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Application of alkoxyamine in self-healing of epoxy

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To provide epoxy with intrinsic self-healing ability, a new alkoxyamine based diol was synthesized and incorporated into an epoxy monomer, which was then compounded with traditional bisphenol A diglycidyl ether and cured by diethylenetriamine. Taking advantage of dynamic equilibrium of thermally reversible reaction of C-ON bond in alkoxyamine, cracked portions of the functionalized epoxy material can be repeatedly reconnected at certain temperature, as characterized by restoration of impact strength and visual inspection as well. Unlike the two-step self-healing approach based on reversible Diels-Alder reaction, the present one only needed one step. Owing to the steric hindrance of tertiary butyl group in the diol, onset of scission of C-ON bonds and radical recombination (i.e. healing reaction) occurred at lower temperature. Additionally, reversibility of the alkoxyamine derivatives was improved with incorporation of Si-O bonds into the epoxy chains. The present work carefully studied thermal reversibility, thermal stability, dynamic mechanical behavior and healing performance of the epoxy in relation to molecular structure. The outcomes might help to optimize the material and guide future design of novel epoxy monomers.

Introduction

Polymers and polymer composites have been used in a variety of applications. However, they are susceptible to damages induced by mechanical, chemical, thermal, and UV irradiation factors. These damages may bring about microcracks deep inside the materials, which are difficult to detected and repaired. To settle the issue, the concept of self-healing emerges as the times require.1 So far, the healing approaches fall into two categories: extrinsic and intrinsic.2 The former takes effect because of the pre-embedded microencapsulated healing agent in the materials. Upon fracture, the healing agent would be released to the cracked portions and rebond the damages.3,4 However, the cracks can not be repeatedly healed when the healing agent is exhausted. The latter relies on the inherent physical and/or chemical interactions of macromolecules between the broken faces. Reversion of covalent bonding,5,6 for example, is found to be an effective means in this aspect owing to its practicality. Intrinsic self-healing system does not require additional healing agents,7,8 and the reversible bonds responsible for repeated healing cycles include Diels-Alder (DA) bonds,9 thiuram disulfide units,10 alkoxyamine moieties,11 coumarin derivatives,12 acylhydrazone bonds,13 disulfide links,14 Ru-catalyzed shuffling of C-C bonds,15 hydrogen bonding,16 ionomers,17 π-π stacking,18 van der Waals’ actions,19 etc.

Epoxy is an important polymeric material widely applied in surface coatings, structural adhesives, printed circuit boards, insulation materials for electronic devices, and advanced composites, because of its high mechanical properties, chemical resistance, thermal stability, ease of handling and processing, etc. application in various fields, easy processing in a wide temperature range, etc. With the development of self-healing technology in recent years, the possibility of imparting intrinsic crack remendability to epoxy has been explored.

By using thermally reversible DA reaction, which proved to be able to reconnect broken chains in thermoset,20 Tian and co-workers prepared self-healing epoxy composed by both thermally reversible DA bonds and irreversible bonds from ring-opening polymerization of epoxide groups.21,22 This molecular structure allows the cured epoxy to possess similar mechanical properties like commercial epoxies, and to eliminate cracks through successive retro-DA and DA reaction below \( T_g \). Unlike the above work by Tian et al. who functionalized epoxy with furan,21 Bai et al. synthesized a diamine carrying DA unit, which served as a healable element and was used to crosslink commercial epoxy monomers to achieve self-healing.24 Canadell et al. incorporated disulfide links into a rubbery epoxy network (i.e. a commercially available disulfide group-contained epoxy cured by tetrafunctional thiol), which was able to fully restore its mechanical property at moderate temperatures (e.g. 60 °C).25 The healing mechanism was further analyzed in detail from the viewpoint of thiol-disulfide exchange.14

Leibler’s group reported that with proper catalyst (e.g., zinc acetate), the topologies of crosslinked networks from epoxy-acid and epoxy-anhydride reactions can be rearranged by transesterification exchange reactions without modification of the numbers of links and average functionality.26 At lower
temperature, the exchange reactions are sluggish, and the materials have properties of classical epoxy thermosets. At higher temperature, however, the polymers behaved like viscoelastic liquids. Lap-shear tests indicated that these networks can be welded after treatment at 150 °C for 1 h. Peterson et al. built up reversible reinforcement/matrix interfaces in glass fiber-reinforced composites taking advantage of DA reaction between a furan-functionalized epoxy-amine thermosetting matrix with a maleimide-functionalized glass fiber.27,28 At room temperature the DA adduct is formed spontaneously and above 90 °C the adduct breaks apart to reform the original furan and maleimide moieties. Significant healing of the interface characterized by single fiber microdroplet pull-out testing was observed.

In this work, a new healing chemistry, reversible covalent bonding through dynamic exchange reaction of alkoxyamines, is introduced to make self-healing epoxy. Under certain homolysis temperature, C-ON bonds in alkoxyamines undergo reversible radical reaction, producing transient carbon-centered and persistent nitroxide radicals in equal amounts.29–34 There exists a fast dynamic equilibrium between dissociation and association with a very high equilibrium constant of $1.7 \times 10^{15}$ [M$^{-1}$] for bulk living polymerization of styrene at 135 °C.30 Our early work demonstrated that crosslinked polystyrene containing C-ON bonds as crosslinkers can indeed rebind fractured surfaces repeatedly.11 Since covalent bond homolysis and radical recombination synchronously take place in this case, the aforesaid two-step healing strategy based on DA bonds is simplified into single-step one, and possible material deformation due to collapse of crosslinked networks in the course of crack remending would thus be avoided even when the healing is carried out above glass transition temperature.

Here, for purposes of obtaining alkoxyamine-containing epoxy (diEP, see Scheme 1), a new alkoxyamine-based diol is designed and synthesized, which should possess lower homolysis/recombination temperature in comparison with the alkoxyamine-based diol we used in our previous work.11 Meanwhile, Si-O bonds are introduced through reaction between the diol and chlorosilane to improve mobility of molecular chains connected with alkoxyamine groups and facilitate the subsequent healing reaction across crack faces. By hydroxylation between silicon hydrogen bond and allyl glycidyl ether, the alkoxyamine-containing epoxy (diEP) is yielded. Considering that the cured version of the alkoxyamine-containing epoxy might be too soft as a result of its flexible long segment structure, traditional bisphenol A diglycidyl ether is incorporated as a rigid component to strengthen the ultimate material. It is hoped that after curing, an epoxy with balanced performance would be yielded (Figure 1), in which the C-ON bonds help to heal cracks via their reversible homolysis/recombination habit.

Figure 1. Thermally remendable epoxy containing alkoxyamines.

### Experimental

Materials and reagents

Benzoyl peroxide (BPO), chlorodimethylsilane, and allylic glycidyl ether were purchased from Alfa Aesar GmbH, Germany. 4-Hydroxy-2,2,6,6-tetramethylpiperidinol (4-OH-TEMPO), dihydroxyamine (DETA), triethylamine, and diethylene glycol diglycidyl ether (DGDE) were supplied by Aldrich. Karstedt’s catalyst solution (divinyltetramethyldisiloxane-Pt(0), 2-3% w/w in xylene) was provided by Gelest, and bisphenol A diglycidyl ether (EPIKOTE 828) by Shell Chemical Company. Dibutyltin dilaurate (DBTL) was supplied by Aldrich. All the above chemicals were used as received. α-Methyl styrene (Alfa Aesar GmbH, Germany) was purified by vacuum distillation after elimination of inhibitor and pre-dried with sodium sulfate. Tetrahydrofuran (THF) and triethylamine were purchased from Aldrich, pre-dried and distilled over Na in advance.

### Synthesis of alkoxyamine-based diol

The alkoxyamine-based diol (4-hydroxy-1-(2’-hydroxy-1’-phenyl-1’-methyl) ethyl-TEMPO) was synthesized as follows. Benzoyl peroxide (14.52 g, 0.06 mol) and 4-OH-TEMPO (20.64 g, 0.12 mol) were dissolved in α-methyl styrene (250 mL), heated at 100 °C under argon for 3 h, and then cooled to room temperature. The excess α-methyl styrene was removed under reduced pressure. Afterwards, ethanol (300 mL) and KOH aqueous solution (3 N, 120 mL) were added into the system and the mixture was stirred at room temperature for 12 h, followed by evaporation to dryness and partitioned between dichloromethane and deionized water. The aqueous phase was extracted with dichloromethane for three times and the organic phases were gathered, dried with anhydrous sodium sulfate for 24 h. After the solvent was removed, the crude product was purified by column chromatography using ethyl acetate and petroleum ether as the eluent, offering the diol as a pale yellow solid (yield = 34.7%).
The synthesis of diEP referred to the route reported in ref. 35 (Scheme 1). The aforesaid alkoxyamine-based diol (3.07 g, 0.01 mol) and triethylamine (3.03 g, 0.03 mol) were dissolved in tetrahydrofuran (100 mL), and then chlorodimethylsilane (2.835 g, 0.03 mol) was added dropwise into the system under argon gas to ensure intimate contact. Healing was conducted at 90 °C under argon atmosphere for 5 h. After the generated triethylamine hydrochloride was removed, the mixture was evaporated to dryness under reduced pressure and partitioned between toluene and deionized water. The organic phase was washed with water for three times and dried with anhydrous sodium sulfate for 24 h. Afterwards, Karstedt’s catalyst (0.018 g, 7.8×10⁻⁶ mol) and allyl glycidyl ether (2.394 g, 0.021 mol) were added into the obtained toluene solution of intermediate product, and the compound was heated at 60 °C under argon atmosphere for 2.5 h. The solvent and excess allyl glycidyl ether were removed by vacuum distillation to give the product as a pale yellow oil (yield = 63.2%). The obtained alkoxyamine derivative with epoxy group at both ends is labeled as diEP. 31H NMR (CDCl₃): δ/ppm 0.89 (3H, CH₃), 0.99 (3H, CH₃), 1.19 (3H, CH₃), 1.20 (3H, CH₃), 1.58 (3H, CH₃), 1.53-1.84 (4H, 2 CH₂), 3.84 (1H, CH), 3.96 (1H, CH), 4.05 (1H, CH), 7.21-7.54 (5H, aromatic); 31C NMR (CDCl₃): δ/ppm 21.96, 22.06, 23.93, 31.49, 49.49, 49.75, 61.01, 61.10, 63.04, 70.12, 81.91, 126.88, 127.19, 128.14, 146.20; mass spectrum for C₁₁H₁₀NO₃[S +1]⁺ found 308.2.

Characterization

1H NMR and 13C NMR spectra were collected by a VARIAN Mercury-Plus 300 (300 MHz) with chloroform (CDCl₃) as solvent. Mass spectrometry (MS) measurement was conducted on a Thermo Finnigan LQCD DECA P LC-MS spectrometer. Electron spin resonance (ESR) spectra were recorded by JEOL JES-FA200 to investigate the effect of thermal reversibility of the resultant epoxy materials. Thermogravimetric analysis (TGA) was performed on a TA Instruments TGA Q50 at a heating rate of 10 °C min⁻¹ using a nitrogen purge. Dynamic mechanical analysis (DMA) was carried out with a 01Db-metavib-DMA25 apparatus under nitrogen atmosphere using tensile mode. Molecular weight between crosslinks of the cured epoxy, Mₛ, was calculated from: 16

\[ E' = \frac{3 \rho}{M_s} \frac{RT}{\left(1 - \frac{2}{\phi}\right)} \]

where E’ stands for storage modulus at rubbery plateau zone, ρ density, R gas constant, T absolute temperature, and φ functionality of epoxy, respectively. In this work, E’ values at T = Tₛ + 30 °C were used for the calculation.

Healing property of the epoxy was characterized by Izod notchched impact tests on the basis of GBT 1843-1996 standard according to the method proposed by Jones et al. 37 Firstly, the specimen (52.8 mm × 12.3 mm × 10.1 mm) was impacted to failure using a JJ-20 impact tester (Changchun Research Institute for Testing Machines Co. Ltd., China). Then, the broken halves of the specimen were recombined, with a pressure of about 0.2 MPa to make sure that their faces were kept in alignment and intimate contact. Healing was conducted at 90 °C under argon atmosphere for 1.5 h. Having been cooled to room temperature, the fixed specimen was tested to failure again. The ratio of impact strength of the healed specimen to that of the virgin one gave a measure of healing efficiency. Each batch included six specimens to yield average value.

The reason why we used impact test rather than tensile test to evaluate healing performance of the material lies in the fact that material loss would take place at the fracture surface when the specimen was failed due to tensile test. As a result, it was hard to ensure intimate contact between the uneven fracture surface of the broken halves of the specimen.

Results and discussions

Thermal reversibility

Since the C-ON bonds in alkoxyamines should play the leading role in self-healing and homolysis-rebonding of C-ON bonds is related to free radicals, ESR was employed to understand the thermally reversible behavior of the materials at the beginning of discussion. Figure 2a shows typical ESR spectra of N-epoxy measured at various temperatures. In addition, Figure 2b gives the normalized absorption lines corresponding to the ESR curves in Figure 2a, from which integrated areas of the relative signal intensities are calculated and plotted as a function of temperature (see Figure 2c). Clearly, radical signal is detectable at 20 °C and its intensity increases with a rise in temperature. The phenomenon resembles the case of crosslinked polystyrene containing alkoxyamine, 11 but the initial temperature for...
appearance of radical signal is much lower than that of the latter (~100 °C). This is because tertiary butyl groups rather than ethyl groups link up with the N-O bonds in the diol (Scheme 1), which produce larger steric hindrance, reducing the bond energy of C-ON bond and lowering its homolysis temperature. On the other hand, the results in Figure 2 and ref.31 confirm that alkoxyamines derivatives attached to different polymers exhibit similar thermal reversibility, which provides us with ample room to develop different thermally reversible polymers for different requirements.

...permanent dissociation of a few alkoxyamines as the combination of tertiary butyl radicals, and then nitroxide radicals is somehow remained in solid state.38 The relatively higher thermal reversibility of N-epoxy than 828/diEP should originate from the larger quantity of soft diEP in the former. On one hand, flexibility of the abundant soft diEP chains increases probability of collision between radicals. On the other hand, molecular chain of diEP (651 g/mol) is longer than that of 828 (330 g/mol), thus making a lower crosslinking density for N-epoxy. It is also conducive to molecular motion and contact with each other. Nevertheless, 828/diEP possesses much better reversible performance than the crosslinked polystyrene with alkoxyamines mentioned above.31 Apparently the higher stability of tertiary butyl radicals together with soft segments in epoxy take the responsibility, which can hinder the combination between carbon radicals but benefit reconnection of the carbon and nitroxide radicals attached to the macromolecular chains.

![Graph](image1)

**Figure 2.** (a) Typical ESR spectra of N-epoxy measured at various temperatures. (b) Normalized absorption lines obtained from the data of (a). (c) Temperature dependence of relative ESR signal intensities calculated from integral areas of the normalized absorption curves in (b).

To further investigate the reversibility of C-ON bond in cured epoxy containing alkoxyamines, its ESR spectra were collected during repeated heating-cooling cycles between 20 and 90 °C (Figure 3), as the change in radical relative intensity reflects homolysis-recombination habit of C-ON bond. Moreover, comparison between the relative signal intensity after thermocycling and that of the original state at 20 °C would help to evaluate thermal reversibility of the epoxy. It is seen from Figure 3 that when temperature alternates between 20 and 90 °C, the amount of free radicals fluctuates as a result of scission of alkoxyamine moieties and recombination of the radicals. These processes are fully reversible, but the valley values of the relative intensity slightly increases with the thermal cycles especially in the case of 828/diEP. The latter behavior might be attributed to permanent dissociation of a few alkoxyamines as the combination of tertiary butyl radicals, and then nitroxide radicals is somehow remained in solid state.38 The relatively higher thermal reversibility of N-epoxy than 828/diEP should originate from the larger quantity of soft diEP in the former. On one hand, flexibility of the abundant soft diEP chains increases probability of collision between radicals. On the other hand, molecular chain of diEP (651 g/mol) is longer than that of 828 (330 g/mol), thus making a lower crosslinking density for N-epoxy. It is also conducive to molecular motion and contact with each other. Nevertheless, 828/diEP possesses much better reversible performance than the crosslinked polystyrene with alkoxyamines mentioned above.31 Apparently the higher stability of tertiary butyl radicals together with soft segments in epoxy take the responsibility, which can hinder the combination between carbon radicals but benefit reconnection of the carbon and nitroxide radicals attached to the macromolecular chains.

![Graph](image2)

**Figure 3.** Relative ESR signal intensities of (a) N-epoxy and (b) 828/diEP measured during heating-cooling cycles between 20 and 90 °C.

### Thermal stability and dynamic mechanical behavior

Considering the fact that the C-ON bonds in alkoxyamines frequently cleave but immediately recombine under certain homolysis temperature, thermal stability of the epoxy materials containing alkoxyamines must be affected accordingly. The TGA curves in Figure 4a show that the presence of alkoxyamines significantly decreases the onset temperature of epoxy, which is in proportion to the concentration of alkoxyamines. The homolysis of C-ON bonds and the resultant radicals should account for this. In addition, the onset temperature of 828/DGDE is 30 °C lower than that of 828 (see the inset of Figure 4a), implying not only alkoxyamines but also soft segments in the
polymer network lower thermal stability of epoxy.

![Graph 1](image1.png)

**Figure 4.** Pyrolytic behaviors of cured epoxies.

When looking at the curves of rate of weight loss (Figure 4b), two peaks are found for N-epoxy. By reference to the peak position of 828 that does not contain any alkoxyamines, it is known that the peak at higher temperature results from destruction of irreversible covalent bonds, and the other reflects the weight loss caused by cleavage of C-ON bonds.

In addition to TGA that provides temperature dependent structural information under quiescent condition, DMA enables study of the issue in a dynamic way. As shown in Figure 5, the N-epoxy specimen can be repeatedly tested, demonstrating the existence of reversible equilibrium between C-ON bonds homolysis and recombination; otherwise, even the second test could not be conducted if the radicals failed to be immediately re-bonded and the material behaved like thermoplastics due to the destruction of the networks. During the repeated heating-cooling cycles, the temperature dependence of storage modulus of N-epoxy keeps almost the same, but the profiles of its tanδ peaks are obviously changed. In fact, there are two peaks on the tanδ curves of N-epoxy. Compared to the higher temperature one, both position and height of the lower temperature one change much more remarkably with the repeated scans. This should be the result of dynamic equilibrium feature of the reversible C-ON bonding. That is, the lower temperature peak on the tanδ curve of N-epoxy is contributed by segment motion of the dangling chains generated by disconnection of C-ON bonds, while the higher temperature one represents the undamaged networks. Owing to the random nature of the homolysis/recombination behavior of C-ON bond, the dangling chains lengths change from time to time so that the position and height of the lower temperature peak are different for different tests. In contrast, the higher temperature peak is basically unchanged due to the relatively definite molecular weight between cross-links of the undamaged networks.

![Graph 2](image2.png)

**Figure 5.** Temperature dependence of (a) storage modulus and (b) tan δ of N-epoxy measured by repeated DMA scans.

With the incorporation of 828 that contains no reversible C-ON bonds and increases crosslinking density of the system, the tan δ curves of 828/diEP become unimodal as the dangling chains lengths of the disconnected chains produced by homolysis of alkoxyamine moieties have to be much shorter due to the existence of irreversible networks, which cannot afford to form to a new damping peak (Figure 6). Nevertheless, it is worth noting that peak temperature and intensity on the tan δ curves decrease after each test cycle. This should be interpreted as the appearance of a few permanently dissociated alkoxyamines originating from the difficulty of recombination of tertiary butyl radicals and nitroxide radicals in solid (Figure 3(b)). Accordingly, crosslinking density of the epoxy network is reduced with the test cycles (Table 1). The analysis is supported by the temperature dependence of storage modulus, which moves downward during repeated DMA tests (Figure 6a). The slight decline of the stiffness should be attributed to the permanently destructed C-ON bonds that could no longer bear load. The decay is marginal on the whole, which is also proved by ESR data, meaning the thermal reversibility of cured 828/diEP would effectively work for crack healing. On the other hand, a comparison of Figure 5 and Figure 6 indicates that the peak temperature of tan δ of 828/diEP is about 20 °C higher than that of N-epoxy. That is due to the reduced concentration of flexible -Si-O- bonds in 828/diEP.
Figure 6. Temperature dependence of (a) storage modulus and (b) tan δ of 828/diEP measured by repeated DMA scans.

Table 1. Molecular weight between crosslinks, $M_c$, of the cured epoxies estimated from repeated DMA scans in Figures 5 and 6 with data of the epoxies without C-ON bonds as references.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Cycle 1</th>
<th>Cycle 2</th>
<th>Cycle 3</th>
<th>Cycle 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-epoxy</td>
<td>1685</td>
<td>1664</td>
<td>1729</td>
<td>1790</td>
</tr>
<tr>
<td>828/diEP</td>
<td>350</td>
<td>371</td>
<td>384</td>
<td>-</td>
</tr>
<tr>
<td>828/DGDE</td>
<td>558</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>828</td>
<td>161</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Figure 7. Repeated impact damaging-healing of an 828/diEP specimen.

Healing performance

As mentioned in the Experimental, healing capability of the materials was evaluated by impact test. Figure 7 shows three successive macro-repairing processes of an 828/diEP specimen. The virgin specimen was firstly impacted apart, and then the broken parts were recombined. Having been healed in argon at 90 °C for 1.5 h, no shape change was observed for the specimen and...
the crack line was absent under visual inspection. It can bear a weight of 200 g (i.e. 15.8 kPa under tensile condition). Afterwards, the healed specimen was subjected to impact loading again, and repaired under the same conditions. The healed version still possessed load bearing ability, and the cracking line was invisible. The third impact-healing tests also gave the same results as before. Clearly, the epoxy has acquired repeated remendability as expected. It is worth noting that the healing temperature is higher than $T_g$ of the material, but the specimen still keep its original shape after rehabilitation, which evidently reflects one of the advantages of employing dynamic reversible C–ON bond as healing group.

In this work, 90 °C is chosen as the healing temperature because of the following reasons. First of all, the materials should be heated above $T_g$ to ensure higher molecular chain mobility for occurrence of the reversible reaction across the crack interface. Secondly, higher homolysis rate or radicals concentration at elevated temperature is important for effective healing.

Table 2 lists that the average healing efficiency of the first healing is 62.0 %, while those of the second and third healing are 59.5 and 55.1 %, respectively. The decline in healing efficiency with healing/re-fracture cycles might result from incompletely alignment of the specimens and/or permanently irreversible C–ON bond caused by radical deactivation at the fractured surfaces. Compared to the crosslinked polystyrene system,[16] the healing efficiency of 828/diEP decreases much more slowly. It is mainly because the long soft segments of diEP in epoxy not only increase the collision probability of radicals to reform covalent C–ON bonds, but also benefit interdiffusion of the dangling chains across the fractured surfaces. Figure 8 depicts the healing efficiency of 828/diEP as a function of healing time. With a rise in healing time, the healing efficiency increases and then levels off when the time exceeds 2 h. It implies that no more reversible C–ON bonds are involved at the interface with prolonged time. A case should be pointed out that although the C–ON healing chemical equilibrium is fairly fast, 2 h is still needed to reach steady state healing. It reflects the importance of interdiffusion of macromolecules and collision probability of radicals between the fractured surfaces, which act as the control step. To investigate the effects of C–ON bonds and long soft segments on healing performance of epoxy, controlled experiments were carried out as follows. Firstly, 828/DGDE was prepared by replacing diEP with DGDE that does not contain any reversible bond but has long soft structure like diEP. It is found that only ~7 % of impact strength can be restored under the same conditions (Table 2), suggesting that the reversible C–ON bonding rather than the soft chains entanglement or reaction of latent functional groups at the interface makes the decisive contribution to the crack healing. Secondly, the impact ruptured specimens of 828/diEP were exposed to air at 90 °C for 1.5 h, and then they were cooled down to room temperature, recombined together and healed in air at 90 °C for 1.5 h. Due to the oxygen induced deactivation of radicals, the reversible reaction of C–ON bonds cannot proceed in air. As a result, ~6 % healing efficiency is detected (Table 2). The result proves the importance of C–ON bonding once again.

### Table 2. Healing efficiencies of 828/diEP measured during three successive impact damaging-healing tests with the data of control specimens as references

<table>
<thead>
<tr>
<th>Materials</th>
<th>First healed</th>
<th>Second healed</th>
<th>Third healed</th>
</tr>
</thead>
<tbody>
<tr>
<td>828/diEP</td>
<td>62.0 ± 3.5</td>
<td>59.5 ± 5.7</td>
<td>55.1 ± 3.2</td>
</tr>
<tr>
<td>828/DGDE</td>
<td>6.8 ± 4.2</td>
<td>7.2 ± 2.5</td>
<td>6.4 ± 2.7</td>
</tr>
<tr>
<td>828/diEP (healed in air)</td>
<td>6.9 ± 3.8</td>
<td>5.4 ± 3.6</td>
<td>6.0 ± 2.9</td>
</tr>
</tbody>
</table>

### Figure 8. Effect of healing time on healing efficiency of 828/diEP.

Healing was conducted in argon at 90 °C.

It is worth noting that the self-healing 828/diEP has not yet achieved full recovery of impact strength owing to the presence of unmendable 828 structure that acts as the stiff backbone of the networks. To further improve healing efficiency of the epoxy while keeping high strength, novel epoxy monomer should be synthesized instead of blending. The current work provides the knowledge of structure-properties relationship for molecular design.

### Table 3 Mechanical properties of the cured epoxies

<table>
<thead>
<tr>
<th>Properties</th>
<th>Materials</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flexural strength (MPa)</td>
<td>828/diEP</td>
</tr>
<tr>
<td>71.4 ± 11.7</td>
<td>124.8 ± 8.1</td>
</tr>
<tr>
<td>Flexural modulus (MPa)</td>
<td>2409.0 ± 62.2</td>
</tr>
<tr>
<td>Tensile strength (MPa)</td>
<td>38.8 ± 8.7</td>
</tr>
<tr>
<td>Young’s modulus (MPa)</td>
<td>991.8 ± 69.7</td>
</tr>
<tr>
<td>Impact strength (J/m²)</td>
<td>380.7 ± 5.9</td>
</tr>
</tbody>
</table>

Mechanical properties of the blend of 828/diEP (at 1.5/1 molar ratio) and 828 are listed in Table 3. The relatively poorer properties of 828/diEP should result from the lower crosslink density in diEP. Therefore, mechanical properties including impact strength of 828/diEP are adversely affected despite that Si-O bonds are known for their flexibility. Further efforts should be made to improve overall properties of this system, as it indeed has potential to become an upgraded version of conventional epoxy without self-healing capability.

### Conclusions

Repeated self-healing ability was successfully imparted to epoxy by introducing alkoxyamines into the networked structure. Owing to the synchronous C–ON bond homolysis and radical
recombination of alkoxyamines, damages in cured version of the functionalized epoxy can be healed at certain homolysis temperature. Compared with the remendable polymers based on DA bonds that healed cracks in a two-step fashion, the present one completed the rehabilitation by only one step.

Blending alkoxyamine-containing epoxy with conventional epoxy proved to be an effective way to produce self-healing epoxy with balanced performance. In the long run, new epoxy monomer coupled with both healability and mechanical strength should be developed according to the molecular structure-properties relationships revealed hereinbefore.

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Notes and references
Cracks in epoxy containing alkoxyamine can be repeatedly healed through dynamic equilibrium of thermally reversible reaction of C-ON bond.