Evaluation of Animal Fats and Vegetable Oils as Comonomers in Polymer Composite Synthesis: Effects of Plant/Animal Sources and Comonomer Composition on Composite Properties

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Rancid animal fats unsuitable for human or animal food production represent low-value and abundant, yet underexploited organic chemical precursors. The current work describes a strategy to synthesize high sulfur-content materials (HSMs) that directly utilizes a blend of partially hydrolyzed chicken fat and plant oils as the organic comonomers, following up on analogous reactions using brown grease in place of chicken fat. The reaction of sulfur and chicken fat with either canola or sunflower oil yielded crosslinked polymer composites $\mathbf{CFS_x}$ or $\mathbf{GFS_x}$, respectively (x = wt% sulfur, varied from 85%–90%). The composites exhibited compressive strengths of 24.7–31.7 MPa, and flexural strengths of 4.1–5.7 MPa, exceeding the value of established construction materials like ordinary Portland cement (compressive strength ≥17 MPa required for residential building, flexural strength 2–5 MPa). The composites also exhibited thermal stability up to 215–224 °C. The simple single-step protocol described herein represents a way to upcycle an affordable and previously unexploited animal fat resource to form structural composites via the atom economical inverse vulcanization mechanism.

1. Introduction

Environmental sustainability that complements economic growth and stability represents a critical challenge for civilization. Industrial growth in the last century has relied heavily on fossil fuels to meet material and energy production demands.[1] Socioeconomic pressures and environmental policies are evolving to address resultant deleterious environmental effects as human endeavors strive towards a zero-carbon-emission future.[2] New technologies that more effectively leverage waste materials and renewable resources to replace extant high carbon-footprint technologies will be critical to achieving these goals.[3] Manufacturing legacy structural materials such as ordinary Portland cement (OPC), for example, is responsible for >8% of the global anthropogenic carbon dioxide emissions, with ≈1 kg of CO_2 released for every kilogram of OPC produced,[4] notwithstanding the tremendous water resource use and environmental damage caused by mining the mineral resources required for the process.[5] With the production of OPC forecast to increase precipitously for at least the next few decades, developing sustainable alternatives such as geopolymers[6,7] or sulfur cement/concrete[8–14] will be central to attenuating climate change and achieving a circular economy.

High sulfur-content materials (HSMs) like sulfur cement represent a potential alternative to traditional construction materials like Portland cement. These HSMs can exhibit excellent mechanical properties including compressive strength exceeding that of OPC, high chemical resistance unattainable with current affordable mineral cement, and abrasion resistance similar to that of marble.[15] The production of HSMs may also be a viable approach to remediating enormous stockpiles (>7 Mt/y) of sulfur accumulated in waste sites from fossil fuel desulfurization.[16–18] HSMs can be conveniently prepared via the atom economical inverse vulcanization reaction wherein sulfur and olefins react to form crosslinked polymers/composites via C–S bond-forming reactions.[19] A panoply of potentially renewable olefin sources have been used in this process, including polysaccharides,[20–24] lignin,[25–28] raw lignocellulosic biomass,[29,30] terpenoids,[31–40] guaiacol,[41] algae oils,[42–44] plant oils,[45–55] and fatty acids.[56–60]

Rendered animal fats and used cooking oils represent abundant, low-value olefin feedstocks for potential use in the inverse vulcanization process. Rancid, partially hydrolyzed animal fats unsuitable for human or animal nutritional use have high free fatty acid (FFA) levels, and have been used in biodiesel production.[61] The high free fatty acid content present in these animal fats, however, represents a challenge for traditional biodiesel production schemes due to the poor compatibility of

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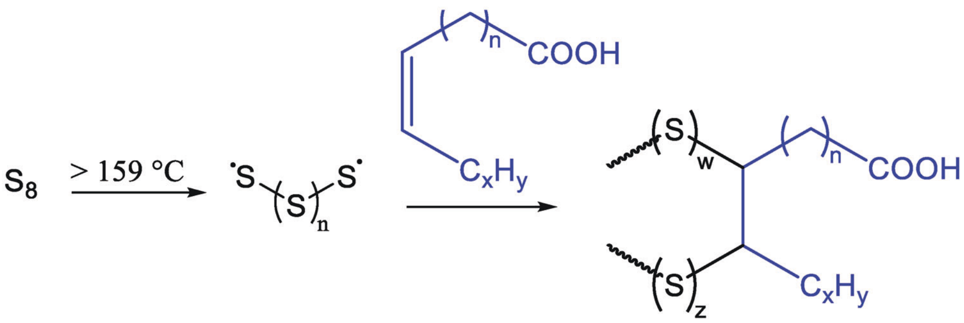

Scheme 1. Inverse vulcanization example wherein the unsaturated units of fatty acid substituents undergo reaction with thermally-generated sulfur radical species.

carboxylic acid moieties with alkaline catalysts. High FFA animal fats thus remain an underutilized but abundant and affordable resource.

High-FFA chicken fat is of particular interest in the context of the current study, with over 2 billion pounds of chicken fat rendered annually in the US alone.[62] The fatty acid chains in chicken fat are a mixture of saturated chains (primarily C14:0, myristic acid; C16:0, palmitic acid; C18:0, stearic acid, where the C*x*:*y* notation indicates the carbon chain length, *x*, and the number of olefins in the chain, *y*) and unsaturated chains (primarily C18:1, oleic acid; C18:2, linoleic acid; and C18:3, linolenic acid). The vulcanization of fats and oils has been used to prepare factice for rubber compatibilization and property modulation for nearly a century.[63–65] We previously reported on similar reactions between oleic acid and sulfur to form HSMs like $\mathbf{ZOS}_x$ (from oleic acid and *x* wt. % elemental sulfur, ranging from 59–99 wt. %) with storage moduli of up to 400 MPa.[60] Similarly, the reaction of sulfur with pure linoleic acid (to give $\mathbf{ZPLS}_x$) or technical grade mixtures of fatty acids (to give $\mathbf{ZLS}_x$) yielded materials having flexural strengths of 1.0–2.0 MPa.[59] Although those FFA-sulfur composites had significantly lower mechanical strength than OPC, a more recent study revealed that more durable composites were achieved when a mixture of plant oil and brown grease (animal fat with FFA content >15%) underwent inverse vulcanization to yield composites $\mathbf{CanBG}_x$ (using canola oil) or $\mathbf{SunBG}_x$ (using sunflower oil, where *x* represents the wt. % sulfur, varied from 85%–90%).[66] Some of these high-FFA fat-containing composites had mechanical properties significantly exceeding those of OPC, with compressive strengths of 28.7–35.9 MPa, and flexural strengths of 6.5–8.5 MPa.

In the current study we evaluate the potential for another high-FFA animal product, partially rancid chicken fat, as a substrate for inverse vulcanization with the goal of forming durable composites analogous to those accomplished using brown grease. Herein, composites were synthesized using chicken fat and plant oils as the organic monomer (**Scheme 1**, in which chicken fat is represented in highly simplified form as an unsaturated fatty acid chain). We abbreviate these composites for discussion as $\mathbf{CFS}_x$ and $\mathbf{GFS}_x$, where we use C for canola oil, G girasol (sunflower) oil, F for fat, and S for sulfur, and *x* indicates the wt. % sulfur, varied from 85%–90%. The thermal, morphological, and mechanical properties of these composites will be discussed.

2. Results and Discussion

2.1. Synthesis and Chemical Characterization of Composites

The fatty acid composition of the chicken fat used in this study was analyzed by FAMES analysis following the previously-reported protocol,[67] confirming that the chicken fat was primarily comprised of saturated fatty acids such as myristic acid (C14:0), palmitic acid (C16:0), stearic acid (C18:0), and unsaturated fatty acids such as palmitoleic acid (C16:1), oleic acid (C18:1), and linoleic acid (C18:2) (Figure S1–S2, Supporting Information).

The chicken fat was also analyzed by ^{1}H NMR spectrometry with added internal standard 2,3,4,5,6-pentafluorobenzaldehyde (full spectrum provided in Figure S3, Supporting Information). The analysis of chicken fat with the internal standard allowed for the quantification of the total unsaturation content present in the mixture of fatty acids. The total unsaturation content was quantified using the ratio of integrations for the olefinic proton resonance from the chicken fat (≈5.5 ppm) versus that for the internal standard aldehydic proton resonance (≈10.5 ppm). This analysis allowed quantification of the total olefin content of the chicken fat to be 2.70 mmol g^{-1}.

The chicken fat used in this study was not readily miscible with elemental sulfur under the reaction conditions (180 °C with rapid mechanical stirring). Similarly poor miscibility was also noted in the previously-reported study on the reaction of high-FFA brown grease with elemental sulfur.[66] In that study, excellent miscibility was achieved by adding plant oils (canola or sunflower oil) to the reaction mixture with an animal fat: plant oil ratio of 1:1 or 2:1. Miscibility was similarly achieved in the current study by blending the chicken fat in a 1:1 mass ratio with either canola or sunflower oil. The reaction of the fat/oil mixtures with sulfur at 180–185 °C with rapid mechanical stirring resulted in a homogeneous reaction mixture that was heated for 24 h to give composites of 90 wt.% sulfur, 5 wt.% chicken fat, and 5 wt.% of either canola oil (to yield $\mathbf{CFS}_{90}$) or sunflower oil (to yield $\mathbf{GFS}_{90}$) (**Figures 1**A–B). Reactions were also successful using 85 wt.% sulfur, 10 wt.% chicken fat, and 5 wt.% of either canola oil (to yield $\mathbf{CFS}_{85}$) or sunflower oil (to yield $\mathbf{GFS}_{85}$) (Figure 1C,D). Composites were formed in quantitative yield in all cases, demonstrating the high atom economy of the inverse vulcanization process. Upon cooling reaction mixtures to room temperature, composites were black solids that could be readily remelted and formed

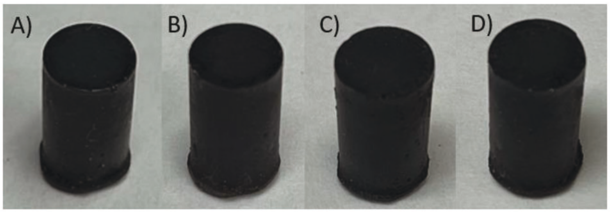

Figure 1. Samples of **CFS$_{90}$** A), **GFS$_{90}$** B), **CFS$_{85}$** C), and **GFS$_{85}$** D) shaped for compressive strength testing.

into various shapes, such as cylinders used for compressional testing (vide infra), by pouring into silicon moulds (Figure 1).

Scanning electron microscopy with elemental mapping by energy dispersive X-ray analysis (SEM-EDX) showed that **CFS$_x$** and **GFS$_x$** form microscopically homogeneous materials. These composites exhibited uniform distributions of carbon, oxygen, and sulfur (Figures S4 and S5, Supporting Information), providing additional evidence for successful homogenization of the comonomer mixture during reaction.

The FT-IR spectra for **CFS$_x$** and **GFS$_x$** composites (Figure S6–S7, Supporting Information) showed the reduction of intensity for the symmetrical and asymmetrical stretches attributable to alkene C–H stretches (2850–2900 cm^{-1}), providing evidence for consumption of olefin units during the reaction. The concomitant emergence of a peak at 795 cm^{-1} was attributed to the C–S stretches for bonds formed during the inverse vulcanization reaction. Similarly, after the inverse vulcanization reaction using a blend of brown grease and triglycerides to yield composites **CanBG$_x$** and **SunBG$_x$**, the emergence of a peak at 795 cm^{-1} and the reduction in the *sp*^{2}-C–H stretches (≈2920 cm^{-1}) was also observed and confirmed the consumption of the olefins during the reaction and the successful formation of the C–S bonds.

The sulfur in HSMs like **CFS$_x$** and **GFS$_x$** has often been reported to exist in the composites as a mixture of entrapped sulfur species and sulfur covalently-incorporated into the crosslinked network via C–S bond formation. The precise nature of the entrapped "dark sulfur" species is not yet fully understood and is the subject of ongoing studies by the Hasell group.[68,69] An initial estimate of entrapped sulfur can be conveniently made by extracting it from the composite using CS$_2$. Predictably, between 69–89% of the sulfur present in the **CFS$_x$** and **GFS$_x$** composites was stabilized as covalently attached crosslinked catenates (Table S1, Supporting Information). Elemental microanalysis confirmed that extractable species comprised ≥98% sulfur and that the organic network material was not extracted into the CS$_2$-soluble fraction. The organic-containing fraction of the composites could not be dissolved in CS$_2$, toluene, hexanes, THF, chloroform, DMSO, methanol, or water.

Using the known covalently-incorporated sulfur content and total initial olefin content in each composite allowed for quantification of the average number of sulfur atoms in crosslinking sulfur catenates (known as the sulfur rank, **Table 1**). Following the convention from previous studies, this calculation is reported here with the assumption that each monomer olefin results in the formation of two C–S bonds in the product, though a recent report indicates that, at least in one case, the actual makeup of products of inverse vulcanization may be more complicated and consist of a mixture of sites having one or two C–S bonds per monomer olefin.[4] In this calculation, we excluded participation of the extractable free sulfur from the calculation and considered only the covalent sulfur. The sulfur rank is then calculated by dividing the number of moles of sulfur atoms by the number of moles of olefin in a given mass of the sample. In the case of the **CFS$_x$** and **GFS$_x$** composites, the sulfur rank calculated in this way varied from 31–61 sulfur atoms, consistent with sulfur ranks previously reported for composites prepared analogously to **CFS$_x$** and **GFS$_x$** but with brown grease in place of chicken fat, which has reported sulfur ranks of 32–60 (Table 1).

2.2. Thermal and Morphological Properties of Composites

Thermogravimetric analysis (TGA) was used to assess the thermal stability of the composites. The **CFS$_x$** and **GFS$_x$** composites exhibited decomposition temperatures (T_d, here defined as the temperature at which 5% mass loss is observed upon heating the samples under a N$_2$ atmosphere) of 215–224 °C (Table 1 and Figure S8, Supporting Information). In all the composites, a major decomposition step was observed attributed to the sublimation of sulfur from the composite. The char yield in the composites increased expectedly with increasing organic content and was relatively low in all cases (2–15 wt.%, Table 1).

Thermal morphological transitions were analyzed by differential scanning calorimetry (DSC, Table 1 and Figure S9–S10, Supporting Information) over the range of −60–140 °C. All the **CFS$_x$** and **GFS$_x$** composites exhibited the characteristic peak attributable to melting of orthorhombic sulfur at ~117°C and both **CFS$_{85}$** and **GFS$_{85}$** exhibited glass transitions (T_g) at −36 °C

Table 1. Thermal and morphological properties of composites with comparison to elemental sulfur.

Comp'd	T_d[a)] /°C	T_m[b)] /°C	$T_{g,\ DSC}$[c)] /°C	Cold xstal peaks/°C	ΔH_m J/g	ΔH_{cc} J/g	%$_{xtal}$[d)]	Percent soluble fraction[e)]	Sulfur Rank[f)]	Char Yield (%)
CFS$_{90}$	224	117.7	NA	–58.8, 38.5	36.5	2.1, 5.3	65	11	61	2
GFS$_{90}$	218	117.7	NA	–58.8, 38.2	31.9	2.6, 5.2	54	16	57	6
CFS$_{85}$	215	117.9	–35.5	–58.8	26.5	3.3	52	30	31	11
GFS$_{85}$	216	116.5	–35.8	–58.8	22.5	3.5	42	31	32	15
S$_8$	229	118.5	NA	NA	44.8	NA	100	0	NA	NA

[a)] The temperature at which the 5% mass loss was observed. [b)] The temperature at the peak minimum of the endothermic melting from the third heating cycle. [c)] Glass transition temperature. [d)] Percent crystallinity: the reduction of percent crystallinity of each sample was calculated with respect to sulfur (normalized to 100%). [e)] Percent of extractable sulfur in each sample after CS$_2$ extractions. [f)] Average number of sulfur atoms per crosslinking catenate assuming the formation of two C–S bonds to each monomer olefin.

Table 2. Physical properties of composites compared to other previously reported high sulfur content materials.

Materials	Compressive strength (MPa)	Flexural strength/ modulus (MPa)	Sulfur Rank	Reference
CFS$_{90}$	24.7 ± 1.6	4.1/130	61	This work
GFS$_{90}$	29.7 ± 0.9	4.4/260	57	This work
CFS$_{85}$	29.7 ± 1.9	5.6/200	31	This work
GFS$_{85}$	31.7 ± 0.9	5.7/140	32	This work
CanBG$_{90}$	32.0 ± 0.9	6.5/420	60	54
SunBG$_{90}$	35.9 ± 0.7	7.7/460	54	54
CanBG$_{85}$	28.7 ± 1.0	8.5/700	37	54
SunBG$_{85}$	33.2 ± 0.2	7.7/560	32	54
CanS	9.3 ± 1.0	ND	ND	39
SunS	17.8 ± 3.1	ND	ND	39
ZPLS$_{90}$	ND	2.0/70	ND	50
ZPLS$_{95}$	ND	1.6/50	ND	50
ZLS$_{95}$	ND	1.3/80	ND	50
Portland cement	17.0[a]	3.7/580	NA	[a]

[a] Minimum required for residential building foundations by the American Concrete Institute, Committee 332, **2006**, ACI 332.1R-06.

attributed to polymeric sulfur chains. Thermograms for **CFS$_{90}$** and **GFS$_{90}$** exhibited cold crystallization peaks at ≈40 °C attributed to the partial organization of the polymeric domains commonly observed in HSMs having crystalline and amorphous domains.

The percent crystallinity of **CFS$_x$** and **GFS$_x$** compared to that of crystalline orthorhombic sulfur was quantified using the integrations of the cold crystallization and melting enthalpies observed in the DSC spectra. These calculations further confirmed that the **CFS$_x$** and **GFS$_x$** composites had amorphous and crystalline domains, with percent crystallinities of 42–65. (Table 1). The percent crystallinities of composites **CFS$_x$** and **GFS$_x$** were somewhat higher than those of composites made from brown grease and sulfur (**CanBG$_x$** and **SunBG$_x$**) which had percent crystallinities between 1–21%, attributable to greater cross-liking afforded by higher olefin content provided by brown grease (3.24 mmol g^{-1}) than by the chicken fat (2.70 mmol g^{-1}) used in the current study.

2.3. Mechanical Properties of Composites

The **CFS$_x$** and **GFS$_x$** composites were remelted at 160 °C and reshaped in cylinders and rectangular prisms (Figure 1) to test compressive and flexural strengths, respectively. The composites were allowed to stand at room temperature for 4 days prior to testing to allow for direct comparison of mechanical properties to those of similarly tested HSMs. Once cooled, the composites are nearly full strength and develop 10%–15% additional strength over the four-day period but then do not change over the next week.[22,39,40,70,71]

The compressive strength of the **CFS$_x$** and **GFS$_x$** composites was measured by mechanical test stand analysis in triplicates (data are summarized in **Table 2** and **Figure 2**A; stress-strain plots are provided in Figures S11–S12 in the Supporting Information). Composites **CFS$_{90}$**, **GFS$_{90}$**, **CFS$_{85}$**, and **GFS$_{85}$** had high compressive strengths of 24.7, 29.7, 29.7, and 31.7 MPa, respectively.

HSMs prepared from the reaction between sulfur with brown grease (**CanBG$_x$** and **SunBG$_x$**) exhibited compressive strengths between 28.7–35.9 MPa. Composites **CanBG$_x$** and **CFS$_x$** were synthesized from the reaction of sulfur with a blend of canola oil and brown grease or chicken fat, respectively. It was observed that **CanBG$_{90}$** exhibited a higher compressive strength (32.0 ± 0.9 MPa) than **CFS$_{90}$** (24.7 ± 1.6 MPa). Similarly, **SunBG$_{90}$** had a higher compressive strength (35.9 ± 0.7 MPa) than **GFS$_{90}$** (29.7 ± 0.9 MPa). The difference between these composites – each made of animal fat, triglycerides, and sulfur – is primarily the chemical composition of brown grease and chicken fat used during these studies. The olefin content per unit mass of brown grease was higher (3.24 mmol g^{-1}) than that of the chicken fat (mmol g^{-1}). The higher olefin content present in brown grease allowed for more crosslinking sites per unit mass of animal fat incorporated in the materials and yielded highly-cross-linked materials such as **CanBG$_x$** and **SunBG$_x$** with overall higher compressive and flexural strengths. The Smith group has also investigated the influence of plant oil olefin content on mechanical properties of HSMs.[48] In this study, the olefins in canola, sunflower, and linseed oils reacted with sulfur radicals to yield composites **CanS**, **SunS**, and **LinS**, respectively. It was observed that an increase in the unsaturation of the triglycerides (canola (monounsaturated)< sunflower (diunsaturated) < linseed oil (triunsaturated)) allowed for more cross-linkable sites and had a direct impact on the mechanical properties of the composites. For instance, **LinS** had the highest compressive strength (22.9 MPa), followed by **SunS** (17.9 MPa) and **CanS** (9.3 MPa). From these studies, it can be concluded that composites **CFS$_x$** and **GFS$_x$** exhibited compressive and flexural properties significantly higher than those of HSMs in which organics were exclusively free fatty acids or triglycerides, but slightly lower than was achieved in HSMs comprising other animal fats like brown grease.

The flexural strengths of the **CFS$_x$** and **GFS$_x$** composites were also assessed at 25°C in single cantilever mode (stress-strain plots are provided in Figure S13–S14, Supporting Information). The flexural moduli for the **CFS$_x$** and **GFS$_x$** composites were 130–260 MPa, with flexural strengths of 4.1–5.7 MPa (Table 2, Figure 2B). Some other HSMs comprised of pure and technical linoleic acid (**ZPLS$_x$** and **ZLS$_x$**; x denotes wt. % sulfur) had reported flexural strengths of 1.0–2.0 MPa, whereas other materials made from brown grease (**CanBG$_x$** and **SunBG$_x$**) had reported flexural strengths of 6.5–7.7 MPa and moduli of 420–700 MPa.

3. Conclusion

The inverse vulcanization reaction of rancid chicken fat and plant oils (either canola or sunflower oil) is an effective route to synthesize composites, **CFS$_x$** and **GFS$_x$**, all of which exhibit higher compressive strengths than that required of ordinary Portland cement for use in residential buildings. The higher incorporation of the organics in the fat/oil blend yielded more highly-crosslinked materials (**CFS$_{85}$** and **GFS$_{85}$**) with increased mechanical strength. The highest olefin content in the monomer feed and the highest compressive and flexural strength (31.7 MPa and 5.7 MPa, respectively) were thus observed for **GFS$_{85}$**. In all cases, **CFS$_x$** and **GFS$_x$** composites exhibited good thermal stability and excellent mechanical properties compared to traditional building materials like ordinary Portland cement. The synthetic approach reported

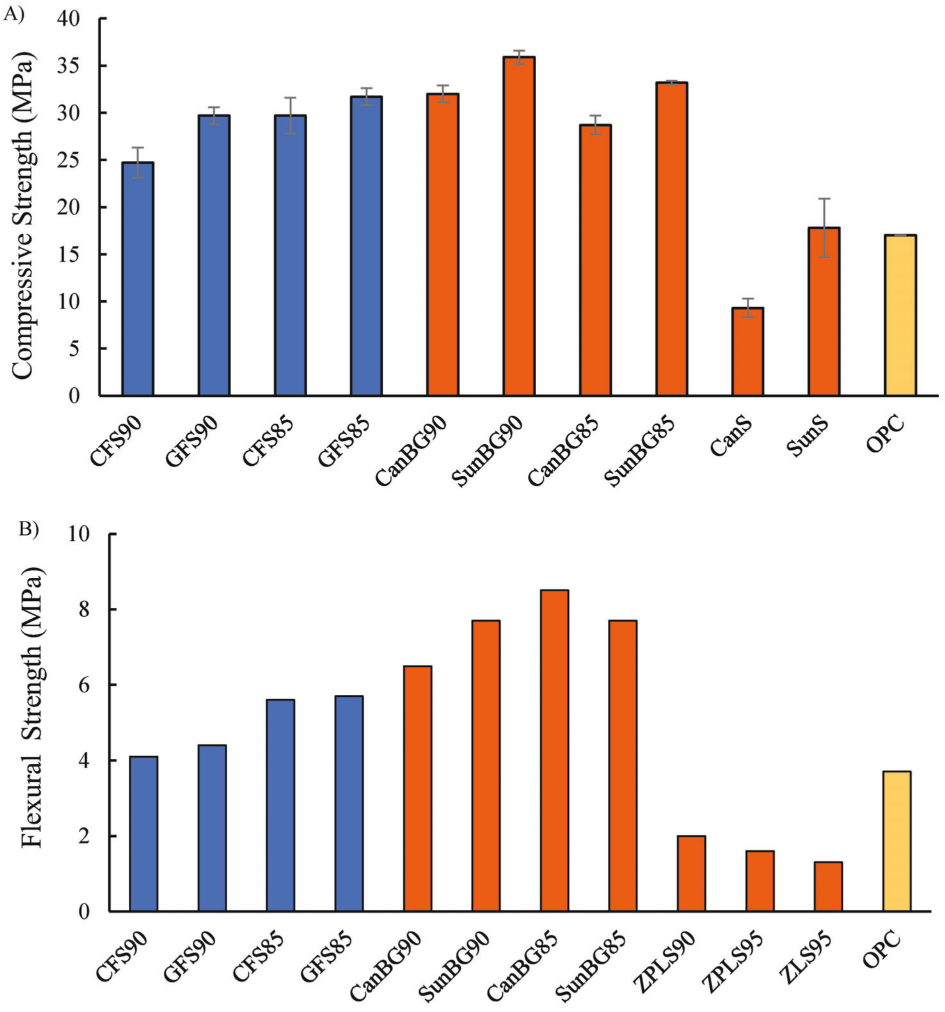

Figure 2. Compressive strength A) and flexural strength B) for composites $\mathbf{CFS_x}$ and $\mathbf{GFS_x}$ compared to other high sulfur-content materials and ordinary Portland cement (OPC).

herein thus represents a potentially impactful method to upcycle lower-value agricultural by-product rancid chicken fat directly in the atom economical inverse vulcanization reaction to yield structural materials of potential commercial value.

4. Experimental Section

General Considerations: 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 with a resolution of 8 cm^{-1}.

TGA data were recorded (Mettler Toledo TGA 2 STARe System) over the range 20–800°C with a heating rate of 10 °C min^{-1} under a flow of N_2 (100 mL min^{-1}). Each measurement was acquired in duplicate and the presented results represent an average value.

DSC data were acquired (Mettler Toledo DSC 3 STARe System) over the range −60–140 °C with a heating rate of 10 °C min^{-1} under a flow of N_2 (200 mL min^{-1}). Each DSC measurement was carried out over three heat-cool cycles.

SEM was acquired on a Schottky Field Emission Scanning Electron Microscope SU5000 operating in variable pressure mode with an accelerating voltage of 15 keV.

Carbon disulfide extractions were performed by suspending 0.3 g of finely ground material in 20 mL of CS_2, allowing the solid to settle for 30 min, pipetting off the supernatant into a separate vial, and adding another 20 mL of CS_2. This process was repeated an additional three times, so that a total of five washes were performed. The residual CS_2 was evaporated under a flow of N_2 and each vial was weighed to determine the soluble (collected as supernatant) and insoluble (remained in the initial vial) fraction masses.

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) with an applied force rate of 3–4 N s^{-1}. Compression cylinders were cast from silicone resin moulds (Smooth-On Oomoo 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 ±0.01 mm resolution. Compressional analysis was performed in triplicate, and the results were averaged.

Dynamic Mechanical Analysis (DMA) was performed using a Mettler Toledo DMA 1 STARe System in single cantilever mode. DMA samples were cast from silicone resin moulds (Smooth-On Oomoo® 30 tin-cure). The sample dimensions were 1.5 × 10.4 × 5.0 mm. The clamping force was 1 cN m and the temperature was 25°C. The samples were tested in duplicates, and the results were averaged.

For percent crystallinity calculations, T_m, ΔH_m, and ΔH_{cc}, the data was taken from the third heat/cool cycles. Melting enthalpies and cold crystallization enthalpies were calculated using DSC data. The reduction of the percent crystallinity of the composites **CFS_x** and **GFS_x** with respect to sulfur was calculated using the following equation.

$$\Delta \chi_c = 1 - \left\{ \frac{\Delta H_{m(CFS_x)} - \Delta H_{cc(CFS_x)}}{\Delta H_{m(S)} - \Delta H_{cc(S)}} \right\} * 100\% \tag{1}$$

$\Delta \chi_c$ – Change of percentage crystallinity with respect to sulfur (2)

$\Delta H_{m(CFS_x)}$ – Melting enthalpy of composite materials (CFS_x or GFS_x) (3)

$\Delta H_{cc(CFS_x)}$ – Cold crystallization enthalpy of composite materials (4)

$\Delta H_{m(S)}$ – Melting enthalpy of sulfur (5)

$\Delta H_{cc(S)}$ – Cold crystallization enthalpy of sulfur (6)

Materials, Methods, and Safe Handling Warning: Canola oil (Crisco), sunflower oil (Maple Holistics), chicken fat (Industrial partners), and sulfur (Dugas Diesel) were used without further purification. Composites were allowed to stand at room temperature for 4 days prior to mechanical testing.

Caution: Heating elemental sulfur with organics can result in the formation of H2S gas. H2S is toxic, foul smelling, and corrosive. Although it was not observed any mass loss attributable to gas generation, temperature must be carefully controlled to prevent thermal spikes, contributing to the potential for H2S evolution. Rapid stirring shortened heating times, and very slow addition of reagents can help prevent unforeseen temperature spikes.

Synthesis of CFS_{90}: Preparation of **CFS_{90}** involved the reaction of chicken fat (2.5 g, 5 wt.%), canola oil (2.5 g, 5 wt.%), and sulfur (45.0 g, 90 wt.%). Sulfur was first melted in an oil bath at 160 °C with rapid mechanical stirring. Then, the temperature was heated further to 185 °C, where sulfur exists primarily as polymeric diradicals. Once the temperature was stable, the chicken fat was slowly added to the sulfur while stirring. Then, canola oil was added dropwise to the chicken fat/sulfur mixture. The reaction mixture was stirred for 24 h at 185 °C. Within the reaction time, a homogeneous solution was produced. Upon cooling to room temperature, the material solidified to a black composite in quantitative yield (50 g). ELEM. ANAL calc'd: C 4.00, H 1.00, S 90.00; found: C 6.18, H 4.41, S 89.23.

Synthesis of GFS_{90}: Preparation of **GFS_{90}** involved the reaction of chicken fat (2.5 g, 5 wt. %), sunflower oil (2.5 g, 5 wt.%). and sulfur (45.0 g, 90 wt.%). Sulfur was first melted in an oil bath at 160°C with rapid mechanical stirring. Then, the temperature was heated further to 185 °C, where sulfur exists primarily as polymeric diradicals. Once the temperature was stable, the chicken fat was slowly added to the sulfur while stirring. Then, sunflower oil was added dropwise to the chicken fat/sulfur mixture. The reaction mixture was stirred for 24 h at 185 °C. Within the reaction time, the desired product, a homogeneous solution was produced. Upon cooling to room temperature, the material solidified to a black composite in quantitative yield (50 g). ELEM. ANAL calc'd: C 5.00, H 1.00, S 90.00; found: C 7.00, H 0.53, S 91.17.

Synthesis of CFS_{85}: Preparation of **CFS_{85}** involved the reaction of chicken fat (5.0 g, 10 wt.%), canola oil (2.5 g, 5 wt.%), and sulfur (42.5 g, 85 wt.%). Sulfur was first melted in an oil bath at 160 °C with rapid mechanical stirring. Then, the temperature was heated further to 185 °C, where sulfur exists primarily as polymeric diradicals. Once the temperature was stable, the chicken fat was slowly added to the sulfur while stirring. Then, canola oil was added dropwise to the chicken fat/sulfur mixture. The reaction mixture was stirred for 24 h at 185 °C. Within the reaction time, the desired product, a homogeneous solution was produced. Upon cooling to room temperature, the material solidified to a black composite in quantitative yield (50 g). ELEM. ANAL calc'd: C 10.00, H 1.00, S 85.00; found: C 20.28, H 1.78, S 76.25.

Synthesis of GFS_{85}: Preparation of **GFS_{85}** involved the reaction of chicken fat (5.0 g, 10 wt.%), sunflower oil (2.5 g, 5 wt.%), and sulfur (42.5 g, 85 wt.%). Sulfur was first melted in an oil bath at 160 °C with rapid mechanical stirring. Then, the temperature was heated further to 185 °C, where sulfur exists primarily as polymeric diradicals. Once the temperature was stable, the chicken fat was slowly added to the sulfur while stirring. Then, sunflower oil was added dropwise to the chicken fat/sulfur mixture. The reaction mixture was stirred for 24 h at 185 °C. Within the reaction time, the desired product, a homogeneous solution was produced. Upon cooling to room temperature, the material solidified to a black composite in quantitative yield (50 g). ELEM. ANAL calc'd: C 12.00, H 1.00, S 85.00; found: C 16.20, H 1.46, S 80.47.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

The authors primarily responsible for particular CRediT roles are provided here. C. V. Lopez: Data curation, Formal analysis, Investigation, Validation, Roles/Writing – original draft. R. C. Smith: Conceptualization, Methodology, Resources, Supervision. R. C. Smith and A. D. Smith: Funding Acquisition, Writing – review and editing.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

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