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Processable crosslinked terpolymers made from elemental sulfur with wide range of thermal and mechanical properties

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Inverse vulcanization has emerged as a popular strategy for transforming the waste material, elemental sulfur, into functional polymers with high sulfur content (>50 wt.%, normally). Inverse vulcanized polymers are intrinsically processable and recyclable, and have been demonstrated as promising for applications in many fields. However, the mechanical properties of inverse vulcanized polymers are currently underdeveloped. If this kind of material is to be widely used in some scenarios to replace some traditional plastics, it is necessary to make them with appropriate thermal and mechanical properties that meet basic application requirements. Here, we report a series of terpolymers copolymerized from two distinct organic comonomers and elemental sulfur to obtain polymers with a wide range of glass transition temperatures (−43 °C to 45 °C) that exhibit good mechanical properties, by blending crosslinkers with varying feed monomer ratio and chain length of linear sections, which expands the application opportunities of inverse vulcanization.

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Inverse vulcanization has recently garnered significant attention as a simple and effective process for transforming elemental sulfur, a by-product, into highly useful sulfur-containing polymeric materials[1–3]. Since inverse vulcanization was created in 2013[4], new crosslinkers for synthesis, and interesting intrinsic properties and unexpected applications of relevant materials have been extensively studied. Plenty of research has demonstrated that inverse vulcanized polymers have unique properties which traditional carbon-based polymers lack, such as affinity for heavy metal (especially mercury)[5–8], chemically dynamic property[9–12], ultrahigh refractive index ($n > 1.8$)[13–15], and they have been proved that they are able to be used in many promising applicable fields, such as antimicrobial material[16,17], water remediation[5,7,8,18], Li-S battery[19–21], infrared thermal imaging[22–24], optics throughout visible range[15,25], and self-healing materials[12,26–28]. Developing a new generation of recyclable plastics is imperative for a sustainable environment and future. Inverse vulcanized polymers form recyclable polymeric materials even when fully crosslinked because of the reversibility of the polysulfide bonds that comprise much of their structure. Crosslinked polymers conventionally form thermoset materials—which are desirable for their mechanical properties, but cannot be recycled because they cannot be melted or dissolved, and so cannot be reformed once made. Recent research has been undertaken into alternative chemistry that allows crosslinked polymers to be recycled by the use of reversible bonding in the crosslinks, and such systems are known as vitrimers[29,30] or covalent adaptable networks[31,32]. Inverse vulcanized polymers, therefore, warrant investigation, since the bulk feedstock of sulfur comes from waste material, can be formed into functional materials, and is intrinsically recyclable[5,9,12]. Considering the long-term development of this type of material, it is necessary for the material to have a wide range of thermal and mechanical properties.

Generally, two main routes have been developed to improve thermal and mechanical properties of inverse vulcanized polymers. One route is a chemical method in which polymers' properties are altered by adjusting crosslinkers[9,13,24,33–43] or further polymerization[12,27,44,46]. R. C. Smith and co-workers fully demonstrated that T_g ($-3\,°C < T_g < 68\,°C$) and strength ($0.5\,MPa < \sigma_{max} < 7.5\,MPa$) of inverse vulcanized polymers could vary with the flexibility of crosslinker[36,38,40,42,45]. S. Park reported that inverse vulcanized polymers with high T_g ($>100\,°C$) could be produced through further polymerization through an annealing process in an oven[46]. T. Hasell and co-workers suggested that inverse vulcanized polymers with a wide range of T_g ($-20\,°C < T_g < 45.6\,°C$), exhibiting both strong or weak, ductile or rigid behavior, can be generated by controlling a secondary cross-linking reaction in a two-step synthesis[12,27]. Another route is a physical method, like fabricating polymer composites by adding organic or inorganic fillers[39,47]. As reported by V. Hanna et al., fillers provide an increase in tensile strength and toughness of inverse vulcanized polymers[47]. Overall, T_g of inverse vulcanized polymers are normally high, which limits the opportunities for some applications in low temperature environments. There is a need for further development of inverse vulcanized polymers with a wider range of thermal and mechanical properties to meet the diverse requirements of various applications. Especially, a kind of inverse vulcanized polymers with low T_g ($<0\,°C$) but still maintaining mechanical properties is waiting to be developed. Copolymerization is an effective method to make terpolymers with controllable properties, resulting from combination of advantages of co-monomers. J. A. Smith et al. have demonstrated that thermal and mechanical properties can be controlled by copolymerization of multiple monomers, however, although a wide range of T_g ($-20\,°C$ to $115\,°C$) was obtained in this work, terpolymers with low T_g ($<0\,°C$) either had unreacted sulfur remaining or had no shape persistence ability[37], which cannot be used even at room temperature if a chemically stable material with sufficient mechanical properties is required.

Hence, it is necessary and meaningful to expand the range of thermal properties of inverse vulcanized polymers and endow the materials with certain mechanical properties, so that the materials can be applied in expanded fields. In this work, inverse vulcanized terpolymers with wide range of T_g ($-43\,°C$ to $45\,°C$) and wide range of mechanical properties (from flexibility and elasticity to stiffness) were generated. Those high sulfur terpolymers are named as S-PEG-TATA and derived from the monomer poly (ethylene glycol) diacrylate (PEG) blending with triallyloxy-triazine (TATA), and elemental sulfur. Herein, the mechanical and thermal properties of inverse vulcanized polymers were modified by not only changing monomer ratio but also changing chain length of linear sections in this work. The PEG used in the synthesis is a relatively small molecule with low polymerization degrees rather than extended macromolecules. Three kinds of molecular weight of PEG were selected, which are 250 g/mol, 575 g/mol and 700 g/mol, respectively. TATA, which has low molecular weight and contains three carbon-carbon double bonds in each molecule, was chosen as the co-crosslinker as it can assist PEG to stabilize more sulfur and bring stiffness to the polymer at same time. The investigation on sulfur load capacity in synthesis and the effect of chain length of crosslinker and feed monomer ratio to polymer's property was carried out. We have demonstrated that thermal and mechanical performance of the obtained polymers can be dramatically modified by changing chain length of linear sections combined with varying molar ratio of two distinct crosslinkers.

Results and discussion

Synthesis and structure characterization of terpolymers. As illustrated above, three types of PEG with different molecular weight (250 g/mol, 575 g/mol and 700 g/mol) were used in this work and co-crosslinker TATA was selected. The chemical structures of PEG and TATA, and the average polymerization degree of three PEGs are shown in the Fig. 1. The reason why blending crosslinkers were used here is that pure PEG is unable to stabilize a high content of sulfur to form a stable sulfur polymer. The higher density of alkene groups of TATA could assist to form fully crosslinked and stable sulfur polymers. When the reaction was attempted without catalyst, an inhomogeneous product was formed as shown in Supplementary Fig. 1. The differential scanning calorimetry (DSC) curve of the product (Supplementary Fig. 2) showed that there are two phase transition temperatures and significant unreacted sulfur in the product, and nuclear magnetic resonance spectroscopy (NMR) spectra (Supplementary Figs. 17–22) show different consumption rates of comonomers, suggesting inhomogeneous and unstable polymer is formed without catalyst. Hence, the catalyst Zn diethyldithiocarbamate (Zn (DTC)$_2$) was used in the synthesis of polymers. It can accelerate the reaction speed between sulfur and both cross-linkers, reducing the difference in reaction degrees between the two reactions. This promotes the formation of more homogeneous polymers (Supplementary Fig. 3).

In principle, the properties of terpolymer can be endowed by the advantages of blended monomers. Here, TATA was proposed to give stiffness to the resultant polymers and PEG was supposed to endow flexibility to the polymers. Hence, the thermal and mechanical properties of terpolymers were proposed to be controlled by varying the feed ratio of sulfur and crosslinkers even by varying the feed ratio of two crosslinkers. It should be note that, in this work, feed ratio of sulfur and blended
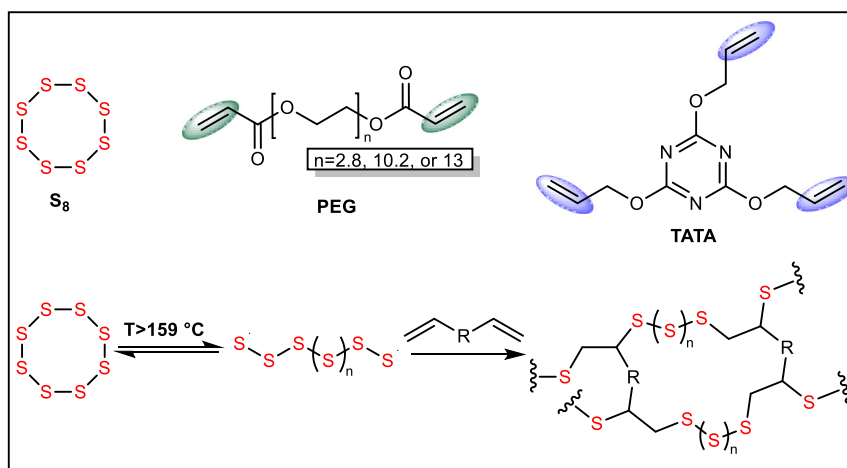
Fig. 1 Reaction scheme. Schematic for inverse vulcanization of sulfur with blending crosslinkers PEG and TATA.

crosslinkers was controlled by changing weight percentage of each part, but feed ratio of crosslinkers was controlled by changing molar percentage of double carbon bonds provided by each crosslinker. Chain length of linear sections was controlled by changing the molecular weight of PEG. The obtained terpolymers are named as 'a S-b (PEG x_c-TATA$_d$)', where 'x' is 1, 2 and 3 which refer to PEG1 (250 g/mol), PEG2 (575 g/mol) and PEG3 (700 g/mol), respectively. 'a' and 'b' represent the weight percentage of sulfur and weight percentage of blending crosslinkers, respectively. 'c' and 'd' represent molar percentage of double carbon bonds provided by PEG and TATA, respectively. Supplementary Table 1 gives all the terpolymers' compositions. The synthesis procedures of the polymers can be found in methods section.

As Supplementary Table 1 shows, sulfur content was adjusted from 50 wt.% to 80 wt.% with 10 wt.% steps and blending crosslinkers content was adjusted from 50 wt.% to 20 wt.%, correspondingly. At constant mass of blending crosslinkers, the carbon double bonds (C = C) molar percentage provided by every single crosslinker varied from 20% to 80% with 20% steps, and the mass of every single crosslinker was determined correspondingly. For the terpolymers with 50 wt.% sulfur, linear chain length was controlled by varying types of PEGs. The terpolymer 50S-50(PEG3$_{20\%}$-TATA$_{80\%}$) was taken as an example to be monitored by using NMR, and the polymers' structure was characterized by using Fourier transform infrared spectroscopy (FT-IR).

From Fig. 2a, we can see that the peaks belonging to C = C in monomers totally disappeared after curing for 3 h, and there are new peaks δ = 1.27, 1.4 and 1.62 ppm and peaks δ = 2.54, 2.65 and 2.87 ppm appeared simultaneously, which are attributed to saturated alkanes and sulfides RS-CH, respectively. Figure 2b further shows that peaks belonging to C = C in monomers were consumed after 12-min reaction and there is a new peak belonging to C-S (peak δ = 69 ppm) appeared. That suggests that the C = C bonds were consumed by sulfur and C – S bonds were formed. The changes of integration of the typical peaks with reaction time are illustrated in Supplementary Information (SI) from Supplementary Fig. 4 to Supplementary Fig. 16. Figure 2c shows that both peak at 1632 cm^{-1} of PEG1 and the peak at 1653 cm^{-1} of TATA disappeared after polymerization, suggesting that C = C bonds from crosslinkers were consumed by sulfur. It is observed from Fig. 2d that there are two new peaks at 534 cm^{-1} and 760 cm^{-1} appeared in copolymer S-TATA and terpolymer 50S-50(PEG1$_{60\%}$-TATA$_{40\%}$), which are belonging to S-S bond and C – S bond, respectively[48,49]. Those results further demonstrate that the terpolymer was synthesized as expected. Other

terpolymers all show same results with that of terpolymer 50S-50(PEG1$_{60\%}$-TATA$_{40\%}$) (in Supplementary Fig. 23).

To check if the terpolymers are crosslinked polymers, solubility investigations of the terpolymers were carried out and the effects of crosslinker feeding ratio, sulfur content and PEG type on solubility of the polymer were investigated. Solvents tetrahydrofuran (THF), chloroform, toluene, acetone and ethyl acetate (EA) were used in solubility investigations here. The procedures of the experiments and calculation of gel content are illustrated in the Methods section. Here, the solubility of the terpolymers are analysed in 3 groups.

In group 1, polymers 50S-50(PEG2$_{20\%}$-TATA$_{80\%}$), 50S-50(PEG2$_{40\%}$-TATA$_{60\%}$) and 50S-50(PEG2$_{60\%}$-TATA$_{40\%}$) were selected, where the only variable is crosslinkers feeding ratio, to research if the blending ratio of crosslinkers has an effect on the solubility. Supplementary Fig. 24 illustrates that insoluble content significantly decreases when the molar ratio of C = C provided by PEG to TATA increases from 20% to 40%, regardless of solvent type. With further increase of the molar ratio from 40% to 60%, insoluble content has a further slight decrease in solvents toluene, acetone and EA. Therefore, all the polymers have a significant insoluble fraction in all five solvents, but they are more soluble in THF and chloroform compared with other 3 solvents. As more PEG and less TATA is introduced, lower insoluble content of the polymer is obtained, as higher PEG proportion leads to lower crosslinking density of the polymer.

In group 2, polymers 50S-50(PEG3$_{20\%}$-TATA$_{80\%}$), 60S-40(PEG3$_{20\%}$-TATA$_{80\%}$) and 70S-30(PEG3$_{20\%}$-TATA$_{80\%}$) were selected, where the only variable is sulfur content, to investigate if sulfur proportion has an effect on the solubility of the polymer. Similarly, all those polymers have an insoluble fraction in all five solvents and have higher soluble fractions in THF and chloroform than other three solvents, as shown in Supplementary Fig. 25. Insoluble contents of the polymers in solvents THF, chloroform, and toluene decrease with the increase of sulfur proportion, while the insoluble content in solvents acetone and EA has a slight increase. Theoretically, higher percentage of sulfur tends to form polymers with lower crosslinking degree and generate the polymer chains with higher sulfur rank. That results in lower gel content when the polymer has higher sulfur contained by mass.

In group 3, polymers 50S-50(PEG1$_{20\%}$-TATA$_{80\%}$), 50S-50(PEG2$_{20\%}$-TATA$_{80\%}$) and 50S-50(PEG3$_{20\%}$-TATA$_{80\%}$) were selected, where the only variable is molecular weight of PEG, to investigate whether the PEG type has an effect on the solubility of the polymer. Supplementary Fig. 26 clearly shows that the insoluble content of the polymer in five solvents significantly
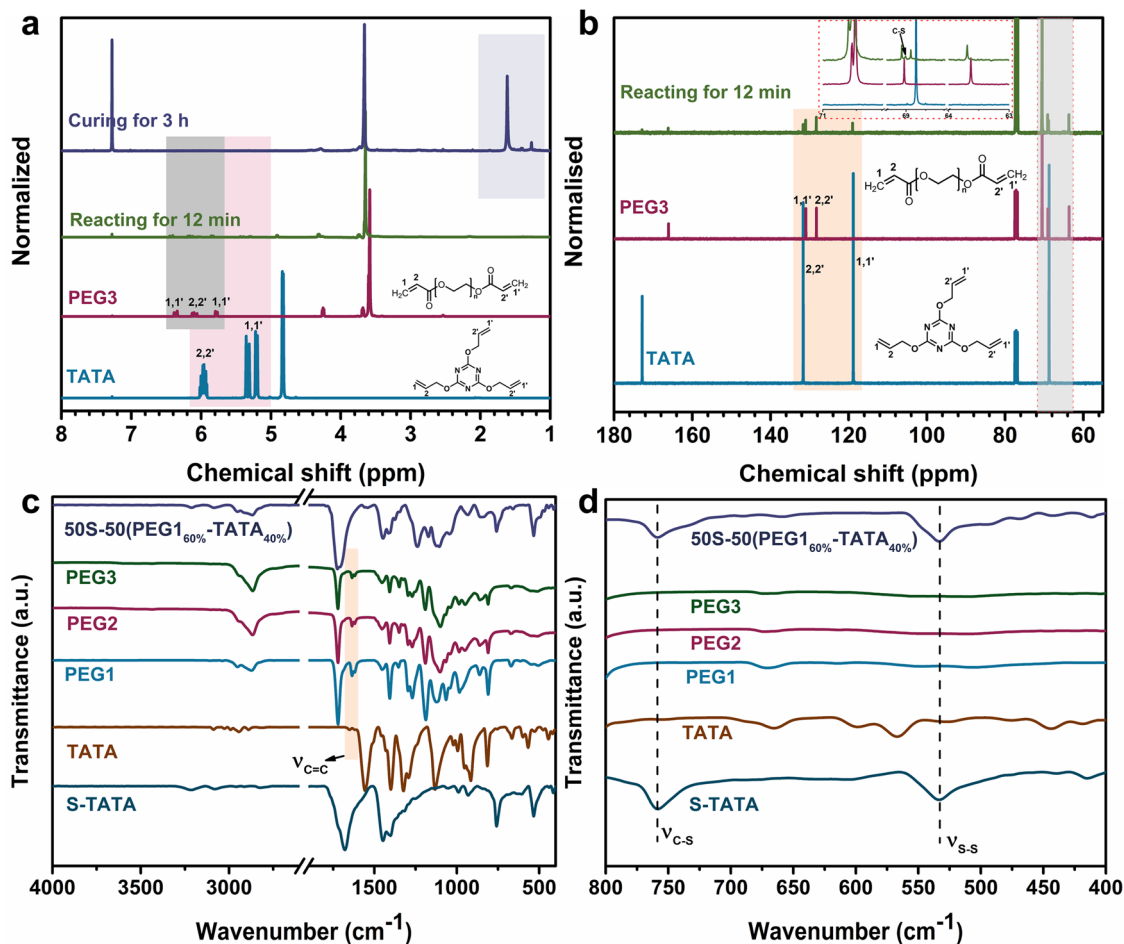
Fig. 2 Polymer structure characterizations. a ^{1}H NMR and (**b**) ^{13}C NMR spectra of monomers TATA and PEG3 and products during reaction or curing. **c** FT-IR curves of monomers, copolymer sulfur-TATA (S-TATA) and terpolymer 50S-50(PEG1$_{60\%}$-TATA$_{40\%}$). **d** partial view of the Fig. 2c with wavenumber from 400 cm^{-1} to 800 cm^{-1}.

decreases with the increase of molecular weight of PEG despite a slight increase of insoluble content in solvents THF and chloroform with changing from PEG2 to PEG3. As higher molecular weight of PEG gives longer chains of linear section of the polymer, the crosslinked degree is decreasing as the increase of chain length, causing the decrease of the insoluble content. In summary, the solubility investigations have demonstrated that all the terpolymers have crosslinked structure due to insoluble performance of the materials in the solvents. Also, it was found that THF and chloroform are good solvents (THF is the best) and the other 3 solvents are bad solvents for the terpolymers relatively. In addition, the photograph records of solubility investigations can be found in from Supplementary Fig. 27 to Supplementary Fig. 29.

Thermal and mechanical properties investigation. Thermal and mechanical properties of the obtained terpolymers are discussed in this section. Supplementary Table 2 gives a summary of thermal and mechanical properties of the relevant materials. DSC was used to test polymers' glass transition temperatures and investigate polymerization degree. From DSC curves of polymers (Supplementary Fig. 30), we can see that there is unreacted crystalline sulfur trapped in the polymers 50S-50(PEG1$_{80\%}$-TATA$_{20\%}$), 60S-40(PEG3$_{60\%}$-TATA$_{40\%}$), 70S-30(PEG3$_{40\%}$-TATA$_{60\%}$), 70S-30(PEG3$_{60\%}$-TATA$_{40\%}$) and 80S-20(PEG3$_{20\%}$-TATA$_{80\%}$). To fully stabilize sulfur, it is suggested that for terpolymers with 50 wt.% sulfur, PEG feed content should not

exceed the content corresponding to a molar ratio of C=C provided by PEG to TATA of 80% of the C=C bonds being from PEG. With the increase of sulfur content from 50 wt.% to 80 wt.%, the maximum allowable PEG content decreases, corresponding to a decrease in the molar ratio of C=C provided by PEG to TATA from 80% down to 20% of the C=C bonds being from PEG. As TATA has higher percentage of unsaturated hydrocarbons than PEG, less TATA means less stability for sulfur. If there is unreacted sulfur remaining in the materials, we think those materials are chemically unstable polymers. The thermal and mechanical properties of all the chemically stable resulting-terpolymers were investigated.

As Fig. 3a shows, when the proportion of sulfur is constant at 50% by mass, T_g of the terpolymer is decreasing with the increase of PEG percentage, regardless of molecular weight of PEG. That illustrates that PEG can endow flexibility to the terpolymer as what expected. When the proportion of sulfur is constant at 50% by mass, and also PEG percentage is controlled at a consistent value by controlling molar ratio of C=C provided by two crosslinkers, like molar ratio of 20%, 40% or 60%, T_g of the terpolymer is decreasing with the increase of molecular weight of PEG. It is observed that at constant molar ratio of C=C provided by two crosslinkers, PEG1 gives much higher T_g to the terpolymer than the other two kinds of PEGs, and T_g is decreasing with the increase of molecular weight of PEG. It means that a longer chain length of the linear section leads to lower glass transition temperature of the terpolymer.
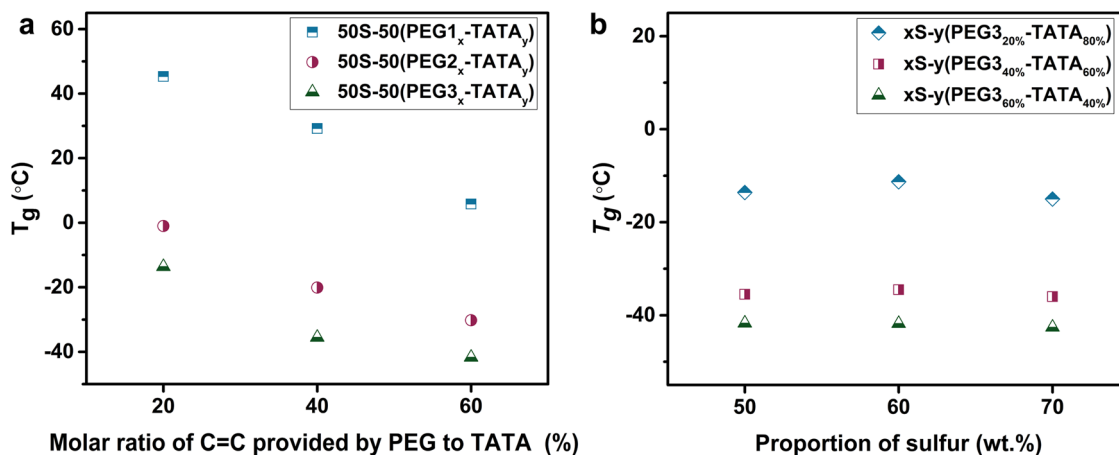
Fig. 3 Summary of T_g changes with monomer feed ratios. a The T_g of terpolymers with composition of 50 wt.% sulfur as a function of molar ratio of C=C provided by PEG to TATA (x is molar ration of C=C provided by PEG to TATA and y is '1-x'). **b** The T_g of terpolymers with composition of PEG3 as a function of sulfur content (x is weight percent of sulfur and y is weight percent of blending crosslinkers).

Figure 3b shows that when the molecular weight and percentage of PEG are controlled at a constant value, sulfur proportion almost has no effect to T_g of polymer. Due to the fact that elemental sulfur serves as both a building block of the polymer backbone and a provider of polymer cross-linking points, an increase in sulfur content leads to an increase in the proportion of polysulfide linear chains within the polymer. This results in a decrease in the glass transition temperature. However, simultaneously, the interconnection of polysulfide chains increases the degree of crosslinking, which leads to an increase in the glass transition temperature. The combined effect of these two factors results in the glass transition temperature not undergoing significant changes with an increase in sulfur content. Additionally, regardless of sulfur content, higher PEG percentage gives lower T_g to the polymer.

Thermogravimetric analysis was performed to evaluate the thermal stability of the obtained terpolymers in N_2. Supplementary Fig. 31 shows that degradation temperatures of all the materials are about 200 °C, which is the normal degradation temperature of inverse vulcanized polymers. Also, with the increase of TATA percentage, the residue percentage increases, due to the higher degree of crosslinking leading to more char residue.

All the obtained polymers have been demonstrated to have a crosslinked structure. However, they are processable due to the existence of sulfur-sulfur bonds, which are a kind of dynamic covalent bonds. These bonds endow the crosslinked polymers recyclable performance. Much research have demonstrated that sulfur-sulfur bonds can give the relevant crosslinked polymeric materials good process ability[12,27,50]. Therefore, the mechanical properties of the crosslinked terpolymers were evaluated using dog-bone samples. These samples were obtained by processing the cured polymers in a hot press (procedure can be found in the 'Methods' section).

Figure 4 shows the typical stress-strain curves of all the polymers. The average values of tensile properties of all those terpolymers, including tensile strength, breaking strain, Young's modulus and toughness, with error bars can be found in Supplementary Table 2. Note that the polymer 50S-50(PEG1$_{20\%}$-TATA$_{80\%}$) is extremely stiff and brittle, making it difficult to make and test dog-bone samples. As a result, only one successful test was obtained. The tensile testing data of the terpolymers, composed of 50 wt.% sulfur with varying blending ratio of 3 different PEGs and TATA, were plotted to molar ratio of C=C provided by PEG to TATA, as shown in Fig. 5.

Additionally, the data of terpolymers composed of blending crosslinkers (PEG3$_{20\%}$-TATA$_{80\%}$) with varying sulfur content were plotted, as shown in Fig. 6. In Fig. 5, color refers to mechanical properties and symbol shapes refer to terpolymers. The effect of chain length of linear section, blending ratio of crosslinkers, and sulfur content on the mechanical properties of terpolymers can be analysed using the data presented in Figs. 4, 5 and 6.

Figures 4a–c and 5a show that the tensile strength of terpolymers, composed of PEG1, is significantly higher than that of the terpolymers, composed of PEG2 or PEG3. The reason behind of this is that PEG1 has a much higher C=C density compared to the other two types of PEGs, resulting in higher crosslinking densities of the obtained polymer products and therefore higher tensile strength in performance. Regardless of PEG chain length, it is observed that the increase of PEG proportion leads to decrease of tensile strength. That cussed by lower crosslinking densities were formed with higher PEG content. Similar results regarding the effect of PEG category and content on Young's modulus can be observed.

Figures 4a–c and 5b show that the effect of PEG content on the breaking elongation of terpolymers, composed of PEG1, is significantly different with the terpolymers, composed of PEG2 or PEG3. For the former polymers, a higher PEG content leads to an increase in soft chain segments, resulting in higher strain. However, the latter polymers are much weaker compared with the former polymers, due to much lower crosslinking degrees, an increase of PEG content leads to lower crosslinking densities and then weaker polymers with lower tensile strains. Additionally, when the PEG content is set to correspond to the molar ratio of C=C bonds provided by two crosslinkers of 20% and 40%, the tensile strain initially increases and then decreases with the increase in the molecular weight of PEG. However, when the PEG content is increased to correspond to the molar ratio of C=C bonds provided by two crosslinkers of 60%, the breaking strain decreases with the increase in the molecular weight of PEG. That is caused by combination effect of flexible chain length and crosslinking densities. Similar results regarding to the effect of PEG category and content on toughness of the terpolymers were observed as well.

Furthermore, mechanical properties of the terpolymers can be adjusted by varying sulfur proportion. As shown in Fig. 4d and Fig. 6, it is revealed that when the molecular weight and percentage of PEG was controlled at consistent values (PEG3, c is 20%), with the increase of sulfur proportion, strength and
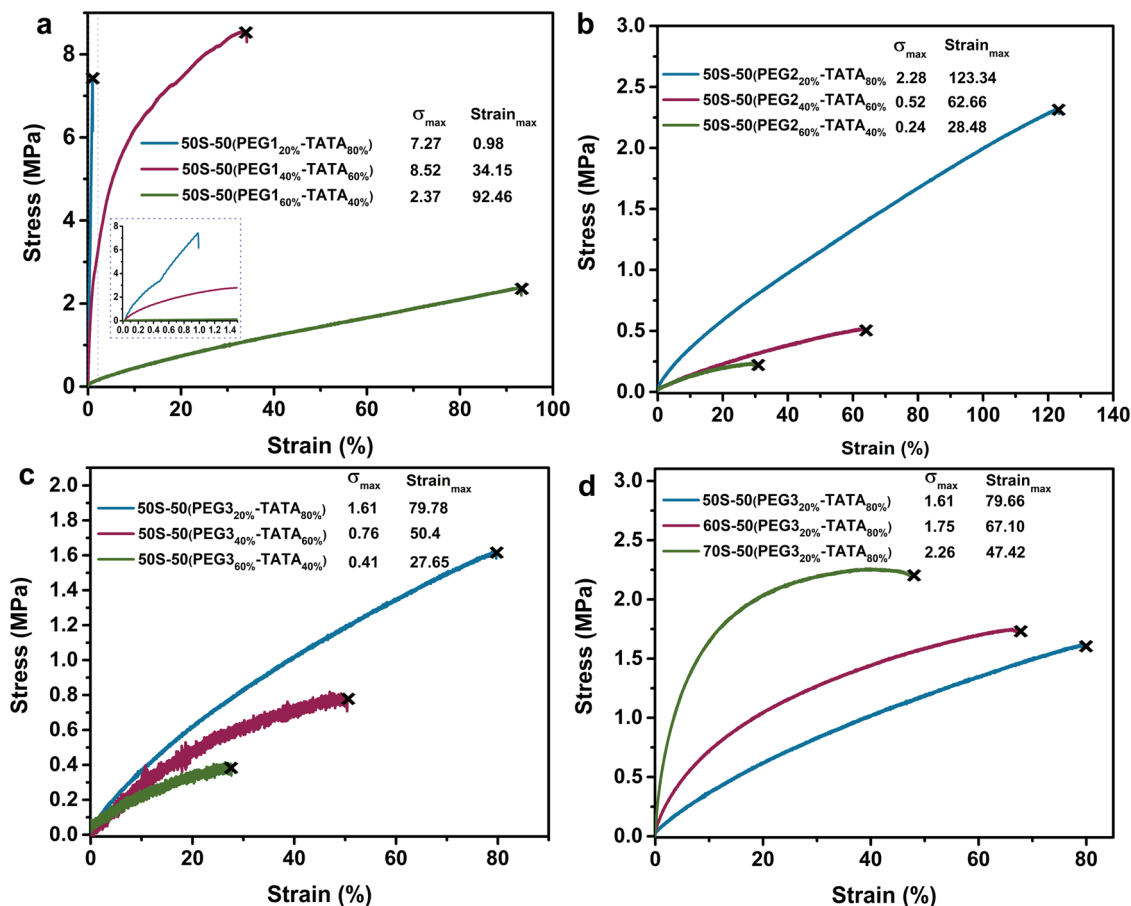
Fig. 4 Mechanical properties of terpolymers. Typical stress-strain curves of (**a**) terpolymers composed of 50 wt.% sulfur with varying blending ratio of PEG1 and TATA, (**b**) terpolymers composed of 50 wt.% sulfur with varying blending ratio of PEG2 and TATA, (**c**) terpolymers composed of 50 wt.% sulfur varying blending ratio of PEG3 and TATA and (**d**) terpolymers composed of varying sulfur content and consistent blending ratio of PEG3 and TATA.

Young's modulus are increasing, but strain is decreasing, and toughness is slightly decreased followed by an increase. That suggests that higher sulfur content leads to higher crosslinking degree, which is able to cause higher strength and modulus and less stretchability. Those results can also be intuitively observed in Fig. 4d, which shows that an increase of sulfur content leads to higher tensile strength but lower strain.

Furthermore, it was found that some of the terpolymers have good elastic properties, which can fully recover the deformation after releasing the stress. Hence, tensile loading-unloading testing was carried out for the selected terpolymers. Supplementary Fig. 32 shows that polymer 50S-50(PEG1$_{60\%}$-TATA$_{40\%}$) can fully recover the maximum strain of 30% in 10 cycles without obvious hysteresis. Additionally, tensile loading-unloading test with maximum strain of 50% to minimum strain of 10% in 18 cycles was performed to this polymer. As shown in Supplementary Fig. 33, the deformations of the material recovered well in 18 cycles, but there is an obvious stress relaxation after 15 cycles. That means the limit strain of the total elastic deformation of this polymer is 50% and cycles should no more than 15. Similarly, terpolymers 50S-50(PEG2$_{20\%}$-TATA$_{80\%}$) and 50S-50(PEG3$_{20\%}$-TATA$_{80\%}$) show elastic properties as shown in Supplementary Fig. 34 and Supplementary Fig. 35. Both of those materials can recover the maximum strain of 30% in 10 cycles, but there are obvious stress relaxations occurred. Compared with the polymer 50S-50(PEG1$_{60\%}$-TATA$_{40\%}$), those polymers have lower elastic deformation limitations and worse recoverable ability. That is caused by the lower crosslinking degree of those polymers compared to the polymer 50S-50(PEG1$_{60\%}$-TATA$_{40\%}$).

As mentioned above, inverse vulcanized polymers are a kind of polymers that are intrinsically recyclable. Recycling performance of the polymers in this work is evaluated by using polymers 50S-50(PEG2$_c$-TATA$_d$) as representative examples. As shown in Supplementary Figs. 36 and 37, regardless of TATA content, the average recovery rates of stress, strain, YM and toughness all reach 80%. In comparison, the polymers with lower TATA content exhibit higher stress recovery rate. That suggests that a higher TATA content results in a higher crosslinking density but lower recycling ability.

Overall, compared with previously published inverse vulcanized polymers, the terpolymers in this work obtained a wide range of T_g, especially at low temperature, to populate an otherwise blank area in the reported values, as summarized in Fig. 7a, which will give inverse vulcanized polymers more opportunities for wider applications. Most of polymers in this work are flexible as shown in Fig. 7b, allowing use in applications that require material with deformation ability.

Conclusion

In summary, the terpolymers S-PEG-TATA with varying monomers feed ratio have been successfully synthesized. It has been demonstrated that thermal and mechanical properties as well as solubility of the terpolymers were effectively modified by adjusting feed ratio of sulfur and blended crosslinkers, or by adjusting blending molar ratio of two distinct crosslinkers, or by changing chain length of PEG. It was illustrated that the polymeric materials with a wide range of T_g (−43 °C to 45 °C) were obtained, and they have variable mechanical properties, some of
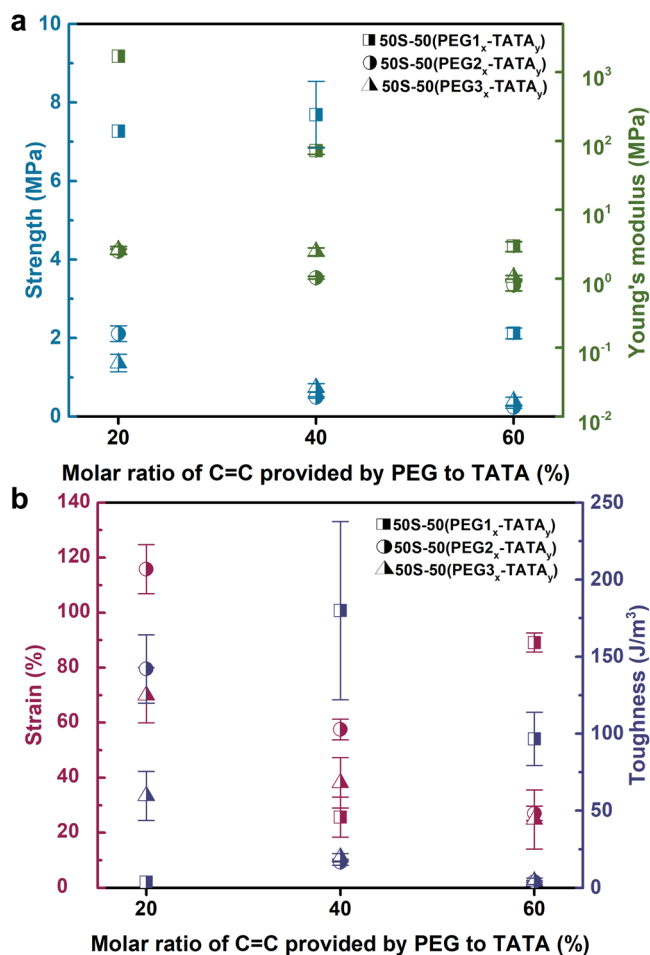
Fig. 5 Summary of tensile properties change with molar ratio of C═C provided by PEG to TATA. Tensile properties including (**a**) tensile strength and Young's modulus and (**b**) breaking strain and toughness of terpolymers composed of 50 wt.% sulfur with varying blending ratio of 3 different PEGs and TATA as a function of molar ratio of C═C provided by PEG to TATA (Here, error bar is standard deviation of 3–5 replicate test results).

them are flexible and elastic, and some of them are stiff and relatively strong, which can be accurately controlled by chain length of linear segment of crosslinker combined with molar ration of two crosslinkers. Combining the wide range of T_g with various mechanical performance of the relevant polymers, those materials themselves or the design principal of this synthesis system both extends the potentials for wider application of inverse vulcanization.

Methods
Materials. Sulfur (S_8, ≥99.5%), poly(ethylene glycol) diacrylate (250 g/mol) (PEG1), poly(ethylene glycol) diacrylate (575 g/mol) (PEG2), poly(ethylene glycol) diacrylate (700 g/mol) (PEG3), triallyloxy-triazine (TATA), Zn diethyldithiocarbamate (Zn(DTC)$_2$), chloroform-d (CDCl$_3$), chloroform, acetone, toluene, THF, and ethyl acetate (EA) were purchased from Sigma Aldrich and used as received without further purification.

Synthesis procedures of terpolymers with catalyst. The total mass of raw materials was set to 10 g, and terpolymers with different compositions were synthesized. The monomer mass for each polymer can be found in the Supplementary Table 1. Standard polymer synthesis procedure can be summarized as follows: sulfur with 100 mg catalyst Zn (DTC)$_2$ was added to a
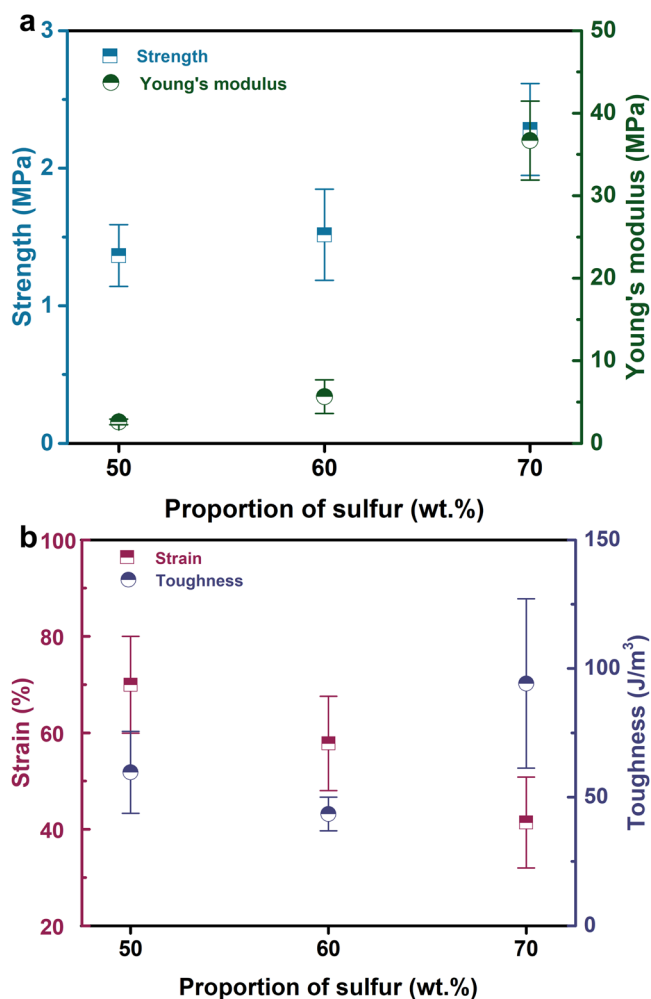
Fig. 6 Summary of tensile properties change with sulfur content. Tensile properties including (**a**) tensile strength and Young's modulus, and (**b**) breaking strain and toughness of terpolymers composed of varying sulfur content and consistent blending ratio of PEG3 and TATA as a function of proportion of sulfur by mass (Here, error bar is standard deviation of 3–5 replicate test results).

40 mL glass reaction vial equipped with a magnetic stir bar and was heated on a hot plate to 160 °C. After the orange sulfur liquid was formed, the mixture of PEG and TATA was added at stirring a speed of 900 rpm. After reacting for 10–15 min accordingly, the viscous liquid was poured into a silicone mold followed by 2 min of cool down and ~15 h curing at 140 °C in the oven.

Synthesis procedures of terpolymers without catalyst. The terpolymer 50S-50(PEG1$_{60\%}$-TATA$_{40\%}$) was used to demonstrate the product properties without catalyst in the synthesis process. The monomer mass of this polymer can be found in the Supplementary Table 1. Sulfur was added to a 40 mL glass reaction vial equipped with a magnetic stir bar and was heated on a hot plate to 160 °C. After an orange sulfur liquid was formed, the mixture of PEG and TATA was added at a stirring speed of 900 rpm. After reacting for 2 h, the pre-polymer was poured into a silicone mold followed by 2 min of cool down and ~15 h curing at 140 °C in the oven. Some photographs and NMR samples were recorded and collected, respectively, during the synthesis.

Solubility investigation. THF, chloroform, toluene, acetone and EA were used as solvents to research the solubility of the terpolymers S-PEG-TATA. For all the samples, the concentrations of
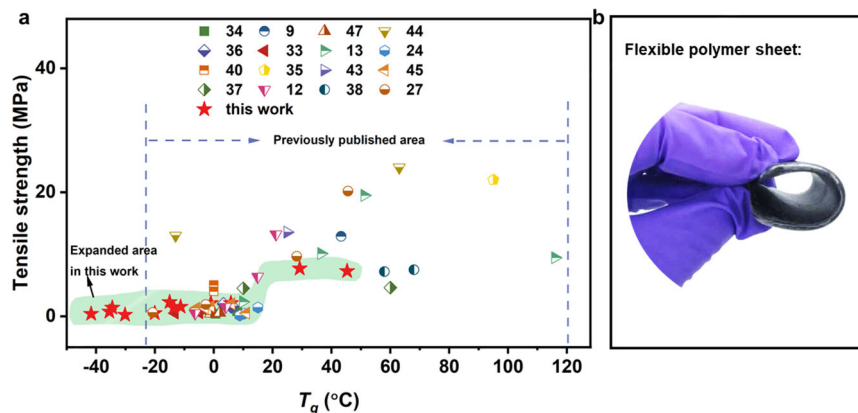
Fig. 7 Comparison of mechanical properties and thermal properties of this work with published work. a Comparison of T_g and tensile strength of polymers exhibited in this work with other inverse vulcanized polymers. (The numbers of the symbols refer to the reference numbers of the papers these results appear in). **b** Photograph of polymer 50S-50(PEG$_{60\%}$-TATA$_{40\%}$).

polymers were prepared as around 3 mg/ml and the mass of each polymer was recorded. All the samples were stirred for ~24 h using agitator at room temperature. Insoluble fractions were filtered using a nylon membrane (0.20 μm), and soluble fractions or insoluble fractions were weighted after solvent evaporation. Then, insoluble fraction of each polymer in each solvent was calculated as Equation 3.1 illustrated. In addition, the soluble polymer could form a transparent liquid with color change theoretically, but insoluble polymer only could be swelled without obvious color change. The changes of polymers' states before and after dissolving by solvents, regardless the solution formed or solid state maintained, were recorded by photographs and that can be found in Supplementary Information.

$$\text{Insoluble fraction}\,(\%) = \text{insoluble fraction}\,(g)/\text{sample mass}\,(g) \times 100\%$$

Dog-bone sample making procedure. Viscous pre-polymer liquid was poured into silicon mold and was cured in the oven at certain temperature first. The solid-state polymer can be obtained after fully curing. The demoulded solid polymer blocks were further shaped into polymer sheet by using hot press with inserting a certain thick steel mold. The temperature and pressure of hot press were controlled at 130 °C and 20 MPa, respectively. Pressing time are varying from 5 min to 15 min depending the crosslinking density of polymer. Once the polymer sheet was obtained, dog-bone samples can be cut off by using specific die cutter, which dimension is following the standard ISO 527-2/5 A.

Reprocess experiment procedures. Pieces of polymers were remolded into polymer films by using hot press with inserting a certain thick steel mold. The temperature and pressure during molding were controlled at 130 °C and 20 MPa, respectively.

Data availability

Data supporting the findings in this study is fully available within the main content and the supplementary information file.

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Author contributions

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Competing interests

The authors declare no competing interests.

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