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# Durable Cellulose–Sulfur Composites Derived from Agricultural and Petrochemical Waste

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**Nature provides a rich panoply of structural motifs comprised of composites whose mechanical properties exceed those of their individual components. The human endeavor to likewise craft value-added structural materials from underappreciated, sustainably sourced feedstocks remains a formidable challenge. Herein, efforts are made to achieve durable composites by synergistic combination of sulfur and cellulose. Composites are achieved in which bulk sulfur is reinforced by a network of 1–20% by mass cellulose cross-linked with polysulfide chains. Composites described herein are remeltable and have flexural strength exceeding that of Portland cement. A thorough analysis of these materials has been undertaken through nuclear magnetic resonance, infrared spectroscopy, Raman spectroscopy, elemental analysis, thermogravimetric analysis, differential scanning calorimetry, and dynamic mechanical analysis. These analyses of both as-prepared composites and fractionated materials unequivocally validate the formulation of these composites and the separability of the bulk sulfur from the reinforcing polysulfide-cross-linked cellulose network. The thermomechanical properties of these recyclable composites portend their tantalizing potential to supplant inherently unsustainable structural elements in numerous commercial applications. Further applications to improve the environmental resistance and flexural strength of Portland cement by treatment with the sulfur–cellulose composites are also discussed.**

Emerging discoveries that feature prominently in the burgeoning green economy continue to facilitate replacement of existing technologies with new, “intrinsically green” surrogates. Unfortunately, this is a gradual process that will require years or even decades to achieve completion. Existing technologies nonetheless contain bountiful unrealized opportunities to mitigate or eliminate adverse environmental impacts and, in doing so, become significantly greener. Petroleum refining, for example, is a non-green industry that may yet provide resources for more sustainable processes. Although most of the materials resulting from petroleum refining have a productive use, only a fraction of the 60 million metric tons of elemental sulfur ($S_8$) produced annually by petroleum and natural gas production has a viable use, whereby millions of tons of $S_8$ remain unused and accumulate in waste storage sites.[1] Likewise, agricultural growing, harvesting, and processing of crops will only increase as the world’s population increases. Agricultural industries generate more than 5 billion metric tons per year of pre-consumer waste consisting primarily of cellulose.[2,3] Collectively, the petroleum refining and agricultural industries generate titanic quantities of $S_8$ and cellulose that are waste. Developing a means to utilize sulfur and cellulose productively,[4,5] such as to replace petroleum-derived plastics, would 1) reduce the amount of petrochemical polymer waste produced each year, and 2) replace petroleum-derived plastics with equivalent materials having organic components manufactured by photosynthesis, thus reducing atmospheric $CO_2$ levels.

A familiar use of sulfur is in Goodyear’s process for vulcanization of rubber, which spurred the multibillion-dollar rubber industry. Vulcanization toughens natural rubber by cross-linking it with small amounts (<5%) of sulfur.[3] More recently, pioneering work by Pyun has shown, using unsaturated organic small molecules, that forming polymeric sulfur cross-links via reaction with $S_8$ is essentially unlimited in substrate scope,[5–7] a process termed “inverse vulcanization” (**Scheme 1**).[6–9] Inverse vulcanization has become an important tool in harnessing waste sulfur to prepare promising materials for environmental remediation, and electronic and optical applications.[6–10] We recently demonstrated that olefin-derivatized polymers can likewise react with $S_8$, which resulted in those polymer chains being covalently cross-linked by polymeric sulfur. Impressively, cross-linking with only 1% of organic material led to at least an eightfold increase in the storage modulus of the material versus that of $S_8$ alone. In addition, these materials could be broken down, remelted, and cast into new shapes without any deterioration in strength, owing to the thermally reversible nature of sulfur–sulfur single bonds.[7]

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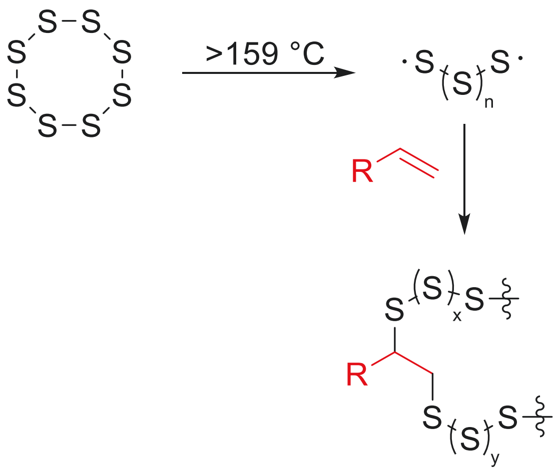
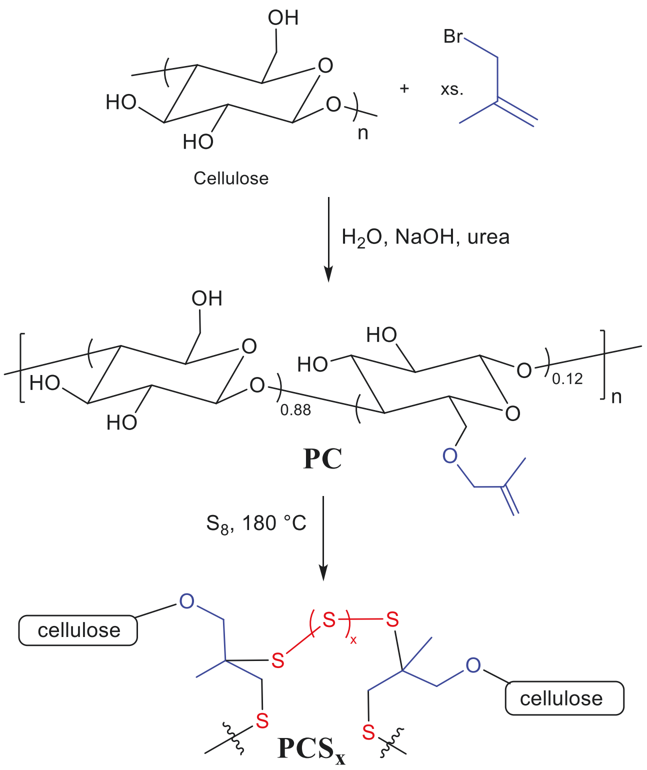


**Scheme 1.** The homologation of elemental sulfur to form sulfur-centered radicals and the subsequent addition across an organic olefin. When the wt% of sulfur is larger than that of the organic species, this process is termed "inverse vulcanization."

We therefore hypothesized that 1) installing C=C bond–containing pendants onto a biopolymer would enable that polymer to be cross-linked by polymeric sulfur upon reaction with $S_8$, 2) the resulting carbon–sulfur composites could be remelted and recast, and 3) these composites would exhibit mechanical properties vastly superior to those of $S_8$, even for composites containing up to 99% sulfur by mass. Herein, we report the cross-linking of methallylated cellulose by polymeric sulfur to yield carbon–sulfur composites, containing 80–99% sulfur by mass, that have flexural strength exceeding that of Portland cement, yet which can be remelted and recast into a variety of different shapes.

Microcrystalline cellulose was selected for modification because its microstructure is well characterized and it is readily prepared from diverse agricultural waste streams.[11] Cellulose derivatives often suffer from inferior processability, but in the current case methylpropene-derivatized cellulose (**PC**, **Scheme 2**) was adequately soluble for facile purification and characterization.

Once the crystalline structure of microcrystalline cellulose had been broken down by a reported dissolution process,[12] olefin-derivatized **PC** was prepared following a method analogous to that used to prepare allylcellulose.[13] Qualitative evidence that substitution had taken place was provided by Fourier-transform infrared spectroscopy, which showed a C—H bending band at 900 $cm^{-1}$ attributable to a geminally substituted olefin (Figure S1, Supporting Information). The degree of substitution (i.e., the percentage of cellulose repeat units that had been alkylated) in **PC** was calculated to be 12 ± 1% from iodometric titration, in which a color change is monitored as alkenes react with in situ generated $Br_2$, a standard method for quantifying unsaturation in carbohydrate research.[13,14] Whereas the substitution of the primary alcohol is shown in Scheme 2, there could be a smaller fraction of substitution at secondary alcohols. Regarding the polymer morphology, X-ray diffraction data (Figure S5, Supporting Information) confirm that **PC** is an amorphous polymer that does not feature fibrous or crystalline structures, so **PC** is appropriate for homogeneous blending with the sulfur comonomer in the subsequent step.



**Scheme 2.** Preparation of **PC** and reaction of sulfur-centered radicals with **PC** to form cross-linked domains within **PCS**$_x$ materials. Here, **PC** is abbreviated to show only the alkylated segments.

**PC** composites with sulfur (**PCS**$_x$) having sulfur wt% values ranging from 80% to 99% (i.e., $x$ = 80–99) were prepared by heating **PC** with molten $S_8$ at 180 °C, which is above the temperature at which $S_8$ ring-opens to form polymeric radical species (Scheme 2). The reaction was allowed to proceed at this temperature until the reaction mixture became homogeneous. These homogeneous mixtures were dark brown to black in the molten state, whereby pouring the melt into a silicone mold and allowing it to cool to room temperature afforded brown to black solids (**Figure 1**). Each **PCS**$_x$ sample is a thermoplastic

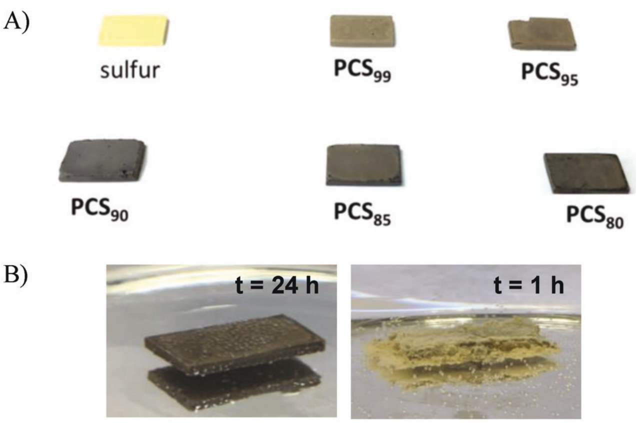


**Figure 1.** A) Digital image of **PCS**$_x$ materials and sulfur. B) Samples of **PCS**$_{80}$ (left) and Portland cement (right) after exposure to 0.5 M $H_2SO_4$ for the specified times.

Table 1. Summary of mechanical analyses.

| Material | S atoms/cross-link | $E'$ [MPa][a] | $E''$ [MPa][b] | tan $\delta$[b] | $T_g$ from tan $\delta$ (°C)[b] | Flexural strength/modulus [MPa] | Modulus of resilience [MPa] |
|---|---|---|---|---|---|---|---|
| **$PCS_{99}$** | ND[c] | ND[d] | ND[d] | ND[d] | ND[d] | ND[d] | ND[d] |
| **$PCS_{95}$** | 58 | ND[d] | ND[d] | ND[d] | ND[d] | ND[d] | ND[d] |
| **$PCS_{90}$** | 24 | 425 | 25, 32 | 0.06 | 9 | ND | ND |
| **$PCS_{85}$** | 31 | 745 | 27, 48 | 0.04, 0.04 | 11, 25 | >3.2[e]/320 | 2.7 |
| **$PCS_{80}$** | 22 | 860 | 34, 54 | 0.05, ND[f] | 6, >80 | >3.8[e]/520 | 1.8 |
| Portland cement | –[g] | –[g] | –[g] | 0.05–0.06 | –[h] | 3.7/580 | 0.6 |

[a] Storage modulus value at –40 °C when each **$PCS_x$** material is below $T_g$; [b] Value at $T_g$, except for Portland cement, which did not exhibit a $T_g$ in the range –100 to 100 °C; [c] Value unattainable due to limited sample size; [d] Sample was too brittle to clamp at 1 cN m; [e] Sample could not be measured beyond this level due to instrumental limitations; [f] Value was outside of measured range; [g] Data not available/applicable; [h] Material exhibited no apparent maximum value in the range –100 to 100 °C.

and could be remelted, poured, and cast into a variety of shapes multiple times in the same manner, as evidenced by the ability to remelt the reaction solution and pour into prismatic molds to give the samples shown in Figure 1A. The origin of the well-known dark red/brown/black color of oligomeric and polymeric sulfur species has been a topic of some discussion in the literature, and is often observed in contexts where several $S_n$ chain lengths are concurrently present.[15] The dark color of such materials is sometimes attributed to carbonation of the organic component, but in the current case it was found that **PC** could be heated at the reaction conditions and times with only slight browning of color and very little degradation as assessed by elemental and thermogravimetric analysis. So, heated **PC** does not develop a dark black color akin to the color of **$PCS_x$**. Numerous other reports in which photos of inverse-vulcanized materials are presented[8,16] show similar or darker coloration to what is observed for **$PCS_x$**, supporting the earlier literature suggesting that the dark coloration is sulfur-derived.

Thermogravimetric analysis (TGA, traces provided in Figure S7 in the Supporting Information) revealed that the decomposition onset temperatures ($T_d$) of the **$PCS_x$** composites were comparable to $S_8$, which is unsurprising given that these composites are 80–99% sulfur by weight. The infrared (IR) spectroscopy, differential scanning calorimetry (DSC), TGA, and dynamic mechanical analysis (DMA) for **$PCS_x$** presented here refer to the as-prepared composites. However, in order to better assess the chemical composition of **$PCS_x$**, the $CS_2$-soluble and $CS_2$-insoluble fractions of **$PCS_x$** were initially studied individually. Free $S_8$ is readily soluble in $CS_2$, whereas **PC** is completely insoluble. Extraction of each **$PCS_x$** sample with $CS_2$ thus enabled removal of all sulfur that was not covalently connected to **PC**. Elemental analysis confirmed that the $CS_2$-soluble fraction of **$PCS_x$** contained only free $S_8$. The ratio of **PC** to sulfur in the $CS_2$-insoluble fractions thus revealed the average length of the polymeric sulfur chain in the **$PCS_x$** composites to be 20–60 sulfur atoms, the average length of the polysulfide cross-link predictably increasing with the wt% S in the composite (**Table 1**).

Raman spectroscopy and DSC support the formulation of **$PCS_x$** as containing polymeric sulfur cross-links. The orthorhombic allotrope of $S_8$ is characterized by strong Raman signals at 143, 209, and 461 cm$^{-1}$ (**Figure 2**).[17] Raman spectra for the **$PCS_x$** samples exhibited major peaks attributable to $S_8$, with a much smaller shoulder at ≈443 cm$^{-1}$ arising from polymeric sulfur.[18] The disappearance of all peaks attributable to orthorhombic sulfur is evident in the Raman spectrum for the $CS_2$-insoluble fraction of **$PCS_{99}$**, whereby the remaining peak at 458 cm$^{-1}$ could be unambiguously attributed to the polymeric sulfur that is covalently linked to **PC**.

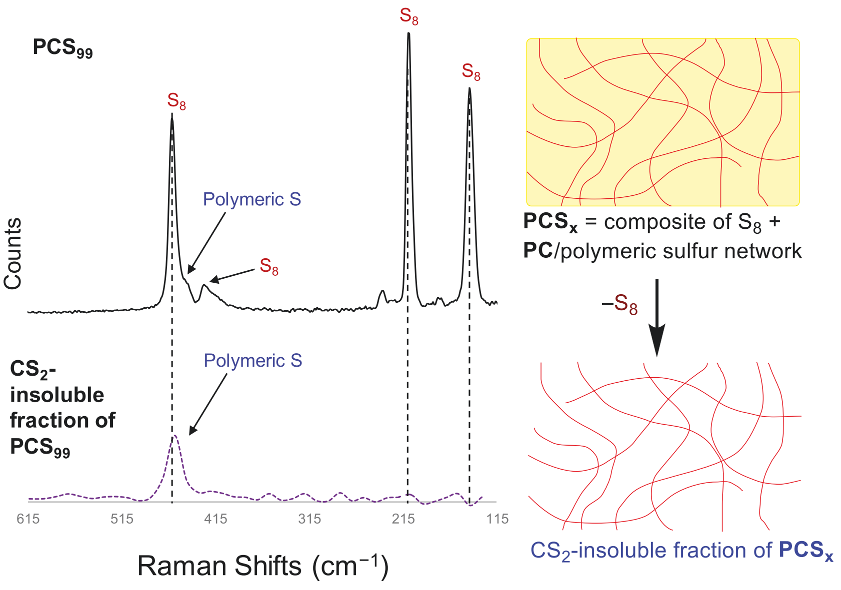


**Figure 2.** Left panel: Raman spectra of **$PCS_{99}$** (solid black line) and of the $CS_2$-insoluble fraction of **$PCS_{99}$** (purple dashed line). Right panel: pictorial representation of **$PCS_{99}$** as a composite of $S_8$ (yellow) reinforced with a network (red lines) of **PC** cross-linked with polymeric sulfur.

DSC data for **$PCS_x$** also featured endothermic phase transitions before the monoclinic melt temperature in the second and later heating cycles for **$PCS_x$**. These transitions were attributable to the oligomeric and polymeric sulfur chains that cross-link **PC**. The first heating DSC traces for both $S_8$ and **$PCS_x$** also show peaks at ≤103 °C attributed to conversion of orthorhombic to the monoclinic allotrope of $S_8$ as well as a feature at ≈120 °C for the melting of monoclinic sulfur. Powder X-ray diffraction data further confirm that the only crystalline regions in **$PCS_x$** are nearly identical to those in elemental sulfur

(Figure S16, Supporting Information); there is no evidence for crystalline or ordered fibrous structures attributable to the cellulose network.

Collectively, the findings of the $CS_2$ extraction/elemental analysis, Raman spectroscopy, and DSC all support a formulation of **PCS**$_x$ as composites comprised by primarily orthorhombic $S_8$ (yellow-colored domains in Figure 2, right panel) reinforced by a network of cellulose cross-linked by polymeric sulfur (red network in Figure 2, right panel).[7]

Given the apparent ability of a small amount of polymeric sulfur-cross-linked cellulose to reinforce a vastly greater abundance of free $S_8$, the mechanical properties of the **PCS**$_x$ composites were investigated in greater detail using DMA. Others have shown that heating free $S_8$ by itself to 180 °C for extended periods of time (e.g., the conditions used to synthesize **PCS**$_x$) affords measurable quantities of polymeric sulfur. In contrast to what is observed in **PCS**$_x$ composites, however, once cooled to room temperature polymeric sulfur in the absence of a supporting organic network gradually reverts to orthorhombic $S_8$ over the course of about 48 h. **PCS**$_x$ samples were thus aged for 15 days prior to analysis to ensure that all polymeric sulfur that is not covalently connected to cellulose has fully reverted to the $S_8$ form. This approach allows testing of the composite structure that would be present in "real-world" applications.

Unfortunately, **PCS**$_{95}$ and **PCS**$_{99}$ were too fragile (i.e., they break at a clamping force of under 1 cN m) for reproducible analysis, so DMA experiments were limited to **PCS**$_{80}$, **PCS**$_{85}$, and **PCS**$_{90}$. Data from DMA are summarized in Table 1 and traces are provided in Figure S17 (Supporting Information). DMA in single-cantilever mode revealed the expected trend of increasing magnitude of storage modulus from the least network-reinforced **PCS**$_{90}$ to the most network-reinforced **PCS**$_{80}$. The loss moduli were relatively low and nearly identical for all three materials, demonstrating that the materials exhibit a more elastic than viscous response. A second transition at ≈25 °C observed in $S_8$ was also evident in **PCS**$_{85}$. Because the loss moduli were nearly the same and the materials exhibited very different storage moduli, the tan $\delta$ values of the three samples differed only slightly across the series. In each case, however, the magnitude of tan $\delta$ over the temperature range studied was rather low in comparison to many synthetic polymers yet on par with traditional structural materials (i.e., Portland cement).[19] Also evident in the storage modulus curves is the appearance of a second glass transition with an onset temperature of ≈40 °C, consistent with the glass transition of **PC**. This transition can also be observed in the loss modulus and tan $\delta$ curves at ≈70 and ≈80 °C, respectively. Due to this transition, the materials' moduli are especially high at room temperature compared to sulfur as is physically evident by the high relative stiffness of the **PCS**$_x$ materials.

The two strongest materials, **PCS**$_{80}$ and **PCS**$_{85}$, were subjected to stress–strain testing to analyze their flexural strength under ambient conditions (Figure S18, Supporting Information).[20] Stress–strain curves showed that **PCS**$_{80}$ exhibited the higher stiffness, flexural modulus, and strength expected from a higher cross-link density. While **PCS**$_{85}$ exhibited a flexural modulus of 320 MPa, **PCS**$_{80}$ exhibited a modulus more than 60% higher (520 MPa). Notably, even after 10 N of applied flexural force—the maximum force available to the dynamic mechanical analyzer—neither material fractured and neither was deformed by more than about 1.25%. The flexural strengths (maximum value of the stress–strain curve) of **PCS**$_{80}$ and **PCS**$_{85}$ are >3.2 and >3.8 MPa, respectively. Note that these values represent lower limits to the flexural strength of the **PCS**$_x$ materials because the samples did not break at maximum instrument force applied. For comparison, the flexural strength of **PCS**$_{80}$ is greater than that of Portland cement (3.7 MPa, with sample breakage upon analysis), while the density of **PCS**$_{80}$ (1.8 g cm$^{-3}$) is also similar to that of Portland cement (1.5 g cm$^{-3}$).

Sulfur has long been explored as an asphalt extender in place of bitumen and as an additive to improve the water uptake and acid resistance of masonry products.[21] The high flexural strength of **PCS**$_{80}$ suggested that it may likewise be a good candidate for further study as a possible Portland cement additive or surrogate. Both Portland cement and high cellulose content building materials are subject to high water uptake such that subsequent expansion of trapped water upon freezing can lead to fissure formation and ultimate material failure. Sulfur, however, is highly hydrophobic, so **PCS**$_{80}$ takes up only 4% of its mass in water (cf. 29% for Portland cement). Portland cement is also susceptible to degradation in acidic environments, leading to diminished operational lifetime. It is immediately evident (Figure 1B) that a block of Portland cement loses its mechanical integrity and shape after just 1 h of exposure to 0.5 M $H_2SO_4$(aq), whereas a sample of **PCS**$_{80}$ is visually impervious to 0.5 M $H_2SO_4$(aq) for at least several days, and after acid exposure, **PCS**$_{80}$ retains its full stiffness, strength, and resilience as determined from post-acid-exposure stress–strain analysis.

The resistance to water uptake and acid degradation afforded by **PCS**$_{80}$ suggested that it might endow **PCS**$_{80}$-impregnated Portland cement with similarly improved resilience. Treatment of Portland cement with sustainable additives that may increase its operational lifetime is an important goal, especially given that nearly a kilogram of $CO_2$ greenhouse gas emission results from production of each kilogram of Portland cement, accounting for 5–7% of global $CO_2$ emissions.[22] A block of previously cured Portland cement was thus impregnated by submerging it in molten **PCS**$_{80}$ in vacuo, whereby the Portland cement took up 18.6 wt% of **PCS**$_{80}$ into its pores. The **PCS**$_{80}$-impregnated Portland cement block only took up 9.5% of its weight in water after being submerged for 24 h (cf. 29% for untreated Portland cement). The **PCS**$_{80}$-impregnated Portland cement block exhibited a flexural strength of >2.8 MPa and, in contrast to untreated Portland cement, did not break during the stress–strain experiment (after 10 N of applied force). Perhaps most impressively, the **PCS**$_{80}$-impregnated Portland cement block retained at least 85% of its flexural modulus after sulfuric acid challenge.

In conclusion, the work described herein has demonstrated a strategy for covalent cross-linking of cellulose with polymeric sulfur chains to form a robust network that forms composites with $S_8$. These composites (**PCS**$_x$) made from waste products are not only remeltable over many cycles but also endowed with mechanical strength on par with commercial Portland cement. When Portland cement pores are backfilled with **PCS**$_x$, the Portland cement takes up significantly less water and is resistant to degradation in acidic environments. Ongoing work on waste-derived and sustainable composites seeks to further improve the properties of such composites and to advance the sustainability of their preparation for deployment in commercial settings.

## Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

## Conflict of Interest

The authors declare no conflict of interest.

## Keywords

cellulose, inverse vulcanization, Portland cement, sulfur, sustainability

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