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Sustainable Composites from Waste Sulfur, Terpenoids, and Pozzolan Cements

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Abstract: Sulfur cements have drawn significant attention as binders because sulfur is a byproduct of fossil fuel refining. Sulfur cements that can be formed by the vulcanization of elemental sulfur and plant-derived olefins such as terpenoids are particularly promising from a sustainability standpoint. A range of terpenoid–sulfur cements have shown compressional and flexural properties exceeding those of some commercial structural mineral cements. Pozzolans such as fly ash (FA), silica fume (SF), and ground granulated blast furnace slag (GGBFS) and abundant clay resources such as metakaolin (MK) are attractive fines for addition to binders. Herein, we report 10 composites prepared by a combination of sulfur, terpenoids (geraniol or citronellol), and these pozzolans. This study reveals the extent to which the addition of the pozzolan fines to the sulfur–terpenoid cements influences their mechanical properties and chemical resistance. The sulfur–terpenoid composites CitS and GerS were prepared by the reaction of 90 wt% sulfur and 10 wt% citronellol or geraniol oil, respectively. The density of the composites fell within the range of 1800–1900 kg/m^3 and after 24 h submersion in water at room temperature, none of the materials absorbed more than 0.7 wt% water. The compressional strength of the as-prepared materials ranged from 9.1–23.2 MPa, and the percentage of compressional strength retained after acid challenge (submersion in 0.1 M H_2SO_4 for 24 h) ranged from 80–100%. Incorporating pozzolan fines into the already strong CitS (18.8 MPa) had negligible effects on its compressional strength within the statistical error of the measurement. CitS-SF and CitS-MK had slightly higher compressive strengths of 20.4 MPa and 23.2 MPa, respectively. CitS-GGBFS and CitS-FA resulted in slightly lower compressive strengths of 17.0 MPa and 15.8 MPa, respectively. In contrast, the compressional strength of initially softer GerS (11.7 MPa) benefited greatly after incorporating hard mineral fines. All GerS derivatives had higher compressive strengths than GerS, with GerS-MK having the highest compressive strength of 19.8 MPa. The compressional strengths of several of the composites compare favorably to those required by traditional mineral cements for residential building foundations (17 MPa), whereas such mineral products disintegrate upon similar acid challenge.

Keywords: sustainable composite; terpenoid; sulfur; hybrid organic–inorganic composite; sulfur cement; polymer cement

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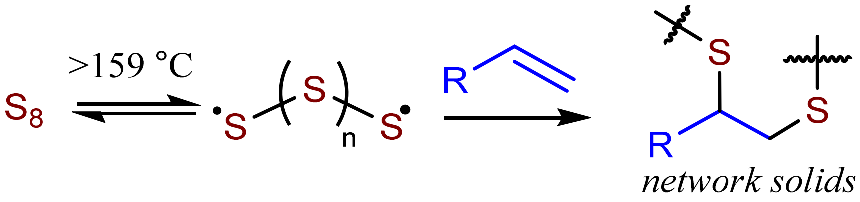
1. Introduction

The modern infrastructure of human civilization—roads, bridges, houses, etc.—is largely built from cement and petrochemical products. The ecological toll of cement and plastic manufacturing is staggering [1–4]. There is a clear and pressing need to develop alternative structural goods that can be recycled or synthesized more sustainably, using renewably sourced or waste-product precursors [5–7]. The materials studied herein have the potential to serve as alternatives for ecologically less advantageous materials. Many terpenoid–sulfur cements have shown compressional and flexural properties surpassing those of some commercial structural mineral cements [8–11].

Terpenes and terpenoids are olefins that can be produced by a variety of plants, algae, and bacteria that have tremendous potential to replace petrochemical olefins and develop a greener economy [12]. In addition to naturally occurring plants, genetically engineered organisms have been designed to efficiently produce terpenoids [13–17], to the extent that techno-economic assessment suggests terpenoids are competitive with petrochemical olefins for some markets [18,19]. In durable structural materials, terpenoids have found use in more sustainable tars and bitumen for asphalt [20–28] and in sulfur cements/composite materials [8–10]. The sulfur used in sulfur cements is a byproduct of fossil fuel refining, which is annually produced in megaton quantities of unutilized material for valorization [29–37]. Upon heating with olefins, sulfur undergoes a low-temperature (<200 °C) reaction to crosslink the olefins via a process known as inverse vulcanization (Scheme 1) [31,38]. Whereas classic vulcanization is a process used for strengthening natural rubber, by reacting it with small amounts of sulfur and, thus, producing primarily materials, inverse vulcanization employs sulfur as the bulk component, so that more mineral-like strength profiles can be attained. The inverse vulcanization route is advantageous because it is both a simple and an up-to-100% atom-economical way of producing recyclable composites, which maintain favorable properties that are competitive with commercial materials [35,39–41]. As such, the inverse vulcanization process has been used to prepare high sulfur-content materials (HSMs) for a wide range of applications [34–36,42–53] in lithium–sulfur batteries [50,51,54–56], infrared imaging [57], water purification [58–62], and fertilizers [46,63,64]. A wide range of sulfur cements has also been prepared by the inverse vulcanization of olefins [65–67]. In previous work, for example, we demonstrated that sulfur cements comprising fatty acids as the sustainable olefin source [7,68–74] could be combined with pozzolanic fines from industrial waste such as fly ash (FA), silica fume (SF), or ground granulated blast-furnace slag (GGBFS) as well as abundant clay resources such as metakaolin (MK), to form a variety of durable composites. Mineral, industrial waste, and fiber fillers are all important for both extending composites and providing them with enhanced physical characteristics. Especially notable advances in these areas have been achieved in fiber-reinforced polymer materials [75–78].



Scheme 1. Heating elemental sulfur produces radicals that add to olefin π bonds to yield cross-linked high sulfur-content materials (HSMs) via a process known as inverse vulcanization.

In the current work, it was of interest to evaluate the extent to which the addition of fines to sulfur–terpenoid cements influences their mechanical properties and chemical resistance. Sulfur–terpenoid cements comprising 90 wt% sulfur vulcanized with citronellol oil (CitS) or geraniol oil to yield (GerS) were used as the binders for these studies. The fines used for this study were FA, SF, GGBFS, and MK. Combination of the fines (10 wt%) with CitS binder yielded CitS-FA, CitS-SF, CitS-GGBFS, and CitS-MK, while combination with GerS binder produced composites GerS-FA, GerS-SF, GerS-GGBFS, and GerS-MK. The density, water uptake, and compressional strength before and after acid challenge were evaluated for the two binders alone as well as for the eight derivative composites.

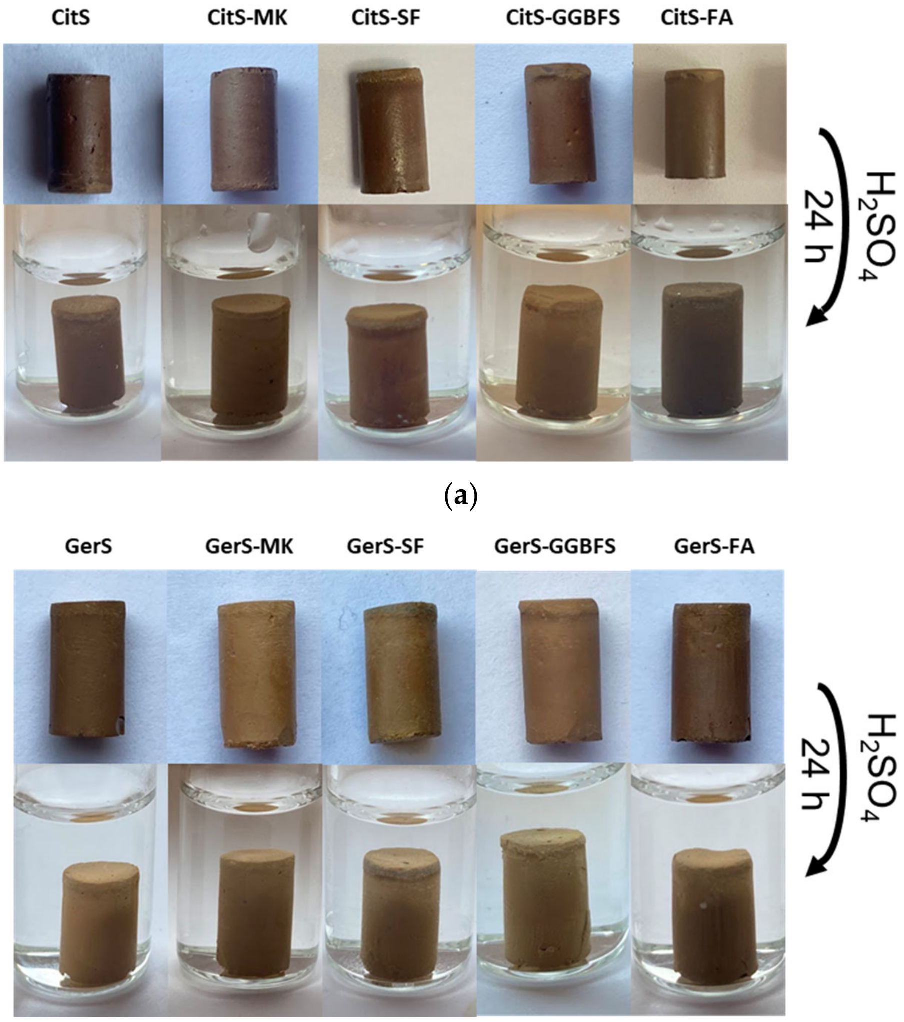
2. Materials and Methods

2.1. Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) data were acquired using a Mettler Toledo (USA) DSC 3 STAR^e System from −60 to 140 °C, with a heating rate of 5 °C min^{-1} under a flow of N_2 (200 mL min^{-1}). Each DSC measurement was carried out over three heat–cool cycles to screen out thermal history. The data reported were taken from the third cycle of the experiment. The first cycle is used for removing solvent impurities. The melting and crystallization transitions as well as the glass-transition temperature were observed in the third cycle.

2.2. Compressional Measurements

Compressional measurements were acquired on cylinders (Figure 1) using a Mark-10 ES30 (USA) Manual Test Stand equipped with a Mark 10 M3-200 Force Gauge (USA) by a modified ASTM C39 standard. Terpenoid–sulfur composite materials were aged for 4 d prior to compressional strength testing. The four-day aging period was selected after assessing material properties over shorter and longer times for one set of samples, and the properties were leveled off after four days. Longer-term stability is not known for these materials.



(**a**)

(**b**)

Figure 1. Representative photos of compressional cylinders of CitS-derived (**a**) and GerS-derived composites (**b**) before (upper row in each image) and after (lower row in each image) acid challenge.

2.3. Chemical Precursor Sources

Terpenoids (Alfa Aesar, Ward Hill, MA, USA or Sigma-Aldrich, St. Louis, MO, USA) and elemental sulfur (99.5%, Alfa Aesar) were used without further purification. Fly ash (FA), silica fume (SF), and ground granulated blast-furnace slag (GGBFS) pozzolanic-cement components were purchased from Diversified Minerals, Inc., Oxnard, CA, USA, while metakaolin was manufactured by Opptipozz, Sandersville, GA, USA.

2.4. General Synthesis of Terpenoid–Sulfur Composites

CAUTION: Heating elemental sulfur with organics can result in the formation of H_2S gas. H_2S is toxic, foul-smelling, and corrosive. This procedure follows the reported method [8]. A 180.0 g sample of elemental sulfur was added to a 2.5 L Erlenmeyer flask. The vessel was placed in a thermostat-controlled oil bath set to 180 °C and stirred with an overhead mechanical stirrer equipped with a stainless-steel stir rod and vane. Elemental sulfur was initially heated at 120 °C. Upon further heating, the viscosity of elemental sulfur increased, and a deep red color characteristic of polymeric sulfur radicals was observed. At this point, 20.0 g of citronellol for CitS or geraniol for GerS was added to the flask dropwise with rapid stirring for 35 min, over which time the color changed to a deep brown color. After cooling to room temperature, the materials were rigid brown to black solids that were readily remeltable and could be shaped into compressive test cylinders by pouring into silicone molds. A total of five independent samples were prepared for each measurement.

2.5. General Procedure for Addition of Fines to Binders

CAUTION: Heating elemental sulfur with organics can result in the formation of H_2S gas. H_2S is toxic, foul-smelling, and corrosive. This procedure follows a reported method for adding fines to fatty acid–sulfur cements [37]. Approximately 27 g of the requisite binder was melted in a 125 mL Erlenmeyer flask equipped with a Teflon-coated magnetic stir bar. The flask was submerged in a thermostat-controlled oil bath set to 180 °C. Once the binder had fully melted, the corresponding pozzolan (10 wt%) was added with rapid stirring. After rapid stirring for 10 min, the mixture was removed from the heat, and cylinders for compressional analysis were prepared by pouring the molten mixture into silicone cylinder molds.

3. Results and Discussion

3.1. Component Properties and Preparation of Composites

The binders for this study were terpenoid–sulfur cements prepared from the reaction of either geraniol oil or citronella oil with molten elemental sulfur at 180 °C for 35 min according to the reported procedure [8]. These particular terpenoids were selected for the current study because citronellol is a monounsaturated compound, whereas geraniol is a diunsaturated compound and, thus, is capable of additional crosslinking. The reaction of citronella oil or geraniol oil with 90 wt% sulfur, thus, led to CitS and GerS, respectively, as homogeneous brown solids (Figure 1). These binders are remeltable to form a free-flowing brown liquid phase at temperatures above 120 °C. The thermal and morphological properties of CitS and GerS derived from differential scanning calorimetry (DSC) are summarized in Table 1. The data in Table 1 are reported for the third heating cycle in each case, such that i) their thermal history effects can be removed and ii) their comparison to the reported data for other HSMs, which are also widely reported from the third heating cycle, is allowed.

Table 1. Properties of terpenoid–sulfur cement binders and comparison to elemental sulfur (orthorhombic).

Materials	T_g/°C	T_m/°C	ΔH_m [a] J/g	ΔH_{cc} [b] J/g	Percentage Crystallinity [c]
S_8	NA	119	45	NA	100
CitS	NA	114	ND	ND	ND
GerS	−37	116	25	20	23

[a] Integrated heat of melting for the orthorhombic sulfur melt transition. [b] Integrated area for all cold crystallization transitions. [c] The reduction in the percentage of crystallinity of each of the samples was calculated with respect to sulfur (normalized to 100%).

The DSC data for all of the composites reflect the typical behavior observed in the third heating cycle of other high sulfur content materials (HSMs) [46,79–83]. The glass-transition temperature (T_g) near −37 °C observable in the DSC thermogram is particularly notable, as it is the diagnostic for the polymeric sulfur domains and, thus, confirms that, as previously reported [8], the binders are covalently crosslinked network materials rather than physical blends of terpenoids with sulfur. The other features in the DSC thermograms correspond to a sulfur melting temperature (T_m) near 118 °C, a monoclinic–orthorhombic crystal morphology transition near 106 °C, and cold crystallization features. Before adding fines, the binder crystallinity can be assessed by integrating thermal features according to Equation (1), reflecting the successful conversion of crystalline orthorhombic sulfur domains to amorphous polymeric sulfur domains in the structures [19].

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

where $\Delta\chi_c$, a dimensionless variable, is the change in the percentage of the crystallinity with respect to sulfur; ΔH_m , in units of J/g, is the melting enthalpy of the binder material; ΔH_{cc}, in units of J/g, is the cold crystallization enthalpy of the binder material; $\Delta H_{m(S)}$, in units of J/g, is the melting enthalpy of sulfur; and $\Delta H_{cc(S)}$, in units of J/g, is the cold crystallization enthalpy of sulfur.

The pozzolans selected for the current study were fly ash (FA), silica fume (SF), and ground granulated blast-furnace slag (GGBFS) and the abundant clay resource metakaolin (MK). These materials were selected on the basis of their established utility as additives to more traditional mineral cements, affordability, abundance, thermal and chemical stability under planned composite preparation conditions, and, in the case of FS, SF, and GGBFS, classification as industrial waste products. Chemically, these fines are oxides or silicates of Ca, Si, Al, and Fe (Table 2). The fineness moduli for these materials (Table 2) were determined by weighing the particles passing through progressively finer ASTM-certified sieves (numbers 18, 30, 50, 100, and 200), according to the reported procedure [37,84].

Table 2. Fineness moduli (*F*) and compositions for pozzolans used in this study.

Materials	Fineness Modulus	Primary Constituents
Silica Fume	3.78	SiO_2
Fly Ash	2.53	SiO_2, CaO, Al_2O_3, Fe_3O_2
Ground Granulated Blast-Furnace Slag	3.35	$2CaO{\cdot}SiO_2$, $CaAl_2Si_2O_8$
Metakaolin	4.63	$Al_2Si_2O_7$

The preparation of composites was effected by following a procedure from the literature for preparing composites of the same fines with an oleic acid–sulfur binder comprising 90 wt% sulfur [37]. Briefly, the binders were first melted down in an Erlenmeyer flask above its melting point of 120 °C. The requisite fine was then added with rapid mechanical stirring, and the stirring was continued for 10 min to ensure homogenization. Each molten composite mixture was poured into a series of cylindrical molds and allowed to set for four days, giving brown cylinders (Figure 1).

Scanning electron microscopy (SEM) imaging with element mapping by energy dispersive X-ray analysis (EDX) was undertaken to assess the distribution of the mineral components in the GerS-derived materials. SEM/EDX data previously reported for GerS showed a uniform, homogeneous distribution of S, C, and O in the absence of mineral additives. In the current case, the distribution of geraniol-derived C and of sulfur remained homogenously distributed in the composites, while well-dispersed particles high in Si and O content were also observed for the minerals (Figure 2).

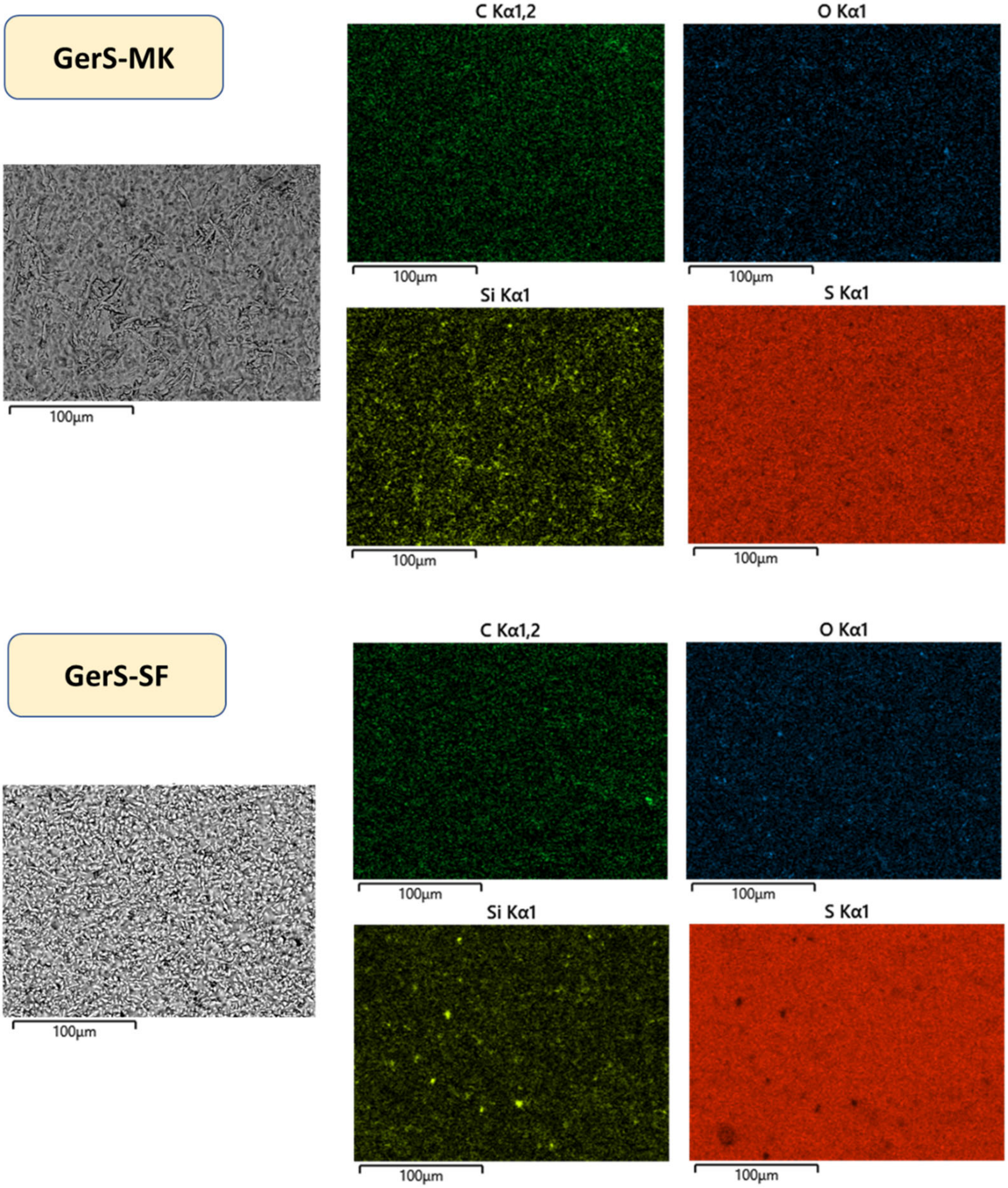


Figure 2. *Cont.*

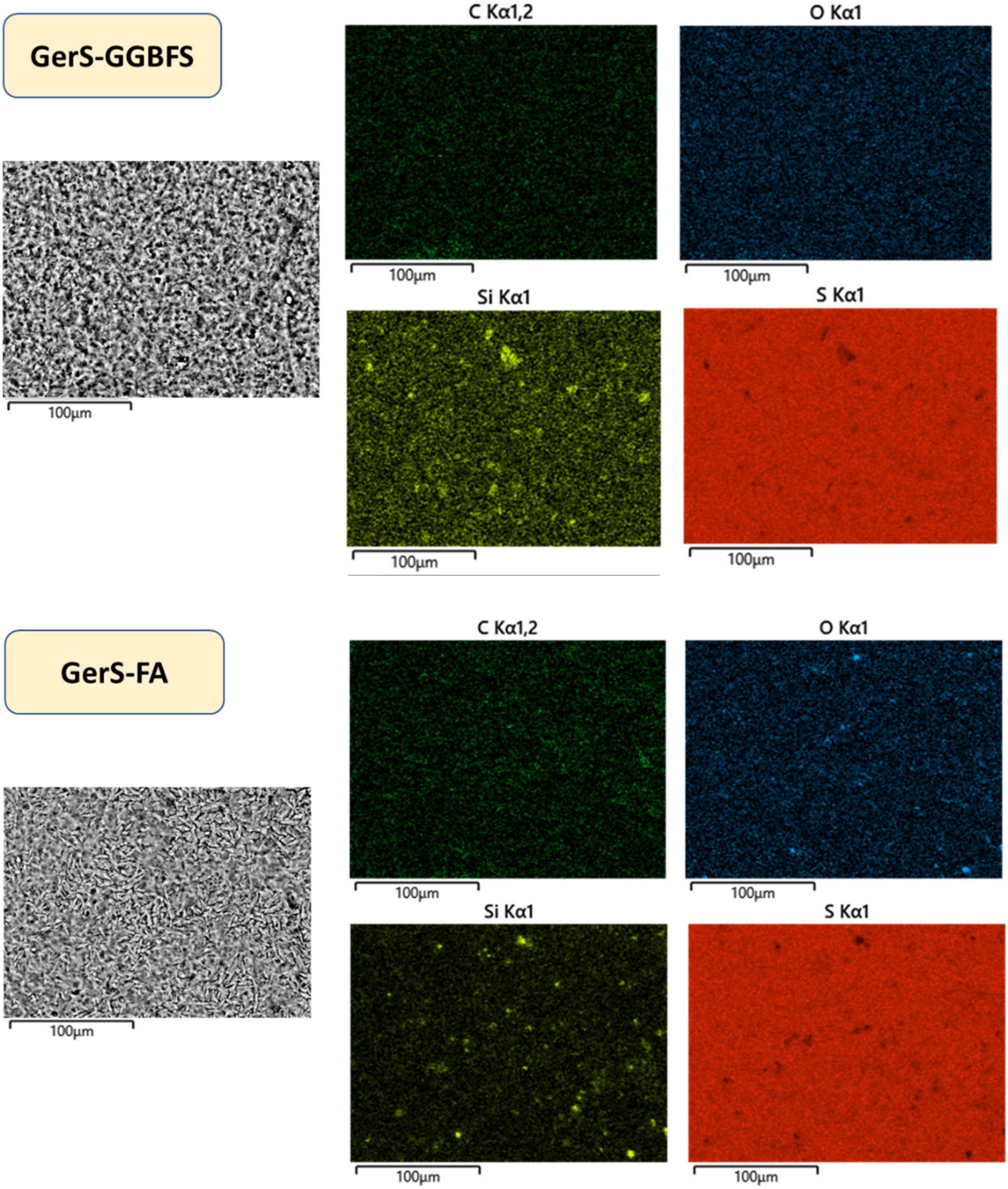


Figure 2. SEM/EDX data for composites reveals the presence of mineral additive well-dispersed in the homogeneous GerS binder for the GerS-derived materials.

3.2. Physical and Mechanical Properties

Several key metrics were assessed to evaluate the composites' viability as structural materials. The density of the materials (Table 3) is 1800–1900 kg/m^3, thus meeting American Concrete Institute (ACI) standard ACI-213R and ASTM 169C guidelines for lightweight structural materials [85,86]. These densities are also similar to commercial composites such as fiber-reinforced resins (i.e., Lyondell Basell product BMC 940-21769, with a density = 1900 kg/m^3) and are slightly higher than the densities of composites made using ZOS$_{90}$ as the binder with FA (giving FAOS), SF (giving SFOS), GGBFS (giving GGBFSOS), and metakaolin (giving MKOS), with densities that range from 1600 to 1700 kg/m^3.

Table 3. Properties of composites and binders.

			Compressional Strength [c]		
Materials	**Density [a] (kg/m^3)**	**Water Uptake [b] (wt%)**	**As-Prepared (MPa)**	**After Acid (MPa)**	**Retained Strength (% of As-Prepared)**
CitS	1800	0.1 ± 0.1	18.8 ± 2.3	15.8 ± 0.5	85
CitS-MK	1800	0.2 ± 0.01	20.4 ± 2.2	19.5 ± 0.4	95
CitS-SF	1800	0.7 ± 0.3	23.2 ± 3.2	18.7 ± 1.3	80
CitS-GGBFS	1800	0.2 ± 0.1	17.0 ± 0.4	16.7 ± 0.6	98
CitS-FA	1800	0.2 ± 0.3	15.8 ± 2.1	17.1 ± 1.2	108
GerS	1800	0.2 ± 0.2	11.7 ± 1.5	9.4 ± 2.1	80
GerS-MK	1800	0.1 ± 0.1	19.8 ± 2.3	23.2 ± 3.6	116
GerS-SF	1900	0.2 ± 0.2	16.4 ± 0.9	14.2 ± 1.3	87
GerS-GGBFS	1900	0.2 ± 0.1	19.4 ± 1.6	18.0 ± 3.1	93
GerS-FA	1900	0.2 ± 0.2	16.5 ± 0.7	16.5 ± 0.7	100
OPC [d]	1500	Up to 28%	17	decomposed	0
ZOS$_{90}$	1700	0.0	19.4 ± 1.8	ND	ND
FAOS	1700	0.0	20.6 ± 5.7	ND	ND
GGBFSOS	1700	0.0	8.50 ± 0.1	ND	ND
MKOS	1700	0.0	9.1 ± 1.2	ND	ND
PCOS	1600	0.1	22.0 ± 0.1	ND	ND
SFOS	1600	0.0	12.4 ± 4.4	ND	ND
GCN0	ND	ND	49.50	ND	ND
GCN5	ND	ND	57.17	ND	ND
GCN10	ND	ND	63.59	ND	ND
GCN15	ND	ND	38.79	ND	ND
GCN20	ND	ND	35.05	ND	ND

[a] Density is reported as the average of three measurements on cylinders used for mechanical testing. [b] Water uptake was calculated by measuring the mass before and after the cylinder was submerged in deionized water for 24 h (average of three trials). [c] Average of three measurements with standard deviations. [d] Values for residential building-grade ordinary Portland cement for foundations and footings.

Water uptake (Table 3) is another critical metric for building applications due to the change in weight and strength of material after water absorption and the potential for product deterioration and failure resulting from cyclic freeze–thaw expansion and contraction. High sulfur-content materials (HSMs) generally have superior resistance to water absorption. The water uptake of the composites, as required under ASTM D570 by 24 h submersion at near room temperature, likewise confirmed that none of the materials absorb more than 0.7 wt% water, which is similar to the parent binder, despite the addition of 10 wt% of potentially hygroscopic mineral oxide/silicate fines. This observation is in line with the similar water-uptake values for the composites made using ZOS$_{90}$ as the binder. The low water uptake of sulfur cement–pozzolan composites stands in sharp contrast to the behavior of traditional mineral cements such as OPC, which absorb up to 28% water under identical testing conditions.

The compressional strengths of the binders and terpenoid–sulfur-cement-derived composites are displayed in Figure 3 and are summarized in Table 1 along with the data for comparison to ZOS$_{90}$ and its derivative composites as well as metakaolin-based geopolymer cements. With the exception of GerS, the binders and derivative composites all exhibited compressional strength that was competitive with or exceeding that required (17 MPa) for cement foundations and footings for residential buildings (ACI specification 332.1R-

06). The incorporation of fines into the already-strong CitS had a negligible impact on its compressional strength within the statistical error of the measurements. In contrast, and unsurprisingly, the compressional strength of the initially softer GerS benefited significantly from incorporating the hard mineral fines. The previously reported ZOS_{90}-derived composites did not show such a predictable trend, with some of the composites showing improved compressional strength and others showing diminished compressional strength. Composites of fatty acid and sulfur, however, suffer from homogenization issues and have been shown to exhibit reactivity between the acidic fatty acid chains and some metal oxides. Such reactivity is not possible for the nonacidic terpenoids selected for the current study.

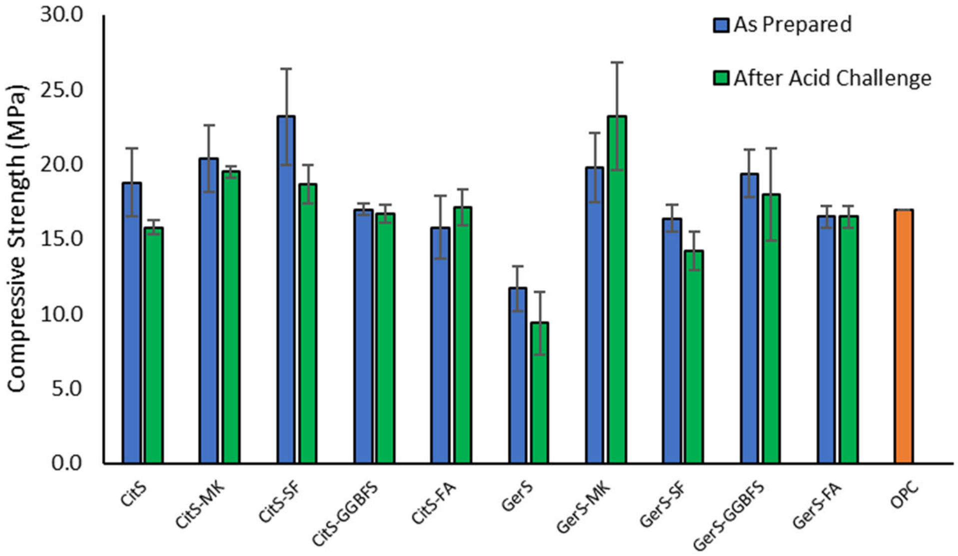


Figure 3. Comparison of compressional strength before (blue bars) and after (green bars) exposure to 0.1 M H_2SO_4 for 24 h.

The compressive strength of the materials studied herein may also be compared to previously studied geopolymer cements with variable quantities of mineral additives. For example, a series of metakaolin geopolymer cements [87] was prepared including GCN*x* having *x* wt% calcium aluminate. These materials exhibited higher compressive strengths compared to the composites reported herein of the previously reported ZOS_{90} and its derivative composites. These data reflect the superiority that purely mineral-based materials can hold over the HSM cements reported to date, despite some HSMs outperforming the ordinary Portland cement used in residential building contexts.

Previous work has demonstrated that sulfur cements can exhibit some properties that are difficult for mineral products to attain, such as exceptional resistance to degradation by acid [88]. Whereas mineral cements such as OPC generally have very low resistance to acidic environments, some HSMs retain their full mechanical strength even after being submerged in acidic solutions for 24 h [41]. To assess the extent to which the current composites could withstand acid challenge, their compressional strengths were measured after the cylinders were submerged in 0.1 M H_2SO_4 for 24 h, conditions under which OPC loses its structural and geometric integrity. The data from these analyses (Table 3 and Figure 3) reveal that neither the binders nor the derivative composites exhibit any significant loss of compressional strength within the range of statistical error.

4. Conclusions

Sulfur cements formed by inverse vulcanization of elemental sulfur and terpenoids show potential as sustainable alternatives for OPC and other traditional materials. Inverse vulcanization offers both a simple and highly atom-economical route for producing recyclable composites with favorable properties competitive with commercial materials. These properties include density, water uptake, compressive strength, and acid resistance. Adding pozzolans to CitS had fairly negligible effects on the compressive strength within standard error of measurements, so they could be used as fillers when economically advantageous, without any significant changes in application. The mechanical properties of GerS, however, benefited from the addition of pozzolans. Except for GerS, the compressional strength of the materials was similar or higher than required for cement foundations and footings for residential buildings (ACI specification 332.1R-06). The pozzolan–sulfur–terpenoid composites reported in this study, thus, hold potential as more sustainable alternatives for traditional cements and can be used in acid-contact contexts where ordinary Portland cement is susceptible to degradation. Work to build on the current study is underway to assess the influence of the quantity of the fines or other additives added to terpenoid–sulfur and other organic–sulfur cements, to explore the mechanical robustness of the composites over time, and to assess the influence of other chemical and physical strains on the long-term viability of the composites as cement surrogates.

Author Contributions: Conceptualization, R.C.S.; methodology, R.C.S.; formal analysis, K.A.T.; investigation, K.A.T.; resources, R.C.S. and A.G.T.; data curation, C.V.L., C.P.M. and K.A.T.; writing—original draft preparation, K.A.T. and R.C.S.; writing—review and editing, R.C.S., K.A.T., C.P.M. and C.V.L.; supervision, R.C.S. and A.G.T.; funding acquisition, R.C.S. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: Data not available in the manuscript may be requested from the corresponding author (rhett@clemson.edu).

Conflicts of Interest: The authors declare no conflict of interest.

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