Chemically activated S-S metathesis for adhesive-free bonding of polysulfide surfaces

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Abstract

A polysulfide terpolymer made from canola oil, dicyclopentadiene, and elemental sulfur was synthesized and evaluated as bulk structural material. The unique polysulfide structure in this material allows the two polymer blocks to be bonded together through amine-catalyzed S-S metathesis. No exogenous adhesive is required: the polysulfide is both the bulk material and the mortar. The strength of the joined polymers was evaluated by a series of shear tests and compared to the bond strength obtained with commercially available superglue. The adhesion obtained via the S-S metathesis was stronger in all tests. To improve the mechanical properties of the terpolymer, carbon nanorods and carbon fibers were embedded in the polymer, with the latter leading to nearly a 16-fold increase in flexural strength. Prospects in sustainable construction are discussed.

1. Introduction

Adhesives, binders, and sealants are critical in the construction, automotive, marine and aerospace industries.[1, 2] Commonly, adhesion is induced by the polymerization of monomers at the interface of the surfaces joined together.[1, 3] Yet, despite the wide use of adhesives, there are a number of limitations that may restrict their use. For example: slow cure times; limited shelf life; and low humidity-, solvent- and temperature-resistance can be detrimental in many contexts.[4] Furthermore, there are increasing concerns for the sustainability and life-cycle management of polymer-based adhesives.[4]

Recently, our lab introduced a different approach to adhesive technology in which the bulk polymer is both the structural material and adhesive. These materials are polysulfide copolymers made from sulfur and polyenes, with dynamic S-S crosslinks enabling covalent bonding between two polymer surfaces. An amine catalyst is simply added to the surface of the polysulfide, which induces S-S metathesis and chemical bonding at the polymer interfaces. (**Figure 1**).[5] This reaction is efficient at ambient temperatures if the sulfur rank (the number of sulfur atoms in a cross-link) is 3 or higher.[5]

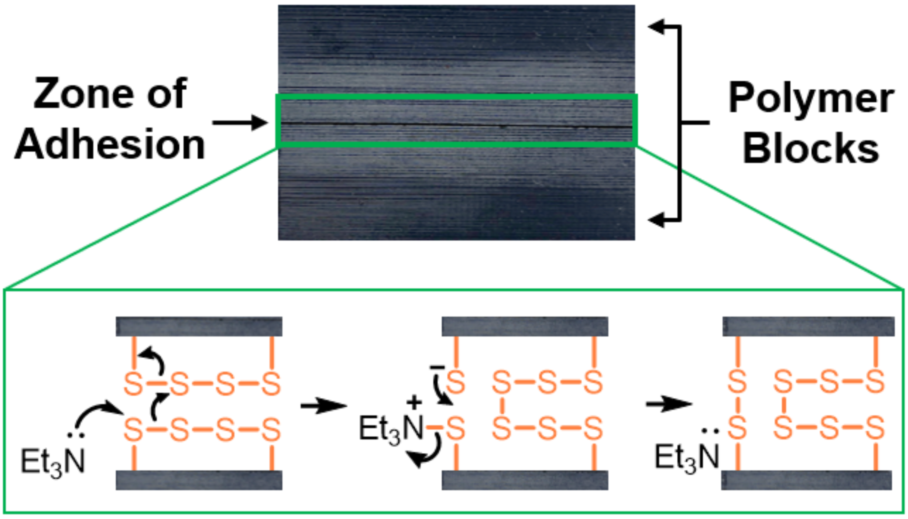

Figure 1: Triethylamine catalyzes the S-S metathesis of polysulfides, joining together two bulk polymer blocks. This reaction occurs for polymers where the sulfur rank is 3 or higher (e.g. trisulfides, tetrasulfides or longer S-S chains).[5]

In that original report, the model polysulfide was useful in establishing the S-S metathesis chemistry, but the polymers themselves had relatively poor mechanical properties, such as low tensile strength. Furthermore, this first report did not assess these polymers as bulk materials for potential use in construction or other structural applications. In this study, we address these issues and investigate the key polysulfide polymers and their potential as bulk structural materials, and the use of amine-catalyzed S-S metathesis to bond these polymers together directly, without the use of an exogenous adhesive. To improve mechanical properties of the polysulfides, a panel of carbon fiber and other carbon-based additives were incorporated into the bulk material. Significant improvements in flexural strength were observed when aligned carbon fiber was threaded throughout the bulk polymer before curing to form the final composite.

In terms of scale and sustainability, the key polymer in this study is made from canola oil, dicyclopentadiene (DCPD), and sulfur. Canola oil is an unsaturated triglyceride derived from plants, with increasing interest for use as a renewable monomer.[6-10] DCPD is a coproduct of ethylene production via naphtha cracking in the petroleum sector.[11] Similarly, sulfur is generated as a coproduct of the petroleum refining industry, with many millions of tonnes produced each year.[12] Because these monomers are all high in abundance, low in cost, and either renewable or derived from surplus industrial streams, they have potential uses as materials for construction and related applications. Due to the unique S-S crosslinks formed in this reaction, these materials also show promise for rapid assembly and adhesion where the polymer is both a structural material and its own chemically active mortar, with bonding achieved by S-S metathesis. These preliminary studies could potentially pave the way towards alternative construction materials where the assembly of components does not require adhesives, mortar, or welding, but rather the material itself contains reactive S-S bonds that can be activated on-demand to bond to another component at the interface.

2. Experimental Section

2.1 Materials

Dicyclopentadiene (DCPD) was purchased from Sigma-Aldrich and used as received. Sulfur was purchased from Sigma-Aldrich (reagent grade, powder, purified by refining, -100 mesh particle size). The carbon fiber tow (fiber type: T300, Filaments 12K, Tensile strength (MPa): 3530, Tensile modulus (Gpa): 230, Elongation (%): 1.5, Density (g/cm^3): 1.76) was purchased from Carbon Fiber Australia. Carbon nanotubes were purchased from Nanografi Nanotechnology (Industrial grade MWCNT, purity: >92%, outside diameter: 48-78 nm, length: 10-30 μm). Canola oil was purchased from Just Fry Oil Australia. Triethylamine (Et_3N, ≥99.0%) was purchased from Sigma-Aldrich.

2.2 Polysulfide Synthesis

The synthesis protocol was the same for all polymer samples irrespective of which mold was used or if carbon fibers were added. The polymer composition of 50 wt% sulfur, 15 wt% DCPD and 35 wt% canola oil and the synthesis protocol were adapted from previous studies of this material in our laboratory.[5] Briefly, 5.00 g of sulfur was added to a 25 mL glass vial and was heated for 3 minutes in a 170 °C hot block with magnetic stirring (200 rpm). Meanwhile in a separate vial, 1.50 g of DCPD and 3.50 g of canola oil were preheated on a 170 °C hot block for 30 seconds. Next, the DCPD-canola oil mixture was added to the preheated sulfur and the stirring speed was increased to 370 rpm. After a reaction time of 9.5 minutes, the mixture appeared as a homogenous dark brown viscous liquid. This liquid was poured into a silicon mold. The various molds are shown in **Figure S1**. For each mold, the liquid pre-polymer from 3 reactions run in parallel was used. Finally, the liquid pre-polymer mixture was cured in an oven at 130 °C for 24 hours. All cured polymers were dark black in color.

2.3 Characterization

Simultaneous thermal analysis (STA) was performed using a Perkin Elmer STA 8000. Between 5-10 mg of sample were held at 40 °C for 4 minutes before the temperature was increased by 10 °C/minute to 800 °C. This was done under a 20 mL/min nitrogen flow.

Differential scanning calorimetry (DSC) was performed using a Perkin Elmer DSC 8000. Between 5-10 mg of sample was cooled to -80 °C and held for 4 minutes. After that the temperature was increased to 80 °C by 10 °C/minute and held for 4 minutes. Next, the sample was again cooled to -80 °C by 10 °C/minute and held for 4 minutes at that temperature. Finally, the sample was heated to 250 °C by 10 °C/minute. This was under a 20 mL/minute nitrogen flow.

CHNS elemental analysis was performed by The Campbell Microanalytical Laboratory at the University of Otago in New Zealand.

Scanning electron microscopy (SEM) and energy dispersive X-Ray (EDX) analysis were obtained using a FEI Inspect F50 SEM fitted with a EDAX energy dispersive X-Ray detector. Samples were sputter coated with silver metal (20 nm thickness) before analysis.

Powder X-ray diffraction (XRD) was carried out on a Bruker D8 Advance Eco diffractometer (Bragg-Brentano geometry) using Co-Kα radiation ($\lambda = 1.78897$ Å). The Bragg angle (2θ) was varied from 10° to 90° with a step size of 0.019°, measurement time of 0.6 s per step and sample rotation at 10 rpm. The samples were deposited onto a sample holder well before analysis.

Mechanical testing: Shear testing and three-point bending testing was performed using an Intron Series XI Materials Testing System fitted with a 5 kN static load cell. For the shear test the samples were mounted in the custom-made sample holder and the cross head was driven up (tension/shear) at a speed of 1.3 mm / minute. For the three-point bending test, the sample was placed on the instrument sample holder and the cross head was driven down (flexure) at a speed of 10 mm / minute. Shear testing was adapted from standard lap-shear testing method ASTM D3163. However, the sample holder was modified for this testing as the grips in the standard method were not compatible with brittle samples. These shear tests are therefore for comparative purposes between all samples tested in this study.

3. Results and Discussion

3.1 Synthesis and characterization of the polysulfide terpolymer

The key polymer was prepared using a protocol adapted from our original studies of sulfur-based terpolymer systems.[5, 13] Specifically, canola oil and DCPD were preheated to 170 ºC and then added directly to a separate vial of molten sulfur at the same temperature. After reacting further at 170 ºC (<10 min) with stirring, the liquid mixture was then poured into a silicone mold and cured for 24 hours at 130 ºC **(Figure 2)**. The feed ratio was based on a previous study that revealed a composition of 50 wt% sulfur, 35 wt% canola oil, and 15% DCPD provides a material with a sulfur rank of approximately 4 (e.g. the sulfur crosslinks are, on average, tetrasulfides based on the molar ratio of sulfur to alkenes in the system) and a glass transition temperature suitable for amine-catalyzed S-S metathesis.[5] However, on this scale in which 30.0 g of polymer was cured, the final material had separated into two phases: a soft top phase and a hard and brittle bottom phase (**Figure 2**).

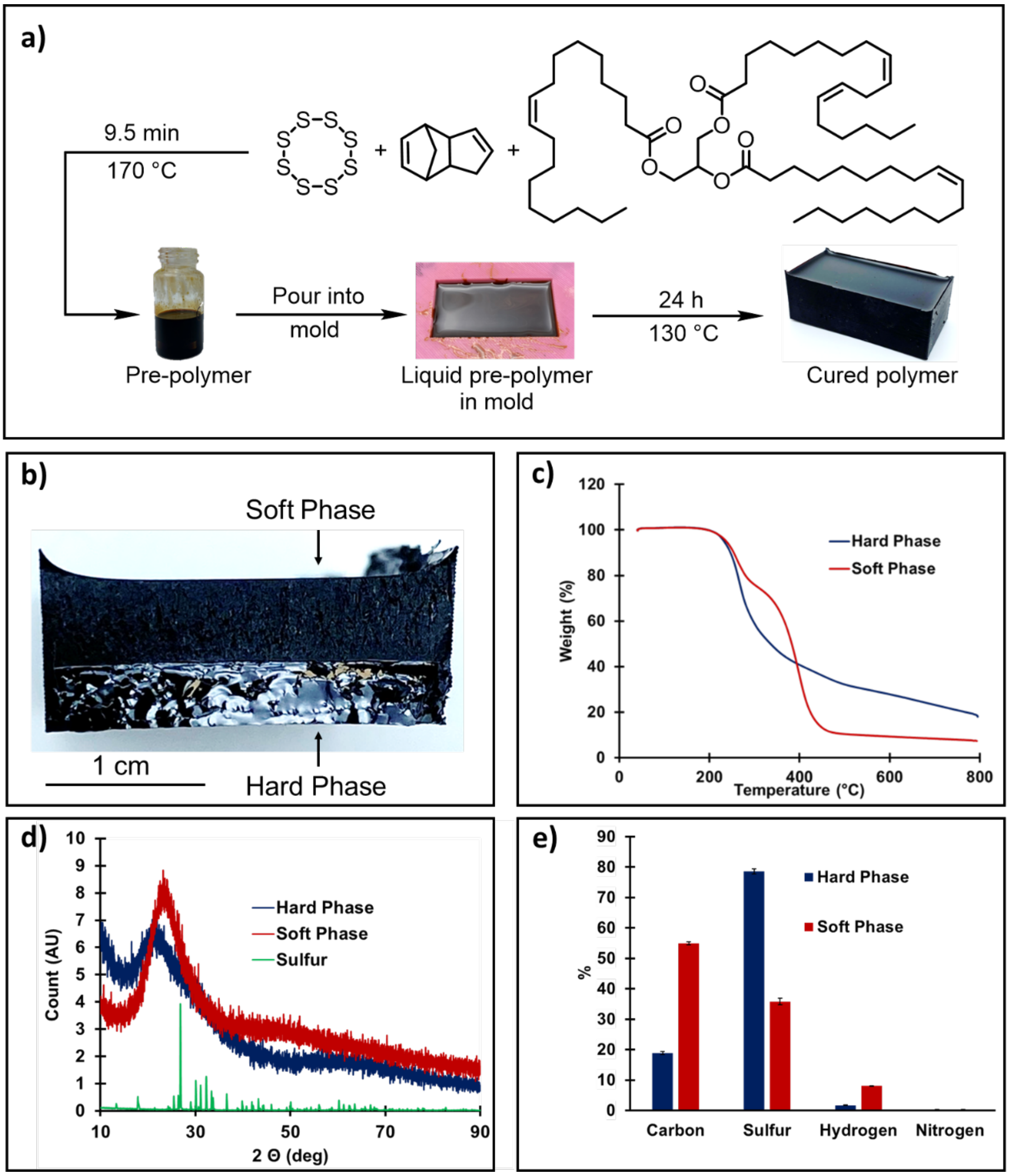

Figure 2: **a)** Synthesis of polymer by direct reaction of canola oil, DCPD and sulfur for 9.5 min at 170 °C. The liquid pre polymer was then poured into a mold and cured for 24 h at 130 °C to give the final product. **b)** The soft phase (top of the molded polymer) and the hard phase (bottom of the molded polymer) can clearly be distinguished within the cured polymer system. **c)** STA analysis showed weight loss onset of both phases at around 180 °C. However, the hard phase shows a single mass loss and retention of more charred material after heating to 800 °C. The soft phase showed two mass losses and more complete thermal decomposition. **d)** XRD of both

phases indicated no crystalline sulfur in the cured material. **e)** Elemental analysis shows different elemental compositions of the soft and hard phase.

This phase separation was not observed in our previous study and was therefore a surprise. We attribute this result to the greater scale in this study (30.0 g) in comparison to the original study in which all samples were <1.0 g.[5] In such a case, because the curing is done without agitation, monomers and oligomers may separate by density throughout the curing process.[5] This phase separation was also observed for polymers with varied amounts of the organic comonomers (see Supporting Information pages 1-5 for additional discussion). Simultaneous thermal analysis (STA) further supported the qualitative observation of this phase separation **(Figure S7 and S8)**: the hard phase of the cured material showed only one weight loss at the onset of 180 °C, having lost 82% of its weight at the final temperature of 800 °C (**Figure 2**). However, the soft phase showed a two-stage mass loss. In the first stage between 180 and 320 °C, around 30% of the weight was lost. During the second weight loss stage between 320 and 500 °C, another 60% of weight was lost (**Figure 2**). Previously, we and others have attributed the two-stage mass loss to a process in which the weaker S-S bonds in the polysulfide domains first decompose, and then the remaining sulfur and organic material decomposes in the second mass loss.[7, 14]

Differential scanning calorimetry (DSC) was used to determine the glass transition temperature (T_g) of the two phases. The hard phase returned a T_g of 41 °C whereas the soft phase had a T_g of -26 °C **(Figure S9 and S10)**. This result is in line with the qualitative physical appearance of the phases, with one soft and rubbery while the other is hard and brittle. The higher T_g of the hard phase may be due to a higher proportion of DCPD in that phase of the polymer, as previous studies of related terpolymers indicated a linear relationship between the feed ratio of DCPD and T_g across a wide range of sulfur content.[13] This explanation was also consistent with combustible analysis (**Figure 2**): the hard phase showed a lower carbon content

(19%) compared to the soft phase (55%), but was much higher in sulfur (79%) than the soft phase (36%). XRD analysis indicated that no crystalline sulfur was present in the bulk material (**Figure 2**), as did DSC analysis (no melting transition of elemental sulfur was observed, **Figure S9 and S10)**. This is consistent with complete consumption of sulfur in the polymerization and curing. However, the surface of the cured material developed a patchy, grey layer over a period of two days after curing. This so-called "sulfur blooming" has been observed in other cured polymer systems made by inverse vulcanization, with elemental sulfur regenerated by depolymerization of the copolymer or polymeric sulfur.[9, 15-17] In our system, we only observed this elemental sulfur on the surface of the polymer. Scanning electron microscopy (SEM) was used to analyse the grey layer on the polymer. This showed particles ranging in size from sub-micron to over 20 microns. Energy dispersive X-Ray analysis (EDX) was used to confirm that these particles were indeed sulfur **(Figure 3)**. As this free sulfur on the surface of the polymer could potentially interfere in adhesion experiments, we investigated simple ways to remove this layer. Fortunately, the free sulfur on the surface could be removed by hand using a simple treatment with sandpaper (**Figure 3**).

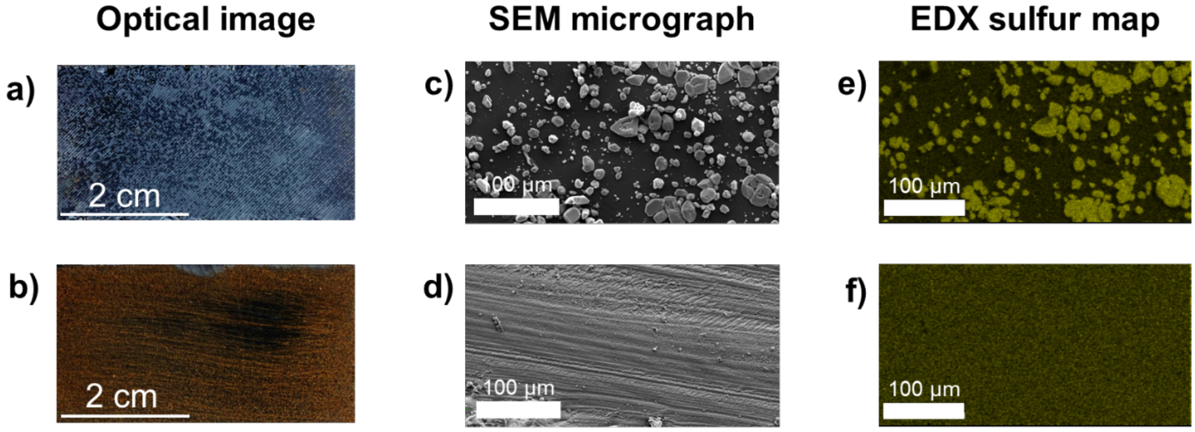

Figure 3: a) Image of polymer with grey layer resulting from sulfur blooming two days after curing **b)** Image of polymer that had grey layer removed using sandpaper **c)** SEM micrograph of grey layer shows particles on surface of polymer **d)** SEM micrograph of polymer that had grey layer removed shows no particles present on the surface **e)** EDX analysis of particles on

surface of polymer with grey layer shows that these particles are sulfur particles **f)** EDX analysis of surface treated with sandpaper shows no large sulfur particles on surface.

3.2 Chemically-induced adhesion and mechanical testing

In our previous study, we noted that the amine-catalyzed S-S metathesis at the polymer interface was most efficient when carried out above the T_g of the polymer.[5] This is due to the chain mobility required for the two polymer interfaces to bond together after cleavage of the S-S crosslinks. In the phase separated system in **Figure 2**, the soft phase with the lower T_g was therefore chosen as the surface for S-S metathesis, while the harder phase with the higher T_g would serve as the more rigid base. In this way, we thought to take advantage of this phase separation when chemically bonding two of the cured polymer blocks together. Initial testing showed that pre-adhesion removal of the grey sulfur layer using sandpaper (P80 grade) resulted in significantly stronger bonding. It was thought that removing the sulfur layer would both expose the reactive polysulfide surface, and also provide a rougher interface with greater surface area for bonding.

Next, triethylamine was evaluated as a catalyst for S-S metathesis for the phase-separated polymer system. Triethylamine was selected because it was the most efficient catalyst screened in our previous report, repairing cut dog bone specimens of the same polymer to their original strength.[5] Accordingly, two polymer blocks (4 cm^2 surface area for each polymer block) were first polished with sandpaper to remove any sulfur and roughen the surface. Then, 100 μL of triethylamine, enough to cover the polymer, was added to the surface of one block before placing the other polymer block on top and adding a 10 kg weight to ensure sufficient surface to surface contact. After 3 hours the weight was removed, providing polymer blocks that were bonded together. The bonded blocks where the cut in half, so that a cross section of the interface could be analyzed using SEM and EDX. No nitrogen could be detected, indicating the triethylamine is not incorporated into the polymer **(Figure S11)**. In this way, the triethyl amine initiates the S-S metathesis, but is effectively traceless.

To test the strength of the bonded polymer interface, a metal plate attached to bolts was embedded into the material **(Figure 4 and S12)**. The liquid pre-polymer was synthesized, poured into a mold **(Figure S13)** containing the metal plate (5 cm × 2 cm, suspended approximately 5 mm above the bottom of the mold) and cured (130°C, 24 hours). The resulting polymer block was 2.5 cm × 6 cm × 1.5 cm, with threaded metal rods protruding out of the material **(Figure 4 and S14)**. Two samples were prepared in this way. To bond the polymer interfaces together, 300 µL of triethylamine was added to one polymer block, the interfaces were placed in contact, and a 5 kg weight was used to force the surfaces into contact for 5 hours **(Figure S15)**. Notably, in this setup it is the harder phase that was bonded together, so it was not clear at the outset is the adhesion would be effective. However, the polymers did bond together and were therefore tested for shear strength. The specimen failed after a displacement of 2.5 mm at a load of 6.2 kg. Interestingly, the failure occurred both in the bulk polymer around the metal plate as well adhesion site.

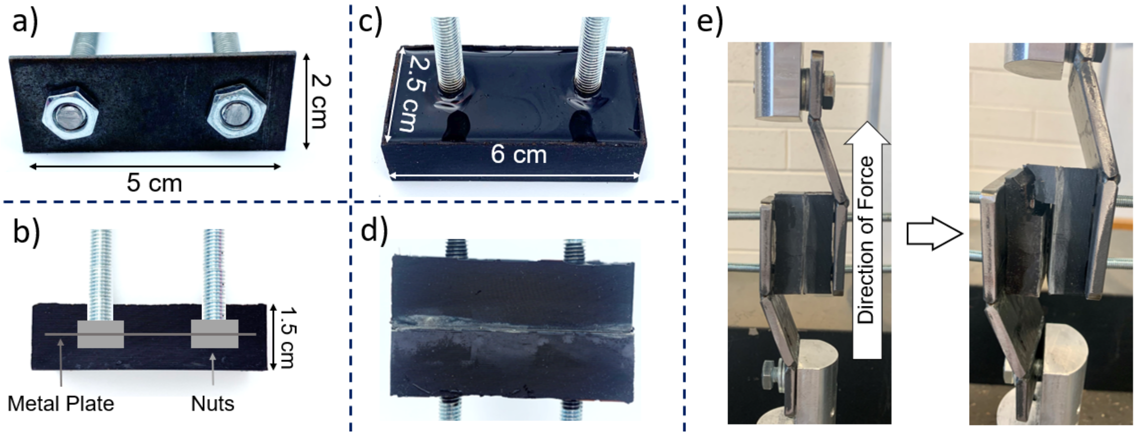

Figure 4: a) The metal scaffold for the polymer was comprised of a 5 cm × 2 cm metal plate to which two threaded rods were fastened using nuts. **b)** The position of the metal plate once

the polymer was cured. **c)** After the polymer had been poured and cured, they were evaluated in the adhesion process. **d)** Two polymer blocks with metal scaffolding after they have been bonded to each other using triethylamine. **e)** Shear tests were conducted to assess the strength of the adhesion. A unidirectional force was applied and the polymer failed at the adhesion interface and also at the bulk material.

While this was an encouraging result, the failure near the polymer-metal juncture meant that this test was not representative of the adhesion at the polymer-polymer interface. Therefore, a new sample holder was developed which was able to hold and test polymer blocks bonded together without any internal metal components that could act as stress concentrators **(Figure 5 and S16)**. Additionally, this holder allowed the polymer blocks to be bonded together at the softer phase with the lower T_g. The new sample holder was able to hold two polymer samples with a width of 2.5 cm, a height of 1.7 cm and a length of 5.00 cm which were adhered to each other **(Figure S17)**. To prepare the samples, the soft sides of the cured polymer blocks were first treated with sandpaper (P 80 grade) in order to remove any surface sulfur and to provide a rough surface **(Figure S18)**. Using the sandpaper also levels the surface which is not always even after the curing step. Then, 300 μL of triethylamine (enough to cover the polymer surface) was added to one of the polymer blocks and then joined to the other polymer block. A 10 kg weight was used to keep the polymer interfaces in contact. A total of 3 hours was used for the adhesion time **(Figure S19 and S20)**. To test the difference of adhesion of the hard phase compared to the soft phase, two polymer blocks were adhered at their hard phase using the same protocol. For comparison, commercial superglue (Bostik Super Glue, Industrial Strength) was used to join two separate polymer blocks together at the soft phase interface. To do this, the surface of one of the polymer blocks was coated with a thin layer of superglue, the other polymer block was placed on top and 10 kg of weight was added to press the blocks together for 3 hours. Shear tests where then carried out on all samples. The sample joined together with triethylamine at the soft phase performed best, with a 25 kg load at a displacement of 8.7 cm. The polymer samples adhered at the hard phase failed at a far lower load of 2.46 kg at a displacement of 1.6 mm. While the super glue adhesion also demonstrated a relatively high load (20 kg at 4.75 mm displacement), the adhesion failed close to the surface of the polymers. In contrast, the polymer adhered with triethylamine at the soft phase failed at the bulk polymer material rather than at the adhered surface. This result means that the amine-catlyzed S-S metathesis provides a strong bond at the interface and that the brittle hard phase is the site of failure. Interestingly, the super glue failing at the interface means that the S-S metathesis is a superior method for bonding the polymer blocks together (**Figure 5**).

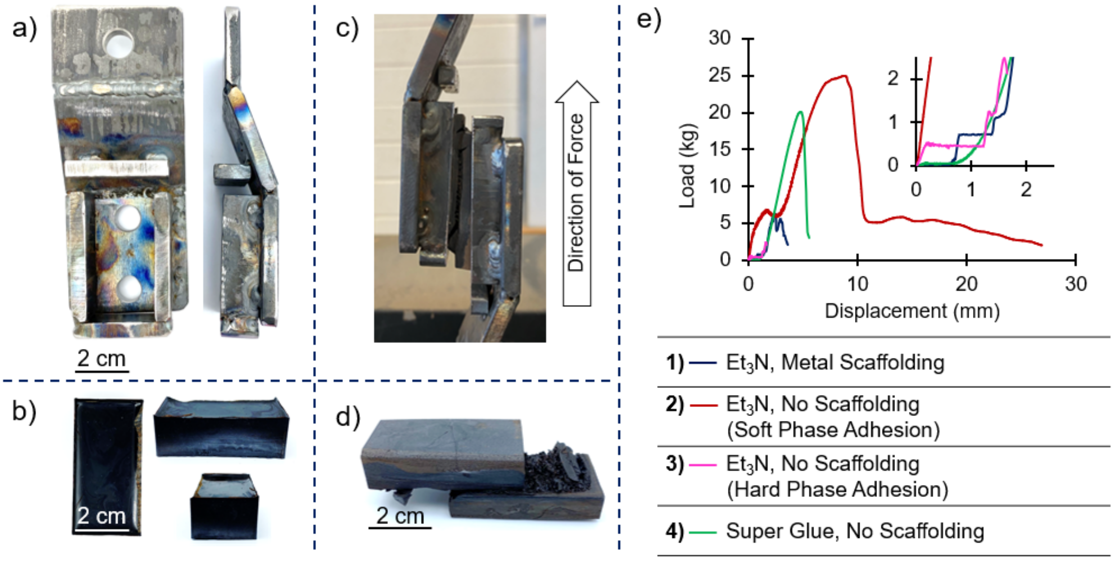

Figure 5: Shear test: a) Modified sample holder. **b)** Side, front and top view of a polymer block after synthesis and curing, ready for adhesion and shear testing. **c)** Sample during a shear test as sample starts to deform and tear. **d)** Polymer sample adhered using triethylamine after shear testing. The sample failed within the bulk material and not at the adhesion surface. **e)** (1) The shear test of the triethylamine adhesion using the polymer containing the metal scaffolding showed a maximum load of 6.24 kg at a displacement of 2.48 mm. (2) The shear test without scaffolding using the modified sample holder showed a maximum load of 25.01 kg at a displacement of 8.7 mm (soft phase adhesion). (3) The shear test using the hard phase as

adhesion surface showed a maximum load of 2.48 kg as a displacement of 1.6 mm. (4) The shear test using super glue as adhesive and the modified sample holder showed a maximum load of 20.05 kg at a displacement of 4.75 mm.

Next, attempts were made to improve the structural strength of the cured polymer by adding carbon fiber as a scaffold. Accordingly, carbon nanotubes and carbon fiber were evaluated as additives for potential structural reinforcement. A three-point bending test was used to assess the flexural strength of the modified materials. Five samples (12 × 2 × 1 cm) were prepared for these tests, using a longer mold that provided the necessary dimensions for the specimens required for three-point bending testing **(Figure S21)**. The polymer synthesis was the same as the one used to make the samples for the shear tests (three 10 g reactions run simultaneously). After pouring the pre-polymer into the new mold, the polymer was cured at 130 °C for 24 hours. The first sample was just cured polymer and did not contain any carbon fiber or carbon nanotubes. The next two samples were reinforced with approximately 0.5 g of carbon fiber. One sample contained loose carbon fibers **(Figure S22)** while the carbon fibers of the other sample were threaded through the mold to ensure alignment and even distribution **(Figure 6)**. The last two samples contained 0.5 g or 1.0 g of carbon nanotubes respectively, which corresponds to a carbon weight % of 1.88 and 3.86 in these samples. After the liquid pre-polymer was poured into the mold, the nanotubes were added and mixed through the pre-polymer using a spatula before curing. Is should be noted that after adding 1.0 g of nanotubes, the polymer mixture was a thick paste. Curing the samples containing nanotubes still resulted in a hard material **(Figure S23)**. The paste-like consistency of the polymer-nanorod mix therefore may be a useful form for applying this polymer as a paste or putty before curing. Unlike the liquid prepolymer, the paste adheres to surfaces without running off.

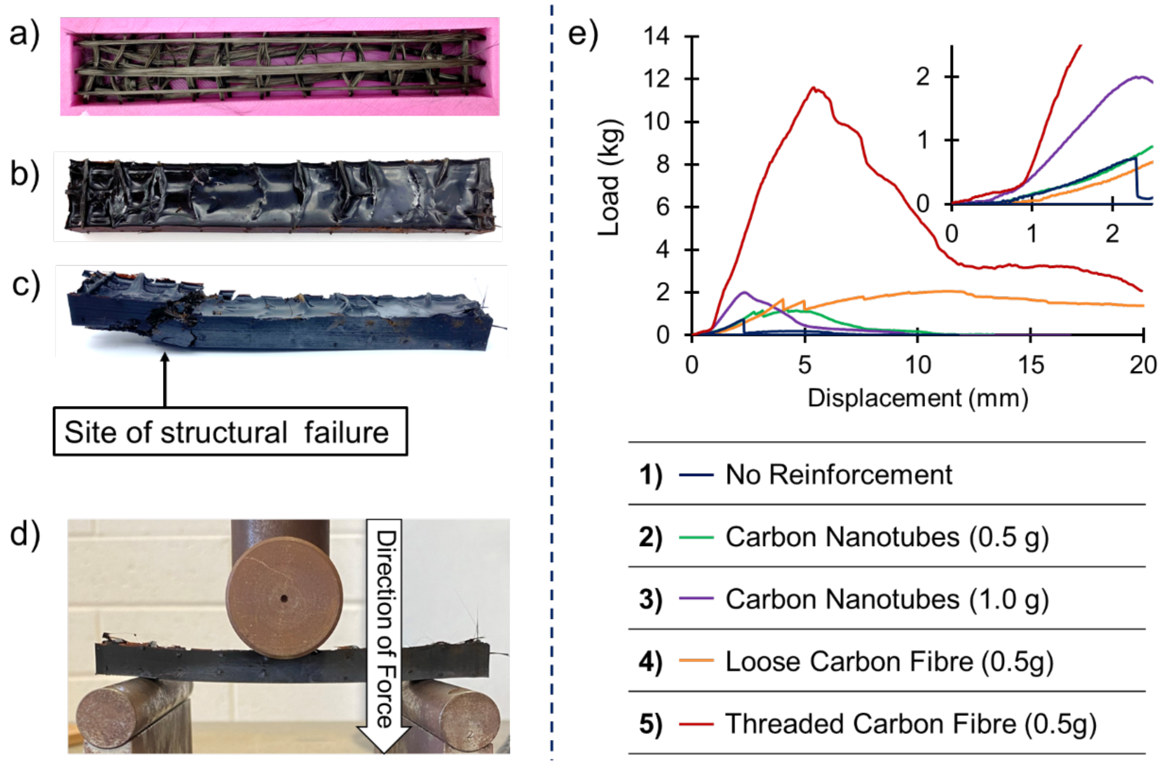

Figure 6: Three-point bending test: a) Mold showing threaded carbon fiber reinforcement. **b)** Carbon fiber reinforced polymer after synthesis and curing, ready for three-point bending test. **c)** Carbon fiber reinforced polymer after three-point bending test. Even after the test, the individual parts of the sample are still connected through the carbon fibers. The carbon fibers did not break in this test, but rather the bulk polymer. **d)** Carbon fiber reinforced polymer sample during three-point bending testing. **e)** Load-displacement curves of three-point bending tests. The weakest polymer was that without any reinforcement, which failed at a load of 0.73 kg (1). This was followed by the polymer containing 0.5 g of carbon nanotubes that failed at a maximum load of 1.21 kg (2). Doubling the amount of nanotubes increased the failure load to 1.99 kg (3) However the highest load was seen in the polymer containing loose carbon fibers with 2.02 kg (4) and threaded carbon fibers with 11.61 kg (5).

Next, the three-point bending tests were performed on all the samples (**Figure 6**). The polymer without any reinforcement was the weakest material, as anticipated, failing at a load of only 0.73 kg. Reinforcement with 0.5 g of carbon nanotubes increased the maximum loads slightly to 1.21 kg. Adding 1.0 g of carbon nanotubes or loose carbon fibers to the polymer increased to maximum load to 1.99 and 2.05 kg, respectively. By far the highest load was seen in the polymer that has been reinforced by threading carbon fibers through the mold before the polymer was poured, with a maximum load of 11.61 kg. The stiffness of the polymers was also affected by the reinforcing material. The samples with 0.5 g of carbon nanotubes or loose carbon fiber had a similar stiffness to the unreinforced polymer (modulus of elasticity of 54.0 MPa, 45.9 MPa and 41.6 MPa, respectively). This indicates that the polymer matrix is the main contributor to the stiffness of these samples. However, when the polymer was reinforced with 1 g of carbon nanotubes, the stiffness was increased greatly, leading to a modulus of elasticity of 121.3 MPa. The sample with the greatest stiffness was the threaded carbon fiber sample with a modulus of elasticity of 256.2 MPa. This indicates that fibre orientation is critical to maximum yield and stiffness. All reinforcement methods showed a much greater displacement at failure than the unreinforced polymer sample. This was particularly noticeable for the carbon fiber reinforced samples. Both the loose and threaded samples reached displacements of over 20 mm before failure, indicating a strong reinforcement at high strain. For the samples containing carbon nanotubes, stiffness increased with increasing nanotube content.

4. Conclusions and Outlook

A polymer made from canola oil, DCPD and elemental sulfur was made by first converting these monomers into a liquid pre-polymer and then curing in a silicone mold for 24 hours at 130 °C. Triethylamine was used to adhere polymer blocks to each other via catalytic S-S bond metathesis. An unexpected phase separation was observed during the curing process. It was found that the softer phase with the lower T_g was better suited for the adhesion chemistry than the harder phase with the higher T_g. The strength of this adhesion was quantified using shear tests and found to be superior to the adhesive strength of commercially available super glue.

Separately, efforts were made to reinforce the flexural strength of the bulk polymers, with aligned carbon fiber providing the best reinforcement in three-point bending tests. This study is a step forward in using polysulfide polymers as bulk structural materials, and ones that can react at their interfaces and covalently bond together. Such systems do not require adhesives when joining surfaces together, only a catalytic amount of an amine such as triethylamine. Furthermore, the renewability of the triglyceride monomer, and sourcing the sulfur and DCPD comonomers from surplus industrial streams are important for sustainability and scalability of these systems, respectively. Considering that the manufacture of construction materials such as cement are energy intensive and major contributors to carbon dioxide emissions,[18] there is a need to identify alternative materials and methods for more sustainable construction. Accordingly, our future research will focus on further improvements to mechanical properties of these terpolymers and methods for upscaling for potential use in industrial applications such as construction. Such studies will help support the expanding interest in using sulfur-rich materials in more sustainable adhesive[19] and composite[20-22] technologies.

Supporting Information

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

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References

[1] Z. Wang, Z. Jia, X. Feng, Y. Zou, *Compos. B. Eng.* **2018**, *152*, 311.
[2] G. Jeevi, S. K. Nayak, M. Abdul Kader, *J. Adhes. Sci. Technol.* **2019**, *33*, 1497.

[3] J. Comyn, "What are adhesives and sealants and how do they work?", Elsevier, 2021, p. 41.
[4] A. C. Marques, A. Mocanu, N. Z. Tomić, S. Balos, E. Stammen, A. Lundevall, S. T. Abrahami, R. Günther, J. M. M. de Kok, S. Teixeira de Freitas, *Materials* **2020**, *13*, 5590.
[5] S. J. Tonkin, C. T. Gibson, J. A. Campbell, D. A. Lewis, A. Karton, T. Hasell, J. M. Chalker, *Chem. Sci.* **2020**, *11*, 5537.
[6] L. Montero de Espinosa, M. A. R. Meier, *Eur. Polym. J.* **2011**, *47*, 837.
[7] M. J. H. Worthington, R. L. Kucera, I. S. Abuquerque, C. T. Gibson, A. Sibley, A. D. Slattery, J. A. Campbell, S. F. K. Alboaiji, K. A. Muller, J. Young, N. Adamson, J. R. Gascooke, D. Jampaiah, Y. M. Sabri, S. K. Bhargava, S. J. Ippolito, D. A. Lewis, J. S. Quinton, A. V. Ellis, A. Johs, G. J. L. Bernardes, J. M. Chalker, *Chem. Eur. J.* **2017**, *23*, 16219.
[8] A. D. Tikoalu, N. A. Lundquist, J. M. Chalker, *Adv. Sustain. Syst.* **2020**, *4*, 1900111.
[9] N. A. Lundquist, A. D. Tikoalu, M. J. H. Worthington, R. Shapter, S. J. Tonkin, F. Stojcevski, M. Mann, C. T. Gibson, J. R. Gascooke, A. Karton, L. C. Henderson, L. J. Esdaile, J. M. Chalker, *Chem. Eur. J.* **2020**, *26*, 10035.
[10] N. A. Lundquist, J. M. Chalker, *Sustain Mater Techno* **2020**, *26*, e00222.
[11] H.-C. Hsu, S.-J. Wang, J. D.-Y. Ou, D. S. H. Wong, *Ind. Eng. Chem. Res.* **2015**, *54*, 9798.
[12] W. J. Chung, J. J. Griebel, E. T. Kim, H. Yoon, A. G. Simmonds, H. J. Ji, P. T. Dirlam, R. S. Glass, J. J. Wie, N. A. Nguyen, B. W. Guralnick, J. Park, Á. Somogyi, P. Theato, M. E. Mackay, Y.-E. Sung, K. Char, J. Pyun, *Nat. Chem.* **2013**, *5*, 518.
[13] J. A. Smith, S. J. Green, S. Petcher, D. J. Parker, B. Zhang, M. J. H. Worthington, X. Wu, C. A. Kelly, T. Baker, C. T. Gibson, J. A. Campbell, D. A. Lewis, M. J. Jenkins, H. Willcock, J. M. Chalker, T. Hasell, *Chem. Eur. J.* **2019**, *25*, 10433.
[14] A. Hoefling, Y. J. Lee, P. Theato, *Macromol. Chem. Phys.* **2017**, *218*, 1600303.
[15] D. J. Parker, H. A. Jones, S. Petcher, L. Cervini, J. M. Griffin, R. Akhtar, T. Hasell, *J. Mater. Chem. A.* **2017**, *5*, 11682.
[16] J. A. Smith, X. Wu, N. G. Berry, T. Hasell, *J. Polym. Sci. A Polym. Chem.* **2018**, *56*, 1777.
[17] J. Wręczycki, D. M. Bieliński, R. Anyszka, *Polymers* **2018**, *10*, 870.
[18] Z. Zhang, J. L. Provis, A. Reid, H. Wang, *Constr. Build. Mater.* **2014**, *56*, 113.
[19] C. Herrera, K. J. Ysinga, C. L. Jenkins, *ACS Appl. Mater. Interfaces* **2019**, *11*, 35312.
[20] M. K. Lauer, M. S. Karunarathna, A. G. Tennyson, R. C. Smith, *Mater. Adv.* **2020**, *1*, 590.
[21] M. K. Lauer, T. A. Estrada-Mendoza, C. D. McMillen, G. Chumanov, A. G. Tennyson, R. C. Smith, *Adv. Sustain. Syst.* **2019**, *3*, 1900062.
[22] M. S. Karunarathna, M. K. Lauer, T. Thiounn, R. C. Smith, A. G. Tennyson, *J. Mater. Chem. A.* **2019**, *7*, 15683.