Supplemental Information for

# Robust, Remeltable and Remarkably Simple to Prepare Biomass-Sulfur Composites

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#### Allylation of Peanut Shells (APS)

Ground peanut shells were obtained from Golden Peanut and Tree Nuts (Product ES). This procedure was based on known procedures for allylating lignin and cellulose.<sup>1, 2</sup> Sodium hydroxide pellets (152.2 g, 3.806 mol) were dissolved in 1.5 L of DI water in a three liter round bottom flask equipped with a Teflon coated stir bar. Once the solution had cooled to room temperature, ground peanut shells (30.38 g) were added and the slurry was rapidly stirred for 10 minutes. The slurry was placed in the freezer until completely frozen. The slurry was thawed in a 25 °C thermostat-controlled water bath over a stir plate with stirring turned on to avoid gel formation. Urea (213.2 g, 3.550 mol) was added portion-wise and the slurry was stirred until the urea had completely dissolved. Allyl bromide (144.0 mL, 201.6 g, 1.666 mol) was added dropwise at 30 °C over two days under the exclusion of light. The reaction was allowed to continue for a total of 5 days. The reaction mixture was acidified with 9.0 M sulfuric acid to bring the pH to 2. Four hundred mL of acetone was added to the slurry. The slurry was filtered in 200 mL aliquots rinsing each aliquot with DI water (4 x 200 mL) and hexanes (2 x 25 mL). The solid was collected and dried at 40 °C under a static vacuum (70 cmHg), the vacuum being released and reapplied frequently. This process yielded 19.120 g of solid material. Due to the heterogeneous nature of the resultant solid, it was passed through an ASTM no. 50 sieve (300 μm cutoff), grinding with a mortar and pestle when necessary. After 2 passes through the mortar and pestle there was 15.076 g of finely ground product termed APS (see S1). The product was determined to contain 1.90 ± 0.04 mmol olefin functionalities/ g product. Moisture content as determined by duplicate TGA experiments: 4.3 wt%. Elemental analysis: C: 52.5% H: 6.4%

#### Allylation of cellulose<sup>2, 3</sup>

Allyl cellulose was prepared by previously reported methods with some modifications. NaOH pellets (151.0 g, 3.776 mol) was dissolved in 1.5 L of DI H<sub>2</sub>O in a RBF equipped with a Teflon coated stir bar. After cooling, microcrystalline cellulose (30.13 g, 185.8 mmol) was added and stirred rapidly to form a suspension. The suspension was placed in the freezer overnight and then thawed over a stir plate to avoid gel formation. Urea (210.8 g, 3.509 mol) was added and the flask was placed in a 30 °C thermostat-controlled water bath. Allyl bromide (144 mL, 202 g, 1.67 mol) was added dropwise under the exclusion of light and the reaction was continued for a total of 5 days. The slurry was neutralized with HCl (6.0 M). The slurry was centrifuged at 7500 RPM for 15 minutes until all of the material had been collected. The solid was resuspended in 1 L of DI H2O and centrifuged 10 times to remove residual allyl bromide and salts. The solid was then suspended in 2 L of 10% (v/v) acetic acid and blended in a commercial blender in 400 mL batches for 1 minute followed by centrifuging at 7500 RPM for 20 minutes. This process was repeated a total of 5 times. The solid was then dried and analyzed by TGA but found to still contain a significant portion of inorganic salts so was, ground, sieved through a number 50 sieve, resuspended in 1 L of DI water, centrifuged at 7500 RPM for 15 minutes and finally washed 3 more times with DI water and 2 times with acetone before final drying. The final purified yield was 1.888 g.

#### **Preparation of mAPS**

Allyl lignin (prepared and characterized in Karunarathna et al.<sup>1</sup>) containing DS = 6.0 mmol·g<sup>-1</sup>, was combined with alkali lignin DS = 0 mmol·g<sup>-1</sup> to obtain allyl lignin with a DS of 4.2 mmol·g<sup>-1</sup>. This was then sifted through an ASTM no. 50 sieve. Allyl cellulose (DS= 0.37 mmol·g<sup>-1</sup>) was also sifted through an ASTM no. 50 sieve. Allyl cellulose (DS= 0.37 mmol·g<sup>-1</sup>) was also sifted through an ASTM no. 50 sieve. Allyl cellulose (DS= 0.37 mmol·g<sup>-1</sup>) was also sifted through an ASTM no. 50 sieve. Allyl lignin (DS= 4.2 mmol·g<sup>-1</sup>) was mixed with allyl cellulose at a 2:3 ratio, respectively to obtain **mAPS** (DS= 1.9 mmol·g<sup>-1</sup>). Moisture content as determined by duplicate TGA experiments: 5.4 wt%.

#### **Preparation of dfPS**

Defatted peanut shells were prepared by taking oven-dried and ground peanut shells (PS) and suspending in hexanes 5% (w/v) and allowing it to stir for 24 hours. The peanut shells were filtered and dried in a vacuum oven at 40 °C (70 cmHg), the vacuum being released and reapplied frequently. Moisture content as determined by duplicate TGA experiments: 9.5 wt%.

The filtrate was dried under reduced pressure at 40 °C. The filtrate residue (~1 wt% of initial PS mass) was dissolved in  $CDCl_3$  and <sup>1</sup>H NMR was acquired (spectrum in MS).

#### **Titration Methods<sup>2</sup>**

#### General Notes:

Deoxygenated water was prepared by boiling for 1 hour. The water was transferred to a round bottom flask that had been purged with nitrogen for 10 minutes and was sealed with a septum. The headspace was purged with nitrogen for 15 minutes after transferring to the round bottom.

Starch solution (1 %) was prepared by suspending soluble starch (1.0 g) in 5 mL of DI water, adding it to 100 mL of boiling water, and boiling the solution for 5 minutes. The solution was stirred as it cooled to room temperature to prevent film formation.

 $K_2Cr_2O_7$  was dried until constant mass was obtained in a 200 °C oven.

Calculations were carried out using the "dry" mass of peanut shells and allylated peanut shells by considering the adsorbed water determined by averaging two TGA runs (taken as % mass at 120 °C).

Pyridinium tribromide (PTB) was freshly recrystallized twice in ethanol and dried under dynamic vacuum at 30 °C for 14 hours. When not in use, PTB was stored in a vial wrapped in aluminum foil in the freezer.

# CAUTION: adding PTB to ethanol may evolve trace quantities of Br<sub>2</sub>. This process should always be conducted in a fume hood.

#### Standardization of Sodium Thiosulfate<sup>4</sup>

Potassium dichromate (0.0712–0.0756 g) was weighed by difference into a 250 mL Erlenmeyer flask. Deoxygenated water (50 mL) was added to the flask. Hydrochloric acid (1.5 mL, 6.0 *M*) and potassium iodide ( $2.0 \pm 0.2$  g) were rapidly added. The flask was covered with parafilm, swirled, and placed into a dark drawer for 10 minutes. The parafilm was removed from the flask, starch solution was added (2.5 mL, 1%), and the solution was immediately titrated. The endpoint was denoted as a transition from a dark blue opaque solution to a clear, light blue solution. Titrant concentration was determined with <0.3% relative standard deviation.

#### Standardization of Pyridinium Tribromide<sup>2, 3, 5</sup>

PTB was weighed by difference (0.156–0.247 g) into a 250 mL Erlenmeyer flask. Ethanol (20 mL) was added and the solution was swirled for 30 seconds. Potassium iodide ( $2.0 \pm 0.2$  g) was added to the flask with 20 mL of DI water and the flask was swirled to dissolve the potassium iodide. Starch solution (1.5 mL, 1%) was added and the solution was immediately titrated. The concentration of PTB was determined with <0.7% relative standard deviation.

#### **Titration of PS and Allylated Peanut Shells**

PTB (0.191–0.247 g) and **PS** or **APS** (0.098–0.140 g) were weighed by difference into a 250 mL Erlenmeyer flask. Ethanol (20 mL) was added and the solution was swirled for 30 seconds.

Potassium iodide  $(2.0 \pm 0.2 \text{ g})$  was added to the flask with 20 mL of DI water and the flask was swirled to dissolve the potassium iodide. Starch solution (1.5 mL, 1%) was added and the solution was immediately titrated. Due to the color of the peanut shells, an over-titrated sample was used as a reference point to determine the endpoint. The flask was allowed to sit undisturbed for 15 minutes once the flask appeared to be the same color as the over-titrated sample. The sample was continually titrated and left for 15 minutes until the color remained unchanged during the 15-minute wait.

## APS have a concentration of 1.90 ± 0.04 mmol alkene/g material

PS was determined to have a concentration of 0.17 ± 0.05 mmol alkene/g material

#### Synthesis of composite materials

## **APS**<sub>95</sub>

Sulfur (9.500 g) and allylated peanut shells (0.522 g) were combined in a 20 mL glass vial equipped with a Teflon coated stir bar. The system was sealed with a polypropylene cap punctured with a needle to prevent sulfur sublimation while allowing water vapor from allylated peanut shells to escape. The reaction was submerged into an oil bath set to 180 °C and allowed to continue, with stirring, for one day. Mass loss (compensating for water loss): 1.3%. Elemental analysis observed: S: 94.70% C: 3.04% H: 0.0%

## APS<sub>90</sub>

Sulfur (9.000 g) and allylated peanut shells (1.048 g) were combined in a 20 mL glass vial equipped with a Teflon coated stir bar. The system was sealed with a polypropylene cap punctured with a needle to prevent sulfur sublimation while allowing water vapor from allylated peanut shells to escape. The reaction was submerged into an oil bath set to 180 °C and allowed to continue, with stirring, for three days. Mass loss (compensating for water loss): 3.0%. Elemental analysis observed: S: 90.94% C: 5.33% H: 0.26%

#### **PS**<sub>95</sub>

Peanut shells were first dried in an oven at 30 °C for 24 h under a static vacuum (70 cmHg), the vacuum being released and reapplied frequently and sieved through an ASTM no. 50 sieve. TGA analysis determined 9.5 wt% residual moisture. Sulfur (9.500 g) and peanut shells (0.552 g) were combined in a 20 mL glass vial equipped with a Teflon coated stir bar. The system was sealed with a polypropylene cap punctured with a needle to prevent sulfur sublimation while allowing water vapor from allylated peanut shells to escape. The reaction was submerged into an oil bath set to 180 °C and allowed to continue, with stirring, for one day. Mass loss (compensating for water loss): 0.4%. Elemental analysis observed: S: 90.66% C: 1.87% H: 0.0%

#### PS<sub>90</sub>

Peanut shells were first dried in an oven at 30 °C for 24 h under a static vacuum (70 cmHg), the vacuum being released and reapplied frequently and sieved through an ASTM no. 50 sieve. TGA analysis determined 9.5 wt% residual moisture. Sulfur (9.003 g) and peanut shells (1.106 g) were combined in a 20 mL glass vial equipped with a Teflon coated stir bar. The system was sealed with a polypropylene cap punctured with a needle to prevent sulfur sublimation while allowing water vapor from allylated peanut shells to escape. The reaction was submerged into an oil bath set to 180 °C and allowed to continue, with stirring, for three days. Mass loss (compensating for water loss): 3.9%. Elemental analysis observed: S: 90.21% C: 6.04% H: 0.0%

#### mAPS<sub>95</sub>

Sulfur (9.498 g) and **mAPS** (0.502 g) were combined in a 20 mL glass vial equipped with a Teflon coated stir bar. The system was sealed with a polypropylene cap punctured with a needle to prevent sulfur sublimation while allowing water vapor from **mAPS** to escape. The reaction was submerged into an oil

bath set to 180 °C and allowed to continue, with stirring, for three days. Mass loss (compensating for water loss): 0.6%. Elemental analysis observed: S: 93.27% C: 2.97% H: 0.12%

## mAPS<sub>90</sub>

Sulfur (9.002 g) and **mAPS** (1.002 g) were combined in a 20 mL glass vial equipped with a Teflon coated stir bar. The system was sealed with a polypropylene cap punctured with a needle to prevent sulfur sublimation while allowing water vapor from **mAPS** to escape. The reaction was submerged into an oil bath set to 180 °C and allowed to continue, with stirring, for three days. A dross had formed on the surface of the reaction indicating a limit in solubility as was seen with other allyl lignin materials so that no further analysis was performed on this material.<sup>1</sup> Mass loss (compensating for water loss): 1.0%.

#### dfPS<sub>95</sub>

Sulfur (9.502 g) and **dfPS** (0.523 g) were combined in a 20 mL glass vial equipped with a Teflon coated stir bar. The system was sealed with a polypropylene cap punctured with a needle to prevent sulfur sublimation while allowing water vapor from **dfPS** to escape. The reaction was submerged into an oil bath set to 180 °C and allowed to continue, with stirring, for three days. Elemental and further analysis was not acquired due to inhomogeneity as determined by SEM analysis.

#### dfPS<sub>90</sub>

Sulfur (9.001 g) and **dfPS** (1.091 g) were combined in a 20 mL glass vial equipped with a Teflon coated stir bar. The system was sealed with a polypropylene cap punctured with a needle to prevent sulfur sublimation while allowing water vapor from **dfPS** to escape. The reaction was submerged into an oil bath set to 180 °C and allowed to continue, with stirring, for three days. Elemental and further analysis was not acquired due to inhomogeneity as determined by SEM analysis.

# Digital Images of APS



**Figure S1.** Allylated peanut shells that were unable to pass through the no. 50 sieve (left vial) after two passes with the material that was able to pass through the sieve and were used to make composites (the three right vials). All analyses and materials preparation were conducted with finely ground allylated peanut shells.





**Figure S2.** IR spectra of microcrystalline cellulose (black curve) and allyl cellulose (purple curve) showing **a**) the spectra from 600 to 4000 cm<sup>-1</sup> and **b**) the regions demonstrating successful allylation on a fragmented axis and with a y-scale to maximize the difference for each region. Stretching for sp<sup>2</sup> hybridized C–H is seen at 3085 cm<sup>-1</sup>. Stretching for C=C can be seen at 1645 cm<sup>-1</sup>. Bending modes for C–H of a monosubstituted alkene can be seen at 1022, 995, and 927 cm<sup>-1</sup>.



**Figure S3.** IR spectra of alkali lignin (black curve) and allyl lignin (purple curve) showing **a**) the spectra from 600 to 4000 cm<sup>-1</sup> **b**) the regions demonstrating successful allylation on a fragmented axis and with a y-scale to maximize the difference for each region. Stretching for sp<sup>2</sup> hybridized C–H is seen at 3075 cm<sup>-1</sup>. Stretching for C=C can be seen at 1645 cm<sup>-1</sup>. Bending modes for C–H of a monosubstituted alkene can be seen at 987, and 922 cm<sup>-1</sup>.

#### IR spectra of PS and APS



**Figure S4**. Stacked IR spectra of **PS** (black curve) and **APS** (purple curve) showing **a**) the spectra from 400 to 4000 cm<sup>-1</sup> and **b**) the regions demonstrating successful allylation on a fragmented axis and with a *y*-scale to maximize the difference for each region. Stretching for sp<sup>2</sup> hybridized C–H is seen at 3080 cm<sup>-1</sup>. Stretching for C=C can be seen at 1645 cm<sup>-1</sup>. Bending modes for C–H of a monosubstituted alkene can be seen at 995, and 924 cm<sup>-1</sup>.



**Figure S5.** TGA of allyl cellulose (purple), allyl lignin (black), and allylated peanut shells (gray) as mass loss curves (upper) and their respective stacked DTG curves (lower) showing the influence of both allyl cellulose and allyl lignin on the thermal decomposition of allylated peanut shells. The inflection points of the major mass losses were 332, 346, and 406 °C due to allyl cellulose, allylated peanut shells, and allyl lignin, respectively.





**Figure S6.** TGA mass loss curves as an average of two runs for starting materials: **PS** (black, bold), **dfPS** (green, overlaid on the black curve), **APS** (red), and **mAPS** (blue) and data obtained from curves (lower). Unsurprisingly, **PS** and **dfPS** produced near identical results while **APS** and **mAPS** also produced near identical results.

material	water adsorbed <sup>1</sup>	onset <sup>2</sup>	char yield <sup>3</sup>	char yield of dry
				sample
PS	9.5	273.7	24.7	22.4
	± 1.0	± 0.8	± 0.6	± 0.8
dfPS	9.5	297.9	22.4	22.4
	± 1.0	± 1.6	± 0.5	± 0.8
APS	4.3	289.4	20.5	19.6
	± 0.0	± 0.0	± 0.4	± 0.4
mAPS	5.4	297.9	18.7	18.7
	± 0.8	± 1.6	± 2.7	± 2.5

Table S1. Data obtained from TGA as an average of two runs.

<sup>1</sup> Water adsorbed was determined by the mass lost by 120 °C. <sup>2</sup> Onset was determined by finding the point of intersection of the baseline (after mass loss) and the line tangent to the major mass loss step. <sup>3</sup> Char yield was determined by the residual mass at 800 °C. <sup>4</sup> Char yield of dry sample was determined by multiplying the char yield by the mass at 120 °C to screen out moisture effects on the char yield.

DSC plots of APS and PS



**Figure S7.** DSC curves of **PS** (black) and allylated peanut shells (purple) from the third heating and cooling cycles. Two glass transition temperatures were observed for **PS** at 82 and 126 °C where allylated peanut shells exhibited only one  $T_g$  at 77 °C (where  $T_g$  was determined by the inflection point of the transition).

#### IR spectra of PS<sub>95</sub>, APS<sub>95</sub>, and mAPS<sub>95</sub>



**Figure S8**. Stacked IR spectra of **PS**<sub>95</sub> (blue curve), **APS**<sub>95</sub> (green curve), **mAPS**<sub>95</sub> (red curve), and allylated peanut shells (black curve) showing **a**) the spectra from 600 to 4000 cm<sup>-1</sup> and **b**) the regions demonstrating consumption of allyl functionalities (for **APS**<sub>95</sub> and **mAPS**<sub>95</sub>) after reaction with sulfur, denoted by gray vertical lines. Stretching for sp<sup>2</sup> hybridized C–H is seen at 3080 cm<sup>-1</sup>. Stretching for C=C can be seen at 1645 cm<sup>-1</sup>. Bending modes for C–H of a monosubstituted alkene can be seen at 995, and 924 cm<sup>-1</sup>.

#### IR spectra of PS<sub>90</sub> and APS<sub>90</sub>





**Figure S9**. Stacked IR spectra of **PS**<sub>90</sub> (blue curve), **APS**<sub>90</sub> (green curve), and allylated peanut shells (black curve) showing **a**) the spectra from 600 to 4000 cm<sup>-1</sup> and **b**) the regions demonstrating consumption of allyl functionalities (for **APS**<sub>90</sub>) after reaction with sulfur, denoted by gray vertical lines. Stretching for sp<sup>2</sup> hybridized C–H is seen at 3080 cm<sup>-1</sup>. Stretching for C=C can be seen at 1645 cm<sup>-1</sup>. Bending modes for C–H of a monosubstituted alkene can be seen at 995, and 924 cm<sup>-1</sup>.<sup>3</sup>

# TGA curves of composites



**Figure S10**. TGA mass loss curves of  $PS_{90}$  (black),  $APS_{90}$  (red),  $mAPS_{95}$  (blue),  $APS_{95}$  (green), and  $PS_{95}$  (purple) with an inset showing the curves from 250–400 °C.

# DTG curves of composites



Figure S11. DTG derivative curves of  $PS_{90}$  (black),  $APS_{90}$  (red),  $mAPS_{95}$  (blue),  $APS_{95}$  (green), and  $PS_{95}$  (purple) where a high temperature transition (>300 °C) can be clearly observed for  $APS_{95}$  and  $PS_{95}$ .

## DSC curve for APS<sub>95</sub>



**Figure S12.** DSC curves of **APS**<sub>95</sub> showing the third heating cycle (solid black) with a cold crystallization peak at 31 °C (7.4 J·g<sup>-1</sup>) and a melting peak due to the presence of crystalline sulfur at 116 °C ( $-38.9 \text{ J} \cdot \text{g}^{-1}$ ) and third cooling cycle (dotted black) revealing a crystallization at 18 °C (22.7

## DSC curve for APS<sub>90</sub>



**Figure S13.** DSC curves of **APS**<sup>90</sup> showing the third heating cycle (solid black) with a cold crystallization peak at 28 °C ( $6.5 \text{ J} \cdot \text{g}^{-1}$ ) and a melting peak due to the presence of crystalline sulfur at 117 °C ( $-36.3 \text{ J} \cdot \text{g}^{-1}$ ) and third cooling cycle (dotted black) revealing a crystallization at 17 °C (18.3

## DSC curve for PS<sub>95</sub>



**Figure S14.** DSC curves of **PS**<sub>95</sub> showing the third heating cycle (solid black) with a cold crystallization peak at 28 °C (6.5 J·g<sup>-1</sup>) and a melting peak due to the presence of crystalline sulfur at 117 °C ( $-36.3 J \cdot g^{-1}$ ) and third cooling cycle (dotted black) revealing a crystallization at 17 °C ( $18.3 J \cdot g^{-1}$ ).

## DSC curve for PS<sub>90</sub>



**Figure S15.** DSC curves of **PS**<sub>90</sub> showing the third heating cycle (solid black) with a cold crystallization peak at 34 °C (5.8 J·g<sup>-1</sup>) and a melting peak due to the presence of crystalline sulfur at 117 °C (-31.6 J·g<sup>-1</sup>) and third cooling cycle (dotted black) revealing a crystallization at 14 °C (16.5 J·g<sup>-1</sup>).

## DSC curve for mAPS<sub>95</sub>



**Figure S16.** DSC curves of **mAPS**<sub>95</sub> showing the third heating cycle (solid black) with a cold crystallization peak at 27 °C (7.4 J·g<sup>-1</sup>) and a melting peak due to the presence of crystalline sulfur at 117 °C ( $-38.0 \text{ J}\cdot\text{g}^{-1}$ ) and third cooling cycle (dotted black) revealing a crystallization at 16 °C (19.4

#### SEM images for APS<sub>95</sub>



**Figure S17.** Images of **APS**<sub>95</sub> generated by scanning electron microscopy (top) with element mapping by energy-dispersive X-ray analysis showing sulfur (red), carbon (green), and oxygen (blue) showing high magnification (left panels, 50  $\mu$ m scalebar) and lower magnification (right panels, 100  $\mu$ m scalebar). Apparent inhomogeneity in the high magnification images (sulfur and oxygen, not apparent in carbon mapping) is a small fragment of silicone from sample preparation observable in the silicon element mapping.

# SEM images for **PS**<sub>95</sub>



**Figure S18.** Images of **PS**<sub>95</sub> generated by scanning electron microscopy (top) with element mapping by energy-dispersive X-ray analysis showing sulfur (red), carbon (green), and oxygen (blue) showing high magnification (left panels, 50  $\mu$ m scalebar) and lower magnification (right panels, 100  $\mu$ m scalebar).

## SEM images for PS<sub>90</sub>



**Figure S19.** Images of **PS**<sub>90</sub> generated by scanning electron microscopy (top) with element mapping by energy-dispersive X-ray analysis showing sulfur (red), carbon (green), and oxygen (blue) showing high magnification (left panels, 50  $\mu$ m scalebar) and lower magnification (right panels, 100  $\mu$ m scalebar).

#### SEM images for mAPS<sub>95</sub>



**Figure S20.** Images of **mAPS**<sub>95</sub> generated by scanning electron microscopy (top) with element mapping by energy-dispersive X-ray analysis showing sulfur (red), carbon (green), and oxygen (blue) showing high magnification (left panels, 25 μm scalebar) and lower magnification (right panels, 100 μm scalebar).

#### SEM images for dfPS<sub>90</sub>



**Figure S21.** Images of **dfPS**<sub>95</sub> generated by scanning electron microscopy (top) with element mapping by energy-dispersive X-ray analysis showing sulfur (red), carbon (green), and oxygen (blue) showing high magnification (left panels, 25  $\mu$ m scalebar) and lower magnification (right panels, 100  $\mu$ m scalebar).

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