A Comparison of Adhesive Polysulfides Initiated by Garlic Essential Oil and Elemental Sulfur to Create Recyclable Adhesives

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A Comparison of Adhesive Polysulfides Initiated by Garlic Essential Oil and Elemental Sulfur to Create Recyclable Adhesives

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Abstract

Despite adhesives having their origins in natural materials, most glues are formed from petroleum-based products. However, many natural adhesives lack the strength to compete with synthetic glues. Therefore, strong, sustainable alternatives are needed. Data presented here builds on prior work that combines elemental sulfur, a petroleum byproduct, and garlic essential oil (GEO) which is composed of allyl sulfides, to make adhesives. Here, we have demonstrated that both sulfur and GEO can initiate polymerization at 160 °C with another petroleum byproduct, dicyclopentadiene, and a variety of natural monomers through the formation of sulfur radicals. In addition to using natural monomers and petroleum byproducts, these processes are solvent free and have high atom economy, limiting waste formation, and meeting many principles of green chemistry. Much of this work has focused on determining the effect of each sulfur source on polymerization and adhesion. A family of polymers were created with varied S: GEO: monomer ratios and characterized to determine differences in their chemical and materials properties. Despite similarities in the reaction mechanism, sulfur tends to polymerize more rapidly and create materials that are more ductile and more easily reprocessed. GEO is slower to react causing more polymerization to take place on the adherend surface yielding a more brittle polymer with higher maximum adhesion strength but lower work of adhesion. Both polymers exhibited effective adhesive recyclability. Overall, a combination of natural oils and petroleum byproducts were combined to make inexpensive, sustainable, recyclable adhesives.

Introduction

Adhesives are a mainstay of modern life and are critical in a wide range of commercial products. Although their origins are natural materials from thousands of years ago, most modern adhesives are made from non-renewable petroleum products making them unsustainable and ecologically damaging.[1, 2] In recent years, a variety of factors have caused a societal shift toward creating biobased products. Plant oils have been specifically used to create a range of adhesives including polyurethanes, polyvinyl acrylates, and epoxies.[3-5] Incorporating these oils can offer solvent resistance, biodegradability, and reduced health hazards. However, current alternatives tend to lack the strength required of more intensive applications.

Sulfur-containing compounds in crude oil lead to the release of SO_2 during combustion, which combines with water in the atmosphere causing acid rain.[6] Therefore, sulfur-containing contaminants are removed during petroleum refinement leading to the annual production of ~70 billion kg of sulfur byproduct.[6, 7] Heating sulfur enables the homolytic cleavage of the S_8 ring forming radical species that can initiate polymerization with unsaturated C-C bonds in a process termed inverse vulcanization.[8] This method expanded rapidly due to the synthetic ease, scalable synthesis, and adherence to many of the principles of green chemistry due to sulfur acting as the solvent, initiator, and monomer, yielding high atom economy and limiting waste production.[9] Inverse vulcanization has been used to create materials for a wide range of applications including cathodes,[8, 10, 11] infrared optics,[12-14] and water purification,[15-21] among others.[22-28] In a prior report we described the first adhesives formed by inverse vulcanization by combining elemental sulfur with garlic essential oil (GEO).[29] Since then, there has been evidence of other polysulfides functioning as adhesives,[30, 31] cements,[32-34] binders,[35] and coatings.[36] Polysulfides are often solvent resistant and flexible with some being able to withstand high temperatures.[37]

An equivalent process utilizing the S-S bonds of allyl sulfides present in GEO make it possible to use this natural feedstock as an initiator for radical polymerization.[29] GEO is a unique plant oil since it is primarily composed of allyl sulfides enabling it to contribute to the overall sulfur content of the material.[38, 39] The effective use of GEO in adhesive copolymers offers a path to synthesize fully renewable adhesives. In order to accomplish this goal, we need to better understand the role of natural monomers and their impacts on adhesives.

Here we have expanded the use of essential oils to form polysulfide adhesives to include naturally sourced monomers linalool, limonene, and myrcene. We have also included analysis of dicyclopentadiene (DCPD) which is a byproduct of ethylene production.[40] Furthermore, this work provides an in-depth analysis into the role of sulfur versus GEO on the chemical and material properties of polysulfides.

Experimental

Materials

Plant Therapy garlic essential oil was used for the majority of testing. However, there were supply issues, so recyclability analysis was conducted with Plant Guru garlic essential oil. All other reagents were purchased from ThermoFisher Scientific or Sigma Aldrich without further modification. Aluminum sheets were purchased from McMasterCarr.

Polymer Synthesis and Characterization

The polymers were synthesized by heating elemental sulfur or garlic essential oil with the monomer of interest at 160 °C for 1 h. A range of S:GEO:monomer ratios were synthesized with 50% monomer by weight, 0-50% GEO, with the remainder composed sulfur. Vials were vented in the hood to allow any hydrogen sulfide that may have formed to escape before further use. In a typical synthesis 0.50 g sulfur and 0.50 g of monomer such as linalool are combined in a 3.7 mL vial with a stir bar and heated at 160 °C for 1 h. The polymer is then collected in a syringe where it is stored and then used to deliver the polymer for adhesion testing. Synthesis could also be conducted on a 5 g scale with similar results. Polymers were characterized on a Bruker 400 MHz NMR in $CDCl_3$ and by ATR FTIR spectroscopy using a ThermoScientific Nicolet iS5 with an iD7 ATR attachment to determine the extent of polymerization. The monomer alkene peaks rather than the allyl peaks from GEO were used to determine the degree of polymerization due to GEO reacting more readily than the other natural monomers. Polymers were further characterized on a TA instruments DSC Q20 with an RCS40 cooling unit and thermogravimetric analyzer Q600 DSC samples were analyzed from -40 to 140 °C, at 10 °C per minute. TGA experiments were conducted from 25 to 550 °C, at 10 °C per minute.

Polymer solubility in dichloromethane (DCM) was tested. After the initial polymerization, ~ 50 mg of polymer was added to a pre-weighed vial and cured at 160 °C for 24 h to mimic adhesive curing. The vials are removed from the oven and allowed to cool to room temperature. ~ 2 mL of DCM was added to obtain a 25 mg polymer per 1 mL DCM ratio. The polymer was vortexed and left overnight to ensure maximum dissolution. It was vortexed again before removing the insoluble portion by vacuum filtration using pre-weighted filter paper. Because these materials tend to be heterogeneous, there is typically a soluble and insoluble portion rather than just a concentration at which the polymer is soluble in a given solvent.[41] Therefore, three, 1 mL washes of DCM were used to wash away any remaining soluble polymer. The filter paper was dried and weighed to determine the insoluble portion. The soluble portion was determined by subtracting the mass of the insoluble portion from the starting polymer mass.

Due to reported hydrogen sulfide gas production during inverse vulcanization, reaction vials were opened in a fume hood to prevent exposure to gasses formed during the reaction and adhesives were cured in an oven with a connection to a ventilation system. To quantify the H_2S produced during the reaction, tubing was connected from the reaction vessel to a flask of 1 M $AgNO_3$, which functioned as an indicator, according to the published protocol.[42] After collection, the resulting Ag_2S precipitate was filtered and weighed. This test was performed for the synthesis and cure of poly(S-linalool) and poly(GEO-linalool).

Adhesion Testing

1/8-inch sheets of T6061aluminum were cut into 3.5 x 1 inch adherends by water jet (**Figure 1**). Adherends were sanded using a random orbital palm sander with 150 grit sandpaper. A 1 cm long area of each adherend was masked off with scotch tape to control the area of polymer application and minimize border irregularity. 25 +/- 1 mg of polymer was evenly spread onto the masked area using razor blades and/or syringe needles. Densities were obtained for some polymer samples, so a volume was used instead utilizing the calculated volume for a 0.025 g sample to the nearest µL. After sample application the scotch tape was removed and a 1 cm^2 piece of scrim cloth was placed on top of one side of the adherend pair to help control bond thickness. The other adherend was overlapped to form a single-lap joint (Figure 1). The joints were cured in a 160 °C oven for 24 h and were allowed to cool a minimum of one hour before testing. Lap shear testing was performed by applying in-line tension to each joint at a rate of 2 mm/min using an Instron TM34-10 universal testing system. Tests were ended automatically after a 70% drop in force once a force of at least 10 N was registered. The adhesion strength was determined by dividing the maximum force by the overlap area. Work of adhesion was automatically calculated by the BlueHill testing software by calculating the area under the force versus extension curve. The failure mode (adhesive vs cohesive) was determined by visual inspection.

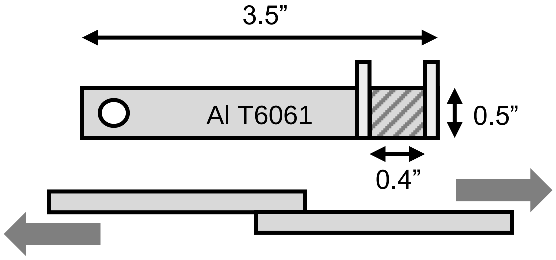
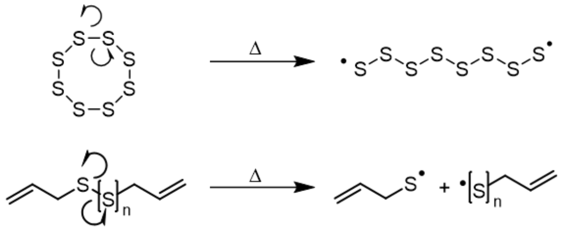


Figure 1: Schematic of aluminum adherends and the single lap joint configuration used for adhesion testing.

Results and Discussion



Scheme 1: Homolytic cleavage of elemental sulfur and allyl sulfides present in garlic essential oil to form thiyl radicals.

To better understand how sulfur and GEO impact adhesion, each was used as the sulfur source and initiator for the polymerization of limonene, linalool, myrcene, and dicyclopentadiene (DCPD). Upon exposure to heat, both sulfur and GEO undergo S-S bond cleavage to form sulfur radicals (**Scheme 1**). Polysulfides were synthesized by heating the monomers to 160 ℃ for 1 h. Limonene, linalool, and DCPD were synthesized with 50% sulfur or GEO and 50% monomer by weight. However, myrcene solidified at 50% sulfur preventing the collection of adhesion data.

Instead, these copolymers are presented with 30% S/GEO and 70% myrcene by weight. Pinene was also tested, but it did not form stable polysulfides with sulfur. The bicyclic structure of pinene with a single unsaturation may limit its ability to stabilize sulfur causing the extended sulfur chains to depolymerize reverting to the S_8 form. This was observed by yellow sulfur rapidly precipitating from solution upon cooling. Each of these monomers has been reported previously to successfully form polysulfides by inverse vulcanization,[9-11, 19, 43] but most have not been used to form adhesives. The exception is DCPD which has been used to form adhesives in conjunction with canola oil.[30, 31]

The polymers synthesized with GEO outperformed those synthesized with sulfur in the case of each comonomer tested: limonene, linalool, myrcene, and DCPC (**Figure 2**). However, the difference in adhesion strength varied substantially. For myrcene, there is almost no difference (0.02 MPa), whereas linalool demonstrated dramatic differences in adhesion strength based on the sulfur source obtaining a maximum adhesion strength of 0.45 MPa for poly(S-linalool) versus 1.78

MPa for poly(GEO-linalool). Regardless of the monomer used, all outperformed poly(GEO), which had a maximum adhesion strength of 0.68 MPa. However, none of the natural monomers outperformed poly(S-GEO), which achieved 1.91 MPa. Sulfur homopolymers could not be used for comparison since elemental sulfur rapidly decomposes after homopolymerization.

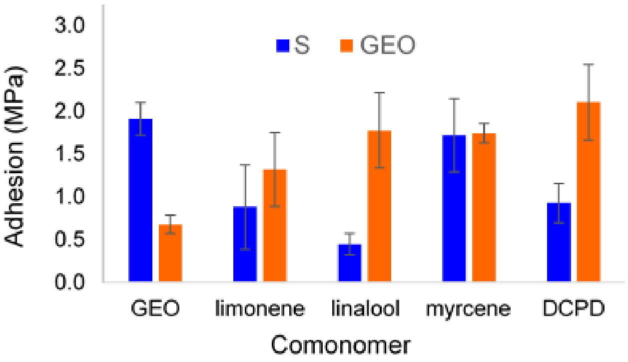


Figure 2: Adhesion strength of polysulfides formed with elemental sulfur (blue) versus garlic essential oil (GEO) (orange) with a variety of monomers. For the GEO comonomer, the orange bar represents the homopolymer poly(GEO).

Altering the comonomer proved to have more of an impact on the failure mode than the sulfur source. DCPD demonstrated adhesive failure indicated by failure occurring at the polymer-Al adherend interface. Linalool, instead, failed within the polymer indicating cohesive failure. Limonene had a mixture of the two. These failure modes were consistent regardless of sulfur source.

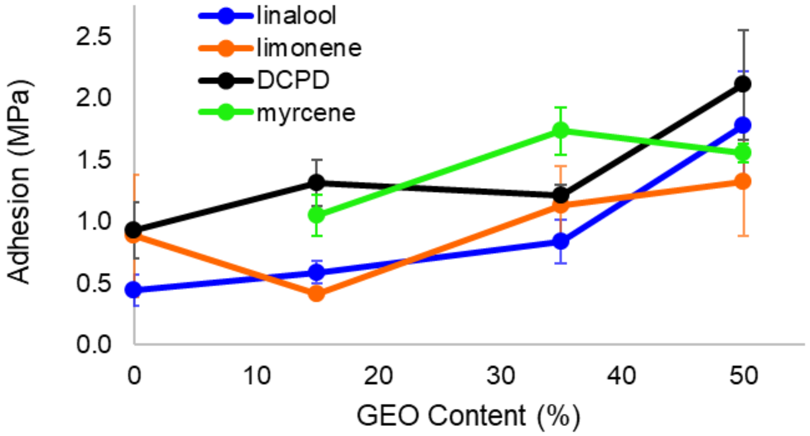


Figure 3: Adhesion strength of polysulfides made with 50% monomer: linalool (blue), limonene (orange), DCPD (black), and myrcene (green), 0-50% garlic essential oil (GEO) and the remainder being elemental sulfur.

To better understand the variations in adhesion strength a series of polymers were made. The monomer of interest was held constant at 50% by weight and the remainder was composed of variable amounts of GEO:S (0:50, 15:35, 35:15, and 50:0). The adhesion strength of these co- and terpolymers was compared (**Figure 3**). These intermediate tests indicate that there is not a balance between sulfur and GEO that provides the best strength, but rather that the higher GEO content led to higher adhesion strength. Although some data are included for myrcene in Figure 3, the full series could not be tested due to solidification above 30% S. Therefore, myrcene was also tested at different ratios. For myrcene, the strongest adhesion was observed with either all S or all GEO and decreased in between (Figure S1). There may be less dramatic changes with this system due to the higher myrcene content, limiting the impacts of S and GEO.

Since linalool demonstrated the largest difference in adhesion strength between sulfur and GEO, it was the focus of further studies to compare the role of the sulfur versus GEO. A variety of chemical and physical properties were analyzed to determine what could be leading to the dramatic differences in adhesion strength. To mimic the adhesive conditions, polymers were analyzed immediately after the initial polymerization as well as after a 24 h cure at 160 °C.

By observing changes in relative abundance of the linalool alkene peaks by ^{1}H NMR, the extent of polymerization could be determined (Figure S2). Since GEO is a natural monomer composed of a variety of chemical species it made NMR analysis difficult. Instead, diallyl disulfide (DADS) was used in the place of GEO to help clarify NMR analysis. DADS is the main component of GEO and demonstrated comparable adhesive performance to GEO in prior work,[29, 39] so it is a viable alternative. However, NMR spectra of poly(GEO-linalool) were also collected (Figures S3-5). When GEO was used instead of DADS, slightly lower degree of polymerization was observed before curing. NMR data indicated that the higher the DADS content, the lower the degree of polymerization before curing ranging from 89% polymerization for poly(S-linalool) to only 32% for poly(GEO-linalool) (**Figure 4**). Due to the decrease in solubility after cure, it

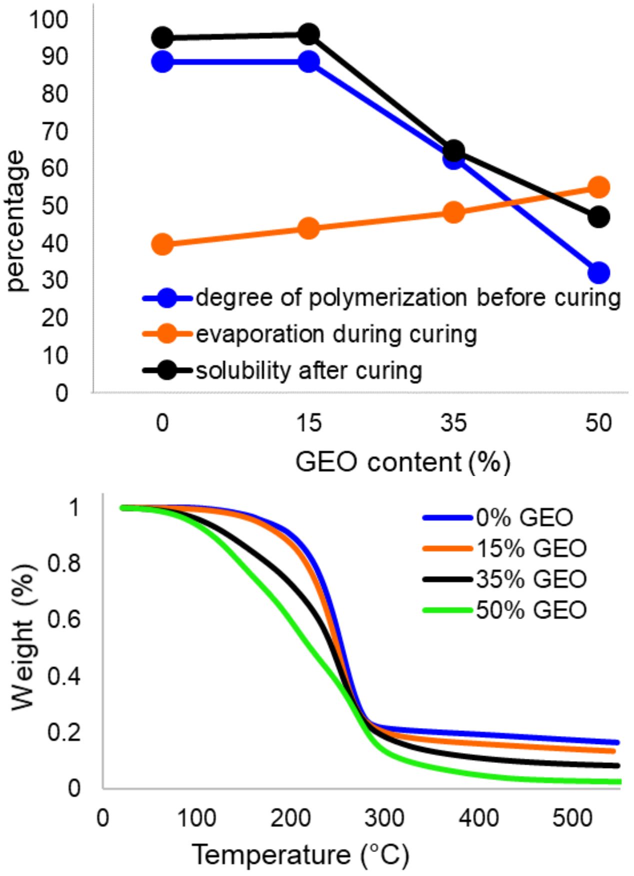


Figure 4: Changes in the degree of polymerization before cure (blue), evaporation during cure (orange), and polymer solubility after cure (black) as well as the thermogravimetric analysis of poly(S-GEO-linalool) based on the S:GEO ratio. Terpolymers all contain 50% linalool by weight.

became difficult to accurately compare the extent of polymerization between these polysulfides. However, the decrease in solubility after curing and the change in consistency from a liquid to a brittle solid indicate that there is likely some polymerization taking place on the adherend surface during the cure.

As the GEO content increases, there was more evaporation during the cure. This is not too surprising since NMR data indicated that these samples still had high monomer content after the initial polymerization making them more susceptible to evaporation. Thermogravimetric analysis provided further insight into these materials. Samples with the highest GEO content demonstrated rapid mass loss at temperatures beyond 100 °C. They also demonstrated much lower char yield at 2.6% for poly(GEO-linalool). As the GEO content decreased the char yield increased to 17% for poly(S-linalool).

After the initial polymerization, all of the linalool polysulfides were fully soluble in DCM. However, after curing, polysulfide solubility decreases with higher GEO content. This indicates that there may be more crosslinking when GEO is present. Analysis by DSC shows that poly(S-linalool) had the lowest glass transition temperature (Tg) at just 21 °C, whereas poly(GEO-linalool) had the highest at 42 °C (Figure S6). Together, these data indicate that the presence of GEO increases polymer crosslinking. This is not surprising due the presence of allyl monosulfides that do not possess labile S-S bonds, and instead are likely acting as a difunctional monomer capable of forming crosslinks.

Polymers formed by inverse vulcanization have been shown to produce hydrogen sulfide gas. H_2S production was quantified by measuring the Ag_2S precipitate formed when exposed to a solution of $AgNO_3$. After the initial polymerization, no H_2S was detected for poly(GEO-linalool). When subjected to a 24 h cure mimicking adhesive cure conditions, 0.29% mass was lost as H_2S. Poly(S-linalool) only produced 0.41% during the polymerization, but during the cure it increased to 1.89%. Both polymers released less H_2S during subsequent 24 h cures.

In addition to examining maximum adhesion strength, the force versus extension curves and work of adhesion were analyzed for the family of linalool polysulfides. As the GEO content was increased, polymers became less ductile and more brittle (**Figure 5**). Although high GEO content led to higher maximum adhesion strengths, they had dramatically lower work of adhesion. Poly(S-linalool) demonstrated the highest work of adhesion at 121 mJ and the lowest maximum adhesion at 0.63 MPa, whereas poly(GEO-linalool) had the lowest work of adhesion, 35 mJ and the highest maximum adhesion, 0.99 MPa. The increased crosslinking caused by GEO may be enhancing the overall material strength, but creating a more rigid network causing brittle failure. The variety of sulfur ranks present at higher sulfur-contents may be providing a range of bond strengths leading to tougher materials.[44]

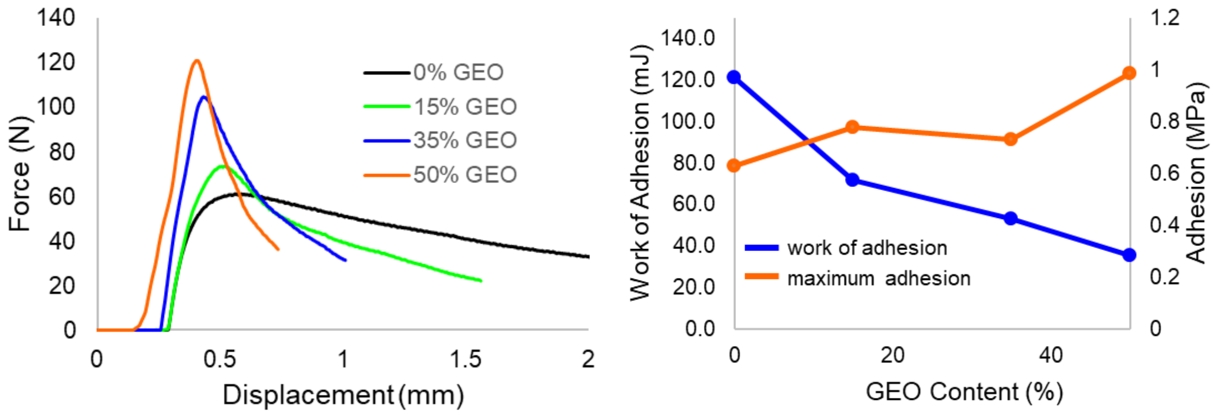


Figure 5: Force versus displacement curves and a comparison of maximum adhesion strength to the work of adhesion for poly(S-GEO-linalool) with varied the S:GEO ratios. Terpolymers all contain 50% linalool by weight.

Other polysulfides formed by inverse vulcanization have demonstrated thermal repair or recycling.[41, 45-48] Therefore, these polymers were subjected to a series of tests to determine if they could be effectively recycled. Qualitative analysis was conducted by taking the polysulfides after one round of curing and placing them into vials. These were heated again at 160 °C for 30 min. For polymers made with linalool and myrcene, samples with higher S content readily melted, whereas those with higher GEO content remained in more discrete pieces with slight melting (Figure S7). However, DCPD was not able to be melted and reprocessed regardless of the sulfur source. It should also be noted that S-linalool will take the form of its container over time at room temperature.

Adhesive recyclability was also tested by placing adherends back in the lap shear configuration and subjecting them to another round of curing at 160 °C for 24 h. Samples were again subjected to adhesive analysis (**Figure 6**). Regardless of sulfur source, all polymers obtained higher strength after the second round of testing. Although some systems have demonstrated comparable tensile strength after recycling, others have shown a decrease, so the improved adhesion strength was unexpected.[30, 48] Polymers with more sulfur achieved both a more dramatic increase in adhesion strength, and a higher maximum adhesion strength. The higher sulfur rank present in these materials likely possess more labile bonds enabling improved recycling. The transition from cohesive failure during round one to adhesive failure upon re-curing support this idea.

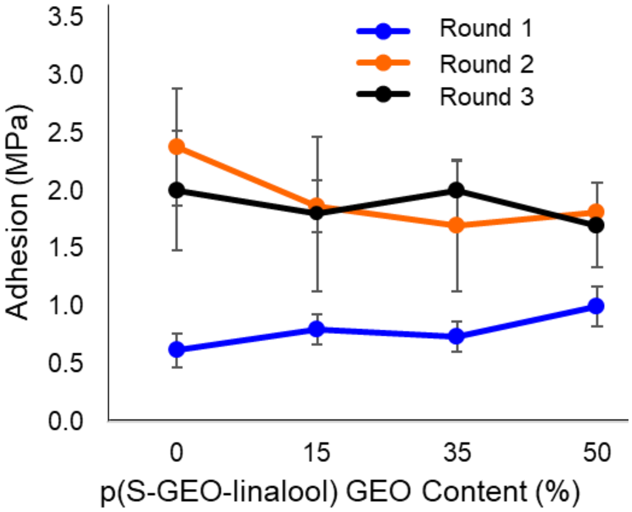


Figure 6: Maximum adhesion strength of poly(S-GEO-linalool) with varied the S:GEO ratios after multiple rounds of testing.

An attempt was made to shape these polymers into dogbone specimens to perform materials analysis. However, evaporation of the GEO-based samples limited our ability to create specimens for further materials analysis. Many polysulfides obtained by inverse vulcanization have demonstrated the formation of flexible films.[45, 49] Initial force versus extension curves obtained during adhesive testing showed some elasticity for sulfur-based samples demonstrated by larger displacement before failure. The materials themselves were also more flexible. However, upon repeated thermal recycling, all polymers lost that flexibility and became more brittle. This could be observed by smaller displacement before failure as well as cracking during handling.

Conclusions

A family of adhesive polysulfides were synthesized using either elemental sulfur or garlic essential oil as the sulfur source and radical initiator. Despite all polymers analyzed being polysulfides, the properties of these materials were quite different. After fully characterizing a series of poly(S-GEO-linool) materials with varied S:GEO ratios, the data indicate that while GEO polymerizes less in the reaction vessel, it undergoes further crosslinking and polymerization during curing ultimately leading to a polymer that is less soluble, more brittle, and has a stronger maximum adhesive strength. The use of garlic essential oil caused the polymers to lose some flexibility that is typical of polysulfide adhesives. Elemental sulfur, however, offers improved work of adhesion, reprocessabilty, and higher adhesion strength after it has been recycled. Both GEO and elemental sulfur offer a path to rapidly form adhesive copolymers from natural sources or petroleum byproducts without the need for solvents, allowing for the formation of more environmentally friendly and sustainable adhesives.

Associated Content

Supporting Information.

Adhesion strength of poly(S-GEO-myrcene) made with 70% myrcene, ^{1}H NMR poly(S-DADS-linalool) with varied S:GEO ratios, ^{1}H NMR poly(GEO-linalool) and poly(DADS-linalool), HSQC NMR of GEO and poly(GEO-linalool), differential scanning calorimetry, image of poly(S-GEO-linalool) before and after additional heating, tables of maximum adhesion and work of adhesion data. (PDF)

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Author contributions

A. Davis was responsible for most of the investigation, validation, and visualization as well as some writing-review and editing. K. Sayer provided some investigation, data curation, some visualization as well as some writing – review and editing. C. Jenkins was responsible for conceptualization, funding acquisition, project administration, resources, and writing- original draft and review & editing.

Conflict of interest

The authors declare no competing financial interests.

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