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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

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

Moira K. Lauer,^a Menisha S. Karunarathna,^a Andrew G. Tennyson^{ib} and Rhett C. Smith^{ib}*^a



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 cellulose¹⁶ 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 lignin¹⁷ or cellulose¹⁶ 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

^a Department of Chemistry, Clemson University, Clemson, South Carolina, 29634, USA. E-mail: rhett@clemson.edu

^b Department of Materials Science and Engineering, Clemson University, Clemson, South Carolina, 29634, USA

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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)
APS ₉₅	20	35.7 ± 1.8	4.8/690	0.2
Portland cement ^c	NA	17	3.7/580 ^b	0.6 ^b
AA95	X	17.1	ND	ND
PCS ₉₀	24	ND	Too brittle	Too brittle
PCS ₈₅	31	ND	3.2 ^c /320	2.7
PCS ₈₀	22	ND	3.8 ^c /520	1.8
CLS ₉₅	31	ND	2.1/156	ND
SAL ₉₅	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 the 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 compressive 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 CO₂. 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.

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