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ARTICLE

Crack healing and reclaiming of vulcanized rubber by triggering rearrangement of inherent sulfur crosslinked networks

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CuCl$_2$ is shown to effectively catalyze reshuffling of the inherent sulfur crosslinked networks of vulcanized rubber. Once activated, CuCl$_2$-based complex catalysis enables disulfide metathesis through circulated crossover reaction among disulfide and polysulfide bonds without forming radicals and ionic intermediates. By taking advantage of this mechanism, the model material of this study, vulcanized polybutadiene rubber, acquires thermal remendability as characterized by repeated restoration of mechanical properties. Moreover, it can be reprocessed like thermoplastics. The compositions and fabrication of the model material simulate those of industrial vulcanized rubber, so as to facilitate formulation optimization under the circumstances close to actual situation for possible future application in practice. It is hoped that the results of the present preliminary exploration would provide basis for extending service life and developing new recycling technique of vulcanized rubber, which is produced, used and scraped in large quantity every day.

Introduction

Vulcanized rubber developed in the 19th century is one of the largest utilized polymers in the world. It has been applied to various industrial products like tyres, conveyor belts, shoe soles, hoses, seals, gaskets, etc. The large quantities of rubber consumption, however, bring about heavy burden to the environment because of the limited disposals of scraps, which contain nonreversible permanent crosslinked networks. To solve the problem, waste rubbers used to be reclaimed by physical, chemical and biological degradation to covert the insoluble and infusible thermoset into small molecular weight fragments with commercial value, or simply burned and buried.[1,2]

Unlike the above methods based on rupture of intermolecular links, the concept of self-healing arising in recent years offers a solution from another angle. That is, extension of service life and reduction of waste of rubber products by re-bonding the damaged materials. Nevertheless, literature survey indicates that the researches in this aspect

have not yet dealt with the widely used vulcanized rubber. Most studies are focused on tailor-made elastomers and elastomer blends, such as polydimethylsiloxane (PDMS) containing encapsulated healing agent,[3] thermoreversible rubber from supramolecular interaction,[4,5] thiol-functionalized silicone elastomer crosslinked by silver nanoparticles,[6] nitrile rubber/hyperbranched polyethylenimines compound,[7] epoxidized natural rubber and its blend with ionomer,[8,9] alkoxyamine crosslinked polyurethane elastomer[10] and epoxy elastomer,[11] polybutadiene with Grubbs' second-generation Ru metathesis catalyst,[12] living crosslinked PDMS,[13] crosslinked poly (urethane-urea),[14] and multiphase supramolecular thermoplastic elastomer.[15]

Considering that vulcanized rubber made of natural rubber or synthetic rubbers possesses optimized structures and properties after years of development, addition of healing microcapsules into the material or introduction of specific reversible bonds into rubber molecules would not be the most suitable way to impart it with self-healability. In fact, rubber is vulcanized mostly by sulfur or sulfur-donor, resulting in crosslinked networks with tremendous monosulfidic, disulfide and polysulfide linkages. (Note: According to the accelerator/sulfur ratio, commercial sulphur vulcanization systems are usually classified into: conventional (0.1~0.6), semi-efficient (0.7~2.5), and efficient vulcanization (2.5~12).[16,17] The produced monosulfide, disulfide and polysulfide crosslinks in the total number of crosslinks amount to 0~5, 30~40 and 60~70 % for conventional vulcanization, 0~20, 50~70 and 10~30 % for semi-efficient vulcanization, and 40~50, 35~50 and 5~20 % for efficient vulcanization, respectively.[16~22]) Disulfide bonds themselves have enabled self-healing of polymers through exchange or metathesis reaction by using their dynamic reversibility.[23~29] If disulfide

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exchange or metathesis among different disulfide and polysulfide linkages can also be triggered in sulfur crosslinked networks of vulcanized rubber by tiny amount of catalyst, the rubber would acquire self-healability accordingly, while keeping its intrinsic quality and original production process. Moreover, reshuffling of macromolecular networks due to dynamic exchange of disulfide and polysulfide bonds would allow vulcanized rubber to be reprocessed without needs of traditional practice of decrosslinking.[2] The key issue lies in finding out proper trigger mechanism and catalyst.

To activate the desired reversible reaction of disulfide and polysulfide linkages in vulcanized rubber, heating, rather than light, pH, etc., should be used as a means of stimulus in view of practicality and work efficiency. Additionally, the matching catalyst had better to be not only thermosensitive but also thermotolerant because of the following reasons. (i) Rubber vulcanization belongs to a typical thermal processing, which requires all the ingredients to be robust enough to survive the manufacturing. (ii) Healing (or reclaiming) temperature higher than the operating temperature of rubber products is necessary for ensuring stableness of structure and properties of the latter during service. Room temperature reshuffling of crosslinked networks[26,28,30] that leads to obvious creep of the material at ambient condition is not encouraged in the present case. According to these criteria, thiol,[25] phosphines[26,31] and rhodium,[32] which have successfully assisted or catalyzed thermal exchange or metathesis of disulfide, are no longer qualified. Thiol is easy to be oxidized in air. For example, thiol-disulfide exchange reaction was hindered at temperature above 70 °C as a result of accelerated oxidation of free thiol groups.[29] Phosphine catalyst is vulnerable to oxygen especially at elevated temperature.[26,31] As for rhodium catalyst, the high cost restricts its large scale application.

Here, for the first time we report $CuCl_2$ as a heat resisting, oxygen insensitive and cost effective catalyst to trigger disulfide metathesis in vulcanized rubber. It was discovered by contrastive analysis of periodic table of elements and probe trial. $CuCl_2$ used to serve as catalyst for radical addition reaction, chlorination and oxidation, additive for electroplating, photoengraving and feed, and colorant for glass, ceramics, etc. To the best of our knowledge, it has not been applied in the manner in which we employ it. To verify the feasibility of our design, $CuCl_2$-loaded polybutadiene rubber is prepared and characterized in the following.
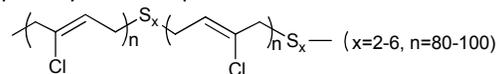
Since this work is a trial towards development of a technology for possible future application, the basic formula of the model material of this study simulates that for tyres (**Table 1**), which contains not only polybutadiene rubber as the base material but also other components like carbon black, nano-silica, sulfur, stearic acid, anti-ager, etc. Nevertheless, fractions of the components of our model material differ from those of the industrial product. To increase concentrations of disulfide and polysulfide bonds and mobility of $CuCl_2$ in the sulfur crosslinked network, bis(3-triethoxysilylpropyl) tetrasulfide, a polysulfide organosilane coupling agent and crosslinking agent for rubber industry, is included. It is expected (i) to take part in the crosslinking reaction of polybutadiene rubber and (ii) to

form complex with $CuCl_2$ in the vulcanized rubber. For achieving the targets, in reality, part of the organosilane is grafted onto nano-silica in advance, while the rest is directly compounded with all ingredients. Although incorporation of the organosilane might somewhat weaken mechanical strength of the model rubber, we prefer to conduct proof-of-concept study at first using the current recipe before working out a solution for real application.

Experimental

Materials

Polybutadiene rubber (trade name: BR 9000) was purchased from Sinopec Group, China. Chloroprene rubber (trade name: CR121) was supplied by Changhui Chemical Co. Ltd., China. Poly (1,2-dihydro-2,2,4-trimethyl-quinoline) (trade name: RD) was purchased from Lanzhou Chemical Industry Co., China. Tris(2,4-di-tert-butylphenyl) phosphate (trade name: 168) was supplied by Tokyo Chemicals Industry, Japan. Dipentamethylenethiuram tetrasulfide (DPTT), bis(3-triethoxysilylpropyl)tetrasulfide (trade name: Si-69), 2,2′-hydroxy ethyldisulfide (HEDS), diethyl disulfide (DEDS), dibutyl disulfide (DBDS), diallyl disulfide (DADS), dipropyl disulfide (DPDS), dimethyl trisulfide (DMTS), dicumyl peroxide (DCP), stearic acid, ZnO, sulfur and $CuCl_2$ were provided by Aldrich. All chemicals were of analytical grade reagents and used as received. **Scheme 1** shows the structures of the substances involved in this study that contain disulfide and polysulfide bonds. Silica nanoparticles (Aerosol A380) with average primary particle size of 7 nm and specific surface area of 380 m^2 g^{-1} was supplied by Degussa. High abrasion furnace carbon black (N330) with average primary particle size of 35 nm was supplied by Cabot Corporation.

Chloroprene rubber

HEDS: $R_1=R_2=$ -C_2H_4OH DEDS: $R_1=R_2=$ -C_2H_5

DPDS: $R_1=R_2=$ -C_3H_7 DBDS: $R_1=R_2=$ -C_4H_9

DMTS: DADS:
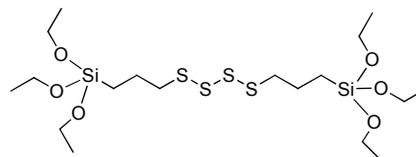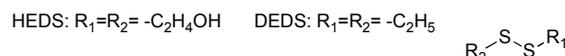
Bis(3-triethoxysilylpropyl)tetrasulfide (Si-69)

Scheme 1 Structures of the disulfide and polysulfide-containing compounds used in this study.

Compounding, vulcanization and molding

According to the recipe listed in **Table 1**, SiO$_2$ nanoparticles (100 g) were firstly mixed with toluene (1000 ml) under ultrasonication. Then, Si-69 (20 ml) was added to the SiO$_2$ sol with mechanical stirring and reflux for 5 h. Finally, the SiO$_2$ grafted by Si-69 (SiO$_2$-g-Si-69) was centrifuged, ultrasonically washed with cyclohexane for three times, and freeze dried for 24 h. The percent grafting was about 10 %, as determined by thermogravimetric analysis (TGA).

The model rubber of this work was fabricated as follows. Firstly, polybutadiene rubber was masticated in a two-roll mill at room temperature. Next, nano-silica (or Si-69 grafted nano-silica) and carbon black were mixed with the matrix rubber. Afterwards, Si-69, CuCl$_2$, ZnO, stearic acid, anti-ager RD, and antioxidant 168 were added. Finally, sulphur and accelerator DPTT were incorporated to the premixed compounds. All the raw materials were poured evenly along the nip with alternating cuts. After uniformly compounding, ten end-roll passes were made before sheeting off. The whole process took about 10 min.

To determine the optimal curing conditions, rheograph of the above compounds (i.e. the model material of this study, named VR-SH) was recorded at 150 °C by a moving die rheometer (UR-2010SD-A, U-CAN Dynatex Inc.). It is seen from (**ESI,† Fig. S1**) that the torque drastically increases at the beginning and then levels off demonstrating the formation of crosslinked structure throughout the material. The characteristic t_{90}, the optimum vulcanization time required for reaching specific torque value which is the sum of minimum torque and 90 % of the differentials between maximum and minimum torque, is estimated to be 6.98 min. Based on this measurement, the rubber VR-SH was cured at 150 °C for 6.98 min under 20 MPa, producing 2 mm thick sheet for the subsequent characterization.

To understand the dispersion status of CuCl$_2$ catalyst, scanning electron microscopic (SEM) micrograph of a model system consisting of only CuCl$_2$ and polybutadiene rubber, and energy dispersive spectroscopy (EDS) image of VR-SH were collected. The observation by means of EDS is conducted because CuCl$_2$ is not the only particulate filler in VR-SH. Mapping of copper is more suitable for identification of CuCl$_2$. As shown in the SEM photo (**ESI,† Fig. S2a**), the CuCl$_2$ particles are well dispersed in polybutadiene rubber except for tiny amounts of small aggregates even when the particles content is as high as 1 phr, which is 10 times higher than that in VR-SH (**Table 1**). Accordingly, the average particle size is estimated to be about 3 µm. The well dispersion of CuCl$_2$ particles is evidenced by the EDS image (**ESI,† Fig. S2b**), which shows that the fillers are separated from each other in the rubber. In fact, well distribution of CuCl$_2$ is important for the proposed disulfide metathesis. If CuCl$_2$ particles were severely agglomerated, the exchange reaction of S-S bonds could not efficiently proceed and hence the crack healing and reclaiming would be hindered.

For comparison, references control 1 and control 2 (**Table 1**) were prepared by the same procedures, except that the curing time of control 1 was 9.70 min and that of control 2 was 1.95 min as suggested by their t_{90} (**ESI,† Fig. S1**).

Table 1 Compositions of the rubbers studied in this work

Rubbers	Polybutadiene rubber	Sulfur	CuCl$_2$	SiO$_2$	Si-69 [d]	SiO$_2$-g-Si-69 [e]	Carbon black	ZnO	Stearic acid	RD [f]	168 [g]	DPTT [h]	DCP [i]
VR-SH [a]	100	1	0.1	0	10	20	5	1	0.5	1	1	1	0
Control 1 [b]	100	1	0	0	10	20	5	1	0.5	1	1	1	0
Control 2 [c]	100	0	0.1	20	0	0	5	0	0	1	1	0	1.5

a) Name of the model material of this study; b) Reference material containing the same components as VR-SH except that CuCl$_2$ is excluded; c) Reference material containing the same components as VR-SH except that peroxide DCP, rather than sulfur, serves as the crosslinking agent; Control 1 and control 2 are used to evidence that both reversible sulfur crosslinks and CuCl$_2$ are necessary for healing and reclaiming of vulcanized rubber. Control 1 contains reversible sulfur crosslinks without CuCl$_2$, while control 2 contains CuCl$_2$ without reversible sulfur crosslinks. d) Trade name of bis(3-triethoxysilylpropyl)tetrasulfide; e) SiO$_2$ nanoparticles grafted by Si-69; f) Trade name of anti-ager poly(1,2-dihydro-2,2,4-trimethyl-quinoline); g) Trade name of antioxidant tris(2,4-di-tert-butylphenyl)phosphate; h) Dipentamethylenethiuram tetrasulfide serving as accelerator; i) Dicumyl peroxide.

Model disulfide metathesis experiments

DEDS (0.24 g, 2.0 mmol), HEDS (0.31 g, 2.0 mmol), CuCl$_2$ (2.5 mg, 18.6 µmol) and acetonitrile (10 mL) were mixed by magnetic stirring at 25 °C. Samples were extracted at different reaction times to estimate the extent of disulfide metathesis. The effects of solvent and structures of disulfide compounds were studied following the same procedure as above.

Characterization

The progress of disulfide metathesis in small molecules was monitored by high-performance liquid chromatography (HPLC) on an Agilent 1100 using a mobile phase of CH$_3$CN/H$_2$O = 3/1 (v/v) at a flow rate of 1 mL min^{-1} with UV detector at 254 nm. Gas chromatography-mass spectroscopy (GC-MS) analyses were performed on a Thermo DSQ-EI mass spectrometer. The GC column oven was heated to 290 °C by 20 °C min^{-1}, followed by a hold at this temperature for 10 min. The disulfide metathesis in macromolecules was characterized by gel permeation chromatography (GPC) on a Waters 1515 with THF as the eluent and polystyrene as the calibration standard. Ultraviolet-visible (UV-Vis) spectra were collected by a Shimadzu UV-300 spectrophotometer. Fluorescence spectra were obtained from a Varian Cary Eclipse with excitation

wavelength of 343 nm. Electron spin resonance (ESR) spectra were recorded on a Bruker A300-ESR spectrometer with 100 kHz modulation frequency. TGA was used to assess thermal stability of the rubbers from 40 to 800 °C with a ramp of 10 °C min^{-1} under N_2 atmosphere on a TA Q50. Stress relaxation was measured on a MetraviB DMA-25N using tensile mode with a deformation of 20 %. Morphological observation and energy dispersive spectroscopy (EDS) analysis were conducted by a Quanta 400 FEG field emission scanning electron microscope (SEM). Prior to the experiment, the sample surface was coated by gold/palladium sputtering.

To evaluate healing ability, tensile tests were conducted on dumbbell-shaped specimens (total length: 50 mm, thickness: 2 mm, width of parallel part: 4 mm) according to ASTM D412 with a SANS CMT 6000 universal tester at a crosshead speed of 50 mm min^{-1} at 25 °C. When the specimen was broken apart, the two parts were placed back in contact. After healing at 110 °C for a period of time, the healed specimen was tested to failure again. Healing efficiency was calculated from the ratio of tensile strength of healed specimen to that of the virgin one.

Reclaiming of the rubbers was conducted by breaking the specimens into small particles through freeze grinding and then compression molding of the rubber particles under 10 MPa at 110 °C for 3 h.

RESULTS AND DISCUSSION

So far, there is no report on the ability of $CuCl_2$ for catalyzing disulfide metathesis. We have to conduct a series of model tests with small molecules first. The high-performance liquid chromatography (HPLC) spectra (**Fig. 1**) indicate that after the addition of $CuCl_2$ into the equimolar mixtures of two disulfide compounds (2,2'-hydroxy ethyldisulfide (HEDS) and diethyl disulfide (DEDS)) in acetonitrile, a new peak appears, whose area increases with time and reaches the equilibrium within 60 min. Meanwhile, the peak areas of HEDS and DEDS decrease. The steady molar proportions of HEDS, DEDS and the reaction product are 24:26:50 (**ESI,† Fig. S3a**), which coincide with the theoretical values supposing the reaction product is hydroxyethyl ethyl disulfide (HEED) according to the assignment of mass spectrum (**ESI,† Fig. S3b**). Evidently, disulfide exchange reaction can be effectively catalyzed by $CuCl_2$ without side-reaction. When the polar acetonitrile is replaced by non-polar *n*-heptane as solvent, moreover, disulfide metathesis between dipropyl disulfide (DPDS) and DEDS also takes place in the presence of $CuCl_2$, despite that reaction temperature has to be higher than 30 °C and longer time is needed to attain equilibrium (**ESI,† Fig. S4**). It means that the mechanism of ionic exchange catalyzed by phosphine,[26,31] which has apparent solvent effect, can be excluded from disulfide metathesis under catalysis of $CuCl_2$. What is more, we also inspected the case in the absence of any catalyst and found that disulfide metathesis did not occur between aliphatic disulfide compounds after long time regardless of solvent polarity and temperature (**ESI,† Fig. S5**).
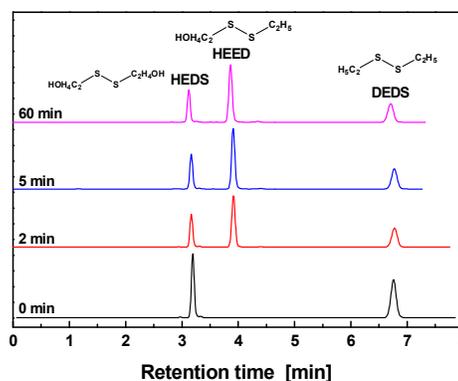

Fig. 1 HLPC analysis of equimolar mixture of HEDS and DEDS as a function of time (25 °C, acetonitrile, 0.5 mol% $CuCl_2$).

The effect of $CuCl_2$ dosage is examined (**ESI,† Fig. S6a)**. It seems there is a critical threshold for the catalyst. In the case of 0.05 mol% $CuCl_2$, for example, the reaction does not equilibrate within 4 h and the conversion is only ~10 %. When the dosage of $CuCl_2$ is raised to 0.25 mol%, however, the reaction manages to reach equilibrium after 2 h. A much faster equilibrium can be achieved due to further increase of $CuCl_2$ dosage to 0.5 mol%. Therefore, the minimum $CuCl_2$ dosage used for the rubber system should be higher than 0.25 mol%. **ESI,† Fig. S6b** studies the effect of initial molar ratio of reactants on the speed of disulfide metathesis. Because the amount of $CuCl_2$ has exceeded the above lower limit, all the reactions are allowed to reach equilibrium within short time.

Quantification of the above reactions offers equilibrium constant, K_{eq}, which only varies with reaction temperature and is not affected by initial molar ratio of reactants and catalyst dose (**ESI,† Table S1-S4**). It is thus known that the disulfide metathesis catalyzed by $CuCl_2$ belongs to dynamic reversible reaction. Besides, activation energy of disulfide metathesis in acetonitrile is calculated to be 22.3 kJ/mol, and that in *n*-heptane is 172.3 kJ/mol (**ESI,† Fig. S7 and S8**). Clearly, more energy needs to be input for the reaction in non-polar environment.

To further understand the effect of structures of disulfide molecules on disulfide metathesis, equimolar mixtures of DPDS/diallyl disulfide (DADS) and dibutyl disulfide (DBDS)/ dimethyl trisulfide (DMTS) pairs as well as DMTS alone were tested with $CuCl_2$ as catalyst, respectively. Allyl disulfide bridge is a common constituent of sulfur cosslinkages in vulcanized rubber[1,16~21] while DMTS simulates polysulfidic bonds. The experiments are expected to get close to the actual situation in vulcanized rubber by choosing these reagents. The mass spectra of the metathesis products indicate that allyl propyl disulfide is generated by DPDS/DADS (**ESI,† Fig. S9**), and methyl butyl disulfide and methyl butyl trisulfide are created by DBDS/DMTS (**ESI,† Fig. S10**). Moreover, there are also metathesis products (i.e. dimethyl disulfide and dimethyl tetrasulfide) in the system of DMTS and $CuCl_2$, which excludes any disulfide at the beginning (**ESI,† Fig. S11**). Clearly, disulfide metathesis is allowed to proceed among not only disulfides

but also polysulfide molecules, probably because of similar bonding energies of S-S and -S_x- ($x \geq 3$) bonds (273 and 256 kJ/mol, respectively[22]). These outcomes suggest that $CuCl_2$ should be applicable to sulfur crosslinks of vulcanized rubber that contain both disulfide and polysulfide bonds.

In fact, $CuCl_2$ can ceaselessly catalyze disulfide metathesis. When the third disulfide DBDS was added into the equilibrated DEDS/DPDS system with ethyl propyl disulfide (EPDS) as the metathesis product, two new products (i.e. ethyl butyl disulfide (EBDS) and propyl butyl disulfide (PBDS)) are yielded and a new equilibrium is reached again (**ESI,† Fig. S12**). Additionally, the high catalytic activity of $CuCl_2$ is also reflected by the control test with triphenylphosphine (PPh_3). It can be seen from **ESI,† Fig. S13** that disulfide metathesis is allowed to proceed with the assistance of PPh_3 at 100 °C, but the conversion efficiency is too low to have use value.

In the formula of the rubber to be studied (**Table 1**), there are quite a few chemical additives having different functions. They might deactivate $CuCl_2$ and disable disulfide metathesis. **ESI,† Fig. S14** checks the influence of two representative additives, anti-ager and antioxidant, on disulfide metathesis catalyzed by $CuCl_2$. The dosages of both anti-ager and antioxidant are intentionally much higher than that of $CuCl_2$, while different pairs of disulfides are employed to investigate the possible structural effect of disulfides. Anyhow, the conversion percentage of the reaction approaches 45 % within 2 h for the tests. Hence, the catalytic activity of $CuCl_2$ should be valid for disulfide metathesis in vulcanized rubbers.

In addition to the low-molecular-weight disulfides, linear macromolecule carrying disulfide and polysulfide bonds on the backbone represented by chloroprene rubber (**Scheme 1**) was also employed as a model compound to examine the catalytic ability of $CuCl_2$ for disulfide metathesis. The molecular weight variation of chloroprene rubber in tetrahydrofuran solution with $CuCl_2$ shows that both number average and weight average molecular weights decrease with time, while the molecular weight distribution increases (**Fig. 2**). It means that disulfide metathesis have proceeded among the main chains of chloroprene rubber. The variation tendency resembles that reported in reference,[33] reflecting the random nature of the metathesis in macromolecules with multiple reversible bonds. As it turns out, disulfide metathesis could occur in disulfide and polysulfide containing macromolecules with the assistance of $CuCl_2$.
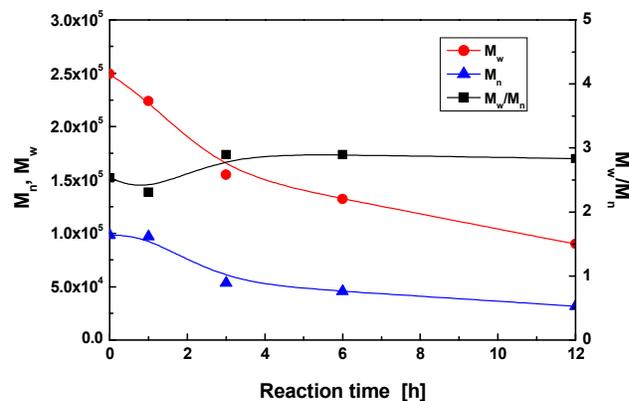

Fig. 2 Time dependences of number average molecular weight, M_n, weight average molecular weight, M_w, and molecular weight distribution, M_w/M_n, of chloroprene rubber in the solution of tetrahydrofuran (3 mg/ml) at 25 °C ($CuCl_2$: 0.5 mol%).

The above results and discussion have revealed that disulfide metathesis is enabled by $CuCl_2$, but the underlying mechanism is still unknown. The UV-Vis spectrum in **Fig. 3a** shows that $CuCl_2$ in acetonitrile has two absorption bands. The strong one at 309 nm results from the absorption of $CuCl_2$, while the weak one at 460 nm is ascribed to the complexation effect between $CuCl_2$ and acetonitrile, i.e. $Cu(MeCN)Cl_2$.[34,35] Once disulfides are added, the strong peak at 309 nm disappears, and the peak height at 460 nm obviously decreases. In contrast, another strong peak due to absorption of disulfide bonds is observed at 248 nm, which is intensified with a rise in $CuCl_2$ concentration. Similarly, electron spin resonance (ESR) spectra indicate that the g value of $CuCl_2$ in acetonitrile changes from 2.12786 (317 mT) to 2.0616 (327 mT) when equimolar HEDS and DEDS are incorporated (**Fig. 3b**), implying variation in the nature of the related chemical bonds.[36] On the other hand, earlier study of fluorescence of disulfides demonstrated that the formation of complex between Cu^{2+} and disulfides led to quenching effect.[37,38] The conclusion agrees with our own observation. **Fig. 3c** exhibits that the fluorescence intensity of disulfides decreases with the concentration of $CuCl_2$. The fluorescence is completely quenched when the concentration of $CuCl_2$ is higher than 1 mol%. All these results manifest that there is complex effect between $CuCl_2$ and disulfides.
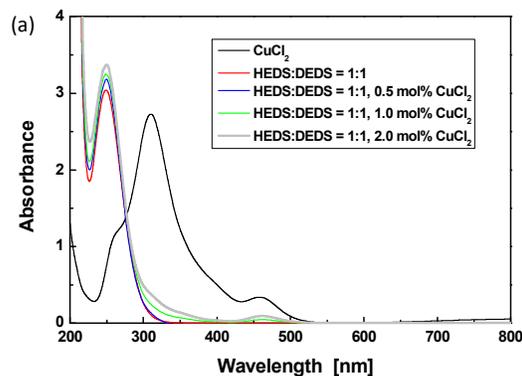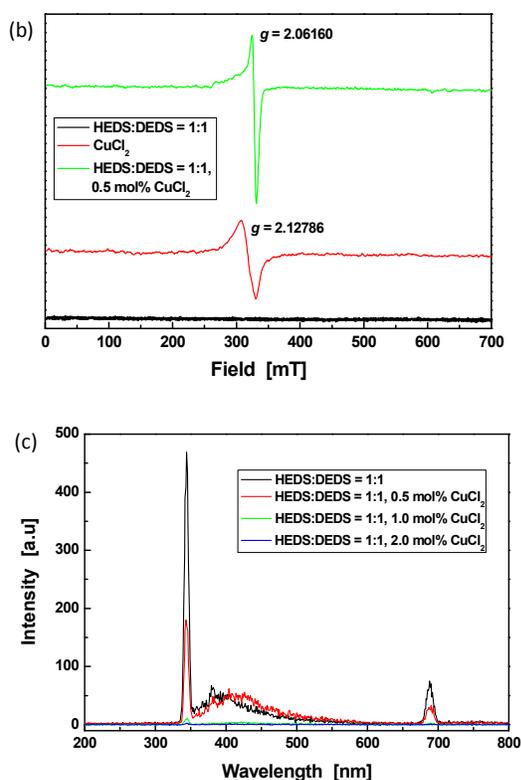
Fig. 3 (a) UV-Vis, (b) ESR, and (c) fluorescence spectra (excitation wavelength: 343 nm) of disulfides and $CuCl_2$ in acetonitrile at 25 °C.

Amamoto et al. suggested that free radicals are involved in reshuffling of thiuram disulfide moieties under visible light.[39] To see whether the present disulfide metathesis is driven by a similar mechanism, TEMPO was included to capture the possible radicals. As exhibited by **ESI,† Fig. S15a**, the conversion of the disulfide metathesis increases with time like the case without TEMPO (**Fig. 1**), but the reaction rate is slowed down after the addition of TEMPO. It might thus be thought that radicals would have been created, which were caught by TEMPO leading to retardation of the reaction. However, the signal intensity of the TEMPO radicals in the reaction system is the same as that in the system without any disulfide under the same conditions (**ESI,† Fig. S15b** and **S15c**). That is, no TEMPO is consumed during the disulfide metathesis. The reduction in reaction rate should result from decay of catalytic activity of $CuCl_2$. **ESI,† Fig. S15d** shows a reaction similar to that recorded in **ESI,† Fig. S15a** except for the feeding sequence. Here no metathesis product is detected only because $CuCl_2$ and TEMPO are mixed for a while in advance. Clearly, the complex effect between $CuCl_2$ and TEMPO restricts the complexation between $CuCl_2$ and disulfide. Besides, if radicals were present in the $CuCl_2$ catalyzed disulfide metathesis, the S-based radicals should have response signals at 350 and 370 mT ($g = 1.925$ and 2.004) in acetonitrile.[39] This is not true for our case as there are no homologous peaks in **Fig. 3b**.

Another possible mechanism is related to formation of ionic intermediates for phosphines catalyzed disulfide metathesis.[26,31] However, the above experiment has shown that $CuCl_2$ works in non-polar solvent (**ESI,† Fig. S4**), which disagrees with the solvent effect of phosphines.[31] **ESI,† Fig. S16a** depicts a group of model tests by introducing diverse inhibitors (i.e. benzoquinone, ethyl acetate, HCl and H_2O) to the disulfide metathesis with $CuCl_2$. The conversion rates of the systems containing inhibitors after 30 min are almost the same as that of the system without any inhibitor. Supposing there were mercaptides (RS^-) or sulfenium cations (RS^+) in the reaction process, the inhibitors would interact with the ions and the conversion rate would be decreased. The truth is the opposite, meaning that the reaction has nothing to do with ions.

On the basis of above results and discussions, it is deduced that neither radicals nor ions are involved in the disulfide metathesis catalyzed by $CuCl_2$, which differs from the cases with light- and phosphines-catalysis.[26,31,33,39]

We found that CuCl can also catalyze disulfide metathesis in the case of higher dosage and reaction temperature, and longer reaction time (**ESI,† Fig. S16b**). Despite the poorer catalytic activity than $CuCl_2$, CuCl takes effect depending on its reducibility,[2] while $CuCl_2$ is often used as oxidant due to the high valence state. The conflicting information manifests that the $CuCl_2$ catalyzed disulfide metathesis should not be a redox process.

Fig. 4a gives quantum chemical study of $CuCl_2$ catalyzed disulfide metathesis in acetonitrile. All structures are optimized using B3LYP method with the 6-31G (d) basis set for C, H, O, S atoms and SDD basis set for Cu element. PCM solvation model in acetonitrile is performed on the basis of optimized equilibrium geometries by Gaussian Package. Vibrational analysis is performed at the same level of theory. The results indicate that there is complex effect between disulfides and $CuCl_2$, which brings forth the reaction intermediates, IM1. Then, IM1 reaches the transient state, TS1, when the potential energy overcomes the energy barrier, which is the rate-determining step.[31] In the course of transformation, bond lengths of S-S and Cu-Cl also change. Finally, two different sulfur atoms of disulfides in the transient state are split and recombined into a metathesis product and $CuCl_2$-disulfide complex.

According to the results of both experiments and theoretical prediction, the mechanism involved in disulfide metathesis utilizing $CuCl_2$ as catalyst is depicted in **Fig. 4b**. Firstly, disulfides and $CuCl_2$ interact with each other as soon as they are mixed together due to the lone pair electrons of sulfur atoms in disulfides and the vacant 3*d* orbit of Cu(II).[34] This leads to the formation of an intermediate. Then, spatial conformation of the complex intermediate is optimized through adjusting bond angle and bond length between disulfide and $CuCl_2$. That is, the system enters the transient state. At last, rearrangement and localization of electrons of disulfide bonds make the latter fracture. Recombination of the two different sulfur atoms offers the metathesis product, while $CuCl_2$-disulfide complex is remained. The newly

generated CuCl$_2$-disulfide complex would rapidly interact with another disulfide, repeating the above processes.
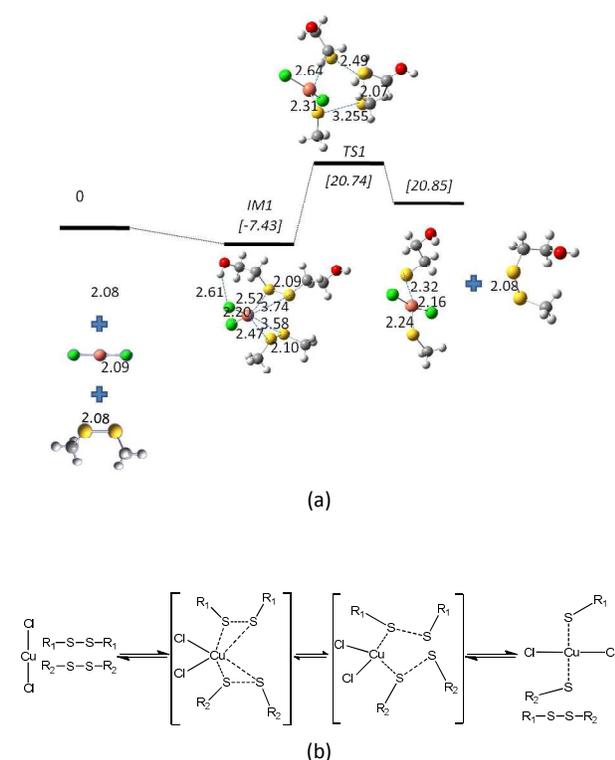

(a)

(b)

Fig. 4 (a) Quantum chemical study of CuCl$_2$ catalyzed disulfide metathesis in acetonitrile. Energies are given in kcal/mol; (b) Mechanism of CuCl$_2$ catalyzed metathesis between low molecular weight disulfides.

As the model experiments and mechanism investigation have revealed the capability of CuCl$_2$, we start with the work of the model material of this study, VR-SH, whose compositions and curing procedures are carefully described in **Table 1** and Experimental section, respectively. The CuCl$_2$ dosage in VR-SH was determined in consideration of speed of disulfide metathesis and ageing resistance of the rubber material. The above model experiments have shown that disulfide metathesis can quickly equilibrate with 0.5 mol% CuCl$_2$. However, if the CuCl$_2$ dosage exceeded 1 mol%, thermal ageing property of VR-SH would be significantly deteriorated. Therefore, the ideal CuCl$_2$ content in VR-SH was chosen as 0.8 mol% (i.e., 0.1 phr as shown in **Table 1**) to have balanced performance. Firstly, some fundamental properties of the materials are characterized. The percentages of disulfide and polysulfide crosslinks in the total number of crosslinks in VR-SH are estimated to be 62 and 31 %, respectively (details of the determination refer to Supporting Information), while the same parameters of the reference material, control 1, are 54 and 42 %. It means that sufficient amount of reversible sulfur crosslinkages are present in the rubbers like the above-mentioned commercial versions. The thermal degradation curves in **ESI,† Fig. S17** exhibit that the initial weight loss temperatures and 50 % weight loss temperatures of VR-SH and

the references (i.e. control 1 and control 2) are close to each other. Only control 2 possesses slightly higher onset temperature because of the higher C-C bond energy than S-S.[22] It is thus known that the rubbers have acquired good thermostability, which is not affected by the addition of CuCl$_2$. Besides, because (i) the dosage of CuCl$_2$ is low, (ii) the complexation between CuCl$_2$ and disulfide bonds weakens the ability of CuCl$_2$ to induce ageing of the rubbers, and (iii) anti-ager is added, thermal ageing tests at 110 °C indicated that the ageing resistance of the rubbers was not deteriorated in the presence of CuCl$_2$.

Fig. 5a plots stress relaxation of VR-SH measured at various temperatures. When temperature is lower than 90 °C, VR-SH behaves like conventional polymers. The significant reduction in stress at the beginning stage due to viscoelastic feature is gradually replaced by a steady plateau. In the case of higher temperature, however, the scenario is quite different. At 110 °C, for example, the stress continues to decrease at slower rate for a long period of time after the initial drastic decline and eventually approaches zero (**Fig. 5a**). It means that multiple stress relaxation mechanisms are involved.[25] In contrast, the curves of control 1 and control 2 (**Fig. 5b**), in which disulfide metathesis is disabled (**Table 1**), resemble that of VR-SH recorded at 30 °C. Naturally, this relaxation manner of VR-SH is associated with disulfide metathesis as it would lead to rearrangement of the sulfur crosslinked networks once triggered, during which stress relief occurs. Our previous study shows that the activation energy of CuCl$_2$ catalyzed disulfide metathesis of small molecules in non-polar solvent is higher than that in polar solvent. Here the main component of VR-SH, polybutadiene rubber, is also non-polar, so that disulfide metathesis takes effect at elevated temperature instead of room temperature.

From a practical perspective, as mentioned in the Introduction, high temperature reshuffling of crosslinked networks of vulcanized rubber is favorable. In this way the crack healing process would not interfere with service stability of rubber products at relatively lower temperature. That is, thermal stability of the material structure is preserved while allowing for reversibility.[40] In normal driving condition, for example, tyre temperature ranges from 30 to 100 °C.[41,42] Compared with this, CuCl$_2$ seems to be quite suitable for vulcanized rubber as disulfide metathesis induced stress relaxation is obvious only above 110 °C (**Fig. 5a**). In this context, 110 °C is selected as the healing (or reclaiming) temperature hereinafter. Such a criterion based on accelerated exchange reaction of reversible covalent bonds was also adopted in recycling of polyimine film.[43]
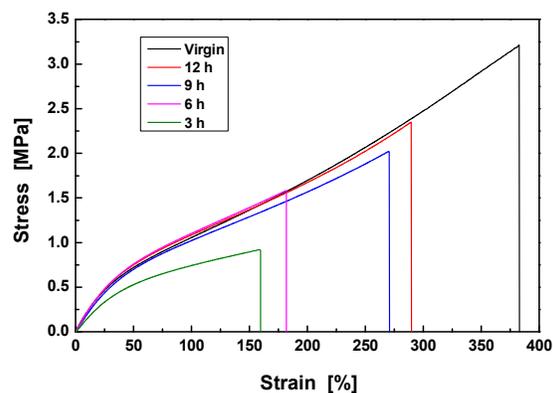
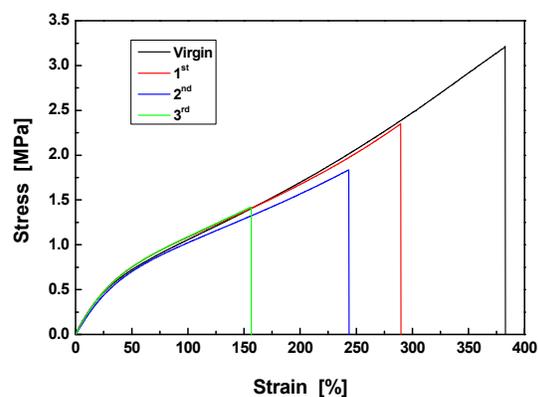**Green Chemistry Accepted Manuscript**
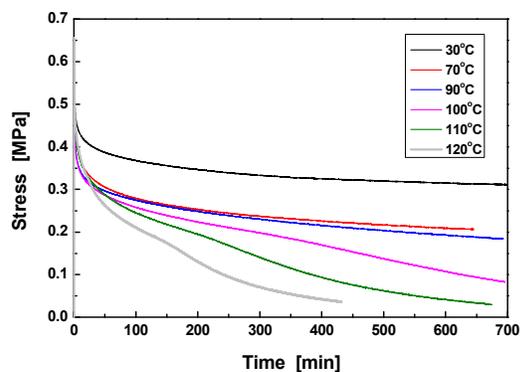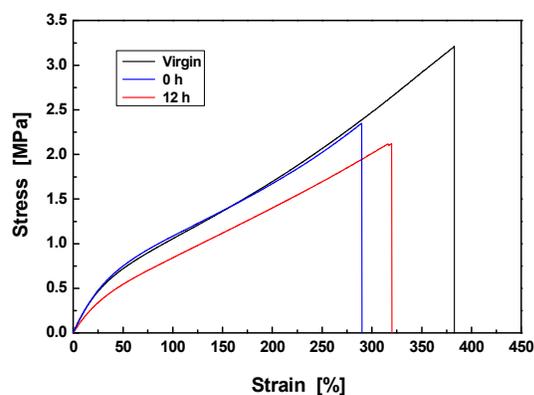

(a)
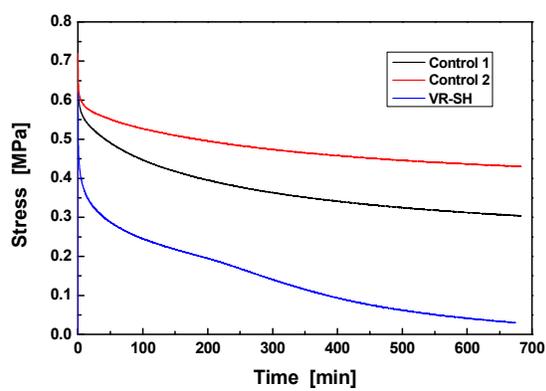
(b)

Fig. 5 Stress relaxation curves of (a) VR-SH measured at various temperatures, and (b) VR-SH, control 1 and control 2 measured at 110 °C.

(a)

(b)

(c)

Fig. 6a shows typical tensile stress-strain curves of virgin and healed VR-SH specimens. Healing can indeed proceed as characterized by the fact that the healing efficiency increases with increasing healing time. About 75 % tensile strength can be restored after 12 h. Furthermore, healing of the same place can be repeated (**Fig. 6b**). To check the contribution of hydrogen bonding, surfaces of tensile-fractured specimens were not immediately recombined but exposed to air for 12 h prior to recombination to eliminate the possible hydrogen bond interaction. Accordingly, the healing efficiency approaches 72 % for healing time of 12 h (**Fig. 6c**). As a matter of fact, the non-polar polybutadiene rubber matrix should not possess any hydrogen bond. The result of **Fig. 6c** instead demonstrates the oxygen insensitivity of the catalytic activity of $CuCl_2$. Comparatively, only ~12 % healing efficiency is measured for control 1 and control 2 under the same condition (**Fig. 6d**) as a result of intermolecular entanglements of dangling chains across the fractured surfaces.[44~46] It can thus be concluded that disulfide metathesis works in healing of the vulcanized rubber by triggering rearrangement of inherent sulfur crosslinked networks under the catalysis of $CuCl_2$.
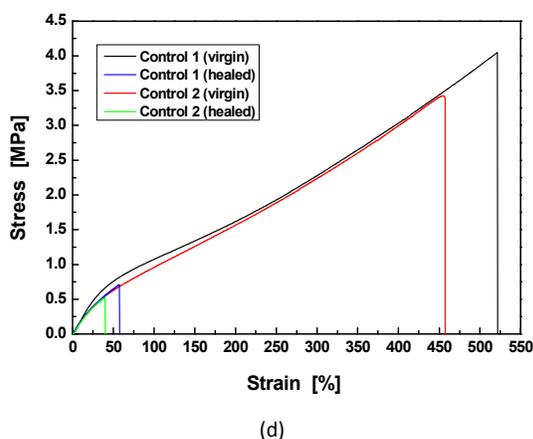
(d)

Fig. 6 (a, b, c) Typical tensile stress-strain curves of virgin and healed VR-SH specimens. (a) Effect of healing time. (b) Effect of repeated healing (healing time: 12 h). Because the tensile strength of the virgin specimen cannot be fully restored, the reconnected interface became the weakest part, and had to break again during the subsequent tensile tests. This ensured that the second and third tensile failures happened to the same healed portion. (c) Effect of waiting time (which is the time for the broken specimens to wait for being reconnected in air at 25 °C; healing time: 12 h). (d) Typical tensile stress-strain curves of virgin and healed control 1 and control 2 specimens (healing time: 12 h). Healing temperature for all the healed specimens in this figure: 110 °C.

During the high temperature vulcanization of the rubber, the catalyst $CuCl_2$ might be turned into Cu_2S, CuS, Cu_2O, and CuO as a result of reaction with the surrounding elements. If so, $CuCl_2$ would lose its ability to catalyze disulfide metathesis, as no metathesis product is generated in the presence of these chemicals (**ESI,† Fig. S18**). The results manifest that $CuCl_2$ must have kept intact in the vulcanized rubber, otherwise no healing behavior would be observed.

It is worth noting that the mechanical property of VR-SH cannot be fully restored (**Fig. 6a**), and the healing efficiency declines with number of healing (**Fig. 6b**). Misalignment of the fractured surfaces should be partly responsible for the phenomenon as it leads to pseudo contacts during healing. The non-contact zones make up 6~10 % of total area of the fractured surface (**ESI,† Fig. S19**). It means that the measured healing efficiency should have been higher, if the non-contact regions were intimately contacted with one another arousing additional disulfide metathesis across the interface. Another reason for the suboptimal healing effect lies in the distribution of $CuCl_2$. Although the catalyst particles are well dispersed in the matrix (**ESI,† Fig. S2**), it is hard to distribute $CuCl_2$ on molecular level nearby each disulfide (or polysulfide) bond (**ESI, † Fig. S20**), so that no disulfide metathesis can be triggered in the regions short of $CuCl_2$ during healing. Although fluidic polysulfide coupling agent Si-69 is introduced to greatly improve mobility (i.e. dispersion) of $CuCl_2$ through the complexation between Si-69 and $CuCl_2$ in the course of compounding (**ESI,† Fig. S21**), which helps to raise the healing efficiency (**ESI, † Fig. S22**), $CuCl_2$ is not homogeneously distributed in the matrix after all. There are always disulfide and polysulfide bonds that fail to take part in the metathesis

reaction due to lack of catalyst to form complex with them, a prerequisite of the reaction (**Fig. 4**).
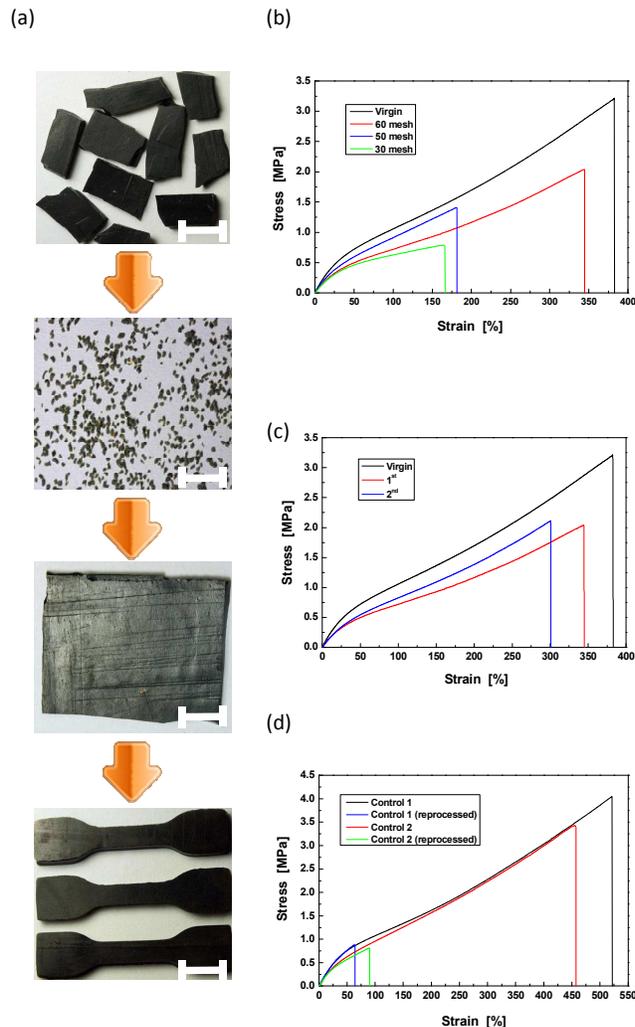
(a)　　　　　　　　(b)

Fig. 7 (a) Reclaiming of VR-SH. Sheeted rubber was cut, cryogenically ground and compression molded. The attached scale bars represent 10 mm in length. (b~d) Typical tensile stress-strain curves of virgin and reclaimed rubbers. (b) Effect of particle size of VR-SH. (c) Effect of repeated reclaiming of VR-SH (particle size: 60 mesh). (d) Control 1 and control 2 (particle size: 60 mesh). To categorize the size of the powdered rubber for reclaiming, the latter was run through sieves with different mesh sizes. The size of the screened particles is characterized by the corresponding mesh size of the sieve. The larger the mesh number, the smaller the particle size of the powder.

Despite all this, VR-SH proves to acquire remendability due to reconstruction of sulfur crosslinked networks in terms of disulfide metathesis in damaged zones. Taking advantage of the same mechanism, reclaiming of the rubber should also be possible, as discussed in the Introduction. Accordingly, VR-SH was frozen by liquid nitrogen, ground into small particles and then hot pressed at 110 °C for 3 h (**Fig. 7a**). **Fig. 7b** shows typical tensile stress-strain curves of the reclaimed VR-SH in comparison with that of virgin VR-SH. Evidently, the ground rubber powders can stick to each other under the reclaiming conditions, reforming a compact bulk material with load

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bearing capability as their ancestor. Careful survey of **Fig. 7b** indicates that tensile strength and elongation to break of the reclaimed VR-SH increase with decreasing rubber particles size. In general, smaller rubber particles mean larger specific surface area and higher surface concentration of exposed disulfide and polysulfide bonds. Therefore, when smaller rubber particles are closely packed, more disulfide and polysulfide bonds are involved in metathesis. The reconstructed sulfur crosslinked networks become stronger. Although the rubber particles size cannot be further reduced due to limit of the grinding machine in our lab, the trend revealed by **Fig. 7b** is straightforward. Additionally, **Fig. 7c** shows that VR-SH can be repeatedly reclaimed owing to the dynamic reversible characteristics of disulfide metathesis. On the other hand, the above-mentioned uneven distribution of $CuCl_2$ catalyst should also partly account for the poorer mechanical properties of the reclaimed VR-SH than the original version.

In the meantime, control 1 and control 2 were also ground and tested under the same conditions. Because of lack of disulfide metathesis, the reclaimed materials possess very poor mechanical strength (**Fig. 7d**) like the cases in **Fig. 6d**.

Unlike devulcanization, a conventional technique of rubber recycling that cleaves sulfur crosslinks of vulcanized rubber, here the reclaiming is based on reshuffling of the crosslinked network through disulfide metathesis. It does not affect the crosslinking density and can maintain strength of the rubber in principle. For example, the percentages of disulfide and polysulfide crosslinks in the total number of crosslinks in reclaimed VR-SH (from the particles of 60 mesh) are 60 and 28 %, respectively, almost identical to the data of the above-mentioned virgin material.

There were also attempts to recycle vulcanized rubber particles by simple thermal molding without using additional catalyst,[47,48] but the operating principle is related to irreversible scission of sulfur crosslinkages and re-formation of irreversible monosulfide crosslingages. The reclaiming cannot be repeated for multiple times accordingly.

Conclusions

This study demonstrates the possibility of healing and reclaiming of vulcanized rubber by triggering rearrangement of the inherent sulfur crosslinked networks. The key issue lies in the application of a novel catalyst, $CuCl_2$, which arouses successive disulfide metathesis among various disulfidic and polysulfidic crosslinkkages via $CuCl_2$-based complex catalysis. Although disulfide metathesis has been known elsewhere,[23,26,28,30~33] the $CuCl_2$ aided version has not yet been reported. $CuCl_2$ is robust enough to survive the rubber vulcanization, and can take effect in multi-component material, being not disturbed by neighboring additives. Either properties restoration of damaged rubber or rubber recycling is allowed to proceed in air at 110 °C, which is higher than working temperatures of many rubber products. Therefore, under conventional conditions the sulfur crosslinks are as

stable as the version excluding $CuCl_2$ without fear of the influence of disulfide metathesis.

Further efforts should be made to develop next generation catalyst, which possesses similar activity like $CuCl_2$ but much higher solubility in rubber matrix. As a result, as many as possible disulfide and polysulfide bonds would be involved in metathesis, leading to higher healing efficiency. Meanwhile, we will try to reduce the content of organosilane and increase the content of carbon black, so that the material would be closer to actual industrial rubber.

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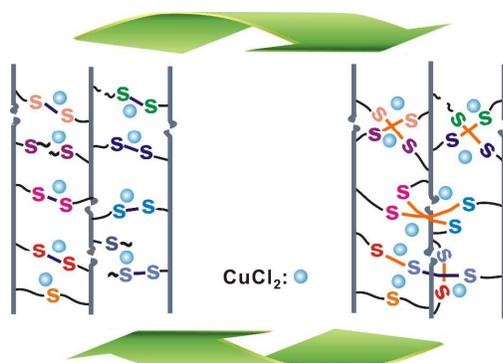
Vulcanized rubber made from an industrial formula can be healed and reclaimed by activating rearrangement of the inherent sulfur crosslinked networks under the catalysis of CuCl$_2$.

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