

Supplemental Information for:

**Inverse Vulcanization of Octenyl Succinate-Modified Corn Starch as a Route to Biopolymer-Sulfur Composites**

Moira K. Lauer,<sup>a</sup> Andrew G. Tennyson,<sup>ab</sup> and Rhett C. Smith<sup>\*a</sup>

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## 1. Instrumentation

Fourier transform infrared spectra were obtained using an IR instrument (Shimadzu IRAffinity-1S) with an ATR attachment. Scans were collected over the range 400–4000  $\text{cm}^{-1}$  at ambient temperature with a resolution of 8. TGA was recorded (Mettler Toledo TGA 2 STARe System) over the range 20–800  $^{\circ}\text{C}$  with a heating rate of 10  $^{\circ}\text{C}\cdot\text{min}^{-1}$  under a flow of  $\text{N}_2$  (100  $\text{mL}\cdot\text{min}^{-1}$ ). Each measurement was acquired in duplicate and presented results represent an average value. DSC was acquired (Mettler Toledo DSC 3 STARe System) over the range –60 to 150  $^{\circ}\text{C}$  with a heating rate of 5  $^{\circ}\text{C}\cdot\text{min}^{-1}$  under a flow of  $\text{N}_2$  (200  $\text{mL}\cdot\text{min}^{-1}$ ). Each DSC measurement was carried out over five heat-cool cycles. Each measurement was acquired in duplicate to ensure consistent results were obtained. Carbon disulfide extractions were performed by suspending 0.3 g of finely ground material (measured to 0.0001 g) in 20 mL of  $\text{CS}_2$ , allowing the solid to settle for 30 minutes, pipetting off the supernatant into a separate vial, and adding another 20 mL of  $\text{CS}_2$ . This process was repeated an additional 3 times so that a total of 5 washes was performed. The residual  $\text{CS}_2$  was evaporated under a flow of  $\text{N}_2$  and each vial was weighed to determine the fraction that was soluble (collected as supernatant) or insoluble (remained in the initial vial). DMA was performed (Mettler Toledo DMA 1 STARe System) in single cantilever mode. DMA samples were cast from silicone resin moulds (Smooth-On Oomoo<sup>®</sup> 30 tin-cure). Samples were manually sanded to ensure uniform dimensions. The sample dimensions were approximately 15 x 8 x 1.5 mm. Sample dimensions were measured with a digital calliper with  $\pm 0.01$  mm resolution. Samples were clamped by hand tightening due to their brittleness. The force was varied from 0 to 10 N with a ramp rate of 0.2  $\text{N}\cdot\text{min}^{-1}$  measured isothermally at 25  $^{\circ}\text{C}$ . Compressional analysis was performed on a Mark-10 ES30 test stand equipped with a M3-200 force gauge (1 kN maximum force with  $\pm 1$  N resolution). Compression cylinders were cast from silicone resin moulds (Smooth-On Oomoo<sup>®</sup> 30 tin-cure) with diameters of approximately 6 mm and heights of approximately 10 mm. Samples were manually sanded to ensure uniform dimensions and measured with a digital calliper with  $\pm 0.01$  mm resolution. Compressional analysis was performed in triplicate and results were averaged.

## 2. Synthesis of OS

**OS** was prepared with slight modifications to a literature procedure.<sup>1, 2</sup> Corn Starch (49.980 g, 10.7 wt% moisture as determined by duplicate TGA experiments, 44.6 g dry basis, 308 mmol dry basis) was dissolved in 93.0 mL of DI H<sub>2</sub>O. The pH was adjusted to 8.0 with 3 wt% NaOH where it was maintained for the duration of the reaction by frequently checking with a pH meter (0.01 unit resolution). Octenyl succinic anhydride (5.031g, 23.93 mmol) was added dropwise over the first four hours of reaction with rapid stirring at 20 °C. The pH was continually monitored until it had stabilized (pH change was ≤ 1.0 pH units per 10 minutes), occurring after 14 total hours of reaction. The pH of the slurry was adjusted to a pH of 6.4 with 3.7 wt% HCl. The slurry was filtered and washed with 100 mL of DI H<sub>2</sub>O. The resultant solid was suspended in 500 mL of DI H<sub>2</sub>O and left overnight. The slurry was centrifuged and separated into 2 fractions, each fraction being resuspended in 500 mL of DI H<sub>2</sub>O. Each fraction was again centrifuged and resuspended in 400 mL of ethanol. Each fraction was filtered and washed with 100 mL of ethanol. The starch was placed into a 35 C vacuum oven (~65 mm Hg), releasing and reapplying the vacuum frequently, for five days. The final yield was 45.654 g, 9.2 wt% moisture as determined by duplicate TGA experiments, 41.4 g dry basis.

### 3. Titrations of **OS**

Titration procedures were based on a reported method<sup>1</sup>, modified to minimize the utilization of product and solvents while maintaining acceptable accuracy. The dry mass of material was used in all cases by determining the mass loss at 140 °C by TGA:

#### Sample Preparation:

**OS** or corn starch were weighed and suspended (~2g weighed to 0.000X) in 2.5 M HCl in isopropanol (20 mL) in a 125 mL Erlenmeyer flask and stirred for 30 minutes. Isopropanol (90% v/v, 80 mL) was added and the suspension was allowed to stir for 10 minutes. The slurry was filtered with a glass frit and washed with isopropanol (90% v/v) until no chloride could be detected in the filtrate by adding a few drops of the filtrate to silver nitrate solution (0.10 M, ~1 mL). The resultant solid was placed in a 250 mL Erlenmeyer flask and suspended in 25 mL of isopropanol. The flasks were covered with parafilm and left until the following day for continued sample preparation and titration. The flask was placed in a 120 °C oil bath while stirring and heated until the isopropanol began to boil (~5 minutes) at which point DI water (100 mL) was added. The slurry was again brought to a boil (this step must be done carefully to avoid boil-overs), removed from the heat, and placed on a magnetic stir plate to cool. Slurries of **OS** were again heated to a boil to ensure complete gelatinization. The slurry was titrated with 0.02 M NaOH with 5 drops of phenolphthalein as an indicator. Samples of native corn starch were prepared and titrated by the same method except they were allowed to boil until complete gelatinization (~ 5 minutes) as they posed no risk of boiling over. Corn starch was used as a blank and the results were subtracted from the values obtained for **OS**.

OS titrated value:  $0.0287 \pm 0.0005$

corn starch titrated value:  $0.0024 \pm 0.0002$

#### Standardization of NaOH:

A 0.02 M NaOH solution was prepared. Potassium hydrogen phthalate (**KHP**) was dried in a 110 °C oven until constant mass was obtained and stored in a desiccator to cool. Deoxygenated DI water was obtained by boiling for 2 hours followed by storage under nitrogen.

To titrate, 0.1 g (weighed to 0.0001 g) of dried **KHP** was weighed by difference into an Erlenmeyer flask. Deoxygenated DI water (50 mL) was added to the flask and it was swirled until complete dissolution of **KHP**. Three drops of phenolphthalein were added, and the solution was titrated. Titrant concentration was determined to be  $0.01998 \pm 0.0005$  based on 4 replicates.

#### Titration of **OS** and starch:

Gelatinized samples (see above for sample preparation) were titrated with previously standardized 0.02 M NaOH four times each. Using **Equation 1** and subtracting out the value obtained from starch as a blank, OS as calculated to contain a DS =  $0.0263 \pm 0.0005$ .

$$DS = \frac{0.162 \times \frac{V \times M}{w}}{1 - \left[ 0.210 \times \frac{V \times M}{w} \right]}$$

**Equation S1**

Where  $V$  = titrant volume delivered (in mL),  $M$  = titrant molarity ( $\text{mol} \cdot \text{L}^{-1}$ ), and  $w$  = the mass of starch or **OS** titrated (dry basis, g)

#### 4. Synthesis of **OSS<sub>x</sub>**

##### Synthesis of **OSS<sub>95</sub>**

Sulfur (9.499 g, 296.2 mmol) and **OS** (0.547) were combined in a vial and which was then sealed with a septum. The vial was purged with a continuous nitrogen flow for 10 minutes. The vial was then placed in a 180 °C oil bath and allowed to stir for 80 min. The sample was removed from the heat and allowed to cool to room temperature, accelerating cooling with a flow of nitrogen for 15 minutes. The OS that had stuck to the walls of the vial above the reaction surface was scraped with a spatula to reincorporate it into the reaction medium. The septum was replaced, and the vial was again purged with nitrogen for 10 minutes. This process of removing from the heat, purging, scraping, purging, and heating was repeated at the following intervals:

t = 0, t = 80 min, t = 140 min, t = 320 min, t = 380 min, t = 440 min

After 380 minutes had elapsed, the reaction media appeared homogeneous but was allowed to continue to emulate the procedures used to prepare **OSS<sub>95</sub>**. Found elemental analysis: S: 94.75%, C: 2.61%, H: 0.20%

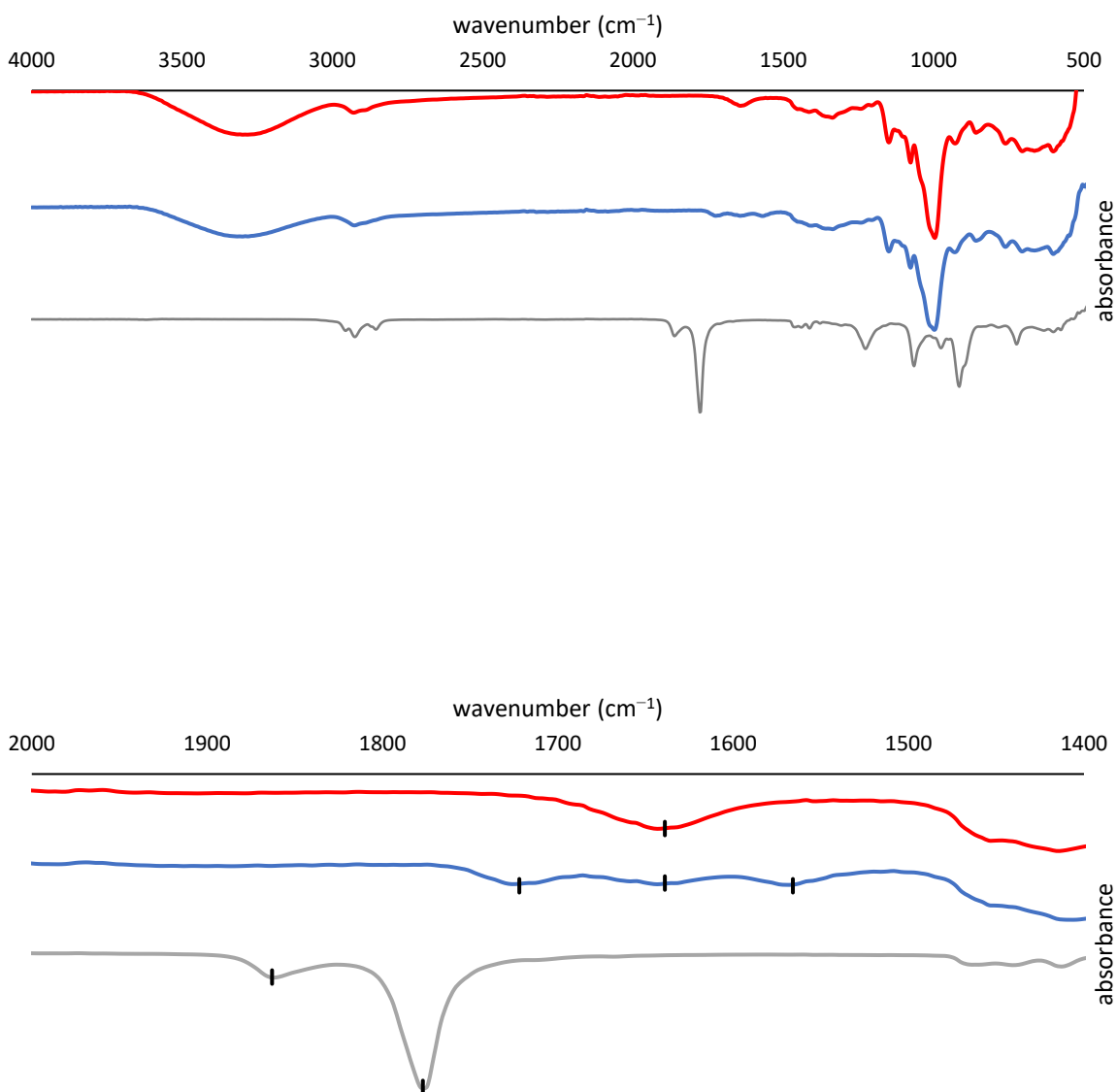
##### Synthesis of **OSS<sub>90</sub>**

Sulfur (9.003 g, 280.8 mmol) and **OS** (1.106) were combined in a vial and which was then sealed with a septum. The vial was purged with a continuous nitrogen flow for 10 minutes. The vial was then placed in a 180 °C oil bath and allowed to stir for 80 min. The sample was removed from the heat and allowed to cool to room temperature, accelerating cooling with a flow of nitrogen for 15 minutes. The OS that had stuck to the walls of the vial above the reaction surface was scraped with a spatula to reincorporate it into the reaction medium. The septum was replaced, and the vial was again purged with nitrogen for 10 minutes. This process of removing from the heat, purging, scraping, purging, and heating was repeated at the following intervals:

t = 0, t = 80 min, t = 140 min, t = 320 min, t = 380 min, t = 440 min

After 440 minutes had elapsed, the reaction media appeared homogeneous but was allowed to continue for 120 additional minutes to ensure complete reaction. Found elemental analysis: S: 89.41%, C: 4.77%, H: 0.53%

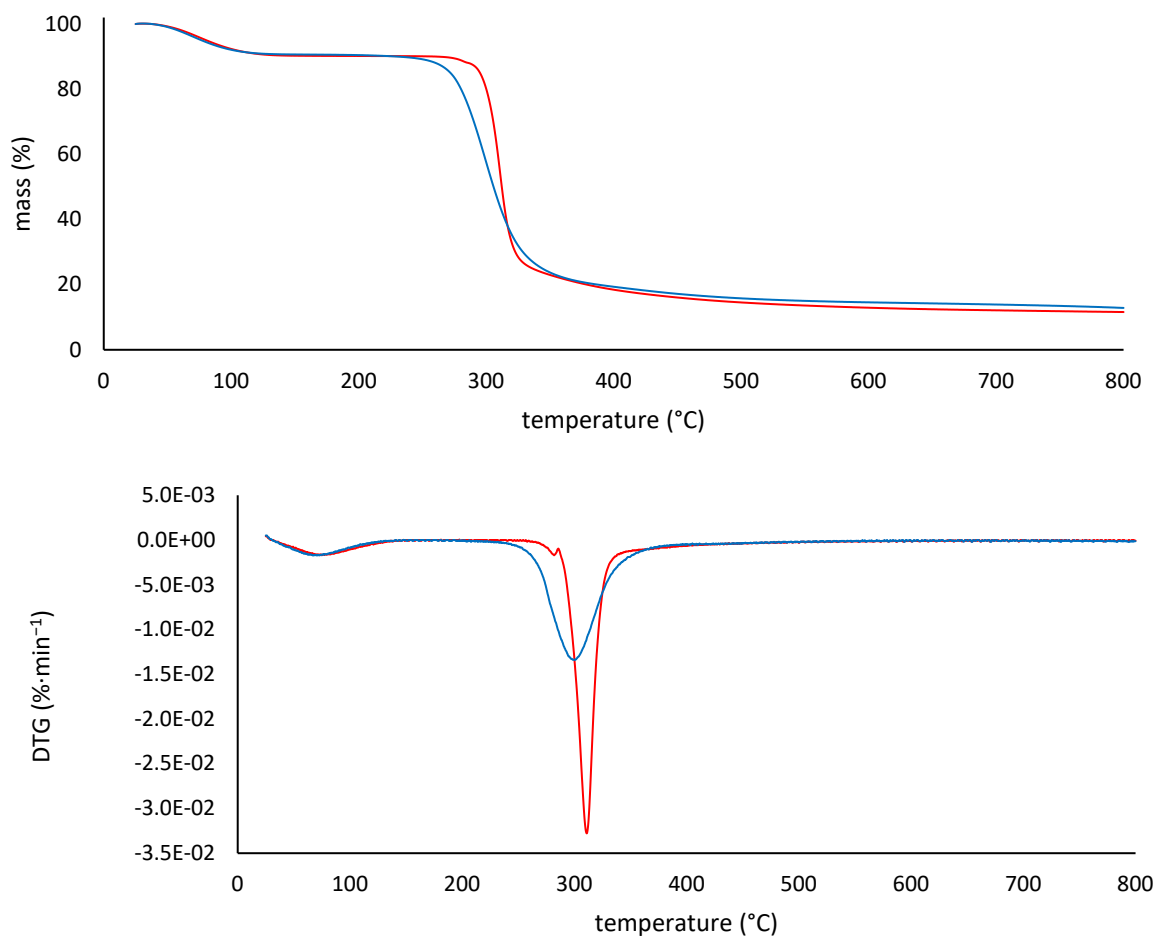
## 5. IR of OS



**Figure S1.** Stacked FT-IR spectra from 500–4000 cm<sup>-1</sup> (top) and from 1400–2000 cm<sup>-1</sup> (bottom) of corn starch (red), OS (blue), and OSA (gray) showing successful octenylsuccinylation. Corn starch shows a signal at 1639 cm<sup>-1</sup> due to residual bound water while **OS** shows additional signals for carbonyls at 1722 cm<sup>-1</sup> due to the ester and at 1566 cm<sup>-1</sup> due to the carboxyl group. The anhydride carbonyls for OSA can be observed at 1863 and 1777 cm<sup>-1</sup>.

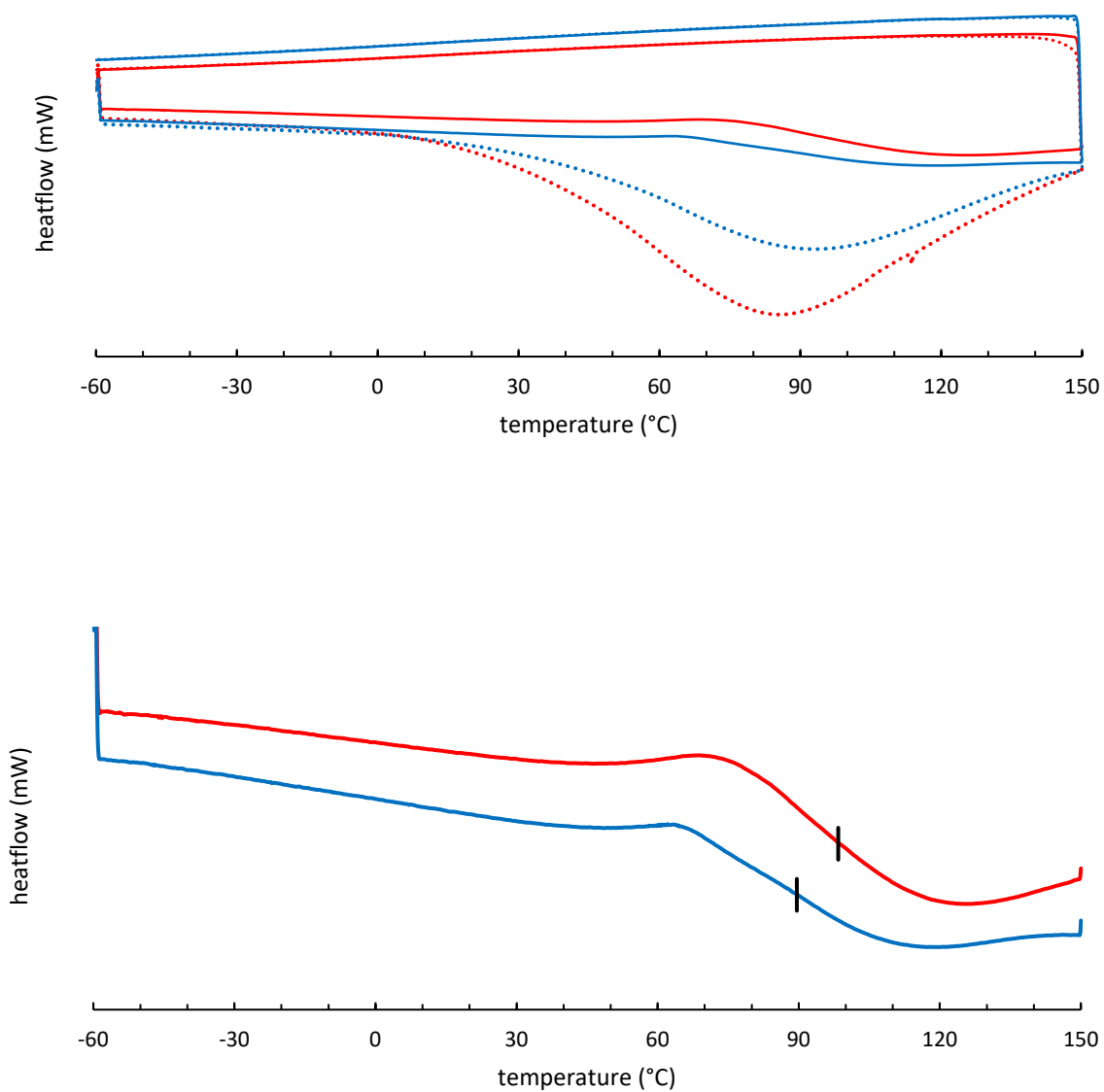


## 6. TGA of OS



**Figure S2.** TGA mass loss curves (top) and DTG curves (bottom) for native corn starch (red) and OS (blue). Modification resulted in a slight decrease in thermal stability and a much broader temperature range of decomposition with a similar char yield.

## 7. DSC of OS



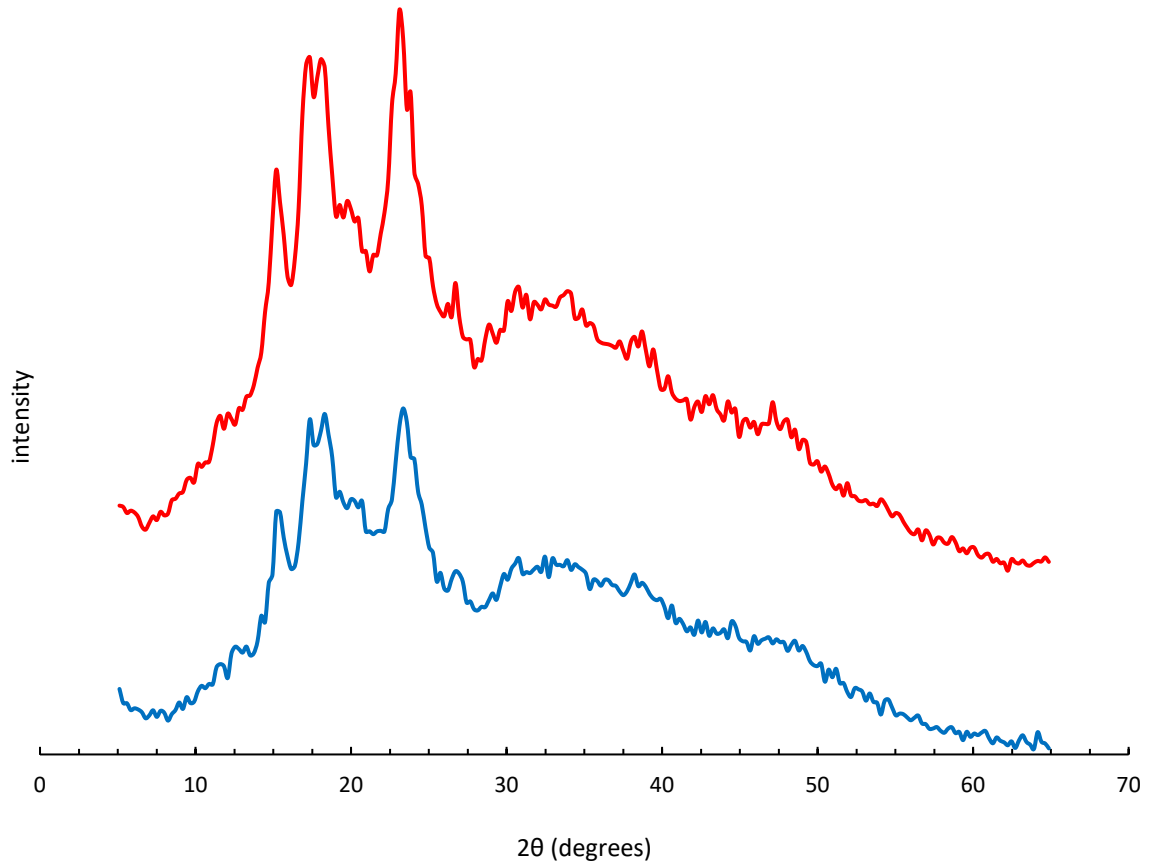
**Figure S3.** DSC curves from the first (dotted curves) and second (solid curves) cycles (top) and the second heating cycle (bottom) with a truncated y-axis to emphasize the glass transition showing starch (red) and OS (blue). The first heating cycles exhibit the desorption of adsorbed water whereas the  $T_g$  (denoted by vertical black line) of native starch (midpoint at 98.4 °C) and OS (midpoint at 89.6 °C) can be observed in the second heating cycles. Cycles three through five were identical to the second heating cycles in all cases. Cooling cycles one through five are nearly overlapping for both samples.

**Table S1.** Average values of thermal properties obtained from duplicate TGA analysis

	moisture (%) <sup>a</sup>	T <sub>d</sub> (°C) <sup>b</sup>	char yield (%) <sup>b</sup>
corn starch	10.7 ± 1.5	293.5 ± 0.5	9.6 ± 1.2
<b>OS</b>	9.2 ± 0.1	268.4 ± 0.4	11.6 ± 0.1

<sup>a</sup> Determined by the mass loss at 140 °C. <sup>b</sup> Defined as the 5% mass loss, normalized to the dry mass to exclude the impact of adsorbed water. <sup>c</sup> The residual mass at 800 °C, normalized to the dry mass to exclude the impact of adsorbed water.

## 8. PXRD of OS



**Figure S4.** Stacked XRD analysis of corn starch (red) and **OS** (blue) showing a slight decrease in crystallinity upon modification (20.9 and 15.8 % for corn starch and **OS**, respectively). A 12-point boxcar average was applied to the data for clarity.

## 9. CS<sub>2</sub> Extraction Data for OSS<sub>x</sub>

**Table S2.** CS<sub>2</sub> Extraction Data

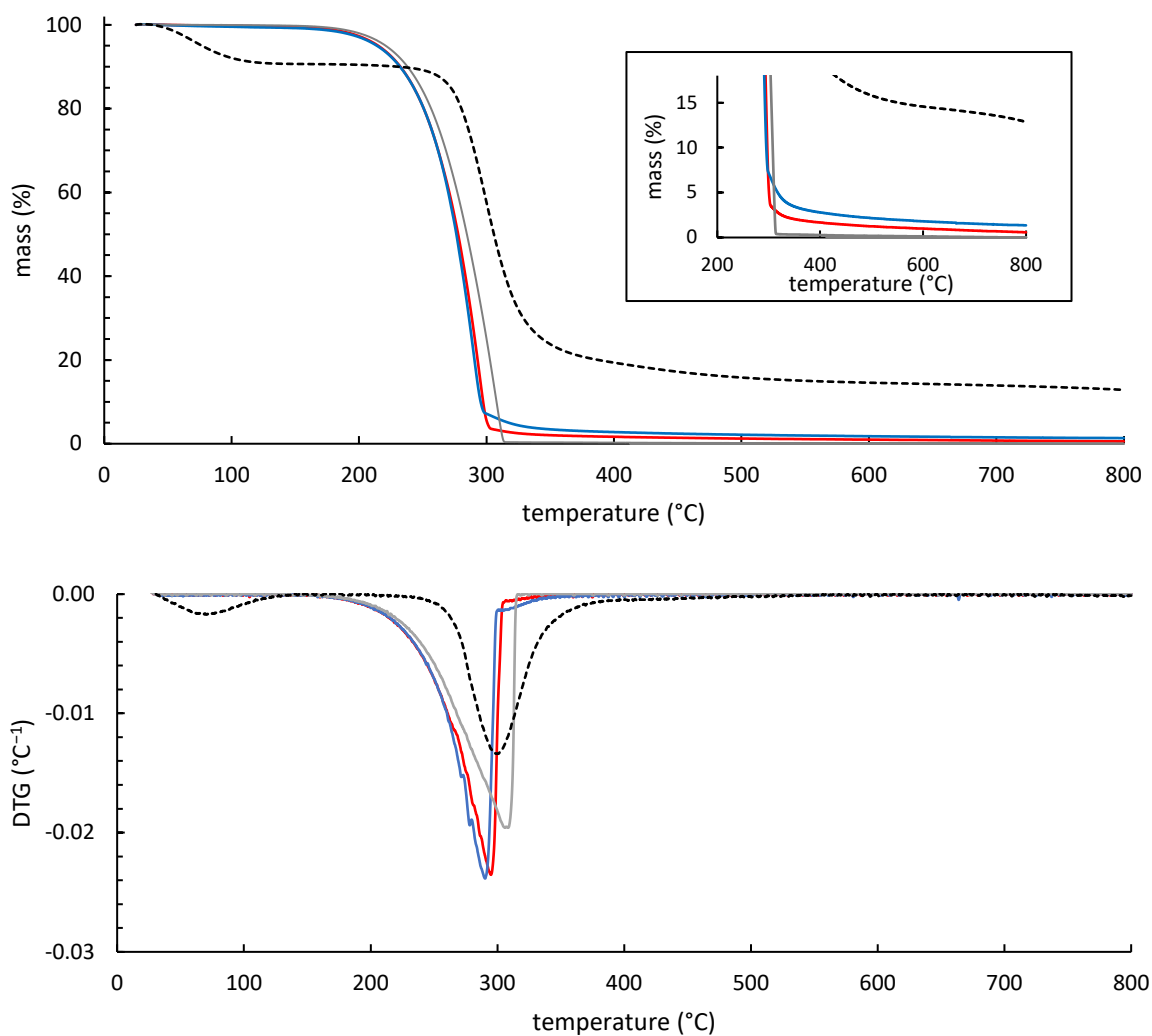
	CS <sub>2</sub> Soluble (%) <sup>a</sup>	sulfur rank <sup>b</sup>
<b>OSS<sub>95</sub></b>	86	340
<b>OSS<sub>90</sub></b>	82	140

<sup>a</sup>Determined by fractionation studies. <sup>b</sup>See equation X for calculations

$$Sulfur\ Rank = \left\{ \frac{S_{cov}}{O_{olefin}} \right\} / 2 = \left\{ \frac{\frac{m_{ins} - m_{org}}{32.06}}{\frac{m_{org}}{167.67 * 0.0263}} \right\} \quad \text{(Supplemental Equation 2)}$$

Data from extraction by CS<sub>2</sub> allowed for the calculation of the number of moles of sulfur atoms covalently incorporated ( $S_{cov}$ ) into the materials by subtracting the amount of organic material ( $m_{org}$  % organic in the composite · recovered total mass) from the total mass of the insoluble fraction ( $m_{ins}$ ) and dividing by the atomic mass of sulfur (32.06 amu). The number of olefins in the insoluble fraction was calculated by dividing the amount of organic material ( $m_{org}$ ) by the average monomer molecular weight determined from titrations (167.67 g·mol<sup>-1</sup>) multiplied by the percentage of monomers containing olefin functionalities.

## 10. TGA of $OSS_x$



**Figure S5.** TGA mass loss curves and inset (top) and corresponding DTG curves (bottom) for  $OSS_{95}$  (red),  $OSS_{90}$  (blue), sulfur (gray solid line), and  $OS$  (black dotted line). The data reveals that the crosslinking reaction decreases the thermal stability of the composite materials relative to both sulfur and  $OS$ . The more crosslinked material,  $OSS_{90}$ , revealed a slightly lower primary decomposition temperature with a more pronounced secondary decomposition and larger residual mass at 800 °C due to the presence of  $OS$ .

**The author primarily responsible for particular CRediT<sup>3</sup> roles is noted below:**

Moira K. Lauer: Data curation, Formal analysis, Investigation, Validation, Formal analysis, Roles/Writing - original draft

Andrew G. Tennyson: Resources

Rhett C. Smith: Conceptualization, Funding Acquisition, Methodology, Formal analysis, Resources, Supervision, Writing - review & editing

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