

Green Synthesis of Thermoplastic Composites from a Terpenoid-Cellulose Ester

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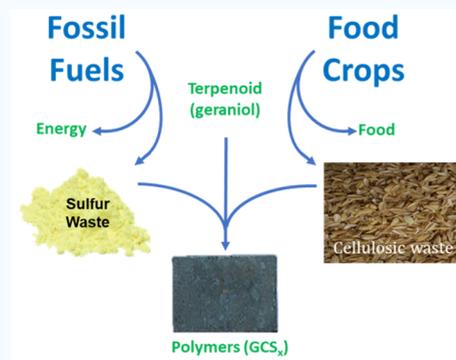
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ABSTRACT: Herein we report a green route to thermoplastics from cellulose, the terpenoid geraniol, and fossil fuel byproduct sulfur with an overall atom economy of 90% over three steps. The only stoichiometric byproducts are NaCl and water. The process involves (1) oxidation of cellulose, (2) amino acid-catalyzed esterification, and (3) cross-linking of olefins with sulfur to give GCS_x ($x = \text{wt } \% \text{ sulfur, varied from } 80\text{--}90\%$). The thermoplastics exhibit flexural strengths and moduli competitive with some commercial materials and are recyclable without loss of strength. The method delineated herein should be applicable to many combinations of saccharide and terpenoid precursors to facilitate similarly green routes to a range of sustainably sourced materials.

KEYWORDS: green chemistry, terpenoid, cellulose, biopolymer, geraniol, biomass



The search for polymers that can be made by applying the principles of green chemistry¹ is central to modern polymer science. Some of the most attractive strategies in this regard employ plant-derived precursors like cellulose,^{2–4} lignin,^{5–7} triglycerides/fatty acids,^{8–11} or terpenoids.^{12–14} One drawback facing efforts in this vein is that synthetic manipulation of sustainably sourced precursors to convert them to appropriate monomers can require multistep processes employing nongreen solvents, driving up cost and lowering the atom economy.

Cellulose, as the most prevalent biopolymer in nature and the primary constituent of agricultural waste biomass, is an attractive target for polymer synthesis. Unfortunately, cellulose itself cannot be thermally processed, and its derivatization is often challenging.¹⁵ Herein we report a green route to thermoplastics from cellulose, a terpenoid alcohol, and sulfur (Figure 1). The only stoichiometric side products of the process are environmentally innocuous NaCl and H₂O, and the process has very high atom economy. The first step was partial oxidation of cellulose by a green variation of classic aqueous NaOCl oxidation of primary alcohols¹⁶ to give oxidized cellulose OC (Scheme 1). Infrared spectroscopy confirmed successful oxidation, while potentiometric titration of OC revealed a degree of substitution (DS, # per anhydroglucose unit) of 0.28 (Figures S1–S3, Equation S1).¹⁷ Oxidation had an atom economy of 91%, and the only stoichiometric byproduct was NaCl.

The carboxylic acid moieties in OC can be esterified with any number of alcohols. In the current case, geraniol was selected as the alcohol because geraniol is a naturally occurring

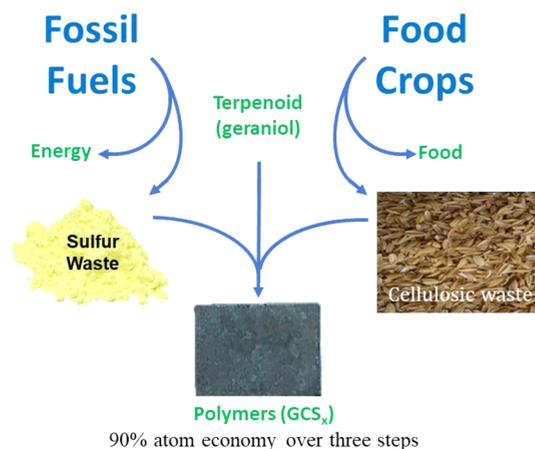
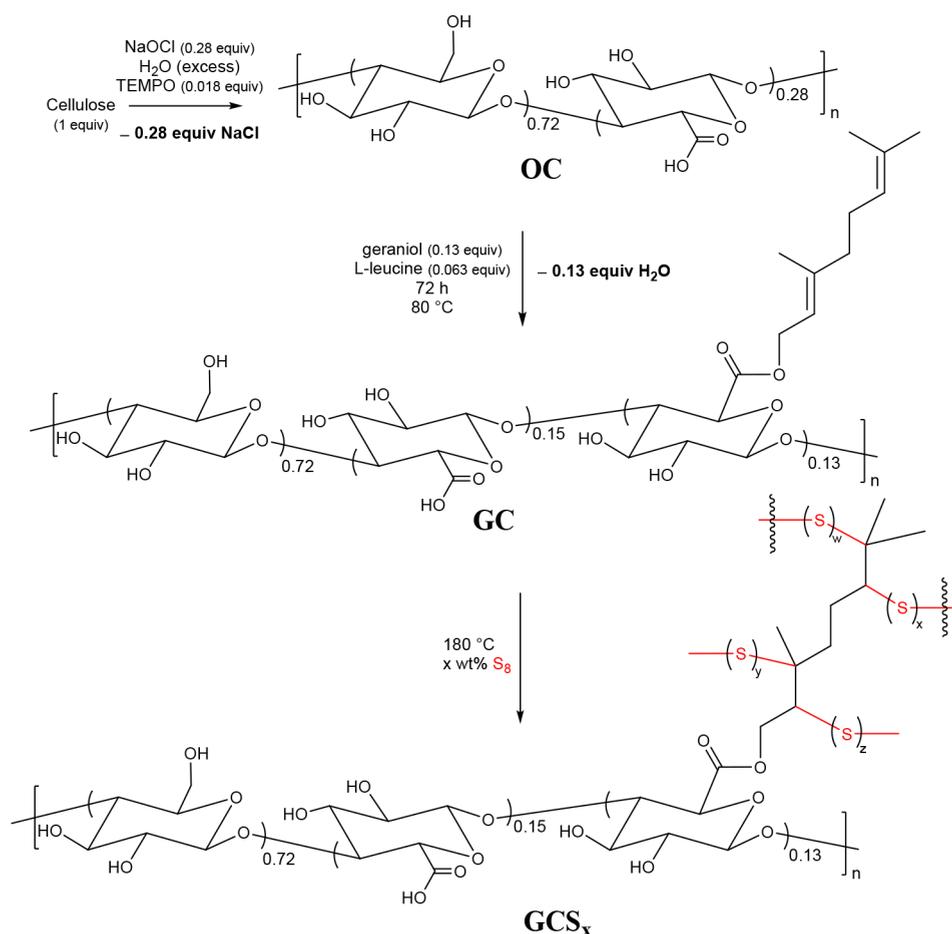


Figure 1. Schematic representation of the preparation of GCS_x and its relation to food and energy production.

monoterpenoid: it is the primary constituent of rose oil and can be efficiently extracted from a variety of other grasses and flowers. Esterification of OC to give GC employed the amino acid leucine as a catalyst and geraniol as the solvent (Scheme

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Scheme 1. Preparation of GCS_x 

1).¹⁸ Water is the only stoichiometric byproduct of esterification by this protocol. Because geraniol was used as the solvent for esterification, it was present in a large excess that was easily, quantitatively recovered by filtration. Recovered geraniol was found to be $\geq 98\%$ pure by gas chromatographic analysis and so could be used in subsequent esterification reactions. Esterification was quantified by iodometric titration of GC,¹⁹ which revealed that esterification at approximately half of the carboxylic acid sites had taken place such that ester DS = 0.128 ± 0.010 in GC. The atom economy of esterification was thus 99%. As anticipated, modifications of microcrystalline cellulose led to decreased decomposition temperatures ($T_d = 305, 226,$ and 213 °C for microcrystalline cellulose, OC, and GC, respectively) as well as slight changes in glass transition temperatures ($T_g = 87, 79,$ and 74 °C for microcrystalline cellulose, OC, and GC, respectively) while the crystallinity remained unchanged (Figures S4–S6).

Olefinic ester GC was then cross-linked by inverse vulcanization with sulfur at 180 °C to yield GC-sulfur composites (GCS_x , where $x = \text{wt } \%$ sulfur, varied from 80–90%). Although not observed in the current case (as deduced by elemental analysis), heating elemental sulfur with organics can result in the formation of toxic H_2S gas, so caution should be exercised in such manipulations. Inverse vulcanization^{20,21} is a 100% atom-economical process in which olefins react with thermally generated sulfur radicals analogous to the reaction of sulfur radicals and olefins in the thiol–ene click reaction. Like

thiol–ene click reactions, inverse vulcanization is quite functional group tolerant, so a wide range of sustainable olefins can be polymerized by inverse vulcanization with many promising applications.^{14,22–25} Elemental sulfur is also an underutilized byproduct of fossil fuel refining prior to combustion (Figure 1). The three-step process to GCS_x employing geraniol, cellulose, and sulfur showed an impressive 90% atom economy.

GCS_x composites were remeltable and range in color from gray to black solids (Figure 2) that can be remelted and reshaped over many cycles by simply melting them and pouring the liquid into molds at temperatures above 130 °C.

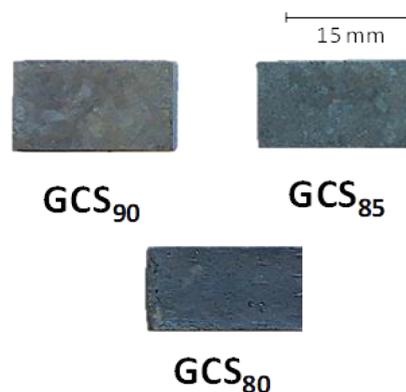


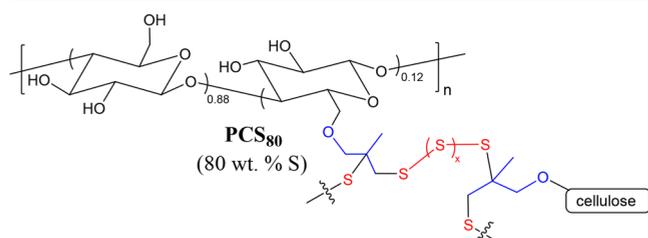
Figure 2. Photographs of GCS_x samples.

Table 1. Select Physical Properties of GCS_x, PCS₈₀, and Some Commercial Materials

material	sulfur rank	E' (MPa) ^a	E'' (MPa) ^b	$\tan \delta^b$	T_g^c	flexural strength/modulus (MPa)	modulus of resilience (kPa)
GCS ₉₀	22	1520	76, 52	0.05, 0.04	-37, 20	>4.9 ^d /950	0.1
GCS ₈₅	13	1564	80, 55	0.05, 0.04	-32, 27	>5.2 ^d /1050	0.3
GCS ₈₀	8	ND	ND	ND	ND	ND	ND
PCS ₈₀	22	860	34, 54	0.05, ND ^h	6, > 80	>3.8 ^d /520	1.8
cement ^e	— ^f	— ^g	— ^g	0.05–0.06	— ^g	3.7/580	0.6
cellulose acetate butyrate ⁱ	— ^f	1100 ^j	50 ^j	ND	80 ^{j,k}	41/1370 ^l	ND
polypropylene-glass fiber composite ⁿ	— ^f	— ^f	— ^f	— ^f	— ^f	3.5/1350	— ^f

^aStorage modulus value at -40 °C when each material is below T_g . ^bValue at T_g , except for Portland cement, which did not exhibit a T_g in the range -100 to 100 °C. ^cAs measured by the maximum of the $\tan \delta$ curve. ^dSample could not be measured beyond this level due to instrumental limitations. ^eData refer to Portland cement that was sifted, mixed with water (1:2, water/cement), and cured very gradually before being dried in an oven. ^fData not available/applicable. ^gMaterial exhibited no apparent maximum value in the range -100 to 100 °C. ^hValue was outside of measured range. ⁱRef 28. ^jCellulose acetate butyrate was plasticized with tributyl citrate, and values were estimated from the provided curves for a 2 mm thick sample. ^kEstimated from loss modulus plot. ^lAverage reported value. ⁿAzdel SuperLite SL550600–100.

Composites prepared by inverse vulcanization are generally composed of a highly cross-linked network in which some free sulfur is trapped. Free sulfur, meaning sulfur that is not covalently attached to the organic network as cross-links, is quite soluble in CS₂, whereas the cross-linked cellulose–sulfur network is completely insoluble in CS₂ (confirmed by elemental microanalysis). Extractable sulfur was thus readily quantified by recursive washing of GCS_x with CS₂, and elemental analysis of the CS₂-soluble fraction revealed that sulfur was indeed the only element present. Elemental analysis GCS_x paired with quantitation of the relative amount of soluble and insoluble fractions confirmed retention of covalently bound sulfur in the network solid (for raw data and calculation information, see Figure S14, Table S2, and Equation S2). Considering that the alkene functionalities had been completely consumed based on IR spectroscopic data and the quantity of covalently bound sulfur, the sulfur rank (average number of S atoms in each cross-link between cellulose chains) was calculated to be 8–22 sulfur atoms (Table 1). These values are larger than the average cross-link length of 4–5 sulfur atoms reported for highly cross-linked composites of sulfur with polystyrene²⁶ or xylenol²⁷ derivatives but on par with those reported for cellulose derivative PCS₈₀ (22, structure provided in Figure 3),⁴ allyl lignin (48–103

Figure 3. Structure of PCS₈₀.

sulfur atoms),⁷ and chlorolignin (12–31 sulfur atoms).⁶ Regardless of the olefin-bearing comonomer used in inverse vulcanization, the average cross-link length correlates expectedly with the ratio of sulfur to cross-linkable olefin sites in the monomer feed.

Although not observable by IR spectroscopy (Figure S5), Raman spectroscopy provided additional evidence that sulfur in GCS_x exists primarily as small rings or chains, as the peak characteristic of polymeric sulfur domains was not observed

(Figure S6). Integration of the orthorhombic sulfur melt peak from differential scanning calorimetry (DSC) measurements of GCS_x likewise confirmed that both free and covalently bound sulfur are present in GCS_x (Figure S9). Because of the confinement of orthorhombic sulfur in the sulfur-cross-linked cellulose network, GCS₈₅ and GCS₈₀ exhibited a depressed melting endotherm in the second and later heating cycles by DSC (Figures S10–S13; DSC for precursors OC and GC are in Figure S5 for comparison).

Thermogravimetric analysis (TGA) of GCS_x reveals that thermal decomposition of the sulfur component occurs at a lower temperature than does decomposition of the cross-linked network. The decomposition temperatures (T_d) for GCS_{80–90} thus range from 234–243 °C, quite similar to that of elemental sulfur (~240 °C). The char yield (at 800 °C) scales expectedly with the amount of organic comonomer present (Figure S8; TGA data for precursors OC and GC are in Figure S4 for comparison).

The data from CS₂ fractionation studies, elemental analysis, IR spectroscopy, Raman spectroscopy, TGA, and DSC are consistent with the formulation of GCS_x as a network of covalently cross-linked cellulose chains wherein each cross-link is composed of short chains of 8–22 sulfur atoms on average. The remaining sulfur is present in the composite but is not covalently attached to the organic component of the network.

Dynamic mechanical analysis (DMA) of GCS_x was undertaken to assess mechanical properties. Because of the high viscosity of molten GCS₈₀ and the difficulty of preparing reproducible samples, DMA was only performed on GCS₉₀ and GCS₈₅, which exhibited very similar mechanical properties to one another (Figure 4 and Table 1). Temperature scans (Figure 4A) revealed that the materials were considerably stronger as they exhibited storage moduli approximately 80% larger in magnitude than in cellulose derivative PCS₈₀ (Figure 3) over the measured temperature range of -60 to +80 °C.⁴ Although GCS₉₀ and PCS₈₀ have a nearly identical cross-link density and sulfur rank, the drastic difference in storage moduli can be attributed to the retention of crystallinity upon modification observed in GC whereas PC became amorphous upon modification, as assessed by powder X-ray diffraction (Figure S16). Stress–strain experiments revealed that the GCS_x materials have flexural moduli of ~1000 MPa, similar to the low end of the range for high impact ABS (acrylonitrile butadiene styrene, 1000–2500 MPa) with low loss moduli and tan delta values indicating their inability to dissipate stress

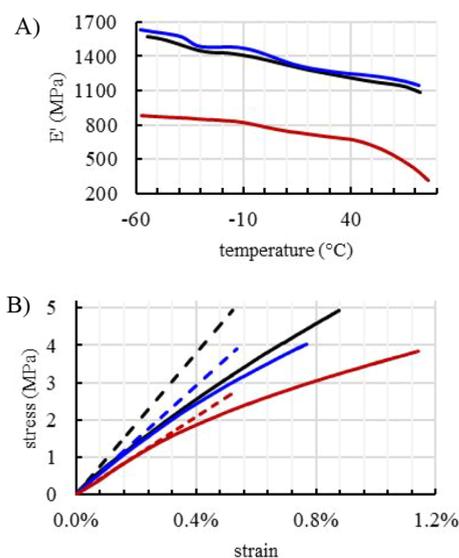


Figure 4. Mechanical properties of GCS₉₀ (black solid line), GCS₈₅ (blue solid line), and PCS₈₀ (red solid line): (A) storage modulus (E') plots and (B) stress–strain curves. Each dashed line in panel B is an extrapolations of the linear region of the curves for the corresponding solid line of the same color.

(Figure S15). As a result of their high flexural moduli and relatively low elastic limits (0.4 and 0.7 MPa for GCS₉₀ and GCS₈₅, respectively), GCS_x materials exhibited considerably smaller moduli of resilience relative to PCS₈₀ but were on par with the moduli of resilience of Portland cement. The flexural strengths of GCS₉₀ and GCS₈₅ (>4.9 and >5.2 MPa, respectively) are higher than the flexural strength exhibited by Portland cement but lower than that exhibited by some other commercial cellulose-based polymers like cellulose acetate butyrate, a material used commercially for applications such as tool handles.²⁸ Both the flexural strength and modulus of GCS_x are comparable to glass fiber–polypropylene composites like Azdel SuperLite that are used commercially in nonstructural automotive door panels.²⁹ It is also notable that GCS_x materials can be thermally processed over many cycles. This property is a result of the thermal reversibility of S–S bond formation and is a notable advantage over some traditional polymers that cannot be repeatedly processed by remelting and recasting.³⁰

A potential industrial application that has been demonstrated for other high sulfur-content materials is as a coating to protect typical mineral cement products from acid corrosion.^{4,11} To evaluate the utility of GCS₉₀ for this application, a block of Portland cement was impregnated by pressure treatment with molten GCS₉₀ following a reported protocol.⁴ The block took up 7 wt % GCS₉₀ to give a material with a density of 1.6 g/cm³. Despite the small weight percentage of GCS₉₀ in the GCS₉₀-impregnated Portland cement block, the mechanical properties were altered drastically. The flexural modulus of GCS₉₀-impregnated Portland cement was found to be 67% greater than that of untreated Portland cement. Additionally, the GCS₉₀-impregnated Portland cement block exhibited significantly improved acid-resistance. Whereas a Portland cement block submerged in 0.5 M H₂SO₄ loses its structural integrity and shape within 30 min, the GCS₉₀-impregnated Portland cement block retained its shape and modulus after acid challenge (Figure 5). The acid-challenged GCS₉₀-impregnated sample exhibited a negligible change in

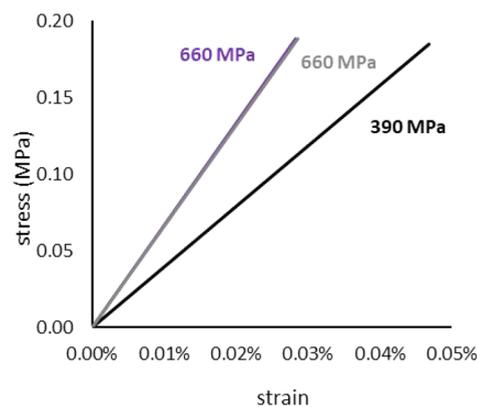


Figure 5. Flexural stress–strain curves for Portland cement (black solid line), GCS₉₀-impregnated Portland cement (purple dotted line), and GCS₉₀-impregnated Portland cement following acid challenge (gray dashed line). Note that the purple and gray lines are coincident and overlapping because there is no loss in modulus of GCS₉₀-impregnated Portland cement following acid challenge. Stresses were maintained below the elastic limit of Portland cement to ensure no permanent deformations were inflicted on the materials between analyses.

flexural modulus relative to the material before soaking. The significant benefits to acid resistance and modulus resulting from a relatively small infusion of GCS₉₀ into Portland cement make GCS₉₀ an especially intriguing material as a cement additive while additionally ensuring that the density of the material is not too high for commercial applications.

In conclusion, we report a three-step green route to thermoplastics from cellulose, terpenoid, and waste sulfur with overall 90% atom economy. The mechanical properties of the resultant polymers display mechanical properties that are competitive with commercially viable materials, and a potential industrial application to improve acid corrosion resistance of cement products was also demonstrated. Perhaps most importantly, the synthetic method delineated herein should be applicable to many combinations of saccharide and terpenoid precursors to facilitate similarly green routes to a range of sustainably sourced materials. Several additional polysaccharide–terpenoid composite formulations are currently being pursued.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsapm.0c00803>.

IR and Raman spectra, DMA data, stress–strain curves, DSC data, TGA data, experimental details (PDF)

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Notes

The authors declare no competing financial interest.

REFERENCES

- (1) Anastas, P. T.; Warner, J. C. *Green Chemistry: Theory and Practice*. Oxford University Press: New York, 1998.
- (2) Foster, E. J.; Moon, R. J.; Agarwal, U. P.; Bortner, M. J.; Bras, J.; Camarero-Espinosa, S.; Chan, K. J.; Clift, M. J. D.; Cranston, E. D.; Eichhorn, S. J.; Fox, D. M.; Hamad, W. Y.; Heux, L.; Jean, B.; Korey, M.; Nieh, W.; Ong, K. J.; Reid, M. S.; Renneckar, S.; Roberts, R.; Shatkin, J. A.; Simonsen, J.; Stinson-Bagby, K.; Wanasekara, N.; Youngblood, J. Current characterization methods for cellulose nanomaterials. *Chem. Soc. Rev.* **2018**, *47* (8), 2609–2679.
- (3) Lauer, M. K.; Karunarathna, M. S.; Tennyson, A. G.; Smith, R. C. Recyclable, Sustainable, and Stronger than Portland Cement: A Composite from Unseparated Biomass and Fossil Fuel Waste. *Mater. Adv.* **2020**, *1*, 590–594.
- (4) Lauer, M. K.; Estrada-Mendoza, T. A.; McMillen, C. D.; Chumanov, G.; Tennyson, A. G.; Smith, R. C. Durable Cellulose–Sulfur Composites Derived from Agricultural and Petrochemical Waste. *Adv. Sust. Syst.* **2019**, *3* (10), 1900062.
- (5) Karunarathna, M. S.; Smith, R. C. Valorization of Lignin as a Sustainable Component of Structural Materials and Composites: Advances from 2011 to 2019. *Sustainability* **2020**, *12* (2), 734–748.
- (6) Karunarathna, M. S.; Tennyson, A. G.; Smith, R. C. Facile new approach to high sulfur-content materials and preparation of sulfur-lignin copolymers. *J. Mater. Chem. A* **2020**, *8*, 548–553.
- (7) Karunarathna, M. S.; Lauer, M. K.; Thiounn, T.; Smith, R. C.; Tennyson, A. G. Valorization of waste to yield recyclable composites of elemental sulfur and lignin. *J. Mater. Chem. A* **2019**, *7* (26), 15683–15690.
- (8) Smith, A. D.; Smith, R. C.; Tennyson, A. G. Carbon-Negative Polymer Cements by Copolymerization of Waste Sulfur, Oleic Acid, and Pozzolan Cements. *Sust. Chem. Pharm.* **2020**, *16*, 100249.
- (9) Smith, A. D.; McMillen, C. D.; Smith, R. C.; Tennyson, A. G. Copolymers by Inverse Vulcanization of Sulfur with Pure or Technical Grade Unsaturated Fatty Acids. *J. Polym. Sci.* **2020**, *58*, 438–445.
- (10) Smith, A. D.; Thiounn, T.; Lyles, E. W.; Kibler, E. K.; Smith, R. C.; Tennyson, A. G. Combining agriculture and energy industry waste products to yield recyclable, thermally healable copolymers of elemental sulfur and oleic acid. *J. Polym. Sci., Part A: Polym. Chem.* **2019**, *57* (15), 1704–1710.
- (11) Lopez, C. V.; Karunarathna, M. S.; Lauer, M. K.; Maladeniya, C. P.; Thiounn, T.; Ackley, E. D.; Smith, R. C. High Strength, Acid-Resistant Composites from Canola, Sunflower, or Linseed Oils: Influence of Triglyceride Unsaturation on Material Properties. *J. Polym. Sci.* **2020**, *58*, 2259–2266.
- (12) Kristufek, S. L.; Wacker, K. T.; Tsao, Y.-Y. T.; Su, L.; Wooley, K. L. Monomer design strategies to create natural product-based polymer materials. *Nat. Prod. Rep.* **2017**, *34* (4), 433–459.
- (13) Wilbon, P. A.; Chu, F.; Tang, C. Progress in Renewable Polymers from Natural Terpenes, Terpenoids, and Rosin. *Macromol. Rapid Commun.* **2013**, *34* (1), 8–37.
- (14) Worthington, M. J. H.; Kucera, R. L.; Chalker, J. M. Green chemistry and polymers made from sulfur. *Green Chem.* **2017**, *19* (12), 2748–2761.
- (15) Onwukamike, K. N.; Grelier, S.; Grau, E.; Cramail, H.; Meier, M. A. R. Critical Review on Sustainable Homogeneous Cellulose Modification: Why Renewability Is Not Enough. *ACS Sustainable Chem. Eng.* **2019**, *7* (2), 1826–1840.
- (16) Janssen, M. H. A.; Chesa Castellana, J. F.; Jackman, H.; Dunn, P. J.; Sheldon, R. A. Towards greener solvents for the bleach oxidation of alcohols catalysed by stable N-oxy radicals. *Green Chem.* **2011**, *13* (4), 905–912.
- (17) Zhuang, C.; Tao, F.; Cui, Y. Eco-friendly biorefractory films of gelatin and TEMPO-oxidized cellulose ester for food packaging application. *J. Sci. Food Agric.* **2017**, *97*, 3384–3395.
- (18) Kumar, M.; Thakur, K.; Sharma, S.; Nayal, O. S.; Kumar, N.; Singh, B.; Sharma, U. Solvent-free, L-Leucine-Catalyzed Direct Dehydrative Esterification of Carboxylic Acids with Alcohols: Direct Synthesis of 3-Alkoxy-1(3H)-isobenzofuranone. *Asian J. Org. Chem.* **2018**, *7* (1), 227–231.
- (19) Hu, H.; You, J.; Gan, W.; Zhou, J.; Zhang, L. Synthesis of allyl cellulose in NaOH/urea aqueous solutions and its thiol-ene click reactions. *Polym. Chem.* **2015**, *6* (18), 3543–3548.
- (20) Chalker, J. M.; Worthington, M. J. H.; Lundquist, N. A.; Esdaile, L. J. Synthesis and Applications of Polymers Made by Inverse Vulcanization. *Top. Curr. Chem.* **2019**, *377* (3), 1–27.
- (21) Chung, W. J.; Griebel, J. J.; Kim, E. T.; Yoon, H.; Simmonds, A. G.; Ji, H. J.; Dirlam, P. T.; Glass, R. S.; Wie, J. J.; Nguyen, N. A.; Guralnick, B. W.; Park, J.; Somogyi, A.; Theato, P.; Mackay, M. E.; Sung, Y.-E.; Char, K.; Pyun, J. The use of elemental sulfur as an alternative feedstock for polymeric materials. *Nat. Chem.* **2013**, *5* (6), 518–24.
- (22) Tonkin, S. J.; Gibson, C. T.; Campbell, J. A.; Lewis, D. A.; Karton, A.; Hasell, T.; Chalker, J. M. Chemically induced repair, adhesion, and recycling of polymers made by inverse vulcanization. *Chem. Sci.* **2020**, *11*, 5537–5546.
- (23) Herrera, C.; Ysinga, K. J.; Jenkins, C. L. Polysulfides Synthesized from Renewable Garlic Components and Repurposed Sulfur Form Environmentally Friendly Adhesives. *ACS Appl. Mater. Interfaces* **2019**, *11* (38), 35312–35318.
- (24) Smith, J. A.; Green, S. J.; Petcher, S.; Parker, D. J.; Zhang, B.; Worthington, M. J. H.; Wu, X.; Kelly, C. A.; Baker, T.; Gibson, C. T.; Campbell, J. A.; Lewis, D. A.; Jenkins, M. J.; Willcock, H.; Chalker, J. M.; Hasell, T. Crosslinker Copolymerization for Property Control in Inverse Vulcanization. *Chem. - Eur. J.* **2019**, *25* (44), 10433–10440.
- (25) Lundquist, N.; Tikoalu, A.; Worthington, M.; Shapter, R.; Tonkin, S.; Stojcevski, F.; Mann, M.; Gibson, C.; Gascooke, J.; Karton, A.; Henderson, L.; Esdaile, L.; Chalker, J. Reactive compression molding post-inverse vulcanization: A method to assemble, recycle, and repurpose sulfur polymers and composites. *Chem. - Eur. J.* **2020**, *26*, 1–11.
- (26) Thiounn, T.; Lauer, M. K.; Bedford, M. S.; Smith, R. C.; Tennyson, A. G. Thermally-healable network solids of sulfur-crosslinked poly(4-allyloxystyrene). *RSC Adv.* **2018**, *8* (68), 39074–39082.
- (27) Karunarathna, M. S.; Lauer, M. K.; Tennyson, A. G.; Smith, R. C. Copolymerization of an aryl halide and elemental sulfur as a route to high sulfur content materials. *Polym. Chem.* **2020**, *11*, 1621–1628.
- (28) Ouajai, S.; Shanks, R. A. Biocomposites of cellulose acetate butyrate with modified hemp cellulose fibres. *Macromol. Mater. Eng.* **2009**, *294* (3), 213–221.
- (29) *Technical data sheet “Azdel Super Lite® SL550600–100”*; Azdel, 2020.
- (30) Thiounn, T.; Smith, R. C. Advances and approaches for chemical recycling of plastic waste. *J. Polym. Sci.* **2020**, *58*, 1347–1364.