

## Crosslinker co-polymerisation for property control in inverse vulcanisation

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# Crosslinker co-polymerisation for property control in inverse vulcanisation

Jessica A. Smith,<sup>[a]</sup> Sarah J. Green,<sup>[a]</sup> Samuel Petcher,<sup>[a]</sup> Douglas J. Parker,<sup>[a]</sup> Bowen Zhang,<sup>[a]</sup> Max J. H. Worthington,<sup>[d]</sup> Xiaofeng Wu,<sup>[a]</sup> Catherine A. Kelly,<sup>[b]</sup> Thomas Baker,<sup>[c]</sup> Christopher T. Gibson,<sup>[d,e]</sup> Jonathan A. Campbell,<sup>[d]</sup> David A. Lewis,<sup>[d]</sup> Mike J. Jenkins,<sup>[b]</sup> Helen Willcock,<sup>[c]</sup> Justin M. Chalker\*,<sup>[d]</sup> and Tom Hasell\*<sup>[a]</sup>

**Abstract:** Sulfur is an underused by-product of the petrochemicals industry. Recent research into inverse vulcanisation has shown how this excess sulfur can be transformed into functional polymers, by stabilization with organic crosslinkers. For these interesting new materials to realise their potential for applications, more understanding and control of their physical properties is needed. Here we report four new terpolymers prepared from sulfur and two distinct alkene monomers that can be predictively tuned in glass transition, molecular weight, solubility, mechanical properties, and colour.

## Introduction

Synthetic polymers are ubiquitous and among the most extensively manufactured materials on earth. However, the vast majority of synthetic polymers are produced from limited resources derived from petrochemicals.<sup>1</sup> More than 60 million tonnes of excess sulfur are produced annually by hydrodesulfurisation of crude oil and gas<sup>2</sup> and it is highly abundant geologically.<sup>3</sup> Although sulfur can be polymerized in a pure form (Fig. 1a), the resultant polymers are not stable and readily depolymerise to S<sub>8</sub>. The recent discovery of inverse vulcanization has heralded a new class of materials, pioneered by Pyun, Char *et al.* in 2013.<sup>4</sup> These polymers are made predominantly from elemental sulfur without the need for organic solvents or initiators. Molten sulfur acts as the reaction solvent itself, as well as monomer and initiator during the molten stage. The growing sulfur polymers are stabilized against depolymerisation by reaction with an organic cross-linker, in a process that is simple, scalable, and highly atom efficient. Inverse vulcanized sulfur polymers offer an alternative to carbon-based materials, exhibiting unique properties for different applications. For example, high refractive indices and infrared transparency allow use as lenses and in thermal imaging applications.<sup>5-7</sup> The low cost of sulfur gives potential for bulk construction applications

derived from their high thermal<sup>8</sup> and electrical insulating properties. Despite a crosslinked structure, the reversibility of sulfur-sulfur bonds allows recycling<sup>9</sup> and repair.<sup>6</sup> Other reported applications include LiS batteries,<sup>4, 10, 11</sup> water purification,<sup>12-17</sup> the stabilization of metal nanoparticles and quantum dots,<sup>18-21</sup> controlled-release of fertilisers,<sup>22</sup> and antimicrobial materials,<sup>23</sup> and there are doubtless many more applications yet to be discovered. Fully realising the potential of sulfur polymers for these applications will depend on the physical properties of the polymers themselves. There is therefore a need to explore and control such physical properties.

Many crosslinkers have already been reported for inverse vulcanisation, both synthetic and renewable.<sup>15</sup> The choice of crosslinker can give very different properties to the sulfur polymer produced, and each with their own advantages and disadvantages. For instance, diisopropenyl benzene (DIB, Fig. 1b) gives a shape persistent solid polymer,<sup>4</sup> but has a relatively high price in comparison to sulfur. Limonene has significant benefits of being sustainable and low in cost, but results in a low molecular weight polymer, and lack of shape persistency.<sup>12</sup> Dicyclopentadiene (DCPD) is a low cost industrial by-product, which gives a hard, rigid, high modulus solid, but it is also brittle.<sup>24</sup> Sustainable vegetable oils, such as rapeseed (canola), linseed, olive, or sunflower oil can be used as a crosslinker,<sup>25, 26</sup> giving a soft compressible solid, the flexibility of which allows recovery of bound oils when this material is used as a sorbent for oil spills.<sup>17</sup> Here we investigate how varying the ratios of two distinct organic crosslinkers (Fig. 1b) can be used to control and tailor the properties of these polymers, with a focus on mechanical properties. We also report four new classes of terpolymers, prepared from sulfur, DCPD and one of the following other monomers; triglyceride, limonene, terpinolene and EDGMA.

Although investigations into the mechanical properties of inverse vulcanized polymers are few, there have been preliminary investigations. Sulfur-DIB copolymers (S-DIB) have been studied for their tensile properties,<sup>4, 6</sup> as have sulfur-diallyl disulphide copolymers.<sup>27</sup> The ductile and hardness properties of S-DIB and sulfur-divinyl benzene copolymers have been compared.<sup>28</sup> Similarly, nano-indentation was used to compare the elastic modulus of sulfur polymers crosslinked with DIB, farnesol, DCPD, and myrcene.<sup>24</sup> The flexibility of a sulfur-rapeseed oil co-polymer was investigated by dynamic mechanical analysis.<sup>17</sup> Most of the previous reports of sulfur polymers use only a single organic crosslinker to react with sulfur, but there are

<sup>a</sup> Department of Chemistry, University of Liverpool, Liverpool, L69 7ZD, United Kingdom. E-mail: t.hasell@liverpool.ac.uk

<sup>b</sup> School of Metallurgy and Materials, University of Birmingham, Edgbaston, Birmingham, B15 2TT, United Kingdom.

<sup>c</sup> Department of Materials, Loughborough University, Loughborough, LE11 3TU, United Kingdom.

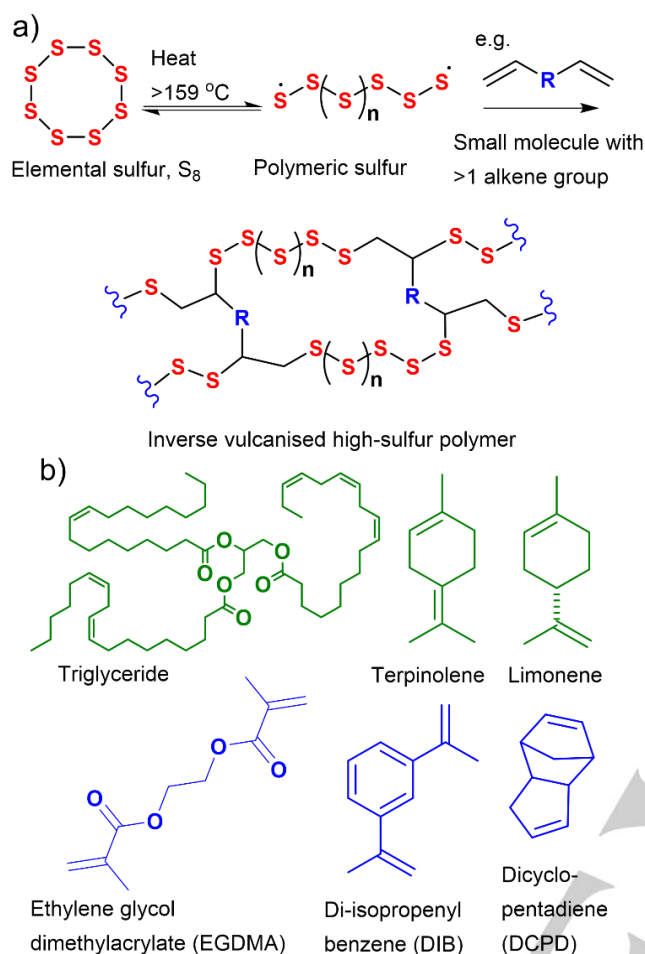
<sup>d</sup> Institute for NanoScale Science and Technology, College of Science and Engineering, Flinders University, Sturt Road, Bedford Park, South Australia, Australia. Email: justin.chalker@flinders.edu.au

<sup>e</sup> Flinders Microscopy and Microanalysis, College of Science and Engineering, Flinders University, Sturt Road, Bedford Park, South Australia, Australia

† Footnotes relating to the title and/or authors should appear here.

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**Figure 1:** a) Schematic for the general synthesis of inverse vulcanised polymers. b) Crosslinkers discussed in this report, clockwise from top left: An example of a triglyceride structure, as found in vegetable oils such as rapeseed or sunflower oil, terpinolene, limonene, DCPD, DIB, and EGDMA.

three notable prior examples of terpolymers obtained by using two organic crosslinkers: initial reaction of sulfur with styrene was shown to then allow the inclusion of a second (acrylate) crosslinker that would not have been reactive with the sulfur otherwise.<sup>29</sup> Similarly, initial reaction of sulfur with divinyl benzene allows later reaction with 1,4-cyclohexanedimethanol divinyl ether which, had it been reacted with sulfur directly, would have required a reaction temperature higher than its boiling point.<sup>30</sup> In a third study, Diez *et al.* produced terpolymers of sulfur and divinyl benzene (DVB) with either DIB or styrene (STY).<sup>28</sup> They showed that by adding a second crosslinker, the ductility can be influenced. A higher DVB content leads to a higher strength and shape retention. The addition of DIB or STY to the Sulfur-DVB polymer was shown to allow control of the glass transition ( $T_g$ ) of the material, at a fixed sulfur content, over a range of almost 20 °C (-1.3 to 17 °C). Intrigued by these discoveries, we set out to investigate if this would be transferable to a wider range of crosslinkers, and if greater

structural variety in the crosslinkers could allow an even greater range of properties to be achieved.

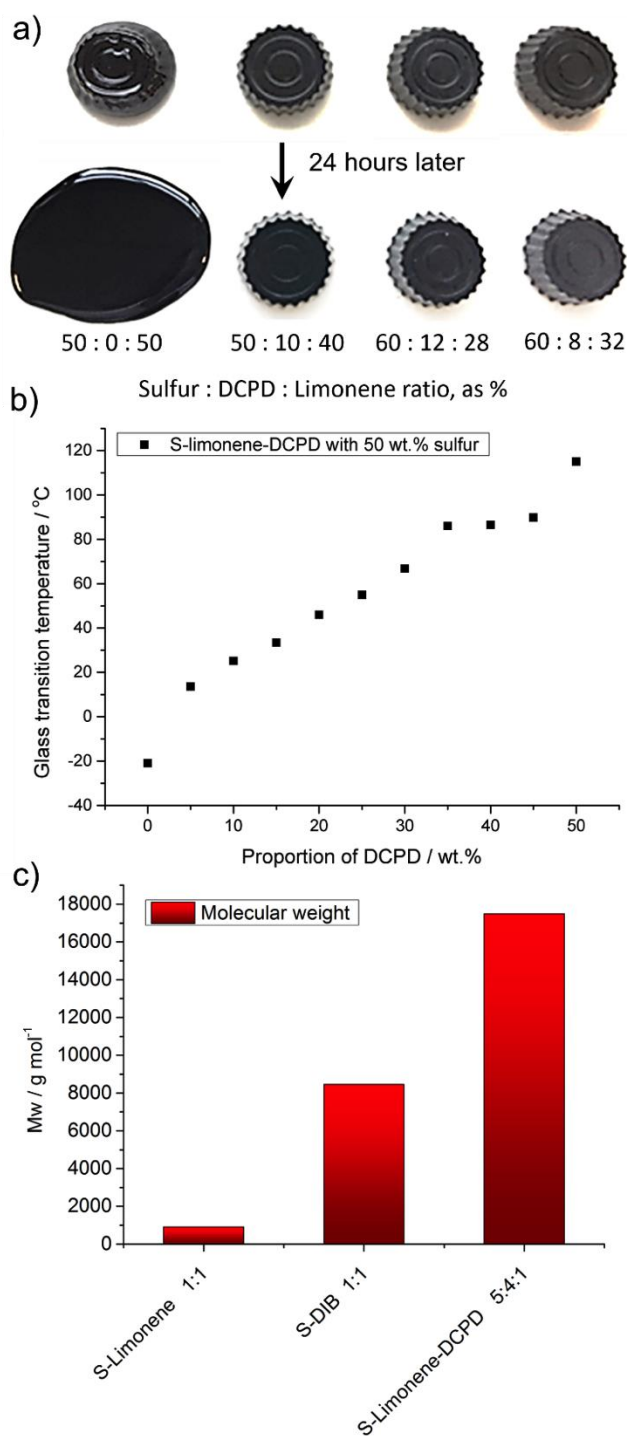
We report several discoveries and new materials which we hope will help guide the synthesis of sulfur terpolymers with bespoke properties. We show that, analogous to classic polyolefin terpolymers such as acrylonitrile butadiene styrene (ABS) plastics and ethylene propylene diene methylene (EPDM) elastomers, sulfur terpolymers can be prepared in diverse forms by simply varying the feed ratio of monomers.

This investigation shows that variation of the organic crosslinker only, at fixed sulfur content, can give controllable  $T_g$  over a 135 °C range (-20 to 115 °C). The monomers used in these reactions are readily available and affordable feedstocks (e.g. sulfur, limonene, terpinolene, triglycerides and dicyclopentadiene (DCPD)) that could be utilized for a range of different applications, by simply varying ratio of three distinct monomers.

Also reported is how the different monomer ratios directly affect mechanical properties. Compression modulus of sulfur terpolymers made from sulfur, triglycerides and DCPD is shown to decrease exponentially with increasing feed ratios of flexible triglyceride co-monomer. Findings also show how flexural strength and modulus of sulfur terpolymers made from sulfur, ethylene glycol dimethylacrylate (EDGMA) can be modulated based on feed ratio. Finally, we report for the first time how feed ratio of sulfur terpolymers can modulate colour.

In this study, 'S-crosslinker' will be used henceforth to refer to a co-polymer of sulfur and the stated crosslinker (or crosslinkers). S-limonene and S-vegetable oil polymers have both shown excellent potential in that they combine sulfur with low cost, renewable materials – and have also both been shown to adsorb mercury,<sup>12, 25</sup> and have improved stability as LiS batteries.<sup>26, 31</sup> However, both also have disadvantages. S-limonene tends to form only low molecular weight polymers which are not shape persistent.<sup>12</sup> Vegetable oils will react with sulfur, but will only bind up to ~30 wt.% sulfur as a stable polymer, with any excess precipitating out as crystals of elemental sulfur ( $S_8$ ).<sup>25, 26</sup> We therefore sought to determine if these challenges could be overcome by including a second organic crosslinker in the inverse vulcanisation. For this we chose DCPD, as it has been shown to produce highly stable and fully crosslinked inverse vulcanized polymers, and while not renewable itself, is at least readily sourced cheaply and at scale as it is an industrial by-product.<sup>24</sup> Also, in terms of the range of  $T_g$ s so far reported for sulfur polymers, vegetable oils and DCPD give amongst the lowest and highest, respectively, so their combination may lead to a broad range of properties.

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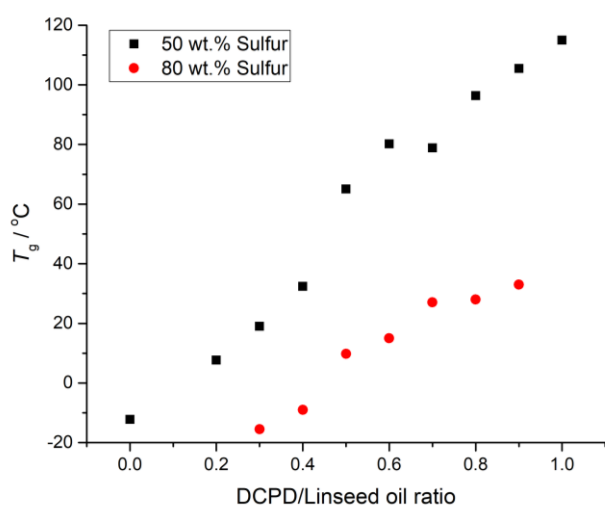
**Figure 2:** a) Photographs of moulded objects produced from sulfur, DCPD, and terpinolene (in the proportions shown). The top row shows the objects as made, and below after 24 hours. Substituting only a small amount of limonene for DCPD is enough to provide shape persistency in the polymers. b)  $T_g$ , from DSC, of co-polymers consisting of 50 wt. % sulfur, with the remaining 50wt.% from either limonene, DCPD, or a mixture of the two. c) Molecular weight, from GPC, of copolymers of S-limonene, S-DIB, and S-limonene-DCPD.

## Results and Discussion

Pursuing the hypothesis that DCPD would increase the  $T_g$  of sulfur polymers, we found that that only a small addition of DCPD was required to make S-limonene copolymers shape persistent (Fig. 2a), and that as the proportion of DCPD added increased, the glass transition temperature ( $T_g$ ) also increased in a controllable and roughly linear manner between that of pure S-limonene, and pure S-DCPD (Fig. 2b). The increase in  $T_g$  is likely the result of the added DCPD inducing a more branched structure, and higher molecular weight in the co-polymer in relation to S-limonene. DCPD is also a more conformationally constrained cross-linker, which could impart rigidity to the polymer structure. Addition of only 10 wt.% DCPD is enough to increase the molecular weight of the copolymer by an order of magnitude, and from below that of S-DIB, to above it (Fig. 2c). The molecular weight of co-polymers with higher proportions of DCPD than this could not be easily measured by gel permeation chromatography (GPC), as the addition of DCPD also results in a marked decrease in solubility, consistent with a greater degree of cross-linking (ESI, Fig. S1). A similar relationship is also seen between DCPD content and  $T_g$  for other sulfur:crosslinker ratios (Fig. S2a) as well as for S-DIB-DCPD terpolymers (Fig. S2b). This could be significant in the optical and electronic applications of S-DIB, as the addition of only 5 wt.% of DCPD can raise the  $T_g$  from 28 °C to 56 °C.

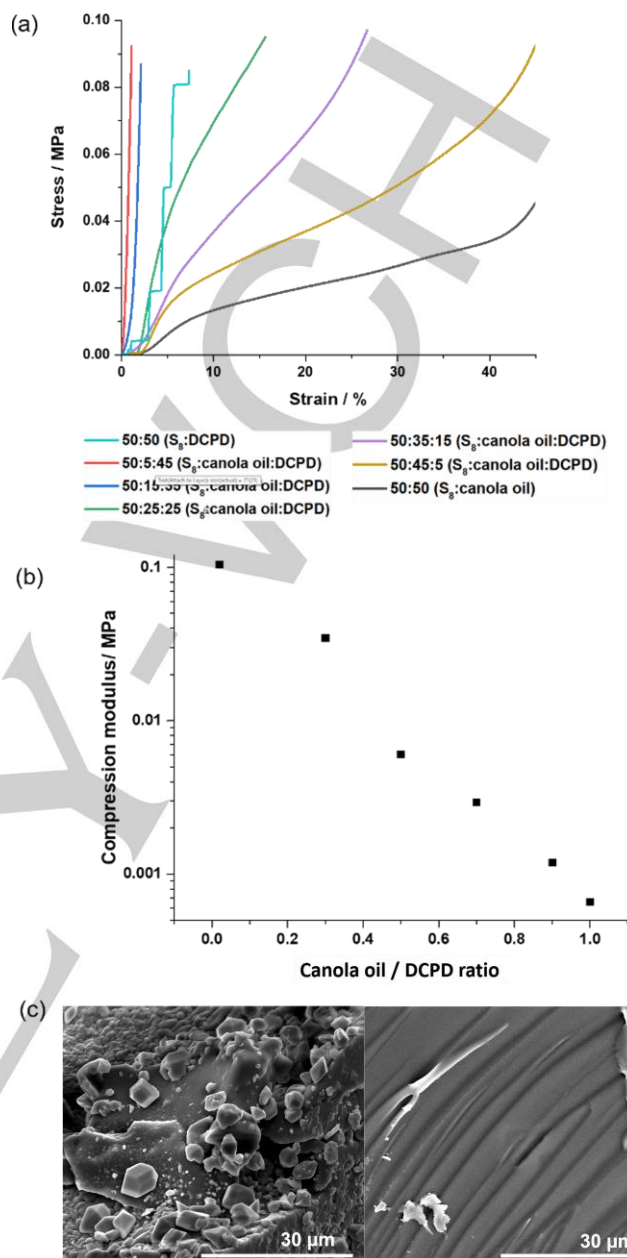
DCPD was included in the synthesis of sulfur and linseed oil to form terpolymers, over a range of different sulfur:crosslinker and DCPD:linseed oil ratios (ESI, Tables S3-S4). The resultant materials were all stable black solids that were either rubbery or brittle depending on the composition. With a 50 wt.% loading of sulfur, polymers with 20 wt.% or higher of DCPD were hard and brittle, and under 20 wt.% DCPD they were rubbery. DSC of the polymers again showed a controlled increase in  $T_g$  with increased addition of DCPD (Fig. 3). As well as increasing the  $T_g$ , the addition of DCPD also allows a higher proportion of sulfur to be stabilized in the polymers without depolymerizing back to  $S_8$ . DSC traces show no evidence of the melting of  $S_8$  crystals, at 50 wt.% sulfur, with only a 10 wt.% loading of DCPD (Fig. S4). At 80 wt.% sulfur, the polymers are stable against depolymerisation above 8 wt.% DCPD, but below this there is evidence of the melting of crystalline  $S_8$  (Fig. S5). Despite the marked difference in the structure of linseed oil in comparison to DCPD, the detection of only one  $T_g$  indicates there is no phase separation in the resultant materials. Thermogravimetric analysis (TGA) of the polymers shows an increased char mass as a function of DCPD loading (Fig. S6). Powder X-ray diffraction (PXRD) can also reveal the presence of depolymerised sulfur by the diffraction of crystalline  $S_8$ . No crystallinity was seen by PXRD, even for the low DCPD samples that showed a slight signal by DSC (Figs. S7, S8).

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**Figure 3:** Glass transition temperature, from DSC, of a range of S-DCPD-linseed oil co-polymers. The DCPD/linseed oil ratio is plotted normalised between 0 (all linseed) and 1 (all DCPD).

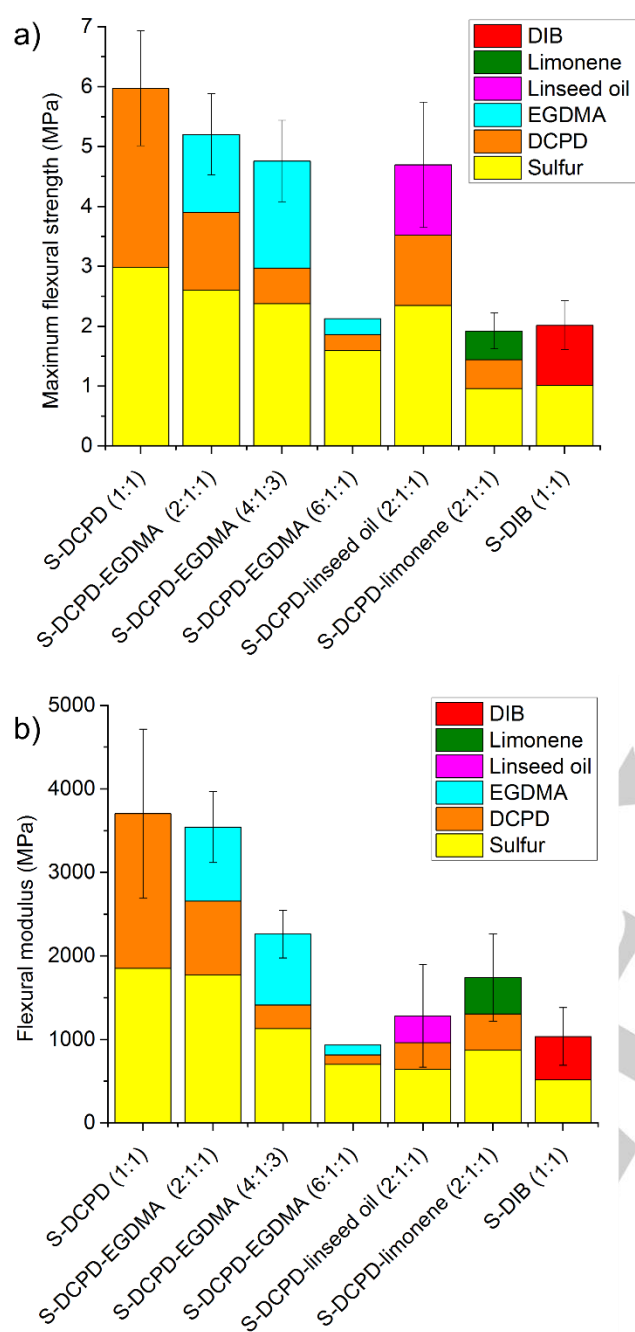
DCPD was also included in the synthesis of sulfur and canola oil (rapeseed oil) to form terpolymers, over a range of different sulfur: crosslinker and DCPD: canola oil ratios (Table S5 ESI). Similar to the other DCPD/vegetable oil polymers the resultant materials were black solids that exhibited different properties as a function of crosslinker ratio (Tables S5, S6). PXRD showed crystalline sulfur present at DCPD levels of 15 wt.% or lower, at 50 wt.% sulfur (Fig. S10). This indicates the depolymerisation of sulfur back to  $S_8$  crystals. At DCPD loadings of 25 wt.% or higher the samples were amorphous. This elimination of free sulfur at DCPD levels of 25 wt.% and above is further confirmed by DSC and Raman spectroscopy (Fig. S11-S14). The DSC also reveals there is sharp increase in  $T_g$  with DCPD loading starting from the 25 wt.% loading level (Fig. S15). A previous study on S-canola oil copolymers used salt templating to create porosity.<sup>17</sup> It was this porosity, and the compressibility of the material, that allowed it to be used for oil adsorption and reclamation, by acting as a sponge. In order to determine how DCPD affected these compressive properties, a range of S-DCPD-canola oil samples were produced and salt templated by the same method (Fig. 4). Stress strain curves were recorded to identify different characteristics (Fig. 4a); the compressive load (stress) and the percentage of compression (strain). From Fig. 4a & 4b it is clear that as more DCPD is included, the polymer can withstand less strain before breaking, and there is a more linear relationship between stress and strain. This is characteristic of a brittle material, with the percentage of compression being much lower for brittle materials. The plateaus in the stress-strain curve for S-DCPD are indicative of when the material is breaking, providing more evidence for how brittle the material



**Figure 4:** a) Stress-strain curves of Sulfur-canola oil-DCPD copolymers at ratios given in the legend. b) There is a direct relationship between the compression modulus of the polymer and the canola oil / DCPD ratio, normalised between 0 (all DCPD) and 1 (all canola oil). c) SEM images of cut surfaces (without salt templating) of: *left*, Sulfur-canola oil-DCPD copolymer at 5 wt.% DCPD, and *right*, at 25 wt.% DCPD. 'Sulfur bloom' of  $S_8$  crystals forming on the new surface can be seen on the left, but only a smooth polymer and fracture marks on the right.

is. Fig. 4a & 4b reveals how doping as little as 5 wt.% of the flexible triglyceride of canola oil can change the compressive properties of the material significantly. Scanning Electron Microscopy (SEM) was conducted to look at the morphology of the polymers. Fig. 4c highlights the presence of depolymerised sulfur in 5 wt. % DCPD loading and shows no free sulfur present in 25 wt. % of DCPD loading. In salt

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**Figure 5:** Maximum flexural strength, a), and flexural modulus, b), of sulfur-crosslinker copolymers with a variety of compositions. The composition of each bar is shown by the relative height of each colour according to the key. Weight ratios of the components of each polymer are given in brackets after the sample name.

templated samples, porosity generated by removal of the salt crystals can be seen (Fig. S16).

In addition to compression tests, co-polymers of different crosslinkers were also tested for their flexural, tensile, and hardness properties. Flexural tests show clear differences in both strength and modulus depending on polymer

composition (Fig. 5). It should be noted that the flexural strength of these sulfur polymers are quite low in comparison to many commodity plastics. Polypropylene for example has a flexural strength of 40 MPa,<sup>32</sup> much higher than the highest of these polymers, 6 MPa for S-DCPD. This may limit some applications of sulfur polymers, but these results will hopefully provide a useful benchmark to be improved upon by the growing research community of inverse vulcanised polymers.

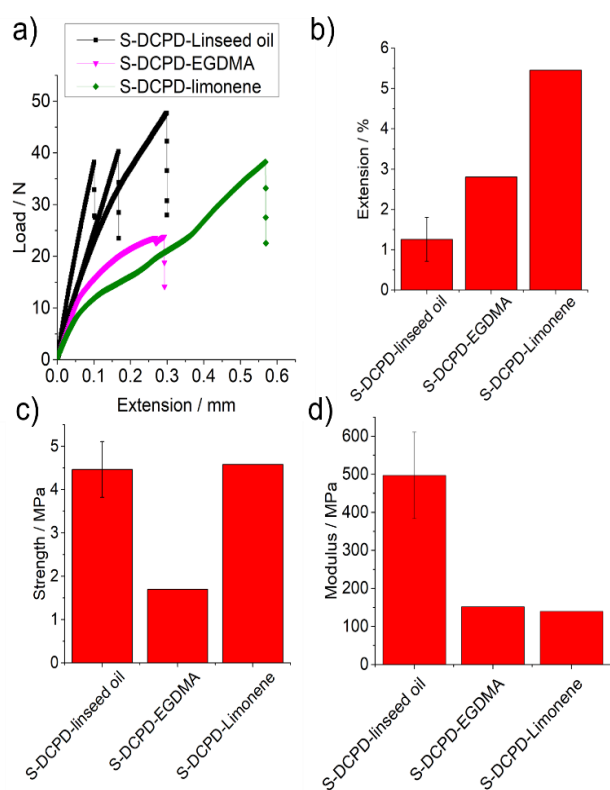
Conversely, the flexural modulus of some of these sulfur polymers is remarkably high; S-DCPD has a flexural modulus of 3.7 GPa, significantly higher than polypropylene (1.5), polycarbonate (2.3), and polystyrene (2.5).<sup>32</sup>

The variation in the flexural strength and modulus with composition demonstrates potential for the properties of sulfur polymers to be tailored for applications by the choice and ratio of crosslinkers. For instance, replacing a proportion of DCPD with EGDMA reduces both the strength and modulus by similar amounts. However, replacing DCPD with linseed oil reduces the modulus significantly, while only having a much lower effect on the strength. The properties of a pure S-limonene sample could not be measured due to its lack of shape persistency. However, it can be seen that incorporation of DCPD along with the sulfur and limonene is sufficient to increase the strength and modulus to comparable levels of S-DIB. Comparing the S-DCPD-EGDMA samples both the strength and modulus are reduced by increasing sulfur loading.

The tensile properties of a set of sulfur polymer terpolymer were tested on samples moulded into 'dog-bone' strips (Fig. S17). Unfortunately not all samples could be tested by this method, as some of the polymers, such as S-DCPD, were too brittle. However, the results showed a marked difference in the properties of a set of three samples produced from sulfur, DCPD, and a third crosslinker, depending on the structure of the third crosslinker used (Fig. 6a). The extension at breaking point of the three polymers varies between 1.3 % for the S-DCPD-linseed oil terpolymer and 5.5 % for the S-DCPD-limonene terpolymer (Fig. 6b). These values are within the range of some commonly used polymers such as polystyrene (1.6 %), epoxy resins (1.3 %), and acrylonitrile-butadiene-styrene (ABS, 6 %) but far lower than others such as polycarbonate (200 %) or polypropylene (80 %).<sup>33</sup>

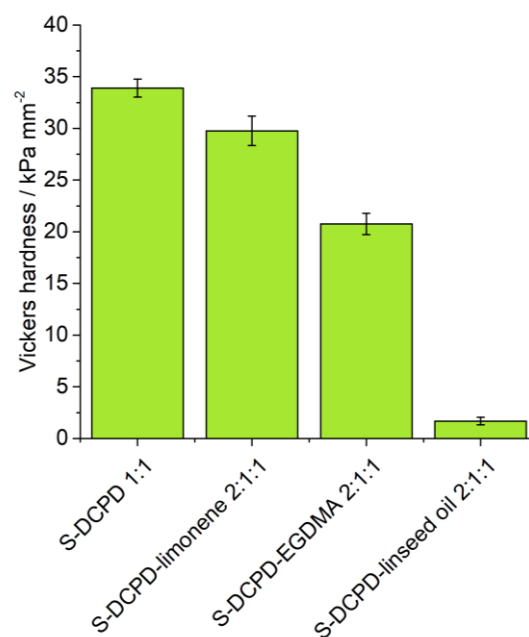
The tensile strength range of these sulfur polymers (up to ~4.5 MPa), in common with their flexural strength, is again poor in comparison to most common polymers, and calls for improvement from future research (Fig. 6c). For example, polyethylene has a tensile strength between 10 to 32 MPa, depending on molecular weight, and polystyrene a strength of 34 MPa.<sup>33</sup> The tensile modulus (Fig. 6d) of the three polymers (up to ~0.5 GPa) is in a similar range to some carbon based polymers (e.g. polyethylene 0.1 to 0.8 GPa) but lower than others (polystyrene 3.0 to 3.5 GPa).<sup>34</sup>

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**Figure 6:** – Tensile testing of sulfur polymers at 50 wt.% sulfur loading, and 25 wt.% loading each of DCPD and another crosslinker: linseed oil, EGDMA, or limonene. Three repeat samples were measured for S-DCPD-linseed oil, and the standard deviation in the results is given. a) Stress-strain curves. b) Extension at break. c) Maximum breaking strength. d) Tensile modulus.

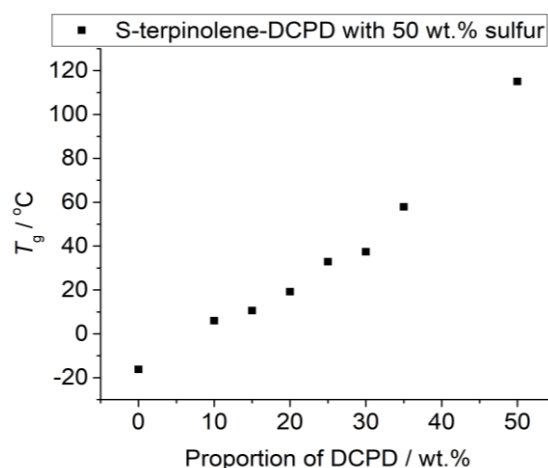
The relative hardness of the polymers was investigated using microhardness Vickers testing (Figure 7). All of the polymers tested contained sulfur reacted with crosslinkers at an equal mass ratio, and all contained DCPD in the crosslinker portion. The difference in hardness as DCPD is replaced with other crosslinkers is clearly apparent. The S-DCPD-linseed oil sample, as the only sample above  $T_g$  at room temperature, has a considerably lower hardness than the other three polymers. The other three polymers all show surprisingly high hardness, the highest of which is S-DCPD at 34 kPa mm<sup>-2</sup>, significantly higher than even many of the hardest conventional carbon-based polymers such as high impact polystyrene, polycarbonate, and poly (methyl methacrylate), at 13, 12, and 21 kPa mm<sup>-2</sup>, respectively.<sup>35</sup> The decrease in hardness of the samples in replacing DCPD with limonene, EGDMA, and linseed oil (i.e. hardness for DCPD>limonene>EGDMA>linseed) inversely correlates with the increase in molecular flexibility across the same series. In addition to changing the mechanical properties, combining crosslinkers can also give the opportunity to modify the colour of the resulting polymers. Terpinolene (see Fig. 1) has not been previously reported as a crosslinker for inverse vulcanisation. When trialled, it was found to successfully



**Figure 7:** Vickers hardness of a range of S-DCPD copolymer and S-DCPD with other crosslinkers added in. Weight ratios are given in the order of the components in the sample name.



**Figure 8:** Photographs of ~5 mm thick blocks of polymers made from 50 wt.% sulfur and 50 wt.% crosslinker, where the crosslinker was composed of copolymers of DCPD and terpinolene, going from all DCPD (left) to all terpinolene (right). Numbers written in pen under the samples can be read clearly for most samples.



**Figure 9:**  $T_g$ , from DSC, of co-polymers consisting of 50 wt.% sulfur, with the remaining 50 wt.% from either terpinolene, DCPD, or a mixture of the two.

react with sulfur through inverse vulcanisation. However, the resultant material had a low  $T_g$  (-16 °C) and lacked shape



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persistence (Fig. S18), similar to materials produced from sulfur and limonene – perhaps unsurprising considering their similar molecular structure. Interestingly though, the resultant sulfur-terpinolene polymer was optically transparent with an orange-yellow colour (Fig. 8). Most inverse vulcanised polymers reported have a colour from black-brown through to deep red. There is interest in the optical properties of sulfur polymers due to their high transmission to infrared light, allowing thermal imaging applications, as well as their high refractive index.<sup>5, 6, 36</sup> For both of these applications, while not always necessary, a greater degree of transparency in the visible light range may be beneficial. By doping DCPD into the sulfur-terpinolene polymer it was possible to improve the physical properties to allow use (10 wt. % DCPD is sufficient to provide shape persistence), while still maintaining the transparent orange-yellow colour (Figs. 8, 9, S19). Pure S-DPCD polymer is too dark in colour to see through in the visible range, and pure S-terpinolene lacks the shape persistence to form a lens. Combining the two crosslinkers therefore allows a compromise of transparency and shape persistence not otherwise afforded. By measuring the refraction of white light through blocks of 50 wt.% sulfur, 25 wt.% DCPD, 25 wt.% terpinolene copolymer the refractive index from Snell's law was calculated as 1.74 +/- 0.03. This is comparable to previously reported refractive indices of inverse vulcanised polymers at the same sulfur content, e.g. S-DIB and S-TIB have refractive indices of, 1.77<sup>5</sup> and 1.72<sup>7</sup> respectively. These indices for high sulfur polymers are significantly higher than those of many other optical materials, such as glass (1.52) or poly (methyl methacrylate) (1.49).

## Conclusions

Polymers with a high proportion of sulfur, made by inverse vulcanisation, have very different properties to carbon based polymers. This offers many unique and interesting potential applications. However, this is still an emerging field, and the physical properties are still largely underreported. As many of the practical applications will be underpinned by the physical properties, it is necessary for them to be investigated, understood, and ideally improved. As well as reporting the tensile, flexural, compression, and hardness properties of a variety of sulfur polymers, we have shown that combining of crosslinkers is a valuable way in which the properties can be tailored. For instance, the  $T_g$  can be varied controllably from -20 °C to 115 °C. This is also the first effort to uncover some design principles so that a given mechanical or optical property can be rationally imparted to this class of sulfur polymers. We hope that these results will

help to set benchmarks to trigger future improvements in the properties of these fascinating polymers.

## Experimental Section

**Polymer synthesis:** Sulfur (wt. % show in Table S3-S6) was added to a 40 mL glass vial equipped with a magnetic stirrer bar and heated on a hot plate to 165 °C. Molten sulfur was formed (transparent, yellow solution) and to this crosslinker was added (sunflower oil/ linseed oil/canola oil /limonene/EDGMA). Following this DCPD was added to the mixture. The mixture was heated until homogenous. The product was then transferred to a silicone mould and allowed to cure for ~14 hours at 140 °C.

### Characterisation:

**Powder X-ray diffraction (PXRD):** Powder X-Ray Diffraction (PXRD) patterns were carried out on samples using a PAN analytical X'pert powder diffractometer using CuK $\alpha$  radiation.

**Differential Scanning calorimetry (DSC):** Differential scanning calorimetry was carried out using Q2000 DSC (TA instruments). The method was a heat/cool/heat for three cycles; heating to 150 °C and cooling to -80 °C at a heating rate of 5 °C/min with Tzero Hermetic pans.

**Thermogravimetric Analysis (TGA):** TGA was carried out in platinum pans using a Q5000IR analyzer (TA Instruments) with an automated vertical overhead thermobalance. The samples were heated at 5 °C/min to 900 °C under nitrogen.

**Fourier-transform infrared spectroscopy (FT-IR):** was performed using a Thermo NICOLET IR200, between 400 cm<sup>-1</sup> to 4000 cm<sup>-1</sup>. Samples were loaded either neat, using an attenuated total reflectance accessory, or in transmission after pressing into a KBr pellet.

**Compression testing:** S-DCPD canola oil porous polymer blocks (45, 35, 15, 5 wt. % canola oil), S-DCPD and S-Canola oil were compressed using TA Instruments Q800 DMA in compression using parallel plates. DMA was ran in controlled force mode using stress/strain experiment. The force was ramped at 0.5 N/ min up to 10 N.

**Flexural testing:** Based on ASTM E290. Flexural testing was carried out using an Instron 5566 in the 3-point bend mode. The force required to deflect the samples, over a 140 mm gauge length, was measured at a rate of 0.5 mm min<sup>-1</sup>. Sample strips were made in a 150 mm x 10 mm x 10 mm silicone mould.

**Tensile testing:** Based on ASTM D638. Tensile properties were measured on an Instron 5944 system. Samples were molded into dog-bone shapes of 63.5 mm length, with a cross-sectional width of 3.18 mm, depth 3 mm and an initial gauge length of 25.4 mm (shown in Fig. S16). The crosshead speed was fixed at 10 mm/min, the capacity of the load cell was 2 kN.

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**Hardness testing:** Microhardness Vickers testing was carried out using a diamond indenter and a 100 g load (HV 0.1) or a 50 g load for the softer materials (HV 0.05).

**Gel permeation chromatography (GPC):** The molecular weight of the soluble fraction of the polymers was determined by gel permeation chromatography (GPC) using a Viscotek system comprising a GPCmax (degasser, eluent and sample delivery system), and a TDA302 detector array, using THF as eluent.

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