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Recyclable, sustainable, and stronger than portland cement: a composite from unseparated biomass and fossil fuel waste†

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A composite was prepared from biomass and waste sulfur from fossil fuel refining. The composite has higher compressive and flexural strength than portland cement. Avoiding expensive biomass separation and achieving metrics exceeding those of commercial products is a notable step towards a green economy.

Effective biomass utilization is the centrepiece of a sustainable future. Fuels, petrochemical plastics and portland cement building materials must ultimately be replaced with greener surrogates such as biofuels, plant plastics and carbon-negative cement products. A primary barrier to the affordability of biomass products is the high cost of separating lignin, cellulose and other components.[1] Current leading technologies for valorising biomass are energy or solvent intensive – pyrolysis, steam explosion, extraction and filtration or pressing, *etc.*[2–10] Herein is reported a method to prepare a composite using unseparated biomass as a starting material. The other comonomer is sulfur, a waste product of fossil fuel refining. The biomass derivative and sulfur are combined to form composite **APS₉₅** (Fig. 1), a material having markedly improved flexural and compressional strength *versus* portland cement.

Efforts to unveil sustainable fuels and plastics have attracted significantly more attention than finding sustainable portland cement replacements, yet portland cement manufacturing is responsible for 7–10% of anthropogenic greenhouse gas emissions as well as accounting for 30% of global material utilization.[11–14] Couple this with the fact that global portland cement production has soared by more than 150% since 2000, and the need for sustainable cement surrogates to counter climate change is evident. Furthermore, only a small percentage of portland cement and traditional plastic produced are recycled,[15] so a more readily recyclable alternative should be sought.[14]

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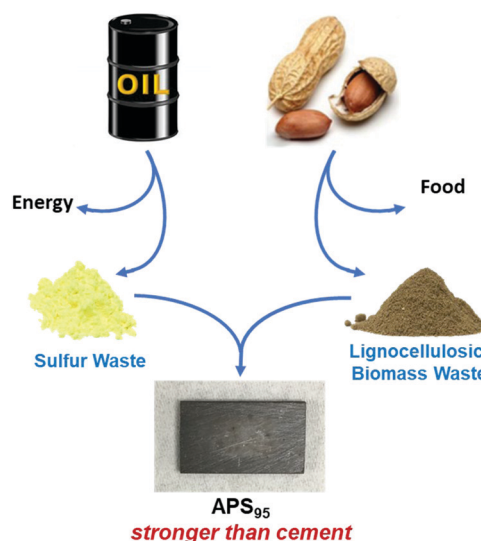
Fig. 1 A carbon-negative cement product (**APS₉₅**) is prepared by harnessing waste products of energy production and agricultural industries.

We previously demonstrated that purified samples of either cellulose[16] or lignin[17–19] could be modified with olefin moieties that allowed them to undergo inverse vulcanization, a 100% atom-economical process whereby the olefin units are crosslinked with sulfur.[20–40] We previously observed that it was necessary to modify lignin[17] or cellulose[16] with olefin moieties for effective mixing with molten sulfur under the typical inverse vulcanization conditions. For the current work, we thus hypothesized that a raw biomass sample treated to incorporate olefinic units could undergo inverse vulcanization to give a composite in an overall two-step process that does not require separation of the biomass. Finely ground peanut shells were used as the biomass source to test this hypothesis. Of the ∼44 megatons of peanuts produced each year, ∼25–30% of the mass – over 11 megaton/year – is peanut shells.[41] The dry mass of peanut shells is comprised by 87% lignocellulose (2:3 lignin:cellulose ratio), with ∼1% peanut oil, 7% total protein, and the balance inorganic salts (ash content). In order to append
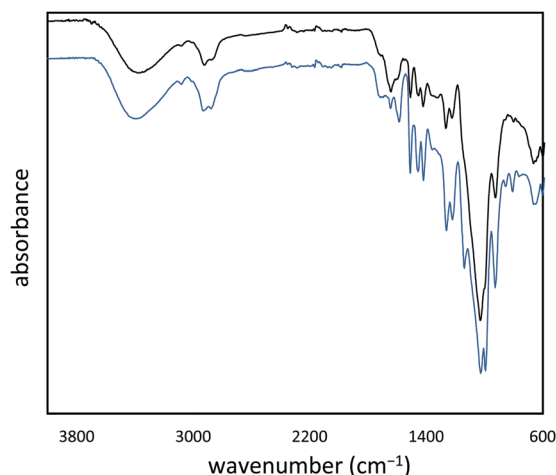
Fig. 2 Stacked IR spectra of allylated biomass (black) and addition spectrum of allyl cellulose and allyl lignin in a 3:2 ratio (blue) demonstrating that the composition of allylated peanut shell material is nearly identical to a mixture of independently-synthesized allyl cellulose and allyl lignin.
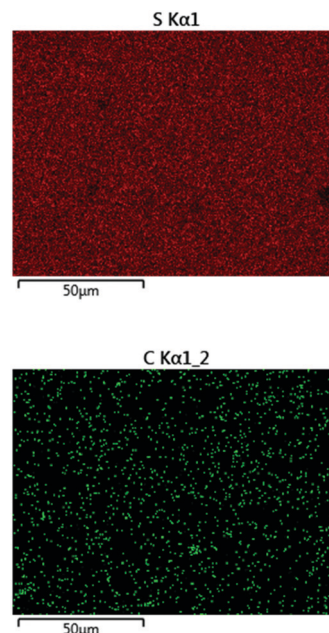

Fig. 3 Surface analysis of **APS₉₅** by EDX revealed the homogeneous distribution of sulfur (upper) and carbon (lower) on the composite surface.

olefin units to the lignin and cellulose components of the shells, they were treated with allyl bromide in alkaline aqueous solution and filtered. The allylated biomass was characterized by infrared (IR) spectroscopy by comparison to spectra for independently prepared samples of allyl cellulose[42] and allyl lignin.[17] The IR spectrum for allylated biomass is nearly identical to the spectrum that results from adding the scaled spectra for ally cellulose and allyl lignin (Fig. 2). The total amount of olefins in allylated biomass was further quantified to be 1.90 ± 0.04 mmol g^{-1} by iodometric titration and elemental composition consistent with the structure was confirmed by elemental analysis. The allylated biomass was subjected to inverse vulcanization (Scheme 1) with 95 wt% elemental sulfur to give composite **APS₉₅** as a visually homogeneous black solid (Fig. 1). The homogeneity was further confirmed by scanning electron microscopy (SEM) imaging with element mapping by energy dispersive X-ray analysis (EDX), which show uniform distribution of sulfur and carbon in the material (Fig. 3 and ESI† Fig. S3). These data confirm the absence of fibres or particles that might be responsible for mechanical reinforcement the material. IR spectroscopy confirms consumption of the alkene units within detection limits (ESI† Fig. S7). **APS₉₅** is remeltable and can be fabricated into various shapes by simple melt processing and shaping in stainless steel or silicone moulds. Many high sulfur- content materials prepared by the inverse vulcanization route contain extractable sulfur in addition to the sulfur that is covalently bound as crosslinking chains. The presence of free sulfur has proven important for the mechanical strength,
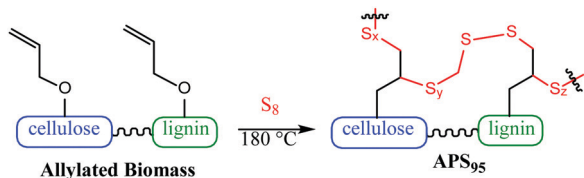
processability and stability of polymeric sulfur domains in previous lignin–sulfur or cellulose sulfur materials prepared by inverse vulcanization.[16,17] Sulfur that is not covalently bound is readily extractable into CS_2. The CS_2-extractable sulfur accounted for 89% of the mass of **APS₉₅**. This data, and the amount of covalently bound sulfur known, allowed a sulfur rank of 20 to be calculated for **APS₉₅**. This sulfur rank compares well to the sulfur rank for other cellulose–sulfur materials but is somewhat lower than the rank observed in lignin–sulfur composites comprising 95 wt% sulfur (sulfur rank of 31–48).

Thermogravimetric analysis (TGA) revealed a major mass loss step characteristic of elemental sulfur with an onset of 252 °C whereas the influence of allyl peanut shells could be seen by a second mass loss step with an inflection point at 316 °C (ESI† Fig. S9). Differential scanning calorimetry (DSC) demonstrated characteristic peaks for sulfur melting (115–120 °C) and crystallization (10–30 °C) as well as a cold crystallization at ~ 30 °C (ESI† Fig. S11). Similar cold crystallization peaks are reported in the DSC analysis of other cellulose–sulfur composites (**PCS$_x$** where x = wt% sulfur) and lignin–sulfur composites (**SAL$_x$** and **CLS$_x$**, where x = wt% sulfur).[16–18]

The mechanical properties of **APS₉₅** are the most striking finding from this study. Many efforts have been undertaken to understand the mechanical and other properties of plant-derived composites having high sulfur content.[43–50] Despite the presence of just 5 wt% organic crosslinker in the composite, significant physical strength enhancement over elemental sulfur was observed. An elemental sulfur sample breaks upon mounting in the instrument at the minimum clamping force. Previous work likewise revealed significant mechanical property enhancement, with an 8-fold increase in storage modulus when sulfur was crosslinked with just 1 wt% of oleic acid.[35] Previous biopolymer–sulfur

Scheme 1 Synthesis of **APS₉₅**.

Table 1 Select physical properties for biopolymer–sulfur composites and portland cement

	Sulfur rank	Compressive strength (MPa)	Flexural strength/ modulus (MPa)	Modulus of resilience (kPa)
APS95	20	35.7 ± 1.8	4.8/690	0.2
Portland cement[a]	NA	17	3.7/580[b]	0.6[b]
AA95	X	17.1	ND	ND
PCS90	24	ND	Too brittle	Too brittle
PCS85	31	ND	3.2[c]/320	2.7
PCS80	22	ND	3.8[c]/520	1.8
CLS95	31	ND	2.1/156	ND
SAL95	48	ND	2.1/90	ND

[a] Compressive strength is for the minimum requirement of ACI 332. Flexural data refers to portland cement without added fines or aggregate, mixed with a 1:2 water to cement ratio, and cured very gradually over an eight-day time period and after drying at 200 °C to screen out humidity effects. [b] Data refers to portland cement without added fines or aggregate, mixed with a 1:2 water to cement ratio, and cured very gradually over a twelve day time period and after drying at 200 °C to screen out humidity effects. [c] Sample could not be measured beyond this level due to instrumental limitations.

composites PCS_x, SAL_x and CLS_x, for example generally have flexural strengths lower or similar to that of portland cement (Table 1).[16–18] The flexural strength of APS95 is 30% higher than that of portland cement, making it a good candidate for certain applications where flexural stress is applied. In contrast to flexural strength, the compressional strength of a material reflects its ability to support a load applied perpendicular to its surface. The high compressional strength of portland cement is the primary feature that has made it the most-produced synthetic product of civilization. When previously-reported biopolymer–sulfur composites are handled, it is clear that they lack substantial compressional strength. In contrast, when APS95 was handled it exhibited substantial resistance to crushing, leading to further study of its compressional strength. When quantified, the compressional strength of APS95 was found to be 35.7 ± 1.8 MPa, more than twice that required by building regulation ACI 332 for residential building (17 MPa, Fig. 4).[51] The compressional strength of APS95 also exceeds that of light bricks used in wall construction (7 MPa). It should be noted that the compressional strength of portland cement varies with aging time and humidity. While much higher values are often quoted for materials referred to as "portland cement",

those are often materials having added fines (sand) and/or aggregate (gravel), which can improve compressional strength by over an order of magnitude. Neither the portland cement nor APS95 had any added fines or aggregate for the current study. The remarkable improvement in compressional strength of APS95 versus previously-reported cellulose– or lignin–sulfur composites must derive from the synergistic combination of lignin with cellulose. Specifically, the allylated biomass could contain naturally-occurring lignin–cellulose crosslinks or potentially base-catalysed esterification of lignin carboxylates during the biomass etherification reaction. It is this same combination primarily of crosslinked lignin and cellulose that provides plants and timber-built structures with their impressive mechanical strength despite the fact that either lignin or cellulose alone has very poor mechanical strength. Prior work on high sulfur content material prepared by inverse vulcanization showed that he modulus can be increased by nearly an order of magnitude upon increasing the crosslink density by only 1%.[35]

In an effort to confirm the hypothesis that the high compressional strength is due to lignin–cellulose crosslinking, separately-prepared allyl cellulose and allyl lignin were blended in the same cellulose:lignin ratio and having the same unsaturation per unit mass as in the allylated peanut shells used to prepare APS95. This synthetic blend was polymerized with 95 wt% sulfur under the same conditions used to prepare APS95, yielding AA95. The compressional strength of AA95 was only about 50% that of APS95 (Table 1 and Fig. 4). Using unseparated biomass thus improves material properties over materials having the same putative composition.

Although the high compressional strength of APS95 is promising for its use as a structural cement replacement, APS95 requires hot casting. This means that blocks of APS95 would need to be made by melting it and pouring it into moulds, while paving with APS95 would require hot-casting in a manner similar to asphalt paving. Shell oil has developed a sulfur asphalt, Thiopave® that can be cast in this way, and several stretches of Thiopave® highways showed durability on par or better than traditional asphalt installations.[52–54]

Conclusions

In conclusion, we report a protocol to prepare a composite from waste products of energy and agriculture industries. The biomass can be used as a comonomer without separation after one simple modification step in aqueous solution, followed by a 100% atom economical polymerization step. The resulting composite (APS95) has mechanical properties that significantly exceed that of portland cement. APS95 also outperforms portland cement in its recyclability by simple melt processing and is a carbon-negative/carbon sequestering product whereas portland cement production is one of the leading sources of anthropogenic CO_2. Given the similar cellulose and lignin content for other agricultural biproducts, we anticipate that the approach herein should be applicable to leveraging a wide range of lignocellulosic biomass waste products, thus allowing for their straightforward conversion to durable structural materials.
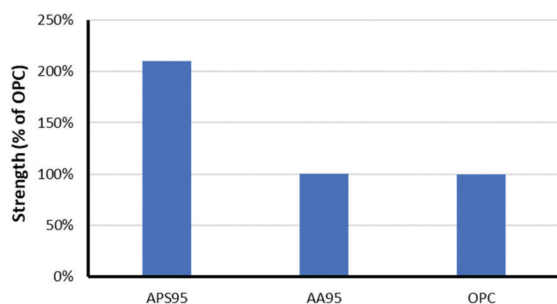

Fig. 4 Comparison of compressive strengths for materials. OPC is ordinary portland cement.

Studies involving application of the current procedure to other biomass resources are underway.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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