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Self-healing polyurethane elastomer with thermally reversible alkoxyamines as crosslinkages

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ABSTRACT

To provide self-healing ability to polyurethane elastomer, alkoxyamine-based diol was synthesized and reacted with tri-functional homopolymer of hexamethylene diisocyanate (tri-HDI) and polyethylene glycol (PEG). Because alkoxyamines acted as crosslinkers of the resultant polyurethane, the thermally reversible fission/recombination of C—ON bonds in alkoxyamine moieties enabled repeated crosslinking and de-crosslinking of polyurethane chains at certain temperature and hence crack healing. Both qualitative and quantitative characterizations demonstrated that the reversibly crosslinked polyurethane was capable of re-bonding ruptured parts and restoring mechanical strength. The remendability was a function of molecular structure and compositions of the components, which can be purposely tuned according to different application demands.

1. Introduction

Polyurethanes (PU) are known for great property variance, ranging from rigid and hard to flexible and soft. As a result, they have been widely used in modern society. Recently, efforts were made to impart intrinsic self-healing capability to polyurethanes in hopes of developing next generation versions with smart functionality [1,2].

Automotive industries have introduced self-healing coating based on PU to attenuate or obscure the scratches [3,4]. By optimizing the crosslink density while keeping the glass transition temperature low, fine scratch could not result in chain scission as in the case of conventional paint but plastic deformation. Under the heat of the sun and outdoor temperature, the deformed parts would be gradually restored due to the viscoelasticity driven plastic flow. However, the paint did not self-repair if scratches were deep enough to sever the bonds. For purposes of creating coating capable of recovering from fracture, Ghosh and Urban synthesized heterogeneous PU networks containing oxetane-substituted derivative of chitosan [5]. Upon mechanical damage of the network, four-member oxetane rings opened to generate two reactive ends. When exposed to ultraviolet light, chitosan chain scission occurred, which formed crosslinks with the reactive oxetane ends, thus offering one-way repairing capability of crack. Ling et al. further coupled coumarin with PU as a photoreversible crosslinker [6,7]. By using its reversible photocyclization habit, cracks on the polymer films were repeatedly mended by ultraviolet illumination or sunlight.

Yamaguchi et al. prepared crosslinked PU with different crosslinking densities by changing the molar ratio of [NCO] to [OH] [8]. The cleaved sample sheet made from a proper reaction ratio was rapidly re-bonded at room temperature within 10 min as a result of the strong topological interaction (physical entanglement) of dangling chain ends. Amamoto et al. [9] reported self-healing crosslinked PU based on radical reshuffling of thiuram disulfide (TDS) units under the stimulation of visible light at room temperature and without solvent. Since the S—S bonds in the incorporated TDS units homolytically dissociated in visible light, the radical reshuffling reactions allowed reorganization of the linking units in the polymer and self-healing of damage. Recently, Du et al. produced linear PU through Diels—Alder (DA) reaction between a PU prepolymer end-capped with furan groups and bismaleimide [10]. The filmy specimen was cut and heated at 120 °C for 5 min, then cooled down to 60 °C and kept for 24 h, recovering 80% tensile strength taking advantage of reversible DA chemistry [11].

On the whole, not many healing mechanisms have been involved in PU, as reflected by the above brief summary. Additional

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healing chemistries should be explored to meet the application requirements of PU in different occasions, such as opaque bulk materials. So far, self-healing approaches can be classified into two categories: extrinsic and intrinsic self-healing [1–3,11–14]. The former takes effect by the embedded microcapsules containing healing agent, while the latter is able to heal cracks by the polymers themselves without the need of additional healing agent. The reversible bonds responsible for intrinsic self-healing consist of covalent and non-covalent ones. Besides DA interactions [11], the former includes thiuram disulfide units [9], coumarin derivatives [6,7], alkoxyamine moieties [15], acylhydrazone bonds [16], disulfide links [17], and Ru-catalyzed shuffling of C–C bonds [18], while the latter involves hydrogen bonding [19], ionomers [20], π–π stacking [21], and van der Waals' actions [8], etc.

Among these candidates, thermally reversible C–ON bond has proved to be an effective measure for realizing self-healing of stiff polymers like alkoxyamine-crosslinked polystyrene [15]. Owing to synchronous bond fission and radical recombination at certain hemolytic temperature, cracked parts can be reconnected repeatedly, without losing integrity and load bearing ability of the material even above T_g. In this context, it is worth verifying whether C–ON bond also enables self-healing of PU elastomer, which has wider range of application.

Here in this work, an alkoxyamine-based diol is synthesized, whose hydroxyl groups can easily participate in the subsequent production of PU. As shown in Fig. 1, alkoxyamine moieties are eventually integrated with PU as intermolecular links attached to the hard segments of the polymer chains responsible for crack rehabilitation, while the soft segments are advantage to interaction of dangling chains across the fracture faces. The design is believed to benefit strength restoration of the polymer.

2. Experimental section

2.1. Materials and reagents

4-OH-TEMPO, α-methyl styrene, benzoyl peroxide (BPO), ethanol, polyethylene glycol (PEG) (PEG200, PEG400, PEG600, M_w = 200, 400, 600, respectively), bisphenol A (BPA) and ethyl acetate were obtained from Alfa Aesar GmbH, Germany. Dibutyltin dilaurate (DBTL) was purchased from Sigma Aldrich Co., whereas the tri-functional homopolymer of hexamethylene diisocyanate (tri-HDI) (Desmodur N3300) was supplied by Bayer Materials Science AG. All the chemicals were used as received.

2.2. Synthesis of 4-hydroxy-1-(2′-hydroxy-1′-phenyl-1′-methyl) ethyl-TEMPO (diol)

The alkoxyamine-based diol was synthesized as follows (Scheme 1). BPO (14.52 g, 0.06 mol) and 4-OH-TEMPO (20.64 g, 0.12 mol) were dissolved with 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 being evaporated 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, to give the diol as a pale yellow solid (12.8 g, yield = 34.7%). ^{1}H NMR ($CDCl_3$): δ/ppm 0.89 (3H, CH_3), 0.99 (3H, CH_3), 1.19 (3H, CH_3), 1.20 (3H, CH_3), 1.58 (3H, CH_3), 1.53–1.84 (4H, 2 CH_2), 3.84 (1H, CH), 3.96 (1H, CH), 4.05 (1H, CH), 7.21–7.54 (5H, aromatic); ^{13}C NMR ($CDCl_3$): δ/ppm 21.96, 22.06, 23.93, 34.19, 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 $C_{18}H_{29}NO_3$ $[M + 1]^+$ found 308.2.

2.3. Preparation of polyurethane crosslinked by alkoxyamines

PU networks were prepared by reacting tri-HDI with diol and PEG (Scheme 2). Firstly, the reaction mixtures were completely dissolved together with the catalyst dibutyltin dilaurate in an appropriate amount of ethyl acetate, offering homogeneous and transparent solution. Then, the solution was poured into a silicone rubber mold at 20 °C under argon atmosphere, allowing reaction for 12 h. Afterwards, the compounds were put in a vacuum oven at 35 °C for 48 h. The molar ratio of the components in the PU (based

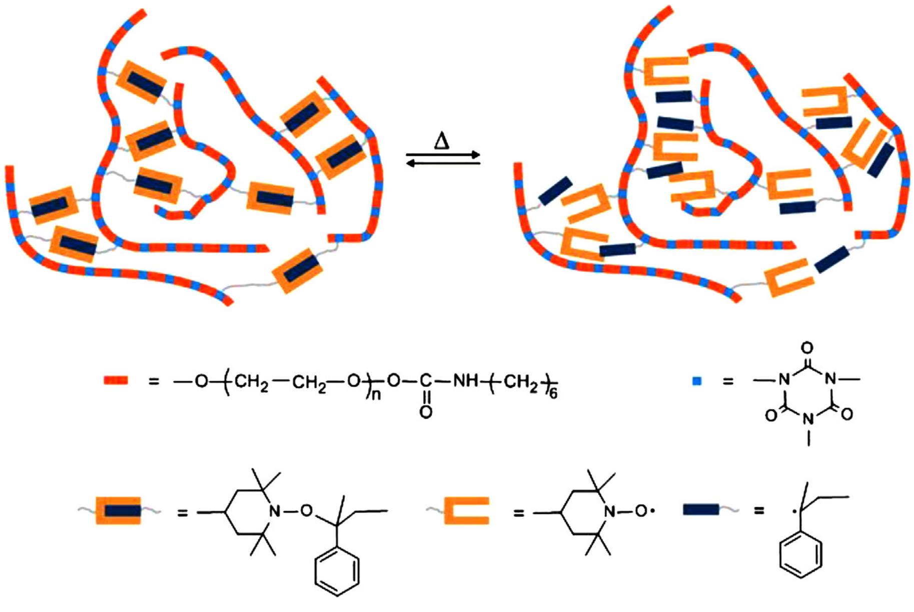
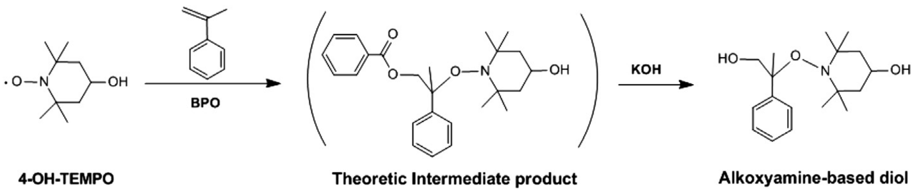


Fig. 1. Healing mechanism of polyurethane crosslinked by alkoxyamines.



Scheme 1. Synthesis of the alkoxyamine-based diol.

on the stoichiometric ratio of NCO and OH), tri-HDI/PEG/diol, was 1:0.58:0.87. Since PEG200, PEG400 and PEG600 were employed as chain extenders to tune the networks, respectively, the corresponding polyurethanes were denoted by HDI/PEG200/diol, HDI/PEG400/diol and HDI/PEG600/diol.

To study the relationship between fission of alkoxyamine moieties and thermal stability of the material when heated, control polyurethane without PEG was prepared, labeled as HDI/diol. In addition, control polyurethanes HDI/PEG/BPA (by replacing diol with BPA) and HDI/PEG were designed to investigate the effect of entanglement of PEG molecular chains on the self-healing performance.

2.4. Characterization

^{1}H NMR and ^{13}C NMR spectra were collected by VARIAN Mercury-Plus 300 (300 MHz) with chloroform ($CDCl_3$) as a solvent. Mass spectrometry (MS) measurement was conducted on Thermo Finnigan LCQDECA P LC-MS spectrometer. Thermogravimetric analysis (TGA) was performed on TA Instruments TGA Q50 at a heating rate of 10 °C/min using a nitrogen purge. Dynamic mechanical analysis (DMA) measurements and creep tests were carried out with a 01Db-metravib-DMA25 under nitrogen atmosphere using tensile mode. Creep stress was set at 0.4 MPa. Electron spin resonance (ESR) spectra were recorded at different temperatures by JEOL JES-FA200 to investigate thermal reversibility of the materials. Molecular weight between crosslinks of the cured PU, M_c, was calculated from Ref. [22]:

$$E' = 3\frac{\rho}{M_c}RT\left(1-\frac{2}{\varphi}\right)$$

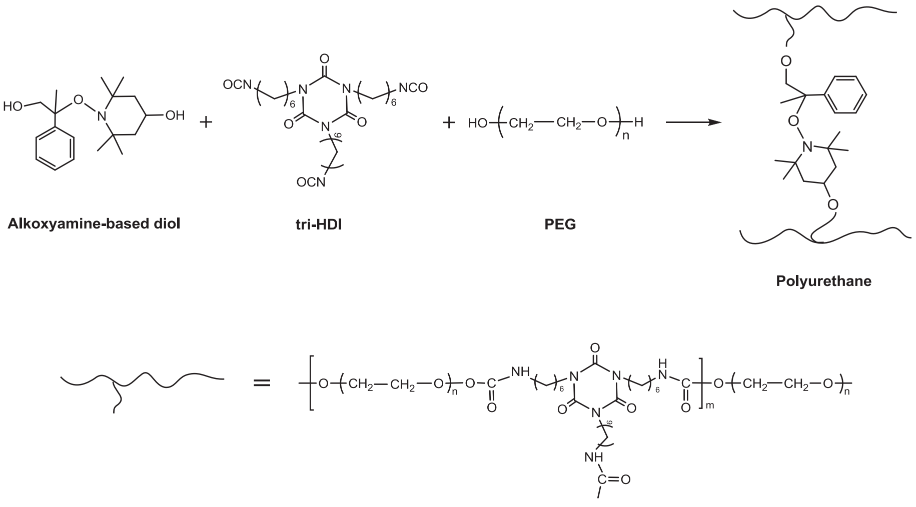
where E' stands for storage modulus at rubbery plateau zone, ρ density, R gas constant, T absolute temperature, and ϕ functionality of PU, respectively. In this work, E' values at $T = T_g + 30$ °C were used for the calculation.

Self-healing performance was characterized by tensile tests, which were performed on rectangle-shaped specimens ($100 \times 10 \times 0.9$ mm^3) at a crosshead speed of 10 mm/min using a universal testing machine (SANS CMT 6103). The fractured parts of the specimens were put together, and treated at 80 °C under argon atmosphere for 2.5 h. Having been cooled to room temperature, the fixed specimen was tested to failure again. The ratio of tensile strength of the healed specimen to that of the virgin one gave healing efficiency. The tests were repeated for several times to study the multiple healing ability. Each batch included six specimens to yield average value. It is worth noting that tensile test is inherently designed to characterize bulk continuum deformation leading up to failure, but gives little information about failure itself. The ultimate stress and strain values might be misleading as the material necks prior to failure (which is not applicable for the polyurethane studied in this work). Crack propagation test focusing on characterizing the regime of material response is the most relevant to self-healing functionality. Employment of suitable specimen geometry is critical for evaluation of self-healing materials [23].

3. Results and discussion

As mentioned in the Introduction (Fig. 1), the planned crack healing of PU depends on dynamic equilibrium of C—ON bond fission and radical recombination. Therefore, ESR spectra of the control polymer formed by the reaction of tri-HDI with diol in the absence of PEG were firstly studied to understand the temperature dependence of radical concentration.

Fig. 2(a) shows that radical signal can be observed from 40 °C. Compared with the crosslinking polystyrene reported in our previous work [15], the initial fission temperature of the polyurethane



Scheme 2. Synthesis of polyurethane crosslinked by alkoxyamines.

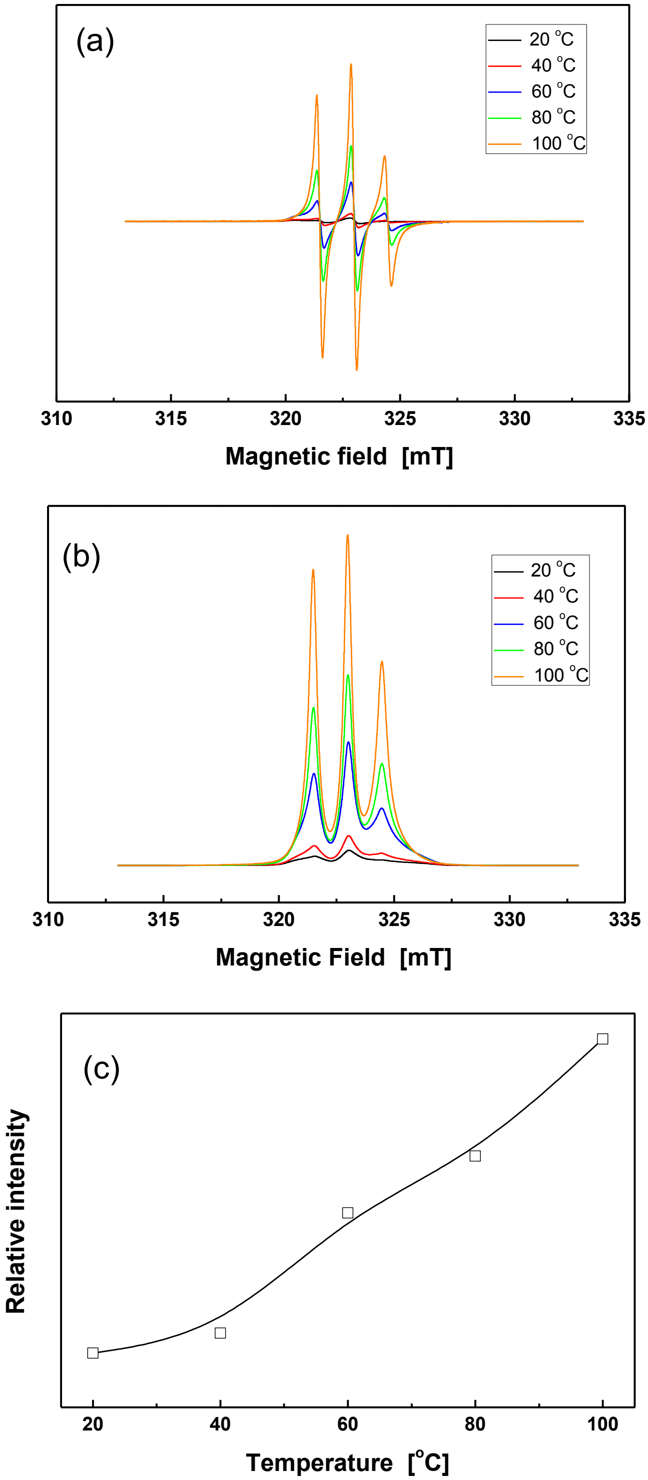


Fig. 2. (a) Typical ESR spectra of HDI/diol measured at various temperatures. (b) Normalized absorption lines converted from the data of (a). (c) Temperature dependence of relative ESR signal intensities calculated from integral areas of the normalized absorption lines in (b).

is much lower because of the methyl group of α-methyl styrene attached to the C atom in C–ON bond. It increases steric hindrance and lowers bonding energy of C–ON bond [24]. By using the data in Fig. 2(a), normalized ESR curves can be calculated (Fig. 2(b)), from which the relative ESR signal intensities are plotted as a function of temperature in Fig. 2(c). It can be seen that the signal keeps on increasing with a rise in temperature, meaning crosslinking and decrosslinking of the PU via dynamic C–ON bonding would be more effective at elevated temperature. No healing would take place below 40 °C.

Since the above study reveals that the C–ON bond in PU can be homolyzed as expected, its thermal reversibility should be known from the ESR spectra collected in the course of repeated heating–cooling cycles. Fig. 3 shows the variation of relative ESR signal intensity. Evidently, radical concentration changes up and down over the thermocycling as a result of reversible C–ON bond fission and radical recombination. A careful survey of the plots indicates that the ESR signal intensity at 20 °C gradually increases despite the fact that difference between the data at 80 and 20 °C remains nearly constant. The trend is more obvious when molecular weight of the PEG segment decreases. It should result from the permanent dissociation of a few alkoxyamines as the combination of methylene radicals and nitroxide radicals is somehow obstructed in solid [25]. The shorter PEG chains lead to higher crosslinking density of the polyurethane network structure and lower molecular mobility, which reduces probability of collision of the radicals to re-form C–ON bonds. Accordingly, HDI/diol and HDI/PEG200/diol exhibit relatively poor reversibility.

In fact, all the polyurethanes studied here possess better reversibility than alkoxyamine-crosslinked polystyrene [15]. This is because T_g of soft segments in polyurethane is generally lower than room temperature, which benefits the movement of molecular chains of the material and hence reconnection of radicals at room temperature. For alkoxyamine-crosslinked polystyrene, when it is cooled below its T_g (~120 °C), the molecular chains have difficulty in moving. Therefore, under the same cooling conditions, higher reversibility of C–ON bond can be achieved in the material with lower glass transition temperature.

To further understand the fission/recombination behavior of alkoxyamine groups in the polyurethanes, isothermal ESR spectra of each sample at 80 °C were scanned for every 5 min. As shown in Fig. 4, the relative radical signal intensities nearly do not change with time. It demonstrates that dynamic equilibrium between homolysis and rebonding of C–ON bonds can be quickly achieved. When the polymer is healed at 80 °C, concentration of the radicals would stay almost the same, which ensures sufficient amount of radicals are involved in the healing action.

Fig. 2 shows that radical concentration of the material increases with increasing temperature. It implies more and more C–ON bonds are involved in the dynamic reversible reaction when heated. Therefore, thermal stability of the PU should be understood to reveal the effect of C–ON bonds.

It is found in Fig. 5(a) that all the polyurethanes possess acceptable thermal stability, as their temperatures of 1% weight loss are higher than 200 °C. Relatively, HDI/PEG400/diol and HDI/PEG600/diol are more stable, showing 1% weight loss at about 260 °C. This is because the concentration of C–ON bond in the two polyurethanes is lower due to the appearance of PEG with higher molecular weight, and hence the reversible crosslinkages are less. The negative influence of homolysis of C–ON bonds on their pyrolytic resistance becomes less significant. Nevertheless, when comparing HDI/PEG400 and HDI/PEG400/diol, we can see that the onset thermal degradation temperature of the latter is about 30 °C higher. The result suggests that the soft PEG segments, rather than thermo-sensitive alkoxyamine moieties, are responsible for the initial decomposition of the polyurethane at lower temperature. In fact, heat resistance of polyurethane itself is not high. After incorporation of alkoxyamines into the molecular chains, the radicals generated by the reversible reaction of C–ON bonds might probably combine with the radicals of pyrolysis products of other bonds, so that thermal stability of the polyurethane is somewhat

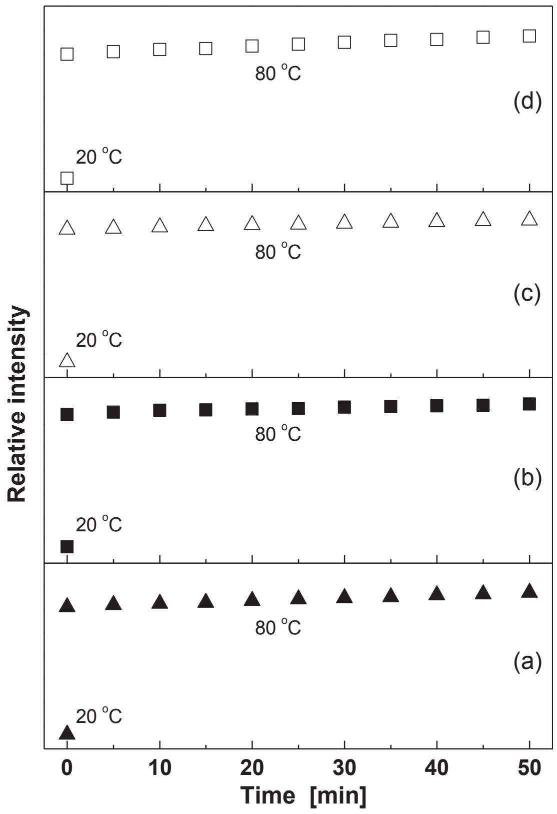


Fig. 4. Relative ESR signal intensities of (a) HDI/diol, (b) HDI/PEG200/diol, (c) HDI/PEG400/diol and (d) HDI/PEG600/diol measured at 80 °C as a function of time.

improved. On the basis of the above discussion, it is known that the multi-peaks on the derivative thermogravimetric curves (Fig. 5(b)) can be respectively attributed to the weight loss dominated by PEG, alkoxyamines and HDI segments with a rise in temperature.

Since the dynamic reversibility of C—ON bonds is temperature dependent, not only thermal stability but also dynamic mechanical property of the polyurethanes should be affected by the alkoxyamine moieties. Fig. 6 plots the results of DMA tests, indicating that longer PEG segments leads to lower T_g of the polymer, narrower width and higher intensity of tan δ peak. It is understandable because in the case of identical molar ratio of hard and soft segments in the polyurethane networks, the higher molecular weight of the chain extender, the lower crosslinking density. Accordingly, T_g of the polyurethane is reduced, and tan δ peak becomes higher. Additionally, with increasing molecular weight of PEG, the fraction of hard segments in the polyurethane decreases and their contribution to the chains motion is weakened. The spectra of internal friction are gradually governed by the characteristics of PEG, so that the tan δ peak narrows down. In contrast, chain lengths of PEG200 and diol resemble each other in HDI/PEG200/diol, which results in two maxima on its tan δ curve representing motions of both soft and hard segments, respectively. With respect to HDI/diol that excludes the chain extender PEG, it has the highest crosslinking density. Consequently, its tan δ peak is the lowest, while T_g the highest.

In accordance with the thermal reversibility study by means of ESR spectroscopy, repeated DMA scans of typical polyurethanes

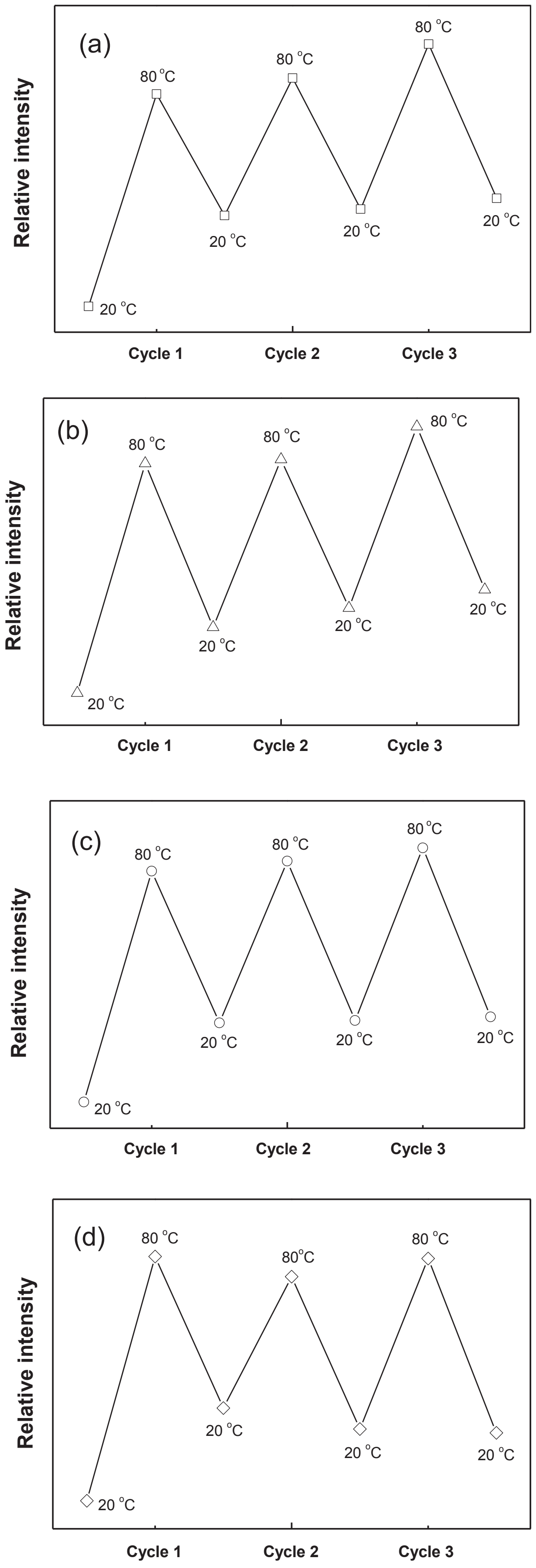


Fig. 3. Relative ESR signal intensities of (a) HDI/diol, (b) HDI/PEG200/diol, (c) HDI/PEG400/diol and (d) HDI/PEG600/diol measured during heating–cooling cycles between 20 and 80 °C.

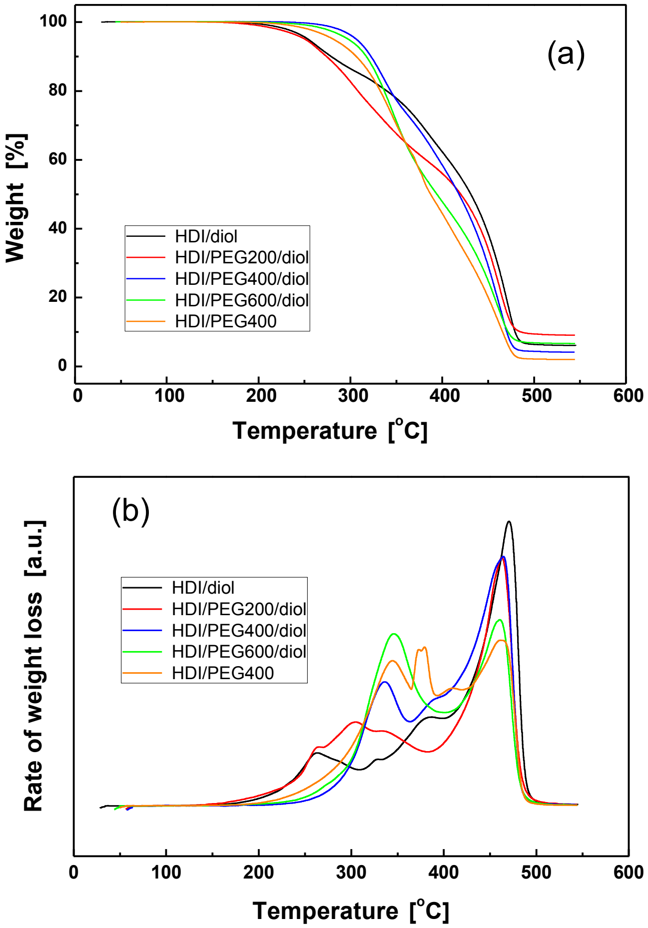


Fig. 5. Pyrolytic behaviors of polyurethanes.

were carried out (Figs. 7 and 8). With increasing the scan numbers, the temperature dependences of storage modulus and tan δ are almost the same, except that the tan δ peaks slightly shift to higher temperature. Moreover, storage moduli of the polyurethanes at elastomeric state do not decay during the multiple scans, demonstrating that the C—ON bonds are not completely debonded even at elevated temperature and the polymers still possess certain load-bearing ability in the course of dynamic reversible reaction of C—ON bonds. It can be regarded as a technical merit of the material, which avoids possible deformation of the end-products even when crack healing is being conducted above T_g.

By using the data of storage moduli of Figs. 6–8, molecular weights between crosslinks, M_c, of the polyurethanes were estimated (refer to Experimental for more details). It can be seen from Table 1 that crosslinking densities marginally decrease with the scan numbers due to appearance of a few permanently cleft radicals, which coincides with the results of Fig. 3.

Fig. 9 shows tensile stress–strain curves of the polyurethanes. Owing to different concentrations of the components, the polyurethanes exhibit different mechanical responses. For the polymers containing PEG with proper molecular weight, balanced performance is acquired offering higher strength and toughness (see the curves of HDI/PEG200/diol and HDI/PEG400/diol in Fig. 9). When PEG600 is used, however, crosslinking density of the PU decreases and the networks have to be more inhomogeneous. As a result, HDI/PEG600/diol possesses the lowest tensile properties. On the other hand, HDI/diol is completely made of hard segments, which provide the material with higher strength and stiffness but lower elongation to break. On the basis of these results and application prospects as well, HDI/PEG400/diol is selected for the healing performance evaluation hereinafter.

Fig. 10 plots creep curves of the polyurethanes, which exhibits their mechanical performance from another angle. In general, the time dependence of creep strain of plastics consists of four stages [26]: (i) initial rapid elongation, which is independent of time and is attributed to the elastic and plastic deformation of the polymer; (ii) primary creep, the creep rate starts at a relatively high value, and then decreases with time; (iii) secondary creep and (iv) tertiary creep, in which the creep rate increases rapidly and final creep fracture occurs. For the polyurethanes shown in Fig. 10, no secondary and tertiary creeps are perceived within the time of interest. HDI/diol has the lowest creep strain because of lack of soft PEG. In contrast, creep strain of HDI/PEG600/diol is the highest owing to its longest soft segment PEG600, which results in low crosslinking density (Table 1) and high deformability. Compared to other materials, the appropriate combination of soft and hard segments of HDI/PEG400/diol provides the best recovery ability of deformation. Its permanent deformation is quickly reduced to zero after removal of creep stress, indicating its application potentiality as elastomeric material.

Prior to quantitative characterization, self-healing performance of the materials was qualitatively characterized (Fig. 11). Firstly, the strip-like specimen of HDI/PEG400/diol was cut apart in the middle. Then, the broken parts were brought together in alignment and treated at 80 °C for 2.5 h in argon atmosphere. It could be found that the crack line disappeared, and the healed specimen can bear a weight of 200 g. In order to verify the repeated healing ability of the material, the repaired specimen was cut again from the upper left to the lower right across the trace of the first cut, followed by the

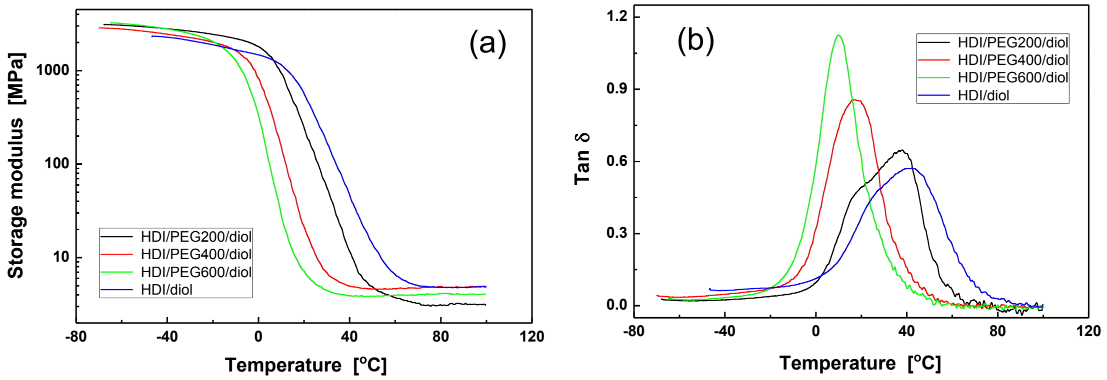


Fig. 6. Temperature dependences of (a) storage modulus and (b) tan δ of polyurethanes.

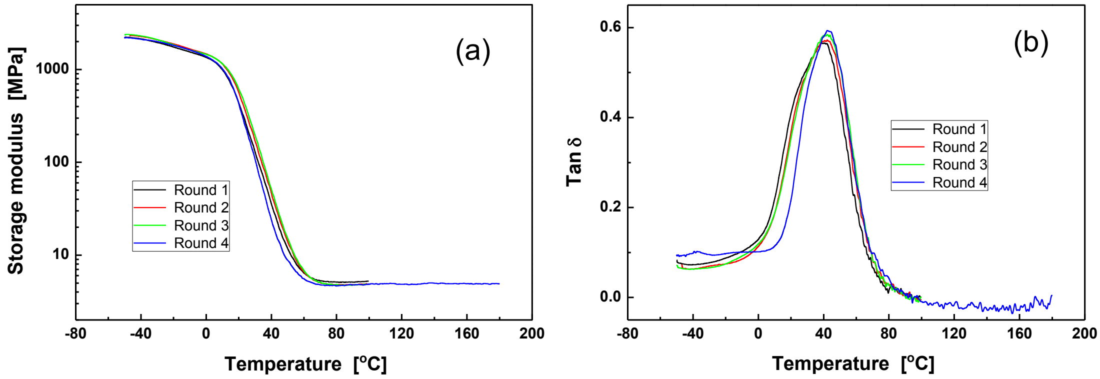


Fig. 7. Temperature dependences of (a) storage modulus and (b) tan δ of HDI/diol measured by repeated scans.

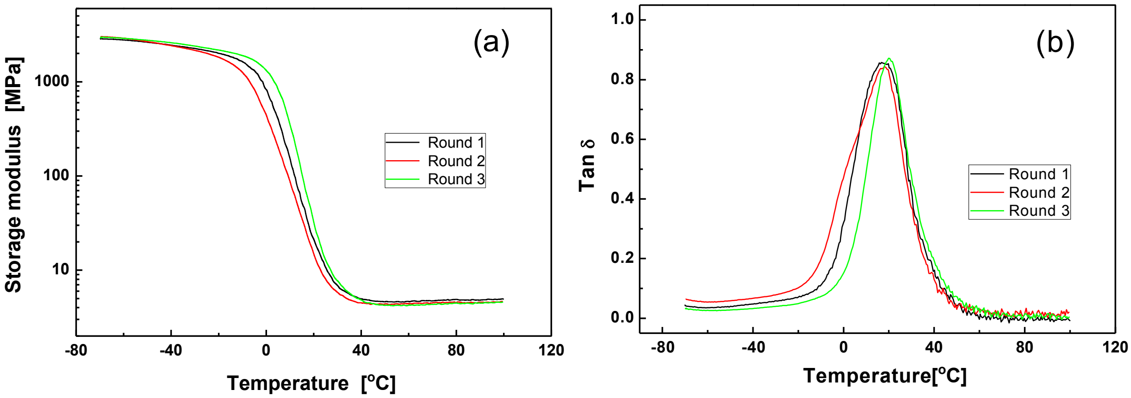


Fig. 8. Temperature dependences of (a) storage modulus and (b) tan δ of HDI/PEG400/diol measured by repeated scans.

Table 1
Molecular weight between crosslinks, M_c, of the polyurethanes estimated from repeated DMA scans.

PU	M_c (g/mol)			
	Cycle 1	Cycle 2	Cycle 3	Cycle 4
HDI/diol	568	605	605	635
HDI/PEG200/diol	524	–	–	–
HDI/PEG400/diol	605	643	660	–
HDI/PEG600/diol	696	–	–	–

second healing as mentioned above. The healed version is also recovered as evidenced by the regained load bearing ability. Finally, the third cut was made on the specimen from the upper right to the lower left in hopes of intersecting the traces of the former two cuts. Having been healed under the same circumstances, the specimen can also be stretched and folded.

Fig. 12 gives the tensile stress–strain curves of HDI/PEG400/diol specimen, which experienced three successive rupture-healing tests. Like the result of above qualitative assessment, the self-healing capability of the polymer is evidenced once more. Tensile

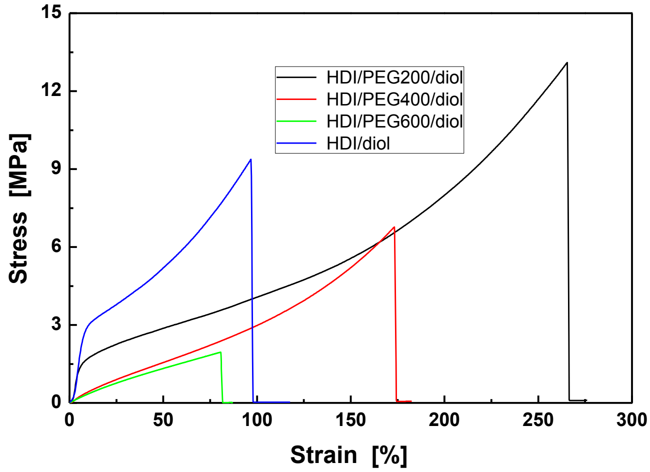


Fig. 9. Tensile stress–strain curves of polyurethanes.

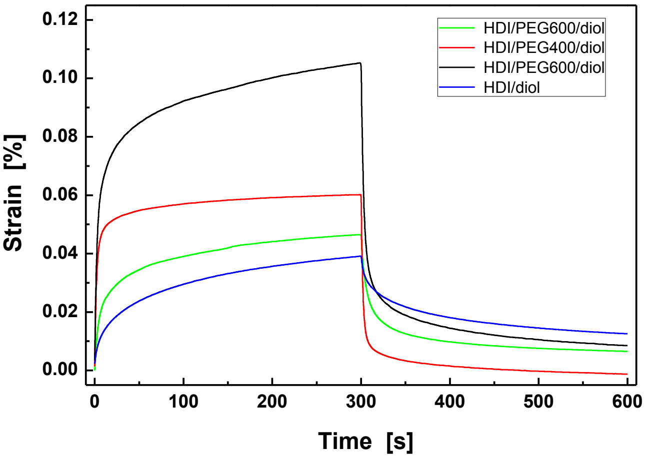
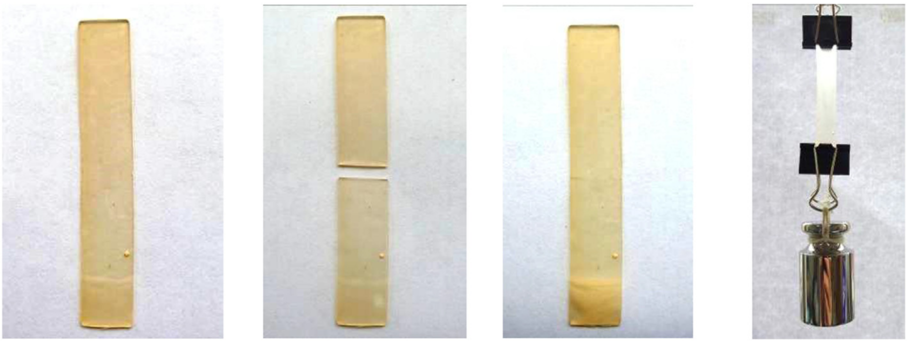
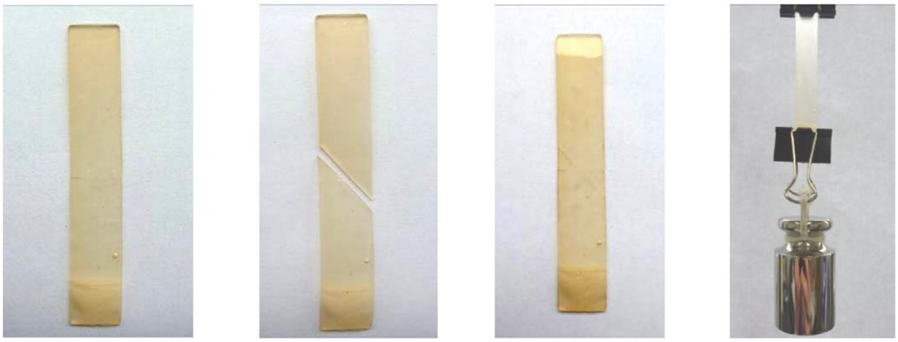


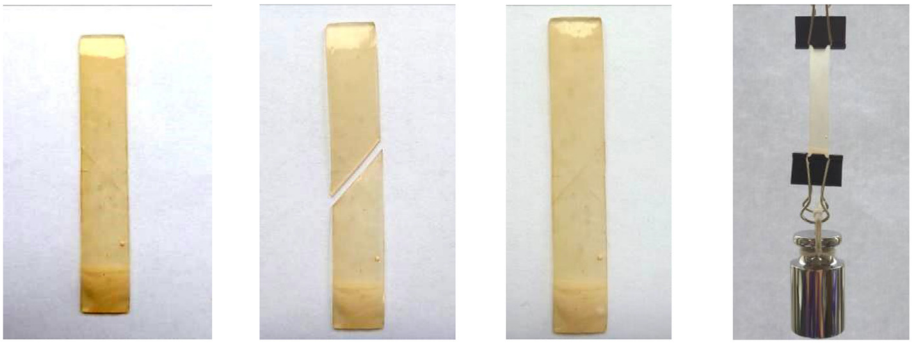
Fig. 10. Typical tensile creep strain–time curves of polyurethanes at 20 °C.



Virgin 1st cut 1st healed Stretching of the 1st healed specimen



1st healed 2nd cut 2nd healed Stretching of the 2nd healed specimen



2nd healed 3rd cut 3rd healed Stretching of the 3rd healed specimen

Folding of the 3rd healed specimen

Fig. 11. Repeated macro-repairing of crossed ruptures of HDI/PEG400/diol.

strength of the specimen can be repeatedly restored, and the efficiency of the first healing event is about 70%. It is worth noting that the healing efficiency decreases after each test. The main reason should lie in the softness of the polyurethane. It was hard to force the fractured surfaces of the broken specimen to have intimate contact during rehabilitation [27]. Therefore, insufficient amount of C—ON bonds were involved in the radical recombination across the interface. In addition, the appearance of permanently disconnected radicals discussed above would also reduce the reaction efficiency.

When PEG400 in HDI/PEG400/diol is replaced by PEG600, the material is also self-healable, but the healing efficiencies determined by successive rupture-healing tests are 51.8 ± 7.3, 40.5 ± 6.4

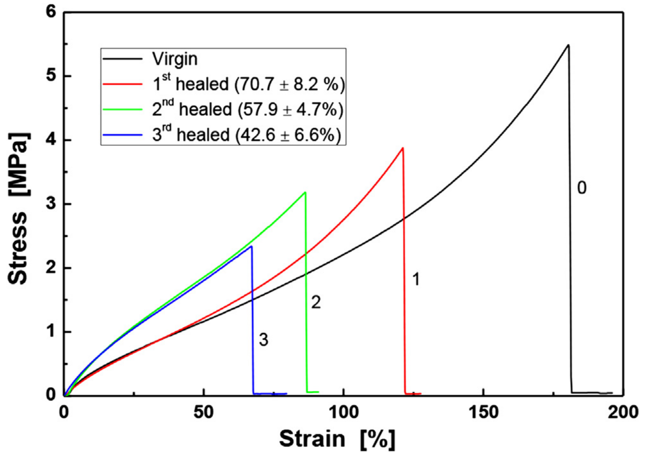


Fig. 12. Typical tensile stress–strain curves of virgin and repaired HDI/PEG400/diol.

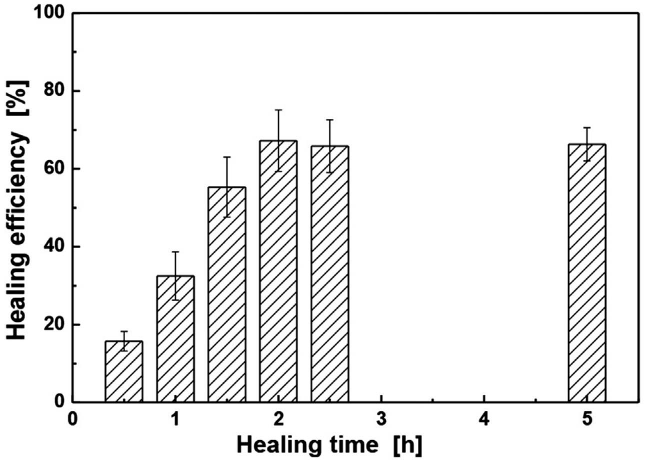


Fig. 13. Effect of healing time on healing efficiency of HDI/PEG400/diol.

and 33.3 ± 5.1%, respectively. It demonstrates that the longer molecular chain of PEG600 leads to lower content of alkoxyamines in the polyurethane. Naturally, lower healing efficiency than the case of HDI/PEG400/diol is observed.

Fig. 13 examines the effect of healing time on healing efficiency of HDI/PEG400/diol. The healing efficiency increases with healing time, and then levels off, which follows the general law of other self-healing materials. The maximum is achieved at 2 h, and further increase of time makes no evident change. It means that the dynamic equilibrium is established after 2 h of healing.

To confirm whether the reversible reaction of alkoxyamines plays the leading role in crack healing, control experiments were done by using HDI/PEG400/BPA specimen, in which BPA substituted diol. It was found that no detectable healing effect was seen after the same procedures as stated above. Furthermore, another control healing experiment was conducted on HDI/PEG400, showing 10.4% of tensile strength can be recovered as a result of chain entanglement. Since tensile strength of virgin HDI/PEG400 is 0.33 MPa, the healing efficiency contributed by physical interaction in HDI/PEG400/diol (with tensile strength of 6.78 MPa for the virgin specimen) can be roughly estimated as: (0.33 MPa × 10.4%)/6.78 MPa = 0.5%, an ignorable figure.

The critical role of C–ON bond was also identified as follows. The fractured surfaces of the tensile failure specimen of HDI/PEG400/diol were firstly exposed to air at 80 °C for 2.5 h. Having been cooled down to room temperature, they were recombined and treated at 80 °C for 2.5 h in air again. No healing effect was detected due to deactivation of the cleft C–ON bonds.

4. Conclusions

Polyurethane elastomer was successfully coupled with self-healing ability by crosslinking the backbone made of tri-HDI and PEG with alkoxyamine-based diol. The thermally dynamic reversible equilibrium between fission/recombination of C–ON bonds in alkoxyamine moieties enables repeated crosslinking and de-crosslinking of polyurethane chains and hence multiple crack healing. Structure of alkoxyamine-based diol is closely related to homolysis temperature of C–ON bonds, while molecular weight of the chain extender PEG exerts important influence on thermal reversibility, thermal stability and remendability. According to the information revealed in this study, not only mechanical properties but also healing performance can be optimized by careful design of the polyurethane molecules.

Compared to self-healing based on reversible DA bonds, which has to be heated up to a certain temperature for disconnecting the intermonomer linkages and then cooled down for reconnection, the present strategy completes the crack healing only by one step dynamic equilibrium of C–ON bonding. As a result, the possible dimensional change of materials due to creep occurring after retro-DA reaction is avoided. However, the reversible reaction of alkoxyamines is somewhat sensitive to oxygen, so that the healing of our polyurethane elastomer has to be conducted in argon. The shortcomings of air sensitivity and manual intervention can be overcome by tuning the structure of alkoxyamines as revealed in a recent work of the authors [28], which helps to further expand the area of application of the healing chemistry.

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References

[1] Zhang MQ, Rong MZ. Polym Chem 2013;4:4878.
[2] Zhang MQ, Rong MZ. Acta Polym Sin 2012;11:1183.
[3] Zhang MQ, Rong MZ. Self-healing polymers and polymer composites. Hoboken: John Wiley & Sons, Inc.; 2011.
[4] Henderson K, Pohl T, Seubert C. Paint Coatings Ind 2009;5:40.
[5] Ghosh B, Urban MW. Science 2009;323:1458.
[6] Ling J, Rong MZ, Zhang MQ. J Mater Chem 2011;21:18373.
[7] Ling J, Rong MZ, Zhang MQ. Polymer 2012;53:2691.
[8] Yamaguchi M, Ono S, Terano M. Mater Lett 2007;61:1396.
[9] Amamoto Y, Otsuka H, Takahara A, Matyjaszewski K. Adv Mater 2012;24:3975.
[10] Du P, Liu X, Zheng Z, Wang X, Joncheray T, Zhang Y. RSC Adv 2013;3:15475.
[11] Liu YL, Chuo TW. Polym Chem 2013;4:2194.
[12] Blaiszik BJ, Kramer SLB, Olugebefola SC, Moore JS, Sottos NR, White SR. Annu Rev Mater Res 2010;40:179.
[13] Guimard NK, Oehlenschlaeger KK, Zhou JW, Hilf S, Schmidt FG, Barner-Kowollik C. Macromol Chem Phys 2012;213:131.
[14] Billiet S, Hillewaere XKD, Teixeira RFA, Du Prez FE. Macromol Rapid Commun 2013;34:290.
[15] Yuan CE, Rong MZ, Zhang MQ, Zhang ZP, Yuan YC. Chem Mater 2011;23:5076.
[16] Deng GH, Tang CM, Li FY, Jiang HF, Chen YM. Macromolecules 2010;43:1191.
[17] Canadell J, Goossens H, Klumperman B. Macromolecules 2011;44:2536.
[18] Lu Y-X, Guan ZB. J Am Chem Soc 2012;134:14226.
[19] Cordier P, Tournilhac F, Soulié-Ziakovic C, Leibler L. Nature 2008;451:977.

[20] Varley RJ, van der Zwaag S. Polym Int 2010;59:1031.

[21] Burattini S, Colquhoun HM, Fox JD, Friedmann D, Greenland BW, Harris PJF, et al. Chem Commun; 2009:6717.

[22] He MJ, Chen WX, Dong XX. Polymer physics. 2nd ed. Shanghai: Fudan University Press; 2000.

[23] Brown EN. J Strain Anal Eng 2011;46:167.

[24] Marque S, Mercier CL, Tordo P, Fischer H. Macromolecules 2000;33:4403.

[25] Wang F, Rong MZ, Zhang MQ. J Mater Chem 2012;22:13076.

[26] Shi XB, Wu CL, Rong MZ, Czigany T, Ruan WH, Zhang MQ. Chin J Polym Sci 2013;31:377.

[27] Wool RP, O'Connor KM. J Appl Phys 1981;52:5953.

[28] Zhang ZP, Rong MZ, Zhang MQ, Yuan CE. Polym Chem 2013;4:4648.