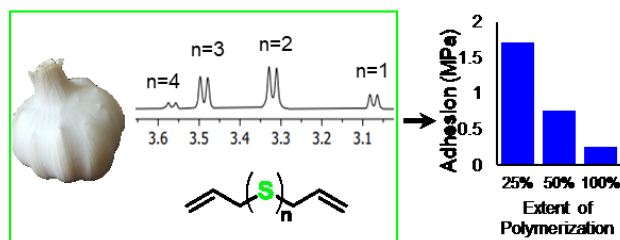


Allyl Sulfides in Garlic Oil Initiate the Formation of Renewable Adhesives

Kyler B. Sayer, Veronica L. Miller, Zackery Merrill, Anthony E. Davis, Courtney L. Jenkins*

Department of Chemistry, Idaho State University, 921 South 8th Ave, Pocatello, ID 83209.

TOC graphic



Garlic essential oil (GEO) was used as the monomer, solvent and initiator to form adhesive polysulfides. Analysis of GEO and the resulting polymer properties improved our understanding of p(GEO) providing a route to develop renewable, S-based materials.

Abstract

The development of inverse vulcanization has provided a simple method to create sulfur-based materials. The low cost, ease of synthesis, and variety of applications has led to a rapid expansion of the field. These polysulfides can be synthesized with a wide range of sulfur contents (20-90% S) depending on the desired properties. Garlic essential oil (GEO) has a high sulfur content, which offers the opportunity to replace sulfur, a petroleum byproduct, with a renewable monomer to make materials with moderate sulfur contents. Using a one-pot, solvent-free synthesis, comparable to inverse vulcanization, GEO can be polymerized to create renewable adhesives at temperatures as low as 120 °C with reaction times decreasing at higher temperatures. Here we have explored the composition of garlic oil from a variety of commercial suppliers by NMR. Through simple ^1H NMR analysis, the major sulfur-containing compounds of GEO can be identified and differentiated by sulfur rank. These data were used to select garlic oils with varied compositions to examine the impact on the poly(GEO) properties using solubility, gel permeation chromatography, differential scanning calorimetry, and thermogravimetric analysis as well as adhesive performance. GEO was then subjected to different reaction times and temperatures and the degree of polymerization was monitored by ^1H NMR. The polysulfides were then evaluated as adhesives at different extents of polymerization to better understand how the reaction conditions impact adhesive performance. The failure mode and mechanical properties of the polymers were analyzed using measurements of maximum adhesion strength and work of adhesion. This study has provided a better understanding of polymers formed from GEO, providing a viable route to developing renewable, S-based materials.

Introduction

Inverse vulcanization is a polymerization method that typically uses heat to cleave elemental sulfur in the presence of difunctional monomers to crosslink and stabilize elemental sulfur.¹ The solventless synthesis, high atom economy, and complete polymerization preclude the need for a solvent-intensive workup allowing this synthetic method to meet many of the principles of green chemistry.² Additionally, the short reactions times, scalability, inexpensive reagents, and widely applicable materials have led to the rapid expansion of inverse vulcanization in creating sulfur-based materials.³⁻⁹

The large excess of elemental sulfur formed by the desulfurization of crude oil has made sulfur an inexpensive reagent for decades.^{2, 10} However, a new study found that society's efforts to move away from fossil fuels may create a sulfur shortage even for common products such as sulfuric acid.¹¹ Garlic essential oil (GEO), rich in allylsulfides,¹²⁻¹⁴ may offer a renewable alternative to making sulfur-based materials.

Garlic (*Allium sativum*) has been used by humans for thousands of years in both traditional medicine and food preparation.^{14, 15} Today, a wide range of garlic varieties are produced worldwide.¹⁶ The volatile sulfur compounds present provide the pungent scent often associated with garlic. The composition of many varieties of garlic oils has been studied. Although there is some variation in the exact composition of a specific type of garlic oil, all of them are dominated by the presence of allyl sulfides.¹⁴

Inverse vulcanization is typically initiated by heating elemental sulfur above 160 °C causing homolytic cleavage, forming thiyl radicals, which can initiate polymerization with unsaturated C-C bonds.¹ A similar process can be achieved with the allyl sulfides present in GEO.^{17, 18} Applying heat to allyl sulfides also leads to the homolytic bond cleavage forming radicals that can initiate polymerization.^{15, 17} Prior reports have combined sulfur with GEO to form co-polymers, limiting our understanding of the role of GEO in polymerization.¹⁷⁻²⁰ Additionally, these publications have used GEO without focusing on how changes to the oil composition could impact polymer structure and adhesive performance.

Adhesives are a critical component of modern life and are found across diverse applications in industry, construction, business, and education among others. While the origin of adhesives is

found in natural systems, most current adhesives are products of petroleum refinement.^{21, 22} These petroleum-based adhesives largely replaced their natural counterparts due to their high strength, solvent resistance, and consistent performance, but they have a variety of drawbacks including their ecological impacts and lack of long-term sustainability.^{21, 22} GEO offers a unique way to create adhesive polysulfides. The use of polysulfides as adhesives offers a variety of benefits including their tendency to be solvent resistant, flexible, and some demonstrating high-temperature resistance.²³

Here we have analyzed the structure of GEO from a variety of different commercial suppliers to determine how the makeup impacts poly(GEO) formation and the properties of the resulting materials. This information has been used to develop fully renewable, adhesive polysulfides. Alterations to the reaction conditions have been analyzed to gain an understanding of the polymerization and adhesion mechanisms.

Experimental

Materials

Garlic essential oils were purchased from Plant Therapy, Green Health, Greenwood Essential Oils, Plant Guru, Fabulous Frannie, and Artizen and were used without modification. All other reagents were purchased from ThermoFisher Scientific or Sigma Aldrich and used without further modification. Aluminum sheets (6061-T6) and scrim cloth used in adhesion testing were purchased from McMasterCarr.

Polymer Synthesis and Characterization

Garlic essential oil (GEO) was initially polymerized by stirring 1 g of GEO in a scintillation vial at 180 °C for 1 h. Additional syntheses were performed at 120, 160, and 180 °C for 15 min to 36 h. Vials were vented in the hood as a precaution since small quantities of hydrogen sulfide gas may be produced during the synthesis. To quantify the production of H₂S over the course of a reaction, the reaction vessel was connected to a sidearm flask containing 1 M AgNO₃ which will react with H₂S to form Ag₂S (s).²⁴ Ag₂S precipitate was collected using vacuum filtration and weighed to quantify the H₂S produced over the course of polymerization and curing.

^1H , ^{13}C , ^{13}C DEPT, and ^1H - ^{13}C HSQC NMR were run using a Bruker 400 MHz NMR with CDCl_3 solvent. ^1H NMR was run with 16 scans and a delay time of 1 s, while ^{13}C NMR, ^{13}C DEPT NMR, and ^1H - ^{13}C HSQC NMR were run with 80-8192 scans and a delay time of 1.5-2 seconds. Integration of the allyl peaks from 5-6 ppm and H-C-S peaks from 3-4 ppm in ^1H NMR spectra were used to determine the relative ratio of allyl sulfide species with varied sulfur ranks. ^1H NMR spectra were also used to monitor the intensity of the allyl peaks over the course of the reaction to monitor the extent of polymerization.

ATR FTIR was performed on a ThermoScientific Nicolet iS5 with an iD7 ATR attachment to compare functionality between different garlic essential oil suppliers as well as an alternative method to determine the extent of polymerization within a sample. The presence and intensity of stretches corresponding to alkenes were used to determine the extent of polymerization.

Molecular weight and polydispersity were determined using gel permeation chromatography (GPC) with an Agilent 1260 GPC system equipped with PLgel MesoPore 3 μm columns purchased from Agilent Technologies (0 – 25000 Da working range) using dichloromethane mobile phase with a flow rate of 1 mL/min. Polystyrene standards with molecular masses between 580 and 27,010 g/mol were used to form a 4th order polynomial model for calibration. For each sample, 10 – 15 mg of polymer per mL of solvent was filtered using a 0.45 μm hydrophobic PTFE filter before 100 μL was injected into the GPC/SEC for analysis.

Glass transition temperatures were determined using differential scanning calorimetry (DSC) with a TA Instruments DSC Q20 with an attached refrigerated cooling system, RSC 40. Samples were initially cooled to $-40\text{ }^\circ\text{C}$ before heating the samples to $150\text{ }^\circ\text{C}$ at a rate of $10\text{ }^\circ\text{C min}^{-1}$. The onset temperature of degradation and char yields were determined by thermogravimetric analysis (TGA) using a TA Instruments SDT Q600. TGA was run from 25 to $550\text{ }^\circ\text{C}$ at a rate of $10\text{ }^\circ\text{C min}^{-1}$.

Adhesion Testing

Aluminum adherends were prepared by sanding the surface using a random orbital palm sander with a 150-grit sanding disk. A 1 cm by 1.25 cm area was then masked with scotch tape on each adherend to control the area of application and to reduce border irregularities. $25 \pm 1\text{ mg}$

of polymer was evenly applied to each adherend within the masked region and the tape was removed. Two adherends were overlapped in a single-lap shear configuration to form a joint with a 1 cm² piece of scrim cloth between the adherends to control for the thickness of the polymer. Joints were then placed in a 160 °C oven for 24 hours to cure.

Adhesion testing was performed using an Instron 34TM-10 Universal Testing System in a tensile configuration pulling joints apart at a rate of 2 mm min⁻¹. Testing was ended when the registered force decreased by 70% from the maximum reading after a force of at least 10 N was achieved. Samples that failed to reach 10 N were ended manually. Following testing, the area of overlap was measured and used to calculate the adhesion strength in MPa. Examination of the post-test adhesive enabled the failure mode to be determined to be adhesive (failure at the adherend-polymer interface) or cohesive (failure at the polymer-polymer interface). Work of adhesion was automatically calculated using the integral of the force-displacement curve over the entire duration of the test.

Results and Discussion

Garlic essential oil (GEO) was purchased from a variety of suppliers. All GEO suppliers used a steam distillation process to obtain a variety of natural products, typically dominated by allyl sulfides.¹⁴ To better understand how the components impact both the synthesis and properties of poly(GEO), a variety of spectroscopy, thermal, and mechanical analyses were conducted.

Spectral Analysis of Garlic Essential Oil

¹H NMR of GEO showed two multiplets at ~5.8 and 5.1 ppm corresponding to the proton environments of the two olefin carbons present in allyl sulfides (**Figure 1**). The extreme degree of overlap between signals of different allyl sulfides in the olefin region causes the multiplicity observed in GEO rather than the clear splitting present for pure monomers. Further analysis of the ¹H NMR of GEO showed a series of apparent doublets of doublets (dd) or doublets of triplets (dt) within the heteroatom region where the S-C-H environments of the allyl sulfides were expected. The use of diallyl sulfide (DAS) and diallyl disulfide (DADS) as model systems provided confirmation of the monosulfide and disulfide assignments in GEO (Figure S1).

Additionally, the difference in chemical shift between peaks in this region was compatible with previously published results relating sulfur rank, number of consecutive S atoms, to chemical shifts in ^1H NMR.²⁵ As the sulfur rank increases, the corresponding peaks become closer and closer together, making it difficult to differentiate allylsulfides with five or more consecutive S-S bonds. Taken together, this provided evidence for the ability to distinguish between allyl sulfides of different sulfur rank by chemical shift alone within ^1H NMR.

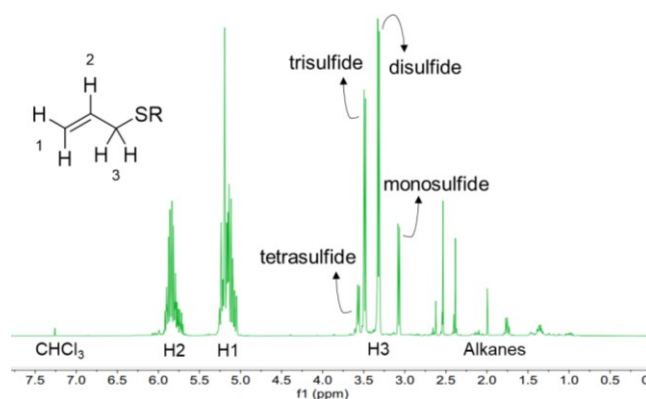


Figure 1: ^1H NMR of garlic essential oil highlighting the allyl groups and peak shifts between the mono-, di-, tri-, and tetrasulfide.

Further analysis by ^{13}C , ^{13}C DEPT, and ^1H - ^{13}C HSQC NMR all confirmed the presence of allyl sulfides of varying sulfur rank in GEO. Monosulfides are easily discernable from all other allyl sulfides with higher sulfur rank (Fig S2-4). ^1H NMR of GEO showed varying alkane peaks, but due to the complexity of the mixture, no effort was made to identify specific compounds. It is noteworthy, however, that GEO from Greenwood Essential was unique in its low alkane content with each sample having no or few peaks present below 2.9 ppm and any peaks that were present having low intensity, representing less than 2% of the overall sample (Fig S5).

The relative abundance of the various allyl sulfide species within a sample of garlic essential oil was measured by integrating each peak of a given species of allyl sulfide relative to the total allyl proton region and expressed as the mol%. This measurement was used to compare the amounts and types of allyl sulfides present within a sample of garlic essential oil. These data were collected for a variety of different commercial GEO suppliers (**Figure 2**). Multiple bottles from each supplier were tested. Very little difference was observed within each supplier except Fabulous Frannie, which had large variation between batches, and were therefore treated as

separate samples. As expected from literature precedent,¹⁴ DADS was the most abundant allyl sulfide in GEO with most samples being composed of 40-50% DADS. Only two suppliers contained diallyl pentasulfide (DAPS) with a sulfur rank of 5, which was the most consecutive S-S bonds observed in these samples. When comparing all suppliers to one another, there was less consistency in GEO composition. The deviation within a given species ranged from 15 – 33% for DAS, DADS, diallyl trisulfide (DATS) and diallyl tetrasulfide (DATeS) and reaching as high as 186% for DAPS content. This difference in consistency can be easily seen when the data is arranged with respect to species first rather than by supplier (Figure S6). However, even with these differences, all samples were still primarily composed of DADS and DATS.

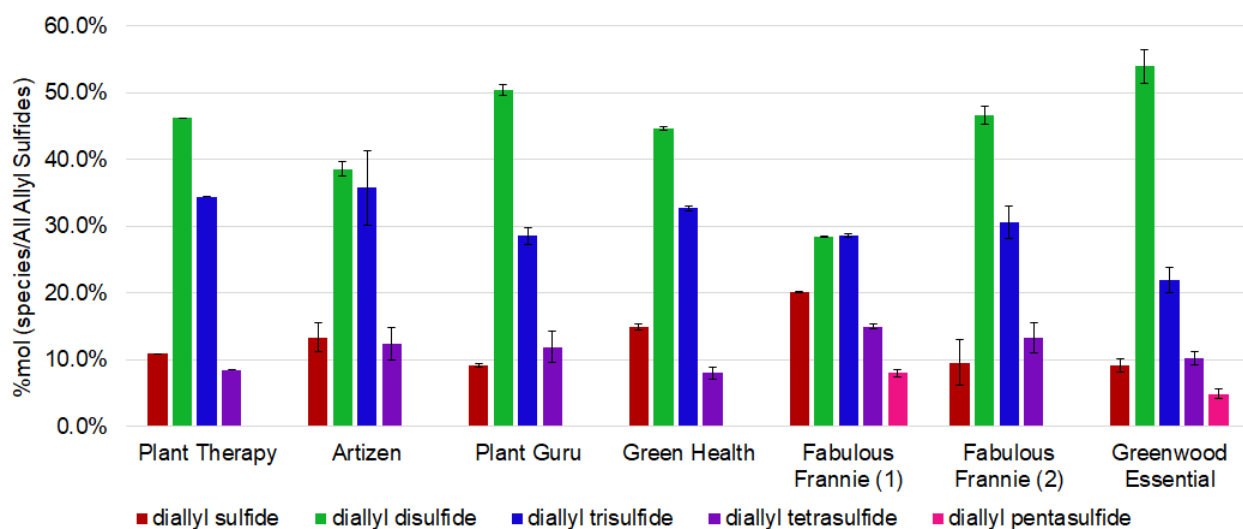


Figure 2: Relative abundance of each allyl sulfide species present in garlic essential oil from a variety of suppliers. Error bars represent standard deviation between bottles.

ATR FTIR analysis of GEO showed expected alkene functionality with a C=C stretch observed at 1620 cm^{-1} and a sp^2 C-H stretch at $\sim 3080\text{ cm}^{-1}$ (**Figure 3**). Additional alkane sp^3 C-H stretches were found at 2980 and 2920 cm^{-1} in all suppliers, including Greenwood Essential samples which showed no alkane peaks in ^1H NMR. This discrepancy can be explained by the presence of allyl methyl sulfides which would be expected to form peaks in similar regions as the diallyl sulfides in ^1H NMR. The FTIR spectra of all samples within and across suppliers appeared identical and denoted the presence of identical functionality.

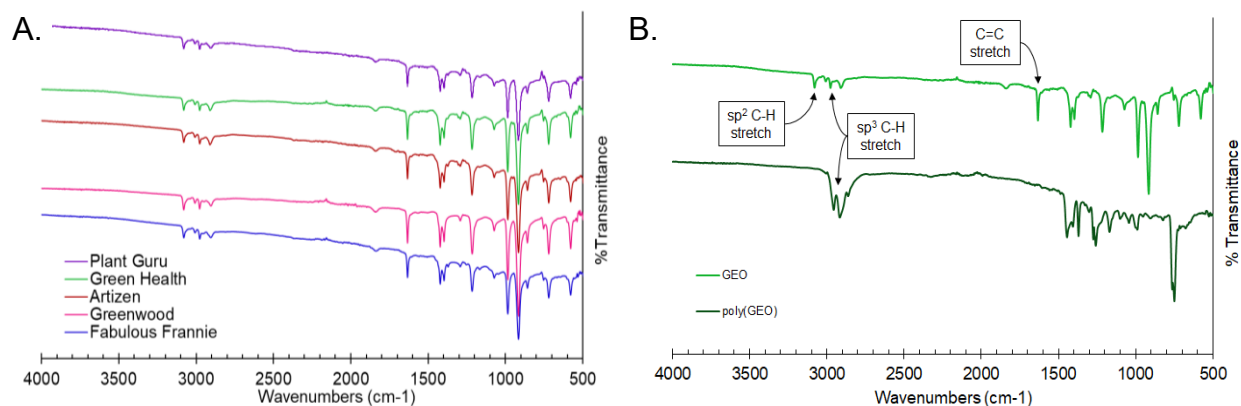


Figure 3: ATR FTIR spectrum of A. GEO from various suppliers and B. of GEO from Green Health before and after polymerization.

Polymerization of Garlic Essential Oil

Although there were differences in composition across the suppliers, most suppliers had an allyl sulfide distribution similar to Green Health. Therefore, only Green Health (GH), Fabulous Frannie (1) (FF1), and Greenwood Essential (GE) were analyzed further. GH is composed primarily of DADS and DATS with small amounts of DAS and DATeS, similar to Plant Therapy, Artizen, and Plant Guru. FF1 has a more even allyl sulfide distribution and includes DAPS. GE has the highest DADS content with much lower proportions of all other allylsulfide species as well as being the only GEO sample composed almost exclusively of allylsulfides (Figure S7).

All samples were polymerized by heating unaltered GEO to 180 °C for 1h. Samples rapidly transitioned from a clear liquid to a dark brown, viscous liquid (**Figure 4**). The color of GEO varied from nearly colorless, to pale yellow, to light brown depending on the supplier. DAS, which contains a thioether, does not homopolymerize, but allyl sulfides with at least a sulfur rank of 2 all possess dynamic S bonds that form radicals when heated, initiating polymerization. For DADS, the homolytic cleavage likely occurs at the C-S bond.¹⁵ As the S rank increases, S-S bonds weaken enabling the formation of two sulfur radicals.²⁶ These sulfur radicals can then initiate polymerization with unsaturated carbons, similar to inverse vulcanization. Pure sulfur homopolymerizes to form a red solid.¹ However, with increasing addition of organic crosslinkers, the polymers often become more brown and opaque.²⁷ Here, the presence of modest S-content relative typical inverse vulcanization, which can have up to 90% S,

and array of different organic components likely lead to the lack of transparency and brown color in the final product.

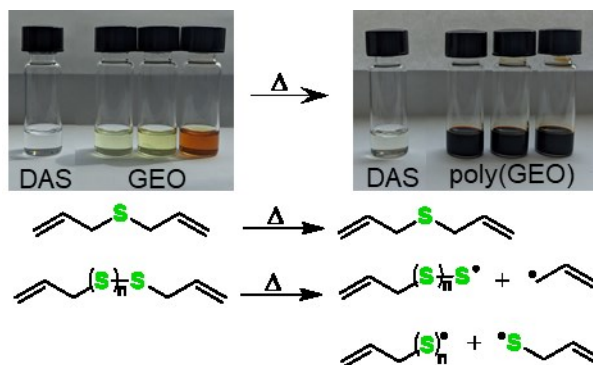


Figure 4: Image of diallyl sulfide (DAS) and GEO from Greenwood Essential, Fabulous Frannie (1), and Green Health (left to right) before and after heating at 180 °C for 1 h. DAS is unaffected by heating, but other allyl sulfides form radicals when heated capable of initiating polymerization.

Polymerization was confirmed by a variety of NMR techniques (Figure S8-11) as well as ATR FTIR analysis (Figure 3B). The clear loss of allyl peaks present in NMR as well as the peak broadening and addition of new peaks in the H-C-S and alkane regions confirm complete polymerization. The loss of the sp^2 C-H stretch and C=C stretch in FTIR further confirms these results.

The sulfur radicals produced during inverse vulcanization have the propensity to produce hydrogen sulfide gas, which is both a health and environmental hazard. Therefore, the production of hydrogen sulfide gas was monitored by connecting the reaction vessel to a solution of $AgNO_3$, which will form Ag_2S in the presence of H_2S , allowing hydrogen sulfide to be quantified. Measurements were taken for typical syntheses of p(GEO) at a 5 g scale at 180 °C for an hour. Additional measurements were taken of the polymer during simulated curing in the closed reaction vessel at 160 °C for 24 hours. Very little sulfur was lost as hydrogen sulfide with no H_2S produced during the initial synthesis of the polymer and only ~0.6% lost during the first simulated curing cycle. Poly(GEO) could be readily synthesized at the 5 g scale. However, when the reaction scale was increased to 10 g, there was a noteworthy increase in temperature leading to the sample boiling. This may indicate that much like inverse vulcanization, large-scale reactions must be conducted at lower temperatures to prevent autoacceleration.^{3, 28}

Poly(GEO) samples were cured for 24 h at 160 °C and subjected to analysis by thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and gel permeation

chromatography (GPC) (Figures S13-15). GH had the lowest onset of degradation at 219 °C and a char yield of 30%. FF1 had a slightly higher onset of degradation and char yield at 227 °C and 35% respectively. GE had a slightly higher onset than both with degradation starting at 238 °C but a slightly lower char yield at 28%. All samples had similar glass transition temperatures of 8.0, 8.5, 10.4 °C for GH, FF1, and GE respectively. GPC analysis showed that poly(GEO) has fairly low molecular weights of 2,800, 1,770, and 2,200 g/mol for GH, FF1, and GE respectively with polydispersity indices ranging from 2.9-3.1, both of which are consistent with other polysulfides formed by inverse vulcanization. Even after complete polymerization and curing poly(GEO), samples synthesized with GH and FF1 remained nearly completely soluble in DCM, 95% and 93% respectively. However, GE was only 63% soluble, typically indicating a higher molecular weight material or the presence of substantially more crosslinking in this sample. However, the dramatic difference in solubility was unexpected especially due to the similarity in both molecular weights and T_g. Instead of just crosslinking contributing to the lower solubility, the presence of alkanes that are likely not fully incorporated into the polymer matrix may provide enhanced solubility of poly(GEO) synthesized with GH and FF1.

Since sulfur in GEO is in a linear form rather than a stabilized 8-membered ring, we anticipated that heating samples above 160 °C to cleave S-S bonds may prove unnecessary. Therefore, the reaction progress of poly(GEO) was monitored by ¹H NMR at 180, 160, and 120 °C (**Figure 5**). Complete polymerization was observed after 25 min and 120 min at 180 °C, and 160 °C respectively. However, when the temperature was reduced to 120 °C, only ~80% polymerization occurred after 24 h. Complete polymerization was not observed until 36 h. The dramatically slower rate of reaction at 120 °C was a bit surprising since 85% of the allyl sulfides present possess dynamic sulfur bonds. Additionally, prior work has shown that once linearized, sulfur radicals form at temperatures as low as 90-100 °C.^{29, 30} However, when these lower temperatures were tested, limited polymerization was observed after 24 h.

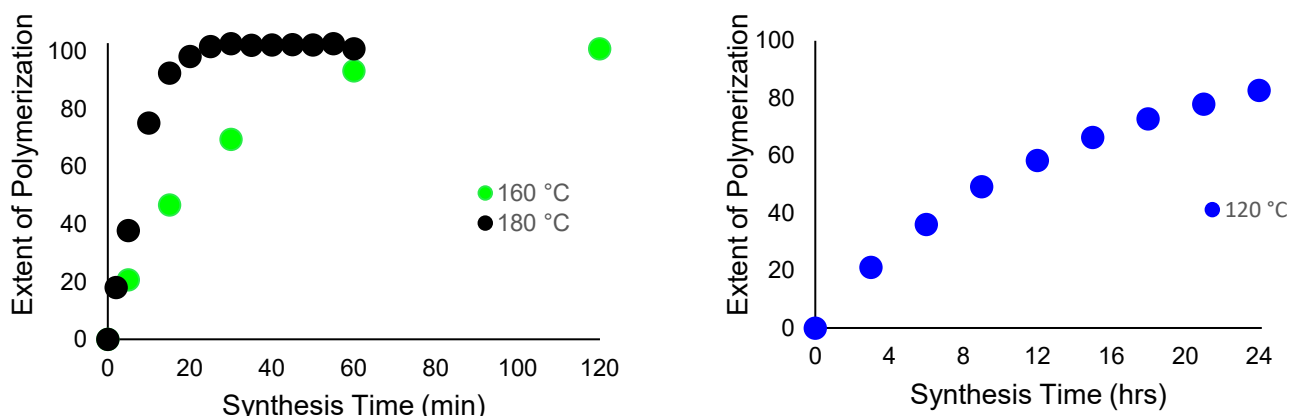


Figure 5: Reaction progression of poly(GEO) at 180, 160, and 120 °C.

Adhesion Testing

To better understand how GEO composition impacts adhesion strength, GH, FF1, and GE were again subjected to polymerization at 180 °C for 1h. Then, 50 mg of polymer was placed between two aluminum adherends in lap shear configuration and cured at 160 °C for 24 h before being pulled apart in tension. The maximum adhesion strength was determined by dividing the maximum force at the breaking point by the overlap area. The work of adhesion was determined by taking the area under the curve of the force versus extension plot. GH had the highest adhesion strength with both FF1 and GE demonstrating much lower maximum adhesion strength. (Figure S16). A similar trend was observed for work of adhesion. This may indicate that both the high DADS and DATS present in GH along with the unidentified alkanes present in most GEO samples improve adhesive performance. Despite these differences in adhesion strength all samples demonstrated cohesive failure, indicating that the material itself failed rather than failing at the Al – polymer interface.

Since poly(GEO) made with Green Health created the strongest adhesives, GH was then subjected to further analysis to determine the synthetic conditions that led to optimal adhesion strength. GEO was heated at 160 and 180 °C for 15, 30, 60, and 120 min before being placed on Al adherends and cured for an additional 24 h at 160 °C. The highest adhesion strength was observed for samples polymerized at 160 °C for just 15 min (**Figure 6**). This indicates that the extent of polymerization likely impacts the maximum adhesion strength.

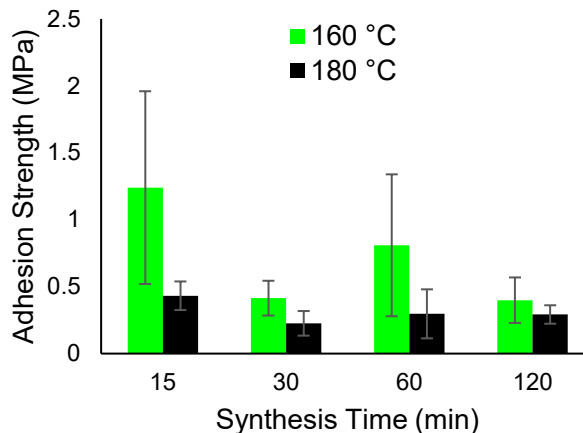


Figure 6: Maximum adhesion strength of poly(GEO) A. synthesized at 160 and 180 °C or 15, 30, 60, and 120 min.

To determine if the extent of polymerization is the key factor impacting adhesion strength, samples synthesized at different temperatures but with the same extent of polymerization were subjected to adhesion testing. Although the reaction progression was monitored by NMR in Figure 5, these data proved inconsistent when performing bulk polymerizations at the same time point. For the NMR study, small portions of polymer were removed from the reaction vessel at given time points and placed in an alternate vessel effectively quenching the polymerization. However, when done in bulk, the polymerization continues even when removed from heat. Ultimately samples were cooled in ice water to halt polymerization, but shorter reaction times still had to be employed. Others have used liquid nitrogen to rapidly quench polymerization in the past. However, work from our laboratory has shown that this rapid cooling alters the polymer properties, which we sought to avoid.³¹

Samples with 25%, 50%, and 100 % polymerization at 120, 160, and 180 °C were subjected to adhesion analysis (**Figure 7**). After samples were 25%, 50%, or 100% polymerized, they were placed on aluminum adherends and cured at 160 °C for 24 hrs. At 25% polymerized the 180 °C sample demonstrated significantly higher adhesion strength than polymers formed at lower reaction temperatures. As the extent of polymerization increased from 25 to 50%, the maximum adhesion strength decreased dramatically. Interestingly, the samples synthesized at 180 °C demonstrate more brittle failure at 25% polymerization yet show more ductile failure at higher extents of polymerization based on the force vs displacement curves. However, there was no significant alteration to the T_g, onset of degradation, or char yield compared to samples fully

polymerized at 180 °C. Samples polymerized at 120 and 160 °C lost even more strength from 50 to 100% polymerized; however, that was not the case for polymers synthesized at 180 °C.

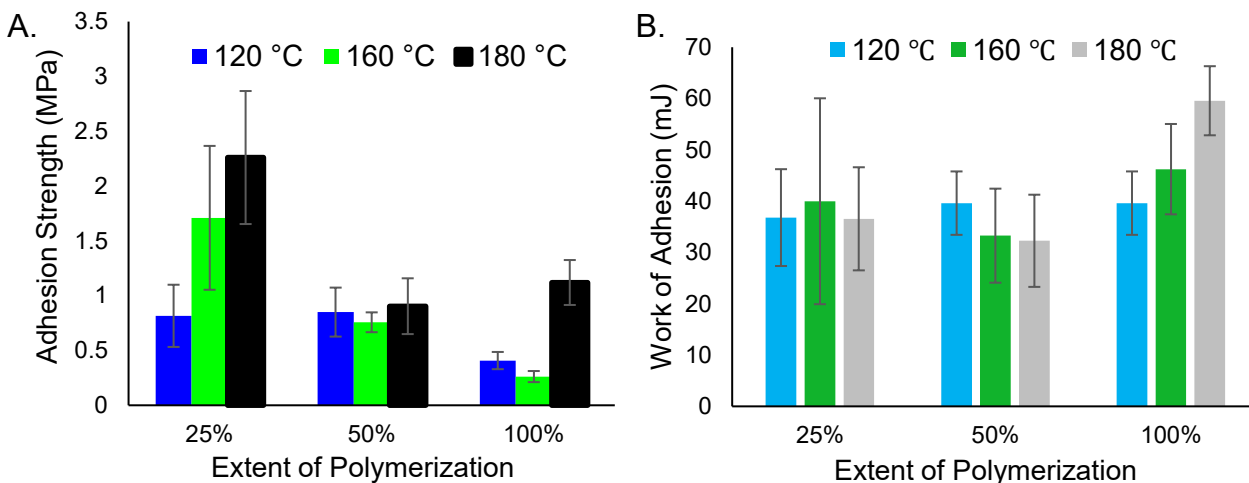


Figure 7: A. Maximum adhesion strength and B. work of adhesion of poly(GEO) based on the extent of polymerization when synthesized at 120, 160 and 180 °C.

These data show that the reaction temperature, not just the extent of polymerization have a dramatic impact on adhesion strength. This may indicate that the high reaction temperatures may drive off a volatile portion of GEO that is not beneficial for adhesion. Overall, these data indicate that poly(GEO) performs best as an adhesive when a portion of the polymerization takes place on the metal surface likely allowing more effective interlocking between the polymer and metal surface. A similar trend was observed in our prior work when comparing S-based adhesive systems, which reached complete polymerization more rapidly than GEO-based systems, and demonstrated lower maximum adhesion strengths.¹⁸ However, when comparing the work of adhesion, the degree of polymerization has a much less dramatic effect (Figure 7B).

Conclusions

Garlic essential oil is readily available from a variety of suppliers. It is primarily composed of allyl sulfides that can be easily differentiated based on the sulfur rank by ¹H NMR. Although the relative abundance of each allylsulfide component differs to some extent based on the supplier, many brands of GEO have very similar allylsulfide distributions. A variety of analysis showed that there seemed to be limited differences in the physical properties of

poly(GEO) when synthesized from GEO with varied composition. However, these differences led to substantial alterations in the maximum adhesion strength. Green Health, which is the most representative of all GEO samples tested, demonstrated the strongest adhesion. Analysis of the synthetic conditions indicate that both the extent of polymerization and the reaction temperature have a significant impact on the properties and adhesive performance of poly(GEO). This work has utilized a renewable material as the monomer, solvent, and initiator to create adhesive polysulfides providing a path to more sustainable sulfur-based materials.

Author Contributions

K. Sayer was responsible for most of the investigation as well as visualization, data management, writing, and editing. Z. Merrill, A. Davis, and V. Miller were responsible for some investigation. C. Jenkins was responsible for conceptualization, funding acquisition, project administration, resources, writing, and review.

Conflict of Interest

The authors declare no competing financial interests.

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