b and Table S7), and the τ^* at 140 °C only increased from 106 to 157 s. The PU CANs containing the filler also were reprocessable after being compression molded at 160 °C for 1 h and showed a recovery in the crosslink density when compared to the 3.2 wt % as-synthesized PU CAN (Figure S24). The effect on the stress relaxation efficiency by the filler incorporation in the PU was lower than in the PC system. This reduced effect by the filler is due to the resulting hydroxyl group from the ring-opening of the cyclic carbonate having the ability to participate in urethane exchange, which is the prevalent mechanism for stress relaxation in the PU system. This makes the filler more dynamic than in the PC system because the cellulose filler is not able to participate in disulfide exchange, making it act as a more static crosslinker and hampering the stress relaxation to a larger degree than in the PU CAN. Regardless, these results demonstrate that the functionalized-cellulose prepolymer can be used to toughen multiple CANs while preserving their ability to relax stress. The incorporation of 3.2 wt % cellulose into the PU/PC network (**9**) provided a similar effect on the mechanical properties compared to **6**.

■ CONCLUSIONS

This study describes a new strategy to functionalize cellulose with cyclic carbonate groups, so that it may be incorporated into CANs at useful loadings (1.3−6.6 wt % or 0.01−0.05 molar equivalents). When 0.01 molar equivalent of the bCC monomer is replaced with functionalized cellulose **3**, the molecular weight between crosslinks decreases 3.6-fold compared to that in control films. The toughness of the composites increased linearly with increasing cellulose content.

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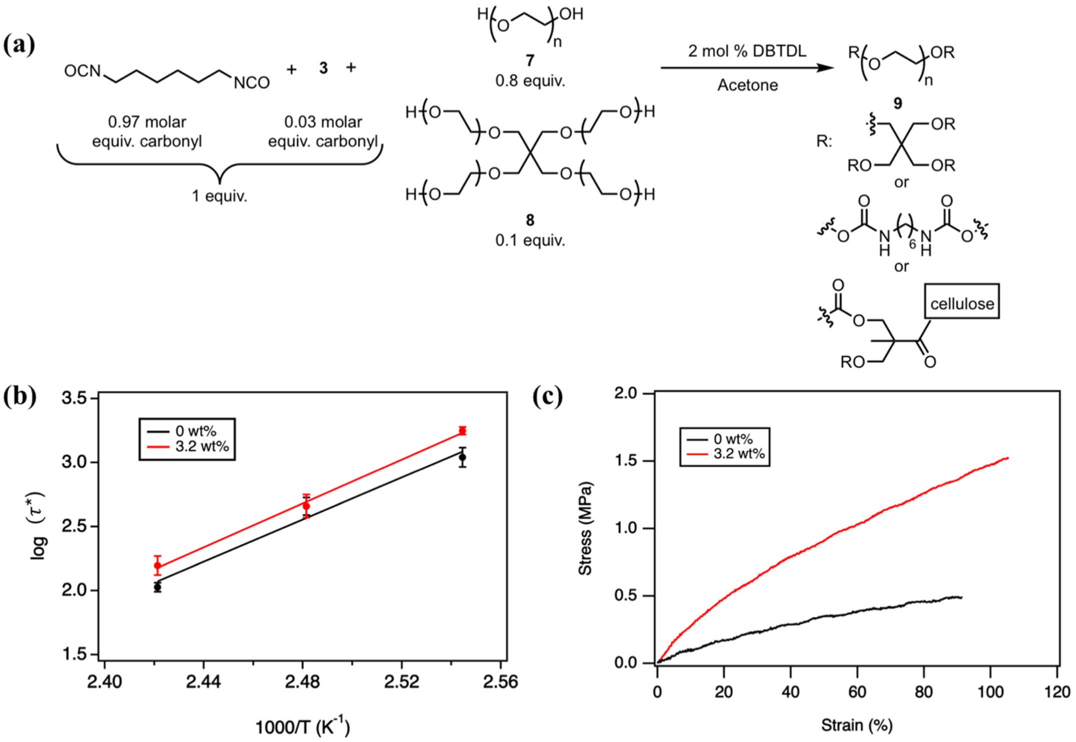

Figure 5. (a) Synthetic scheme of PEG-based PU CAN containing 3.2 wt % of **3**. (b) Plot of log(τ*) versus 1000/T to determine the activation energy for the urethane exchange for films with and without 3.2 wt % cellulose. (c) Stress versus strain plot comparing the PU films with or without cellulose incorporated.

The dynamic behavior of this CAN was retained in the cellulose-containing composites, with the τ* at 180 °C increasing from 63 to 365 s. PC composites were reprocessed and retained greater than 80% of their tensile stress and toughness relative to the as-synthesized materials. The same cellulose monomer was also incorporated into a PU CAN, which likewise increased its toughness while retaining reprocessability. These results demonstrate a general means to improve the mechanical properties of CANs using an inexpensive and sustainable reactive filler.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.0c09215.

Materials and instrumentation, filler synthesis schemes, FTIR spectra, DMTA plots, SRA, SEM images, stress-strain plots, and NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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