Electronic Supplementary Material (ESI) for Materials Advances.

Electronic Supplementary Information for:

A Role for Terpenoid Cyclization in the Atom Economical Polymerization of Terpenoids with Sulfur to Yield Durable Composites

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Additional experimental details on using the Mark 10 test stand to determine mechanical strength

Sample Preparation:

- Cylinders were prepared with uniform geometry
- At least two diameter measurements were taken at the top and the bottom of the sample at a 90° angle, for example at diameters d_1 and d_2 in the figure at right (4 total measurements)
- The difference between the highest and lowest measurement must be no more than 0.1 mm. If the difference was greater, the sample was discarded
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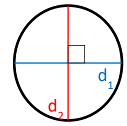
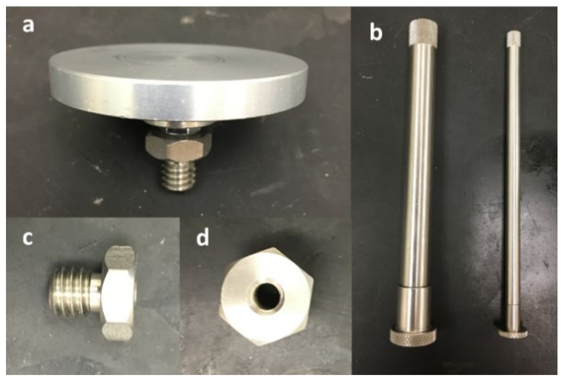


Instrument Setup:

- Compression analysis requires the attachment of a base plate to the base of the test stand (a) and one of two compression rods to the force gauge (b). The 1,000 N or 2.5 N force gauge require the larger compression rod whereas the 10 N force gauge can utilize the small compression rod or the large compression rod with the appropriate fitting (c, side view or d, top view).



Compression Sample Analysis:

- Sample was placed onto base plate in the center
- Compression rod was lowered until it rests just on the top of the sample (with force gauge still at 0 N)
- A dust shield was placed about the sample without contacting the mechanism or sample to prevent pieces of the sample from escaping and possibly causing injury upon sample rupture.
- Stress was applied at the lowest rate of travel while force and distance were simultaneously recorded by the instrument (plots of the raw data are provided in Figures S7 and S9) until the sample broke and the force rapidly dropped off.

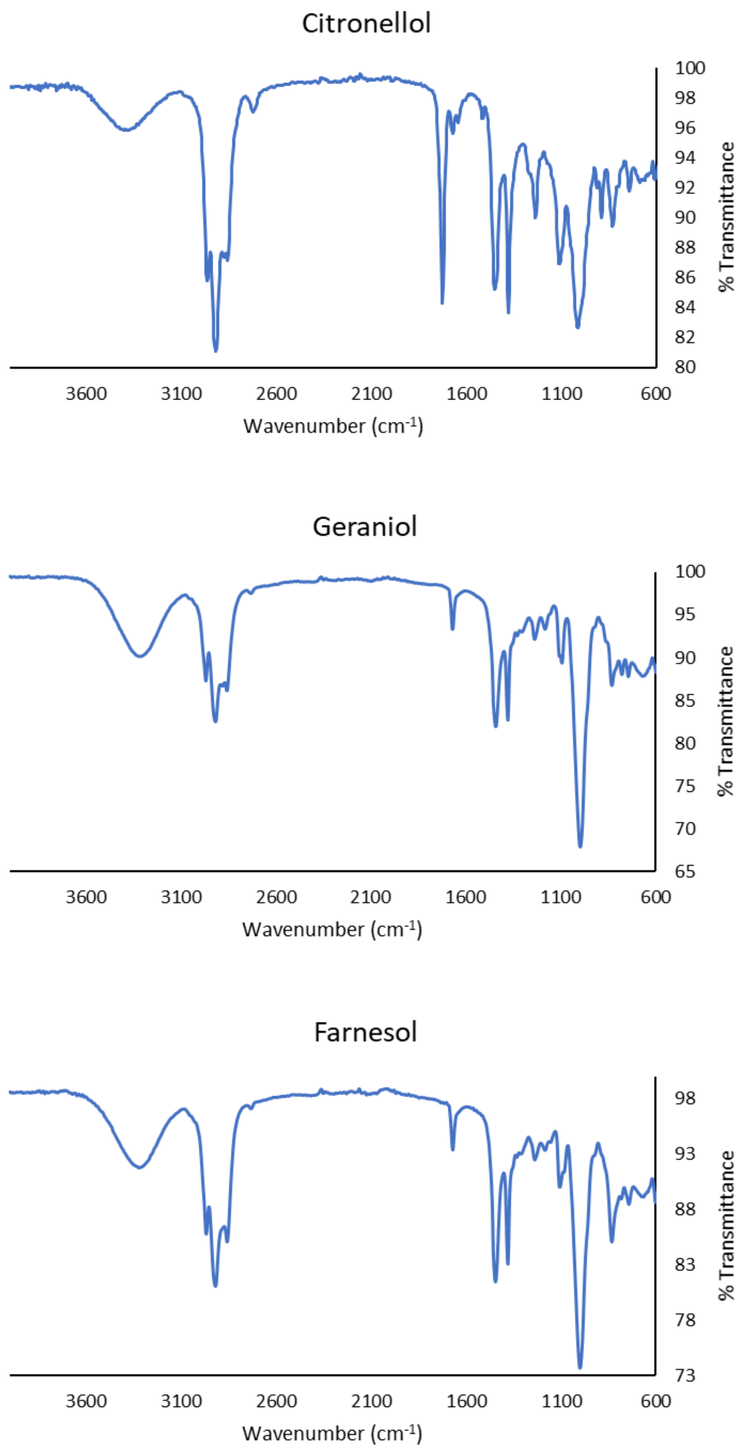


Figure S1. IR spectra for terpenoids used in this study.

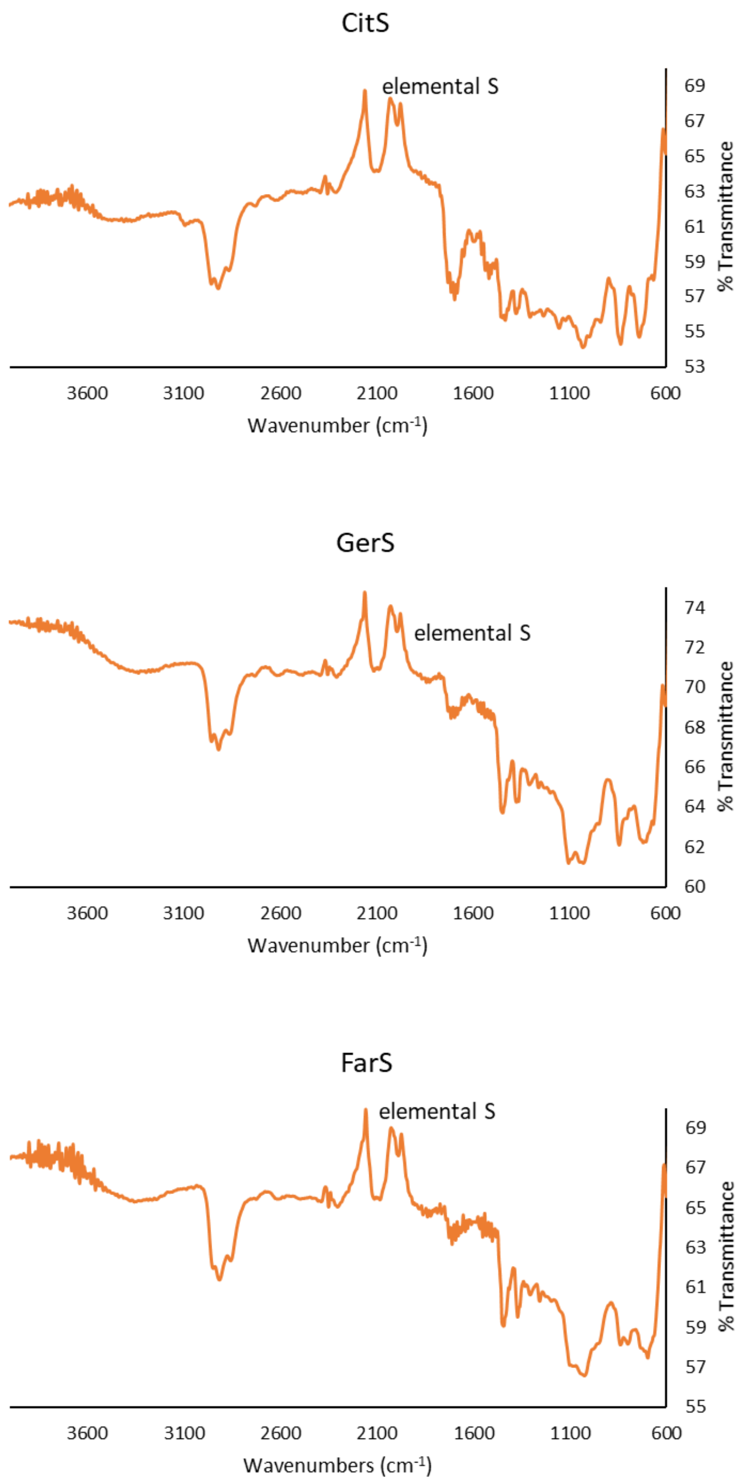


Figure S2. IR spectra for terpenoid-sulfur composites. The feature from ~1800–2200 cm^{-1} is attributable to elemental sulfur.

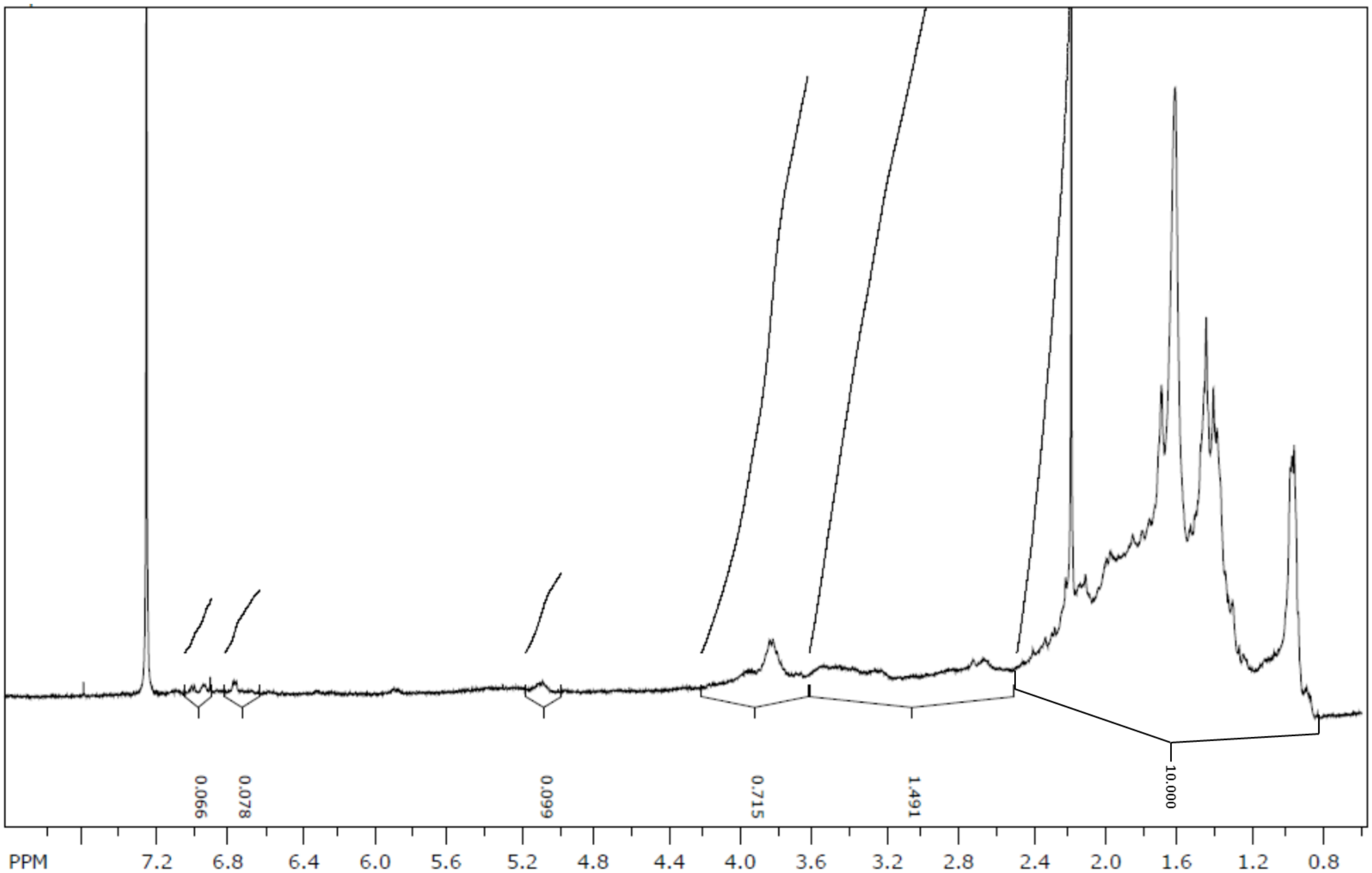


Figure S3. Proton NMR spectrum for the product of reaction between geraniol and 4 equiv S (300 MHz, $CDCl_3$).

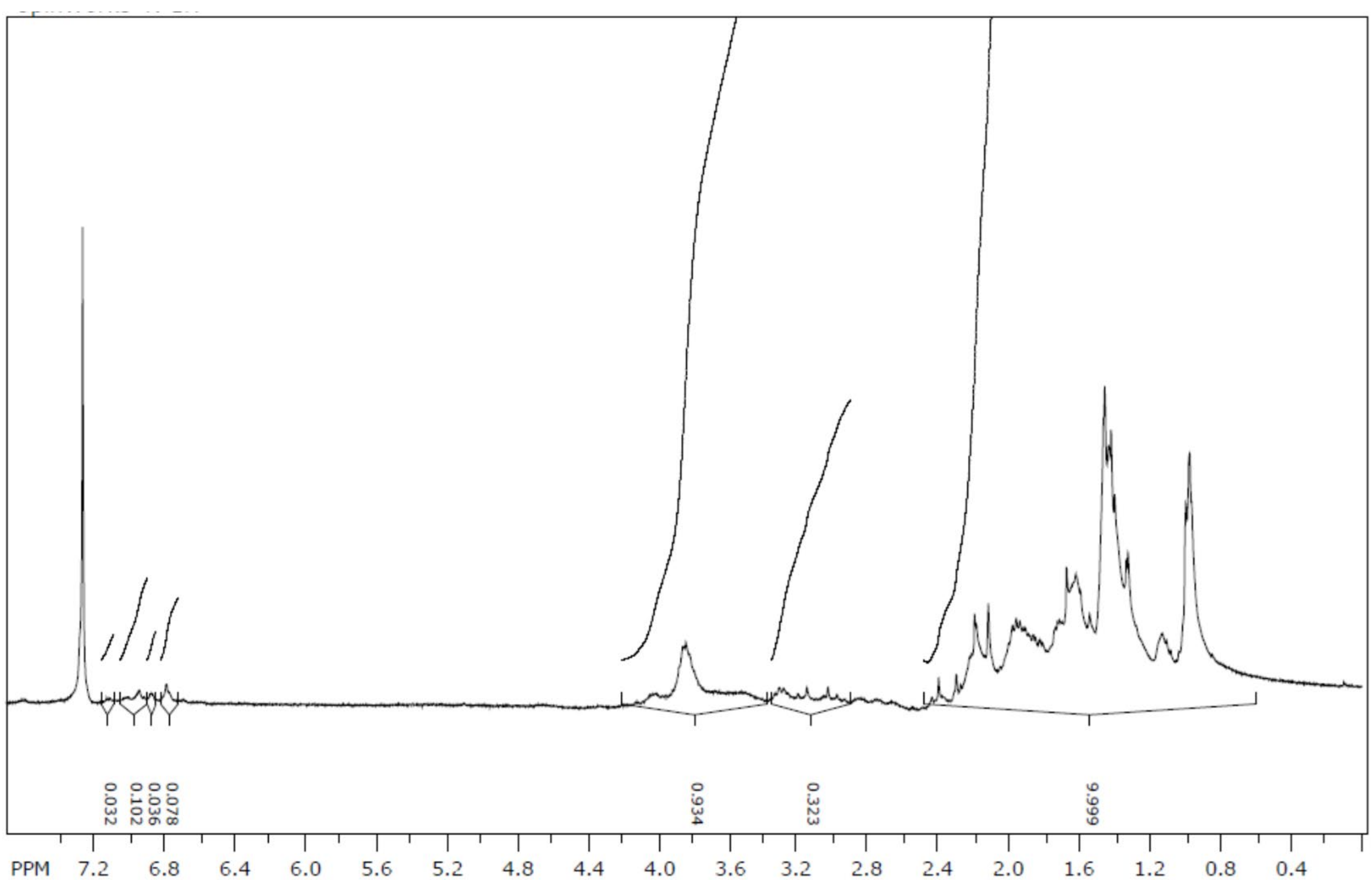


Figure S4. Proton NMR spectrum for the product of reaction between farnesol and 4 equiv S (300 MHz, $CDCl_3$).

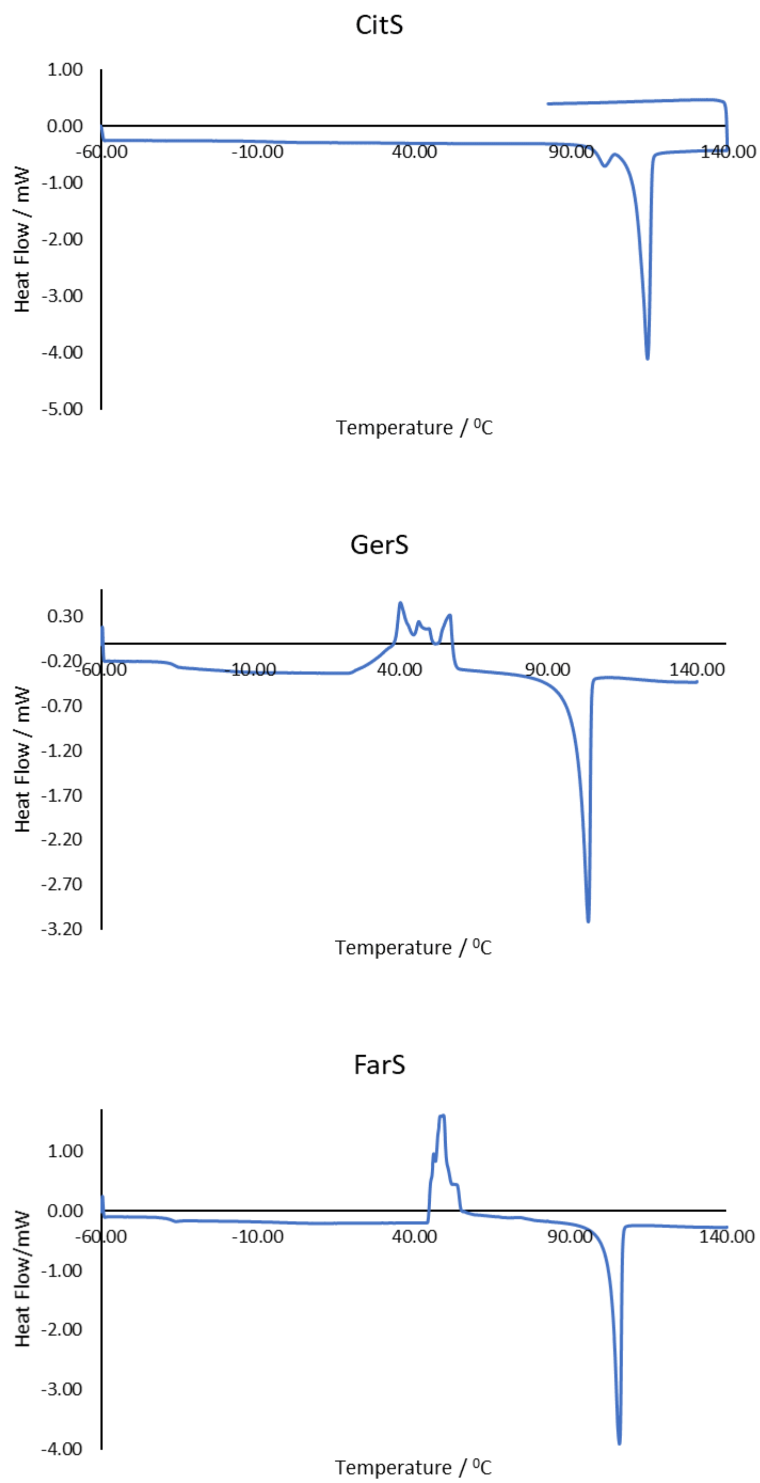


Figure S5. DSC traces for terpenoid-sulfur composites. The traces are given for the third heating cycle.

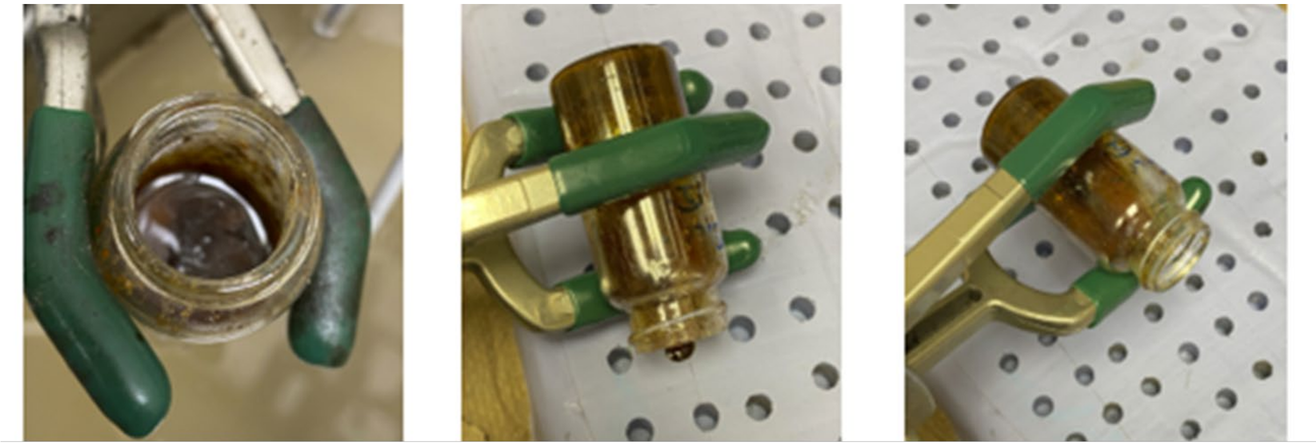
Table S1. Quantification of sulfur and crystallinity from integration of the DSC traces for terpenoid-sulfur composites

Materials	$T_m^{[b]}$/°C	ΔH_m J/g	ΔH_{cc} J/g	Wt% S[c]
CitS	114.4	–36.6	NA	82
GerS	103.3	–25.4	36.81	57
FarS	105.4	–24.9	21.02	56
S_8	118.5	–44.8	NA	100

[a] The temperature at which the 5% mass loss was observed. [b] The temperature at the peak maximum of the endothermic melting. [c]The reduction of percent crystallinity of each samples was calculated with respect to sulfur (normalized to 100%). [c] Refers to free sulfur that is not covalently bound to the organic crosslinker.

For T_m ΔH_m and ΔH_{cc}, data were taken from the third heat/cool cycles. Melting enthalpies and the cold crystallization enthalpies were calculated using DSC data from the third heating cycle.

$\Delta H_{cc(LS_x)}$ - Cold crystallization enthalpy of composite materials (LS_X)
$\Delta H_{m(S)}$ - Melting enthalpy of sulfur
$\Delta H_{cc(S)}$ - Cold crystallization enthalpy of sulfur



Step 1: Melt the composite at 120–150 °C. Tilting the vial so that the side glass remains hot is helpful to maintain fluidity as the liquid is poured in step 2.

Step 2: Begin pouring at a height that is high enough above the mold opening that the liquid stream is narrow enough to avoid the sides of the mold. The is determined through trial and error and requires a steady hand for small molds.

Step 3: Pouring must be done in one single rapid motion to avoid solidifying. Sample is discarded if an all-liquid pour fails. Although it was not necessary in this case, it can be helpful to clamp a heat gun pointed at the sample during pouring to ensure it is liquid as well as to warm the mold. Samples that cool or harden too quickly for this technique may be effectively made in stainless steel molds heated in an oven to about 120 ° C prior to pouring. The mold pictured is made of silicone as described in the experimental section.

Figure S6. Annotated photographs depicting the manner in which terpenoid-sulfur composites were fabricates for compressive testing.

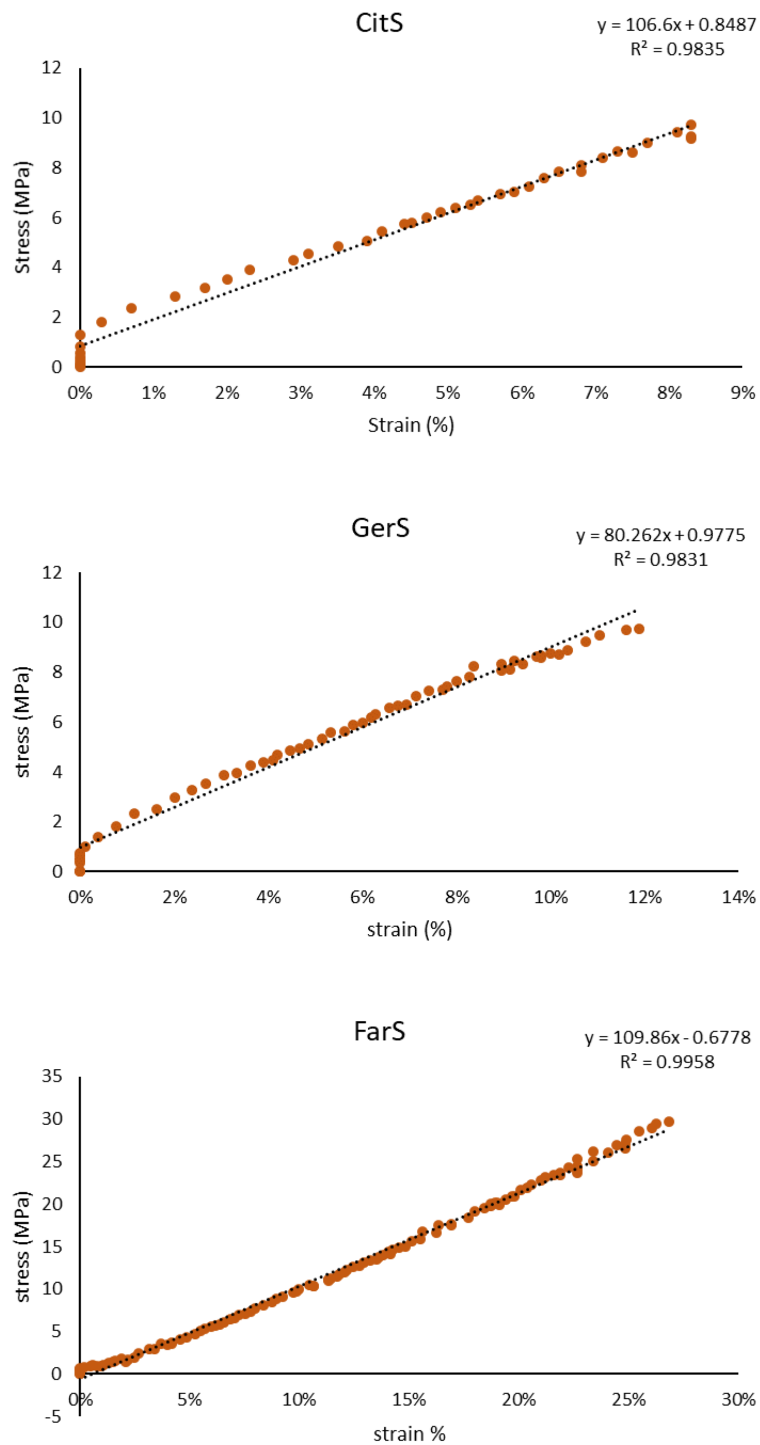
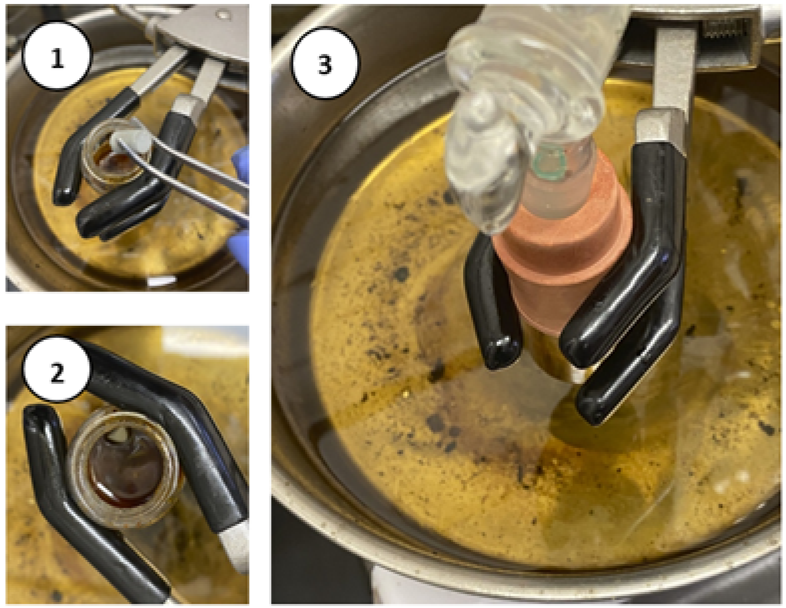


Figure S7. Compression stress-strain plots for measurements on the cylinders prepared as described in the previous figure. The blue circles are data points, while the black dotted line is the trendline for which the linear trendline equation and R^2 values are provided in each plot.

Step 1: A pre-made cement compression cylinder that has been measured in all dimensions by calipers is added to molten composite at 150 °C.

Step 2: Cement and these composites have similar densities (note the only half-submerged cement cylinder in this photo). The cylinder should be pushed into the liquid. If necessary a needle can be pushed through the septum to a length that will keep the cylinder submerged.



Step 3: A vacuum is applied to the sample. Caution should be exercised as some such samples are viscous so that they can foam up quite a bit as dissolved gas is pumped out when vacuum is applied – more so than non-viscous organic solvents. Introduce vacuum quite slowly (note the barely-opened stopcock in the photo). Once bubbling subsides, full vacuum is applied for 1 h.

Step 4 (no photo): Most of the molten composite comes off of the hot cylinder easily when it is removed from the liquid. A Teflon spatula or rubber policeman works well for this purpose. The excess can be carefully removed using 220 or 330 grit sandpaper until the dimensions match the original cylinder dimensions measured using calipers as in Step 1.

Figure S8. Annotated photographs depicting the manner in which samples **CitS**, **GerS**, and **FarS** are infused into cement cylinders to give **CIP**, **GIP**, and **FIP**, respectively.

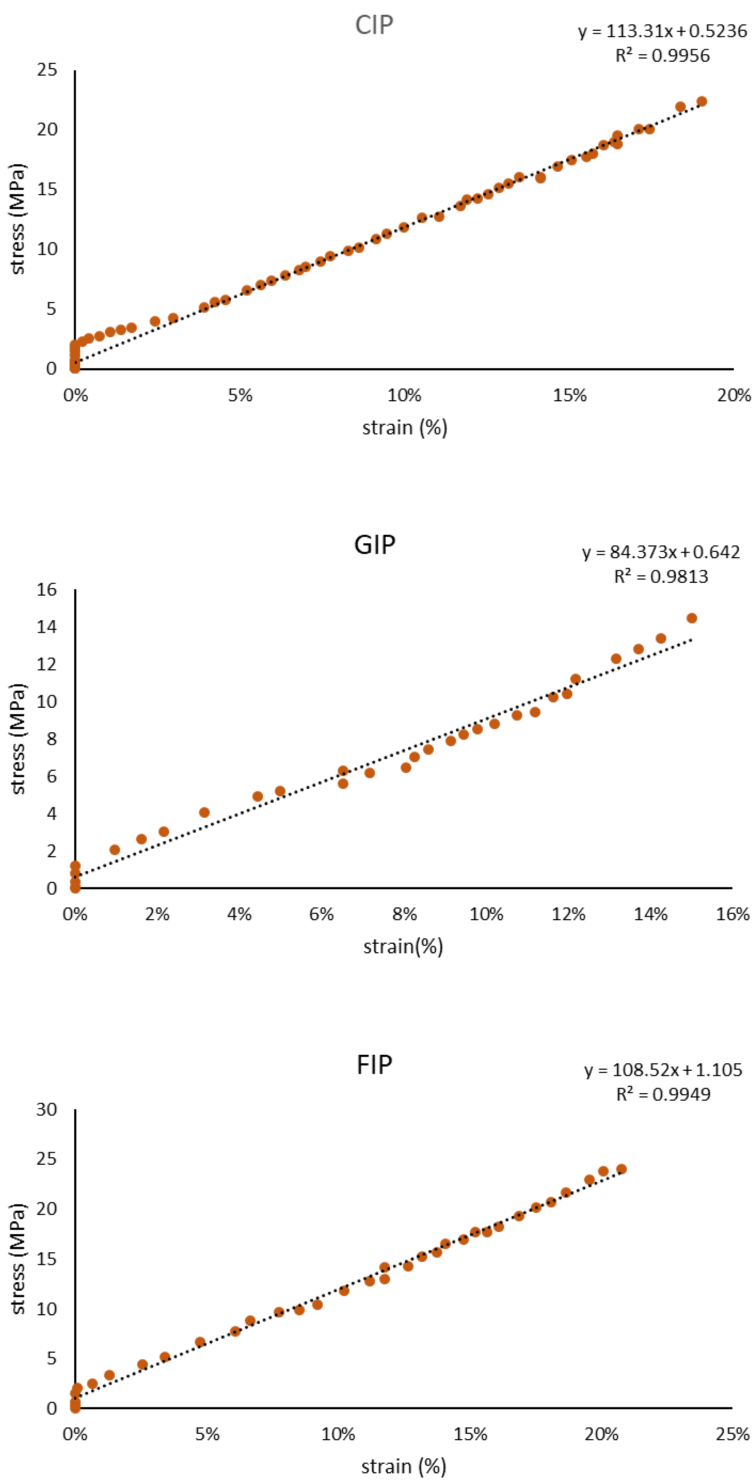


Figure S9. Compression stress-strain plots for measurements on the cylinders prepared as described in the previous figure. The blue circles are data points, while the black dotted line is the trendline for which the linear trendline equation and R^2 values are provided in each plot.