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Self-Healing Materials Based on Disulfide Links

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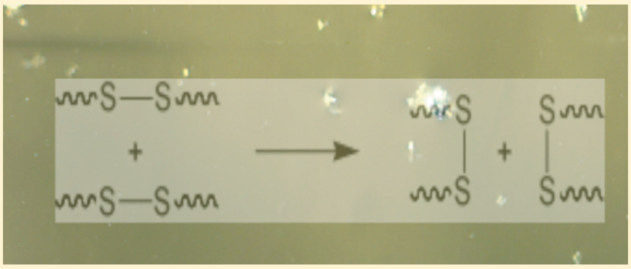
S *Supporting Information*

ABSTRACT: Autonomous healing of damage is a common phenomenon in living organisms but is hardly ever encountered in synthetic materials. Disulfide chemistry is used to introduce a self-healing ability in a covalently cross-linked rubber. Autonomous healing of a cut takes place at moderate temperatures and leads to full recovery of mechanical properties. This result is achieved by introducing disulfide groups in the network that are able to exchange, leading to renewal of cross-links across the damaged surfaces. The healing process can be repeated many times. The combination of their unique self-healing properties and applicability for a large variety of polymers makes this approach ideal for coatings.



INTRODUCTION

When our body suffers an injury, in many cases the damage is autonomously repaired and full recovery of the materials' properties takes place. Several approaches for introducing this self-healing concept in synthetic materials have been explored in recent years, and various reviews have been published on this field.[1−3]

To date, the most successful examples are based on encapsulation and reversible chemistry, including both covalent and noncovalent chemical bonds. The encapsulation approach[4−8] is one of the most studied self-healing concepts and is based on the introduction of microcapsules with a healing agent, which polymerizes upon release from the microcapsules. The system has a great potential for healing internally developed microcracks but fails to repair a macroscopic cut in the material. Furthermore, the irreversible nature of the healing mechanism is a limitation. A method to overcome this last limitation is by making use of reversible chemistry. Intermolecular interactions, such as hydrogen bonding[9−13] and metal−ligand coordination,[14−16] have been demonstrated to be especially useful to introduce the capacity to heal a polymer multiple times. However, the dynamics of the network differ significantly from a covalently cross-linked material, since for example for hydrogen bonding the bond strength is much weaker. Alternatively, in the case of reversible chemistry based on strong covalent bonds, such as thermoreversible Diels−Alder reactions,[17,18] the healing process usually takes place at high temperatures. Therefore, weaker covalent bonds, such as disulfide groups, can be beneficial to introduce a healing functionality at lower temperatures, meanwhile keeping a reasonable level of bond strength. Disulfide chemistry is quite versatile. In the classic work by Tobolsky et al., stress relaxation by the introduction of disulfide and tetrasulfide links was demonstrated. The exchange of sulfur−sulfur links was shown in polyurethanes[19] as well as in poly(ethylene disulfide) and poly(ethylene tetrasulfide).[20] On the basis of the work by Tobolsky, it can be envisaged that a disulfide-containing material is amenable to creep. It is also known that disulfide groups can be cleaved by a reduction reaction to form two thiol groups and can be re-formed by an oxidation reaction. Tesoro et al. used this chemistry to introduce a recyclable functionality in a thermoset epoxy resin.[21,22] Also, redox-reversible hydrogels have been prepared by interconversion between disulfide and thiol groups.[23] Finally, Tsarevsky et al. synthesized poly(styrene) blocks bridged by disulfide groups that could be split via a reduction reaction yielding the corresponding thiol-terminated poly(styrene) and coupled back to the starting disulfide by oxidation.[24] Furthermore, vulcanized rubbers can undergo sulfur cross-link scission at elevated temperatures or in the presence of nucleophilic reagents, such as amines, alcohols, or thiols, or by rearrangement with disulfides.[25,26]

In this work, we investigate a self-healing concept that is based on the use of disulfide links incorporated in a rubber network, which is able to fully restore its mechanical properties at moderate temperatures. The key element of this self-healing concept is found in the exchange reaction of disulfide groups at

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Scheme 1. Disulfide Interchange Reaction

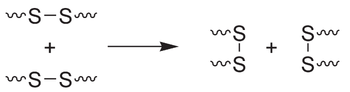


Table 1. Compositions of the Epoxy Resins with Different Disulfide Group Concentration Given in Molar Ratios

sample	EPS25 (mmol)	DER732 (mmol)	Tetrathiol (mmol)	S−S (wt %)
1	3.44	3.82	3.63	20
2	2.58	5.97	4.27	15
3	1.72	8.08	4.9	10
4	0.86	10.23	5.5	5
5	0	4.95	2.47	0

moderate temperatures as depicted in Scheme 1, leading to renewal of cross-links across damaged surfaces.

EXPERIMENTAL SECTION

Materials. Compound **1** (EPS25, epoxy equiv = 930 g/equiv) was purchased from Akzo Nobel; DER732 (Dow Chemicals, epoxy equivalent = 303 g/equiv), pentaerythritol tetrakis(3-mercaptopropionate) (**2**, Tetrathiol), 4-(dimethylamino)pyridine (DMAP), and poly(ethylene glycol-*block*-propylene glycol-*block*-ethylene glycol) (PEG-*b*-PPG-*b*-PEG, M_n ~ 1900 g/mol) were purchased from Aldrich. Glycidyl end-capped PEG-*b*-PPG-*b*-PEG was prepared according to a literature procedure with some adaptations.[27] Briefly, a mixture of 138.5 g (1.5 mol) of epichlorohydrin, 84 g (1.5 mol) of potassium hydroxide, and 1 g (2.94 mmol) of tetrabutylammonium hydrogen sulfate was prepared, to which 50 g (26.3 mmol) of PEG-*b*-PPG-*b*-PEG was slowly added under vigorous stirring in an ice bath. Subsequently, the mixture was stirred for 18 h at room temperature. The reaction mixture was filtered and evaporated to dryness. The obtained product was purified by precipitation of the dissolved polymer in 40 mL of chloroform into pentane, yielding 39 g of glycidyl end-capped PEG-*b*-PPG-*b*-PEG (epoxy equiv = 900 g/equiv).

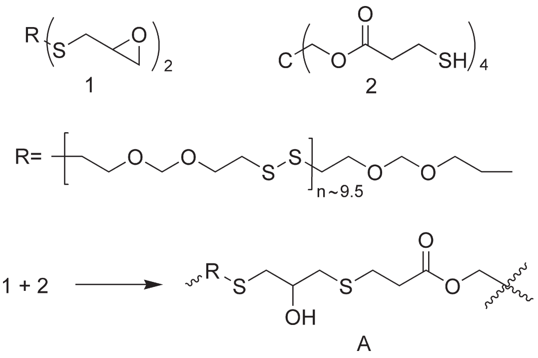
The epoxy equivalent was determined by the Jay-Dijkstra-Dahmen method, variation Ciba.[28]

Preparation of Polymer A. The sample was prepared by mixing and manual stirring in a mortar: 10 g (5.37 mmol) of EPS25 and 1.31 g (2.68 mmol) of Tetrathiol with 0.11 g of DMAP (1 wt %). The resulting homogeneous mixture was then heated at 60 °C for 2 h in a glass mold to obtain a yellowish, transparent material.

Preparation of Polymers with Different Disulfide Group Concentration. A typical procedure was as follows: The sample was prepared by mixing and manual stirring in a mortar using a stoichiometric mixture of two epoxy resins (DER732 and EPS25) and Tetrathiol. Then, 1 wt % of DMAP was homogeneously mixed into the composition. Finally, the polymer sheet was obtained by heating at 60 °C for 2 h in a glass mold. The compositions of the epoxy resins in molar ratios as well as the disulfide concentration in wt % are summarized in Table 1.

Characterization Methods. The isothermal cross-linking reaction was monitored at 60 °C by using FTIR spectroscopy. Spectra were obtained by placing the material on the diamond crystal of a Specac Golden Gate attenuated total reflection (ATR) setup placed in a BioRad Excalibur 3000 spectrometer. 160 spectra with a resolution of 4 cm^{-1} over a spectral range of 600−5000 cm^{-1} were signal-averaged, and the resulting spectra were analyzed using the BioRad Merlin 3.0 software. The intensity of the absorption band assigned to the symmetric ring deformation of the epoxy group between 860 and 815 cm^{-1} and the band assigned to the stretching vibration of the thiol group at 2536 cm^{-1} were used to calculate the epoxy and thiol conversion. The carbonyl stretching band at 1739 cm^{-1} was used as internal reference to correct for changes in the penetration depth of the evanescent wave.

Scheme 2. Curing Reaction of Epoxy Resin 1 with a Tetrafunctional Thiol 2



Raman spectroscopy of the initial monomer mixture and the cured epoxy resin was performed using a RamanStation spectrometer from Avalon Instruments with a laser with an excitation line of 784 nm.

Dynamic mechanical thermal analysis (DMTA) on the specimen with approximate dimensions of 6 mm long × 4 mm wide × 2 mm thick were carried out on a TA Instruments Q800 with film tension clamps from −100 to 140 °C at a heating rate of 3 °C/min. The DMTA experiments were strain-controlled with a constant amplitude of 10 μm. A preload force of 0.01 N and a force track factor of 110% were used.

Dynamic shear measurements were performed on a strain-controlled AR-G2 rheometer (TA Instruments) by using an 8 mm parallel-plate geometry and disk-shaped specimens (8 mm diameter, 1.5 mm thick). Frequency sweeps from 10^{-3} to 5×10^{2} rad/s were performed at 40, 60, 70, 80, and 100 °C with a strain of 0.2%, which is within the linear viscoelastic regime. Creep measurements were performed on a stress-controlled AR-G2 rheometer (TA Instruments) at a constant shear force of 100 Pa.

Tensile tests were performed on dumbbell-shaped tensile bars (20 × 5 × 2 mm) at 0.5 mm/s using a 20 N force cell on a Zwick Z010 tensile tester. The equipment was controlled with TestXpert v11.02 software. Healing experiments for material A and B were performed at 60 °C by bringing cut or broken samples together manually. The materials with varying disulfide concentration were healed at 80 °C for 2 h using this method to ensure that the healing process was completed.

Optical microscope images were obtained on Zeiss Discovery V20 stereo microscope with magnification of 125×.

The healing process can be seen in action in the Supporting Information. The epoxy resin-based rubber is cut through but left attached at the top to ensure a good fit of the surfaces. Without any force, the material is heated to 60 °C. A picture is taken every minute. The pictures are combined into a movie, which is played at 13 frames/s. Hence, the 1 h healing process is condensed in a 4.7 s movie.

RESULTS AND DISCUSSION

Epoxy resins were cross-linked with thiols in a base-catalyzed addition reaction.[29,30] An epoxy resin **1** containing disulfide groups (ca. 29 wt %) in its structure was cross-linked with a tetrafunctional thiol **2** in the presence of 1 wt % of 4-(dimethylamino)pyridine at 60 °C (Scheme 2). The cross-linking process was monitored

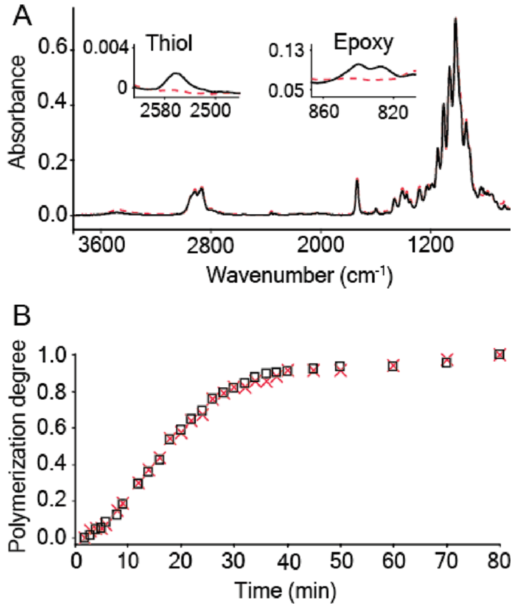


Figure 1. (A) FTIR/ATR spectra before (—) and after (---) curing at 60 °C. (B) Conversion of epoxy (☐) and thiol (×) groups versus time.

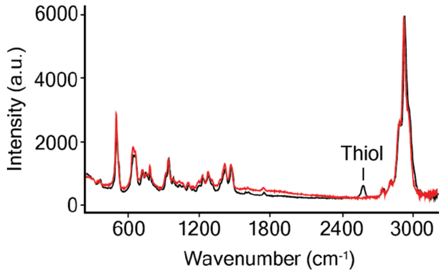


Figure 2. Raman spectra before (—) and after (---) curing.

by FTIR spectroscopy. This technique allowed us to monitor the evolution of the groups involved in the reaction by means of the variations in the intensities of the corresponding absorption bands. In Figure 1A, the FTIR spectra of a stoichiometric mixture of **1** and **2** are shown before and after cross-linking. In the FTIR spectrum of the unreacted sample, a broad absorption band between 860 and 815 cm^{-1}, which can be assigned to a stretching vibration of the oxirane ring, is observed together with a weak absorption band at 2536 cm^{-1}, which can be assigned to the S−H stretching vibration of the thiol group. The complete disappearance of these two absorption bands indicates that the conversion of the cross-linking reaction is close to 100% and that the monomers are incorporated into the network. The functional group conversion versus time is shown in Figure 1B. Since the intensity of the thiol absorption band is very weak in FTIR spectroscopy, Raman spectroscopy experiments were performed to confirm the complete disappearance of this band (Figure 2). The cross-linking process reaches completion in 80 min at 60 °C.

The resulting material **A** is a transparent thermoset rubber, with a glass transition temperature (T_g) of approximately −35 °C. Conventionally cross-linked polymers show a rubber plateau modulus that extends to the temperature at which the material decomposes.[31] The modulus of the rubber plateau can be obtained

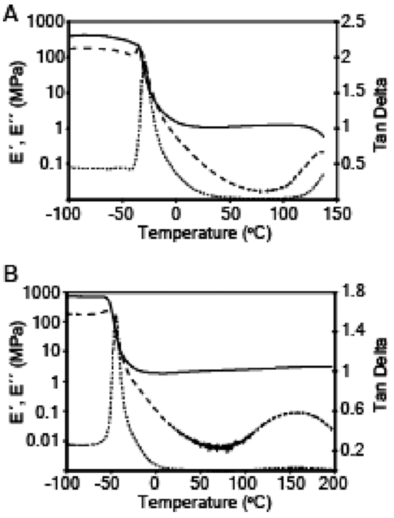


Figure 3. Temperature dependence of log storage (—, E') and log loss (— —, E'') modulus and tan delta (· · ·) for (A) the epoxy resin **A** and (B) control material.

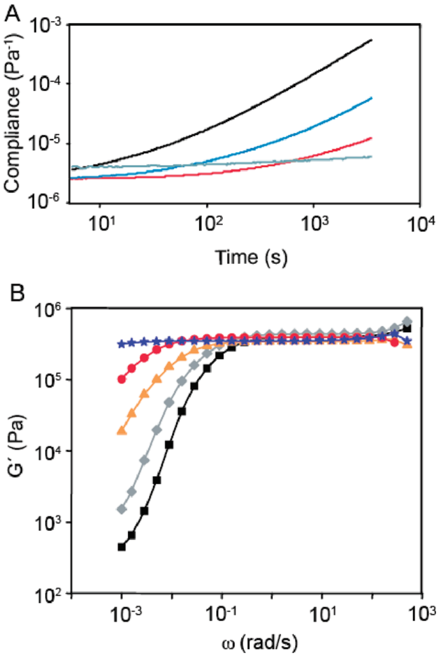


Figure 4. Rheological properties. (A) Compliance as a function of time for the material **A** and control material **B** at 60, 80, and 100 °C: (black) **A**, 100 °C; (blue) **A**, 80 °C; (red) **A**, 60 °C; (gray) **B**, 60−80−100 °C all overlapping. (B) Frequence dependence of storage modulus of the material **A** at 40, 60, 70, 80, and 100 °C: (★) 40, (●) 60, (▲) 70, (◆) 80, and (■) 100 °C.

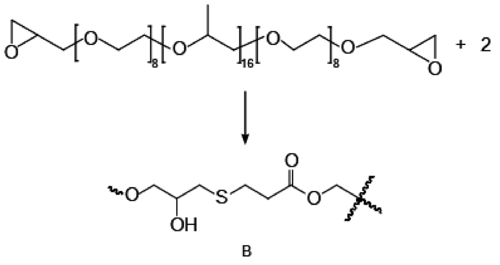
by dynamic mechanical thermal analysis, where the sample is sinusoidally deformed during a temperature ramp. However, our cross-linked rubber (Figure 3A) shows an unusual ability to flow at temperatures above 100 °C.

This indicates that the disulfide links disconnect and the chain segments gain enough mobility to induce macroscopic flow. Another typical feature of conventional cross-linked polymeric networks is the insolubility in common organic solvents.[32] However, our material shows solubility after immersion of the sample for 3 days at room temperature under stirring in nitrogen-containing solvents, such as *N,N*-dimethylformamide, and thiol reagents, such as 1,6-hexanedithiol. This observation can be explained by the selective scission of disulfide groups in the cross-linked network.[33]

Creep experiments were performed at constant low shear stress (100 Pa) to study the flow behavior at different temperatures. At moderate temperatures (60 °C), the material shows flow after ~100 s. This is in agreement with the observed healing capability at this temperature. The increase of the creep compliance with temperature (Figure 4A) can be explained by higher disulfide group dissociation in the network, which is in agreement with the previously cited studies from Tobolsky et al.[19,20] To confirm that this behavior is only due to the disconnection of disulfide groups and not due to physical effects, a control experiment was performed with a material obtained from the polymerization of an epoxy resin without disulfide groups but with similar epoxy end-groups and the same cross-linking agent. The reference material, which did not show any self-healing capability, is obtained by a copolymerization of **2** with poly(ethylene glycol-*block*-propylene glycol-*block*-ethylene glycol) end-capped with glycidyl moieties (Scheme 3). The glycidyl end-capped triblock copolymer was selected for the synthesis of the reference material, since it yields an amorphous cross-linked polymer. The use of glycidyl end-capped poly(ethylene glycol) would have led to a semicrystalline cross-linked polymer with quite different properties.

As depicted in Figure 4A, the control material does not show a critical stress to induce flow. Furthermore, the storage modulus shows a rubber plateau, which is typical for cross-linked polymers (Figure 3B). There is a discrepancy in the storage and loss moduli of the materials in Figure 3A,B. This is most likely due to a difference in cross-link density caused by the difference in epoxy equivalent of the starting materials as well as to a difference in chemical structure of the starting materials (see above). However, it cannot be completely ruled out that the different moduli are in part the result of a side reaction during the curing process, where the thiol bites the disulfide bond in the chain, giving more loops in the network. Since the network structure is different, it cannot be excluded that physical effects, such as diffusion of chains, play a role in the self-healing process. In Figure 4B, the storage moduli G' are plotted as a function of angular frequency for different temperatures. Each storage modulus G' curve shows a transition from the rubbery plateau to the terminal zone, where the curve has the slope of ~1.5, which is clearly different from linear polymers,[34] and is in accordance with the cross-linked nature of the material, but the transition shifts to higher frequencies on increasing the temperature.

Scheme 3. Curing Reaction of Control Material



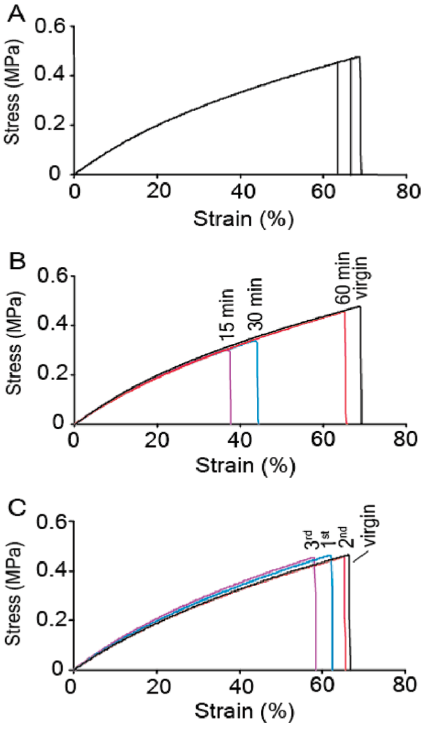


Figure 6. Evaluation of self-healing properties. (A) Stress–strain curves for three samples are shown to illustrate the reproducibility of the experiments. (B) Stress–strain curves as a function of the healing time. Broken samples during the tensile test experiments are put into contact at 60 °C and allowed to heal for different times. (C) Stress–strain curves after repetitive healing experiments.

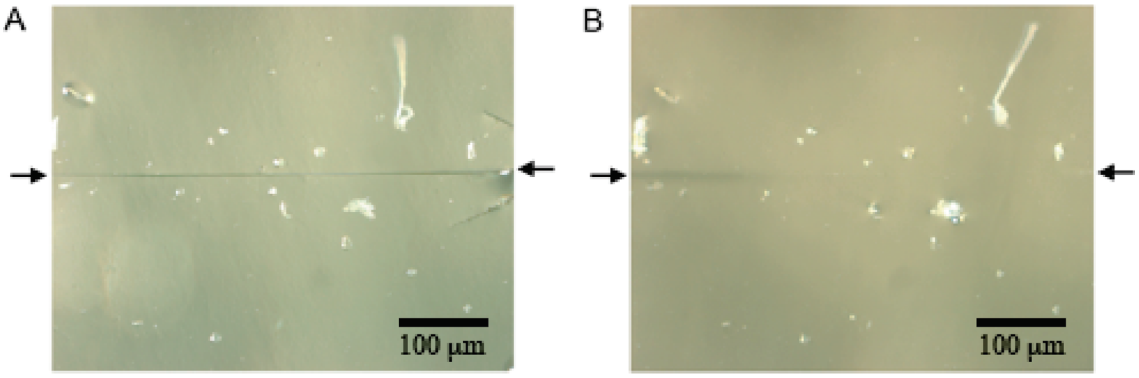


Figure 5. Optical microscope images (A) before and (B) after the healing process.

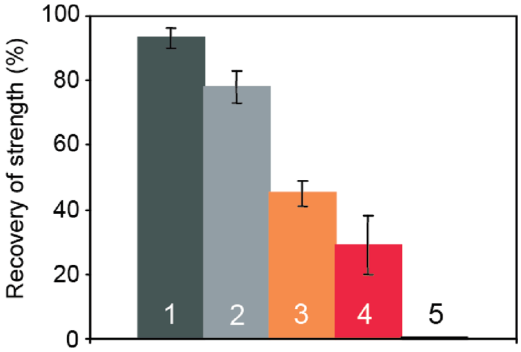


Figure 7. Recovery of strength (%) of healed samples with different concentrations of disulfide groups. Sample 1: 20 wt %; sample 2: 15 wt %; sample 3: 10 wt %; sample 4: 5 wt %; sample 5: 0 wt % disulfide.

Supporting Information movie 1 shows the healing process. The initial cut in the material disappears after 1 h at 60 °C. Optical microscopy images before and after the healing process are shown in Figure 5. Figure 5B shows that the cut heals almost completely to produce a homogeneous material. A minor defect can be seen on the left side, which is most likely due to a slight offset when putting together the surfaces.

To quantify the healing efficiency, tensile testing experiments were performed to quantify the recovery of strength.[10] Representative stress−strain curves for the original material are plotted in Figure 6A, showing that the elongation at break is ~65 ± 5%. When a sample breaks during the tensile test and the fracture surfaces are immediately put into as close as possible contact and heated at 60 °C, the mechanical properties are fully restored in just 1 h (Figure 6B). As expected, longer healing times lead to better healing, but even when the contact time between the two broken parts is as short as 15 min, a repaired sample shows an elongation at break close to 40%. Surprisingly, for all healing times, the stress−strain curves superimpose and show only different elongations at break, indicating that the healed samples have similar elastic properties as the original material. This material can be healed efficiently multiple times, and the mechanical properties after the second and third healing process are, within experimental error, fully restored, i.e., elongation at break of ~63 ± 5%, and no systematic decrease for consecutive breaking−healing cycles (Figure 6C).

To determine the influence of the disulfide concentration on the self-healing properties, several polymers were prepared using different ratios of epoxy resins, one free of disulfide groups (DER732) and another containing disulfide groups in its structure (EPS25). In all experiments the tetrafunctional thiol was used as the cross-linker. The compositions are listed in Table 1. The disulfide concentration was varied from 0 to 20 wt %. As can be seen from Figure 7, the recovery of the strength depends on the concentration of the disulfide groups present in the material. The material with the highest disulfide concentration shows the best self-healing efficiency, whereas material 5, without disulfide groups, does not show any self-healing property at all.

■ CONCLUSIONS

We have shown a novel concept for self-healing materials based on disulfide bonds. Our present understanding of the system indicates that the exchange of disulfide groups is responsible for the observed self-healing properties. This method is expected to be widely applicable to low-T_g materials, e.g., polyurethanes and polyesters. The applicability for higher T_g materials may be restricted due to the limited mobility of chains in glassy polymers. Obviously, the self-healing process needs to take place above the T_g of the material, since the chain segments in the network need mobility to allow for the interchange reaction to take place. The disulfide groups do not need to be introduced exclusively via the anionic ring-opening copolymerization of an epoxy resin as performed in this work. Other monomers (e.g., diamines, dithiols) containing the disulfide functionality can be used with various polymerization methods, potentially resulting in a large variety of cross-linked materials. Further work is needed to determine the full scope of this concept.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. A movie of the healing process. This material is available free of charge via the Internet at http://pubs.acs.org.

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