Recyclable, Sustainable, and Stronger than Portland Cement: A Polymer from Unseparated Biomass and Fossil Fuel Waste

Moira K. Lauer, Menisha S. Karunarathna, Andrew G. Tennyson, and Rhett C. Smith*

Table of Contents

1. Instrumentation and experimental methods	.1
2. Allylation of peanut shells	.2
3. Ordinary Portland cement (OPC) sample preparation and analysis	.3
4. Titration Methods	4
5. Synthesis of APS ₉₅	6
6. Synthesis of AA95	.7
Figure S1 Digital image of allylated peanut shells	.8
Figure S2 Digital images of APS95	.9
Figure S3 SEM image and EDX results of APS ₉₅ 10	0
Figure S4 IR of allylated cellulose1	11
Figure S5 IR of allylated lignin1	12
Figure S6 IR of peanut shells (PS) and allylated peanut shells1	13
Figure S7 IR of APS ₉₅ 1	14
Figure S8 TGA of allyl cellulose, allyl lignin, and APS1	٤5
Figure S9 TGA of APS ₉₅ 1	16
Figure S10 DSC of PS and allylated peanut shells1	L 7
Figure S11 DSC of APS ₉₅ 1	18
Figure S12 Stress-strain plot of APS95 in a flexural deformation mode1	19
Figure S13 Stress-strain plot of APS ₉₅ plotted with OPC in a flexural deformation mode2	20
Table S1 CS2 extraction data for PS, allylated peanut shells, and APS95	21
References	22

1. Instrumentation and Methods

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 cm⁻¹ at ambient temperature. TGA was recorded (Mettler Toledo TGA 2 STAR^e System) over the range 20–800 °C with a heating rate of 10 °C min[−] ¹ under a flow of N₂ (100 mL·min⁻¹). DSC was acquired (Mettler Toledo DSC 3 STAR^e System) over the range -60 to 150 °C with a heating rate of 5 °C·min⁻¹ under a flow of N₂ (200 mL⁻¹min⁻¹). Each DSC measurement was carried out over five heat-cool cycles. DMA was performed (Mettler Toledo DMA 1 STAR^e System) in single cantilever mode. DMA samples were cast from silicone resin molds (Smooth-On Oomoo® 30 tincure). Samples were manually sanded to ensure uniform dimensions. The sample dimensions were approximately 18 x 7 x 1.5 mm and the clamping force was 5 cN·m. The force was varied from 0 to 10 N with a ramp rate of 0.2 N·min⁻¹ measured isothermally at 25 °C. CS₂ extractions were prepared by suspending 0.3 g of finely ground material in 20 mL of CS₂, allowing the solid to settle for 30 minutes, pipetting off the supernatant into a separate vial, and adding another 20 mL of CS₂. This process was repeated an additional 3 times so that a total of 5 washes was performed. The CS₂ was evaporated under a flow of N_2 and each vial was weighed to determine the fraction that was soluble (collected as supernatant) or insoluble (remained in the initial vial). SEM was acquired on a Schottky Field Emission Scanning Electron Microscope SU5000 operating in variable pressure mode with an accelerating voltage of 15 keV. Compressional analysis was performed on a Mark-10 ES30 test stand equipped with a M3-200 force gauge (1 kN maximum force with ±1 N resolution). Compression cylinders were prepared by pouring the molten polymer sample into silicone resin molds (made from Smooth-On Oomoo® 30) and allowing the samples to solidify as they cooled to room temperature. Cylinders had diameters of approximately 6 mm and heights of approximately 10 mm. Samples were manually sanded to ensure uniform dimensions.

2. Allylation of Peanut Shells

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.¹⁻² 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 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 μ m 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 (see S1). The product was determined to contain 1.90 ± 0.04 mmol olefin functionalities/ g product.

3. Ordinary Portland Cement Sample Preparation and Analysis

Making cement samples:

- Ordinary Portland cement was first sifted through as ASTM no. 50 sieve (300 µm cutoff)
- OPC was mixed w/ DI water (2 parts by weight OPC to 1 part DI water)
- Cement was injected into a silicone mold with a disposable syringe

Curing cement samples:

- Day 0- the mold was wrapped tightly in plastic wrap and left at ambient conditions
- Day 2- the plastic wrap was removed from the mold and the mold was placed in a humidity chamber (~70–50% humidity)
- Day 5- The samples were removed from the mold and placed in a different humidity chamber (~85% humidity)
- Day 7- The cylinders were moved to ambient conditions
- Day 8- The samples were placed in a 100 °C oven
- Day 9- The samples were moved to a 200 °C oven
- Day 12- The samples were removed from the oven, allowed to cool, and their densities and compressive strength were measured

Based on this curing procedure and 5 replicates analysis

density= $1.5 \pm 0.0 \text{ g} \cdot \text{cm}^{-3}$

compressive strength= 19.1 ± 4.4 MPa

4. Titration Methods²

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.

K₂Cr₂O₇ 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 140 °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 Br₂. This process should always be conducted in a fume hood.

Standardization of Sodium Thiosulfate

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 *M*) and potassium iodide (2.0 ± 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

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 ± 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 allylated peanut shells (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.

Allylated peanut shells 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

5. Synthesis of APS₉₅

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 24 hours. After reaction had completed, the vial was weighed to determine a mass loss of 1.3% (accounting for moisture in allylated peanut shells). The solid was then remelted at 170 °C and cast into silicon molds for mechanical analysis. Elemental analysis: S: 94.70% C: 3.04% H: 0.0%

6. Synthesis of AA95

Allyl lignin (prepared and characterized in Karunarathna, et al.¹) with DS = 6.0 mmol·g⁻¹, was combined with alkali lignin DS = 0 mmol·g⁻¹ to obtain allyl lignin with a DS of 4.2 mmol·g⁻¹. This was then sifted through an ASTM no. 50 sieve. Allyl cellulose (prepared based on a literature procedure³) with DS = 0.37 mmol·g⁻¹ as determined by iodometric titration, was also sifted through an ASTM no. 50 sieve. Allyl lignin (DS = 4.2 mmol·g⁻¹) was mixed with allyl cellulose at a 2:3 ratio, respectively to obtain the allylcellulose/allyllignin material **AA** (DS = 1.9 mmol·g⁻¹).

Sulfur (9.498 g) and **AA** (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 allylated peanut shells to escape. The reaction was submerged into an oil bath set to 180 °C and allowed to continue, with stirring, until homogenized, for 72 hours. After reaction had completed, the vial was weighed to determine a mass loss of 0.6% (accounting for moisture in AA). The solid was then remelted at 170 °C and cast into silicon molds for mechanical analysis. Elemental analysis: S: 93.27% C: 2.97% H: 0.12%.



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. Digital images of **APS**₉₅ **a)** cylinder for compressional analysis, top view, **b)** cylinder for compressional analysis, side view, and **c)** cuboid for flexural analysis



Figure S3. SEM image of **APS**₉₅ with EDX mapping for sulfur (red), carbon (cyan), and oxygen (purple) and calculated composition based on EDX showing good dispersion of elements in the composite material. Note: this data is of a larger area than that in the manuscript to show that dispersion was consistent even at lower magnification.



Figure S4. IR spectra of microcrystalline cellulose (black curve) and allyl cellulose (purple curve) showing **a**) the spectra from 600 to 4000 cm⁻¹ 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 sp² hybridized C–H is seen at 3085 cm⁻¹. Stretching for C=C can be seen at 1645 cm⁻¹. Bending modes for C–H of a monosubstituted alkene can be seen at 1022, 995, and 927 cm⁻¹.



Figure S5. IR spectra of alkali lignin (black curve) and allyl lignin (purple curve) showing **a**) the spectra from 600 to 4000 cm⁻¹ **b**) the regions demonstrating successful allylation on a fragmented axis and with a y-scale to maximize the difference for each region. Stretching for sp² hybridized C–H is seen at 3075 cm⁻¹. Stretching for C=C can be seen at 1645 cm⁻¹. Bending modes for C–H of a monosubstituted alkene can be seen at 987, and 922 cm⁻¹.



Figure S6. Stacked IR spectra of **PS** (black curve) and allylated peanut shells (purple curve) showing **a**) the spectra from 00 to 4000 cm⁻¹ 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 sp² hybridized C–H is seen at 3080 cm⁻¹. Stretching for C=C can be seen at 1645 cm⁻¹. Bending modes for C–H of a monosubstituted alkene can be seen at 995, and 924 cm⁻¹.



Figure S7. IR spectrum of **APS**₉₅ showing **a**) the spectra from 600 to 4000 cm⁻¹ and **b**) a fragmented axis with selected regions of interest showing quantitative consumption of alkene functionalities within limits of detection. Purple lines denote the stretches attributable to olefin functionalities in allylated peanut shells.



Figure S8. 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 S9. TGA data for **APS**₉₅ showing **a**) the mass loss curve and **b**) the DTG curve. The inflection point of the major mass loss, which could be attributed to sulfur, occurred at 288 °C while the inflection point for the secondary mass loss occurred at 316 °C attributable to the influence of allylated peanut shells.



Figure S10. 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).



Figure S11. DSC curves of **APS**₉₅ showing **a**) the third heating cycle (solid black) with a cold crystallization peak at 31 °C and a melting peak due to the presence of orthorhombic sulfur at 116 °C and third cooling cycle (dotted black) revealing a crystallization at 18 °C. Also shown is **b**) five consecutive cooling cycles showing the variability of the crystallization exotherm: cooling cycle 1 (black), cooling cycle 2 (red), cooling cycle 3 (blue), cooling cycle 4 (green), and cooling cycle 5 (purple).



Figure S12. Characteristic stress-strain curve of **APS**₉₅ (purple) with the region of plastic deformation denoted (black). Based on the average of replicate runs, **APS**₉₅ was determined to have a flexural strength of 4.9, a flexural modulus of 690 MPa and a modulus of resilience of 180 Pa.



Figure S13. Stress-strain curve of **APS**₉₅ (black) and **OPC** (purple) undergoing a flexural deformation. The red lines indicate material failure. While initial behavior is similar, **APS**₉₅ exhibited a 30% higher flexural strength of 4.8 MPa compared to the flexural strength of **OPC** (3.7 MPa). Additionally, outside of the linear range, **APS**₉₅ exhibited a lower strain for the same stress, indicating that it's a stiffer material when undergoing a flexural deformation.

material	amount of sample extracted	% soluble	% insoluble	EA of insoluble fraction	sulfur rank
PS	0.302	99	1	N/A ¹	N/A ²
APS	0.304	90	10	N/A ¹	N/A ²
APS ₉₅	0.307	89	11	99.3%	20

Table S1. CS₂ extraction data, elemental analysis (EA), and resulting calculation of sulfur rank for PS, APS, and APS₉₅

¹elemental analysis was not acquired for these results. ² No sulfur was present in the material

The author primarily responsible for each particular CRediT role is noted below: ⁴

Moira K. Lauer: Data curation, Formal analysis, Investigation, Validation, Formal analysis, Writing – review and editing

Andrew G. Tennyson: Resources

Rhett C. Smith: Conceptualization, Funding Acquisition, Methodology, Formal analysis, Resources, Supervision, Writing - original draft

References Cited

1. 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. *Journal of Materials Chemistry A: Materials for Energy and Sustainability* **2019**, *7* (26), 15683-15690.

2. 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. Sustainable Syst.* **2019**, *3* (10), 1900062.

3. 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. *Polymer Chemistry* **2015**, *6* (18), 3543-3548.

4. Allen, L.; Brand, A.; Scott, J.; Altman, M.; Hlava, M., Credit where credit is due. *Nature* **2014**, *508*, 312-313.