ORIGINAL ARTICLE

A thermal self-healing polyurethane thermoset based on phenolic urethane

Shan Cao, Shouhai Li, Mei Li, Lina Xu, Haiyang Ding, Jianling Xia, Meng Zhang and Kun Huang

Thermosetting polyurethanes have excellent elastic properties and solvent resistance, but they cannot be reshaped like thermoplastic polymers after molding. In this study, we designed a thermosetting polyurethane based on a reversible reaction between isocyanates and phenolic hydroxyls instead of alcoholic hydroxyls. The phenolic urethane partially decomposed above 120 °C, but the phenolic hydroxyl and isocyanate groups reconnected upon cooling. These reversible urethane bonds contributed to the thermal self-repair of the thermosetting polyurethane network. This thermosetting elastomer was organic-insoluble below 120 °C. Compared to the original material, the healed thermoset preserved approximately 70% of its tensile strength and exhibited 86% elongation at break. This thermosetting polyurethane can be applied in self-healing coatings or adhesives.
Polymer Journal (2017) **49**, 775–781; doi:10.1038/pj.2017.48; published online 6 September 2017

INTRODUCTION

It is desired to create coatings and adhesives that can autonomously repair the damage incurred upon scratching or cracking and fully recover the material properties. These self-healing coatings or adhesives save huge amounts of resources[1–3] and avoid frequent repair. Thermoplastic materials can be reshaped by melting, and, owing to their higher dimensional stability, thermal stability and solvent resistance than plastics,[4] thermosets are irreplaceable in coating or adhesive applications. However, thermosetting resins cannot be reshaped as well as thermoplastic resins because they tend to crosslink and are implastic.[5]

The introduction of microcapsules with a healing agent can be used as a shortcut to heal the microcracks of thermosets, but this method fails to repair macroscopic cuts.[6–10] The noncovalent method based on hydrogen bonding[11–15] or metal-ligand[16–18] coordination is able to heal a polymer multiple times, but the noncovalent bonding becomes much weaker. To solve these problems, series of reversible covalent bonds (for example, disulfide-bonds,[19,20] acylhydrazone bonds,[21] nitroxide bonds,[22] and Diels–Alder addition bonds[23,24]) that can disconnect and reform have been receiving increasing attention. These reversible covalent bonds are especially contributive to the healing ability of polymers. The unstable disulfide groups can cleave by a reduction reaction to form two thiol groups, which can reform disulfide groups through an oxidation reaction.[25,26] Two thiuram disulfide units under visible light can release reshuffling radicals, which in turn generate two new thiuram disulfide units.[27] Thus, a macroscopic self-healing polymeric system was designed depending on the reshuffling of the carbon radicals photoinduced from the trithiocarbonate units.[28] The C–ON bonds in alkoxyamines easily cleave when subjected to temperatures that can induce homolysis, and they immediately recombine through exchange and crossover reactions between the radicals from the original alkoxyamine groups.[29] However, radical systems are prone to unavoidable termination reactions that reduce the reversibility of the networks. Self-healing can also be achieved through the exchange reactions of two acylhydrazones.[21,30] The reversible Diels–Alder reaction[11,12,31,32] between maleimide and furan enables damaged crosslinked polymers to self-heal. Since the retro-Diels–Alder reactions occurs at 60–70 °C, the material is applied at relatively low temperatures. Nevertheless, special chemical groups must be introduced to polymers to obtain the self-healing capacity for reversible covalent bonds, but such treatment is usually expensive or unachievable. These approaches are obviously far from being applicable for commercial thermosetting resins.

Transesterification is also one way to prepare reversible ester bonds. Leibler et al.[2] designed epoxy networks that could topologically rearrange during transesterification without depolymerization and found they were insoluble and processable, but zinc acetate was required as a catalyst. Ying et al.[33] discovered the dynamic exchange of hindered urea bonds between a few molecules and polymers and thereby synthesized poly(urethane-urea)s and polyureas, which can self-repair at low temperature without a catalyst. However, the hindered urea bonds decreased the cohesive energy of the macromolecules and thereby led to poor mechanical properties.

In these studies on reversible covalent bonds, the applications of these self-healing thermosets have been limited by the need of either special non-versatile chemical groups or rigorous operation conditions, such as high temperatures or inert gas environments and low applied temperatures. However, regarding commercial thermosetting resins, these demands obviously limit the practical applications of these self-healing polymers.

As for polyurethane, we wanted to determine whether it was possible to make thermosetting polyurethane self-heal. The urethane bonds in traditional polyurethane are made of alcoholic hydroxyl and isocyanate groups, and thus are stable and indecomposable. Likewise, phenolic hydroxyl can also react with isocyanate, and this reaction (Figure 1) is usually utilized to block the isocyanate and thereby improve its water resistance.[34,35] The phenolic urethane can decompose into phenol and isocyanate again through a reversible reaction.

Under this inspiration, we chose propyl gallate (PG) as a polyphenol instead of using a polyol and synthesized a crosslinked polyurethane that can self-heal under heating. The thermosetting and self-healing properties of this polyurethane were investigated. In addition, the applied temperature could be higher than that required to introduce Diels–Alder reactions in the polymer system. Polyphenol is a raw material that is easy to obtain, and the reversible reaction of phenol and isocyanate is versatile for coating or adhesive applications.

EXPERIMENTAL PROCEDURES
Materials and reagents
Propyl gallate was purchased from Aladdin Industrial Corporation (Shanghai, China). Dibutyltin dilaurate was purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd (Shanghai, China). The polyurethane prepolymer (PTHFT) was synthesized using propyltetrahydrofuran and toluene diisocyanate, the content of isocyanate was 6.2%, and the relative molecular weight was 1350. The PTHFT was purchased from Shanghai Jiren International Trading Co., Ltd (Shanghai, China). *N,N*-Dimethylformamide was purchased from Chinasun

Specialty Products Co., Ltd (Nanjing, China). 1,2,3-Trichlorobenzene was purchased from Aladdin Industrial Corporation (Shanghai, China).

Synthesis of the self-healing polyurethane
A charge of 5.76 g of PG, 60 g of PTHFT (the molar ratio of phenolic hydroxyl and isocyanate was 1:1.08) and 0.33 g of dibutyltin dilaurate was added into a 250 ml stand-up bottle. After the PG was dissolved in the PTHFT, the temperature of the mixture was raised to 100 °C, the bubbles were eliminated under vacuum conditions (0.098 MPa), and then the mixture was poured into tetrafluoroethylene plastic plates, cured at 120 °C for 14 h, and cooled to ambient temperature for 2 h.

Characterizations
Fourier transform infrared spectroscopy analysis. Fourier transform infrared spectroscopy and variable-temperature Fourier transform infrared (FT-IR) were performed using an IS10 FTIR instrument (Nicolet, Waltham, MA, USA). The samples were smeared on a NaCl window plate and scanned from 4000 to 400 cm^{-1}. The temperature ranged from 120 to 190 °C.

Dynamic mechanical analysis. A dynamic mechanical analysis was conducted using a TA DMA-Q800 instrument with a film tension configuration. All samples had dimensions of 50 mm × 6.5 mm × 20 mm and were swept from −80 to 150 °C at a heating rate of 3 °C min^{-1} and a frequency of 1 Hz.

Tensile properties analysis. Tensile properties were measured using a CMT4303 universal test machine (MTS) with a large deformation configuration following the GB/T 528-1998 standard. The test speed of the machine was 500 mm min^{-1}, and the test region of the samples was 20 mm × 4 mm × 2 mm. Five replicates were tested for each sample to reduce the error.

Differential scanning calorimeter. Differential scanning calorimeter was performed using a Perkin-Elmer Diamond DSC calorimeter. The samples for differential scanning calorimeter were weighed in an aluminum pan, which was then sealed. The scanning differential scanning calorimeter measurements were carried out at heating rates of 5, 10, 15 and 20 °C min^{-1} from 20 to 200 °C in a nitrogen atmosphere.

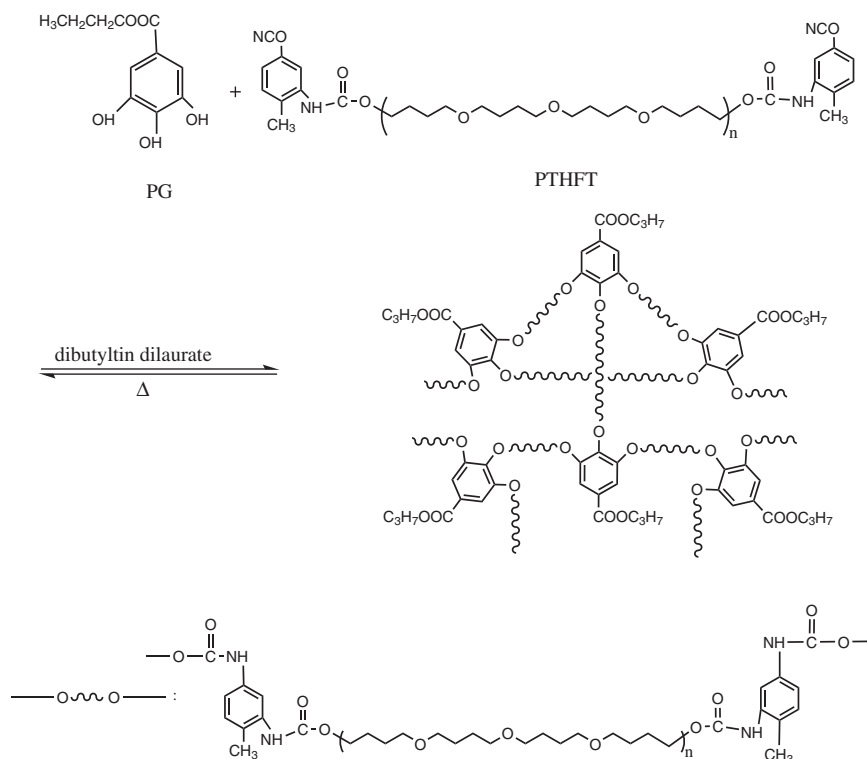**Figure 1** The reversible reaction of phenol-type urethane.

Figure 2 Thermosetting polyurethane network based on phenol-type urethane.

RESULTS AND DISCUSSION

Polymerization and characterizations of the self-healing network

propyl gallate has three phenolic hydroxyls, which undergo additional reactions with PTHFT. The crosslink and reversible reactions between PG and PTHFT are shown in Figure 2. Infrared spectroscopy was conducted on the PG, PTHFT and polyurethane (Figure 3) to verify the polymerization reaction. For PG and PTHFT, the characteristic peak at 2250–2270 cm^{-1} is indicative of the isocyanate stretching vibrations, while the peak at 3500 cm^{-1} is the infrared absorption of the phenolic hydroxyls. The self-healing polyurethane does not exhibit an obvious peak in these ranges, which indicates that the isocyanate was nearly completely consumed by the phenolic hydroxyl. In addition, the presence of N–H (3275–3343 cm^{-1}) and C=O (1700–1780 cm^{-1}) indicates the formation of urethane bonds, and the strong stretching vibration peak at 1210–1220 cm^{-1} is attributed to the appearance of C=O connected to N–H.[35,36] The infrared spectroscopy confirms the polymerization of PG and PTHFT and proves that the network of phenolic hydroxyl-based thermosetting polyurethane was successfully prepared.
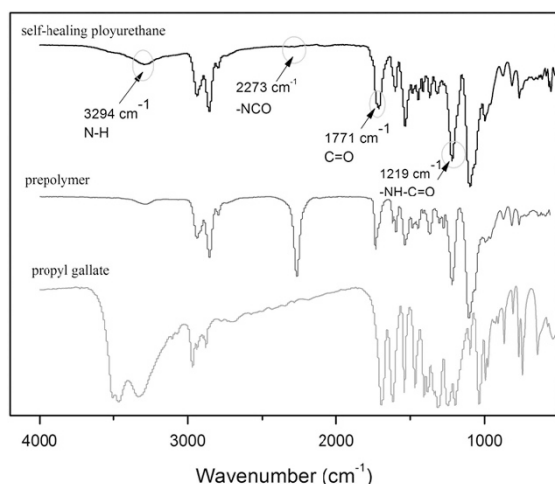

Figure 3 Infrared spectroscopy of the monomers and polyurethane. A full colour version of this figure is available at the *Polymer Journal* journal online.

Because of their dimensional network, thermosetting polymers are hard to dissolve and only swell in organic solvents, even at high temperatures. As shown in Figure 4a, after soaking in N,N-dimethyl-formamide at 25 °C for over 100 h, the polyurethane was insoluble and swollen. The polyurethane was then placed into trichlorobenzene at 25 °C, and the temperature was raised to 80, 100 and 120 °C in sequence to observe the volume changes (Figure 4b). The volume of the original samples at 25 °C was 1 cm^3; after 1 h of soaking at 80 and 100 °C, the volumes of the swollen samples became 4 and 5 cm^3, respectively. When the temperature increased to 120 °C, the sample was still insoluble. However, after 5 h of immersion at 120 °C, the samples became partially dissolved in trichlorobenzene, and the volume of the swollen sample dramatically increased to 10 cm^3. The reason for this increase was that the networks of the polyurethane were no longer stable and became partially damaged due to the temperature rise in the solvent. After being further soaked in trichlorobenzene at 120 °C, the sample completely dissolved in the solvent, indicating that the polyurethane networks were completely damaged after the temperature increased. The dissolution experiments revealed that portions of the covalent bonds disconnected in the polyurethane network, and then, the network was able to dissolve as the solvent temperature increased to 120 °C.

Depolymerization of the self-healing network

The dissolution experiments confirmed that the polyurethane network was damaged at approximately 120 °C. To obtain more information about the depolymerization, we used DMA to scan the polyurethane from −80 to 150 °C (Figure 5). Its glass transition temperature (T_g) is −10.28 °C. The storage modulus profiles in Figure 5 show a two-stage decrease process. The first drop in the storage modulus can be attributed to the glass transition between −50 and 10 °C, and the second drop occurs above 120 °C. Conventionally, the dissipation factor (tanδ) of a material can be obtained from a DMA in which the sample shows a sinusoidal trend during a temperature ramp. However, our sample exhibited an unusual trend on the tanδ curve after the plateau above 120 °C, and the storage modulus dropped rapidly. This result was most likely due to the drop in the modulus caused by depolymerization. The urethane bonds disconnected at approximately 120 °C, which was confirmed from the dissolution experiments. Therefore, the second decrease in the storage modulus can be attributed to the disassociation of the urethane. The dissolution
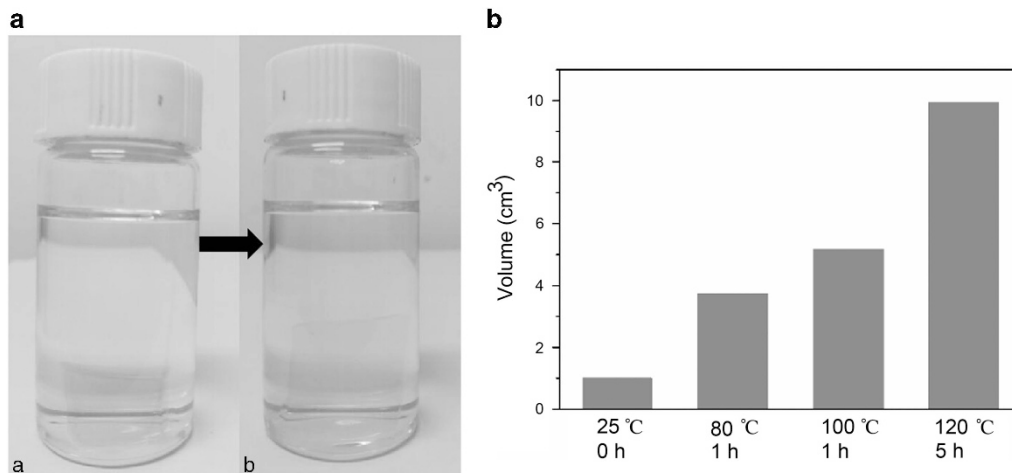
Figure 4 (a) Swelling of the polyurethane sample in DMF at room temperature and (b) the volume variations of the samples in trichlorobenzene at different temperatures. DMF, N,N-Dimethylformamide. A full colour version of this figure is available at the *Polymer Journal* journal online.

experiment and DMA results agree very well and indicate that the reversible reaction between the phenolic hydroxyl and isocyanate occurred at approximately 120 °C.

Variable-temperature FT-IR, which intuitively displays the changes in the covalent bonds, was used to track the dynamic process of the disconnection and reconnection of the reversible urethane bonds. The mixture of PG and PTHFT was cast on the NaCl window and cured at 120 °C for 14 h after pretreatment (dissolution, bubble elimination and homogeneous mixing). The FT-IR spectra were scanned from 25 to 190 °C and then to 120 °C in 0.5 h and are shown in Figure 6.

Herein, a –NCO peak was not observed from 25 to 110 °C. The absorption peak of –NCO (2273 cm^{-1}) appears above 120 °C, at which temperature the urethane started to cleave. This result highly agrees with the dissolution experiment and DMA results. Above 170 °C, the peak of –NCO did not become stronger, indicating that the reversible reaction between the phenolic hydroxyl and NCO groups reached a new chemical equilibrium. The peak of NCO disappeared again when the sample was cooled down to 120 °C in
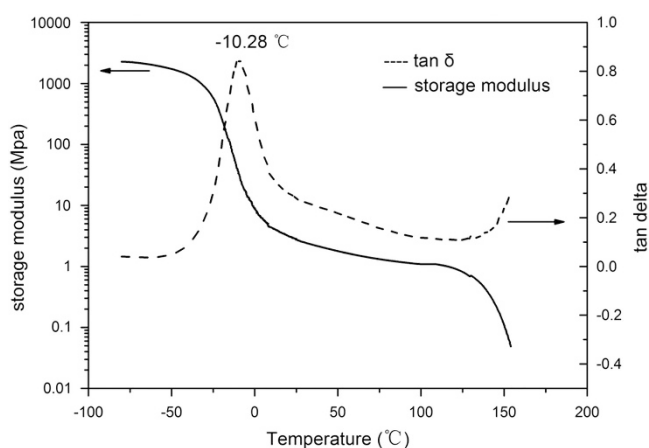
0.5 h; during this slow cooling process, the isocyanate and phenolic hydroxyl groups reconnected, which enabled reversible polyurethane bonding.

Since this polyurethane could self-heal, we sought to determine whether the mechanical performance could recover after breakage and self-healing. In fact, the self-healing process is due to 'disconnecting and reconnecting' between the NCO and phenolic hydroxyl groups. From the FT-IR spectra and storage modulus data, the disconnecting process occurred above 120 °C, so we chose 120 °C as the temperature for self-healing. A dumbbell-shaped specimen was cut through the middle with scissors, and the two cut surfaces were immediately placed in close contact without any applied pressure (Figure 7). The two pieces were heated to 120 °C in a convection oven, and they self-healed after 8 h. The two pieces sustained large deformations and recovered their shape and size when the stress was released, although a fracture scare was still observed (Figure 7f).

The tensile properties (including the tensile strength and elongation at break) of the original and self-healed samples were tested to evaluate the healing ability of the polyurethane (Figure 8).

The tensile strength and elongation at break of the broken samples after healing were 3.7 MPa and 443.3%, respectively, while the original values were 5.2 MPa and 510.7%, respectively, indicating that, compared to the original material, the self-healed thermoset maintained approximately 70% of its original tensile strength and 86% elongation at break. The variable-temperature FT-IR results indicate that the phenolic urethane only partially dissociated. Thus, when the fracture surfaces of the broken samples became interconnected, the healed material did not fully recover its original tensile properties. Furthermore, since isocyanate react with water in the air, when the fractured surfaces were exposed to the air, the isocyanate interacted with moisture to form urea bonds, which were not reversible covalent bonds under the tested conditions. Thus, the fractured surfaces of the thermoset could be passivated by water, and consequently, the broken samples had a reduced self-healing ability. We exposed two pieces of a broken sample to air at room temperature for 1 h, then placed them together at 120 °C for over 8 h, but they did not exhibit self-healing.
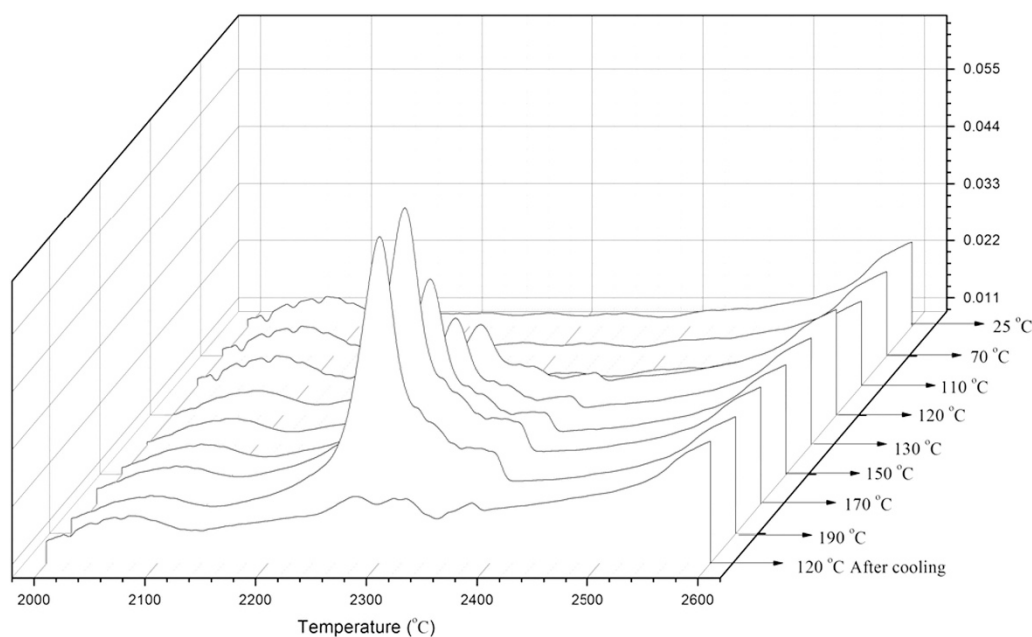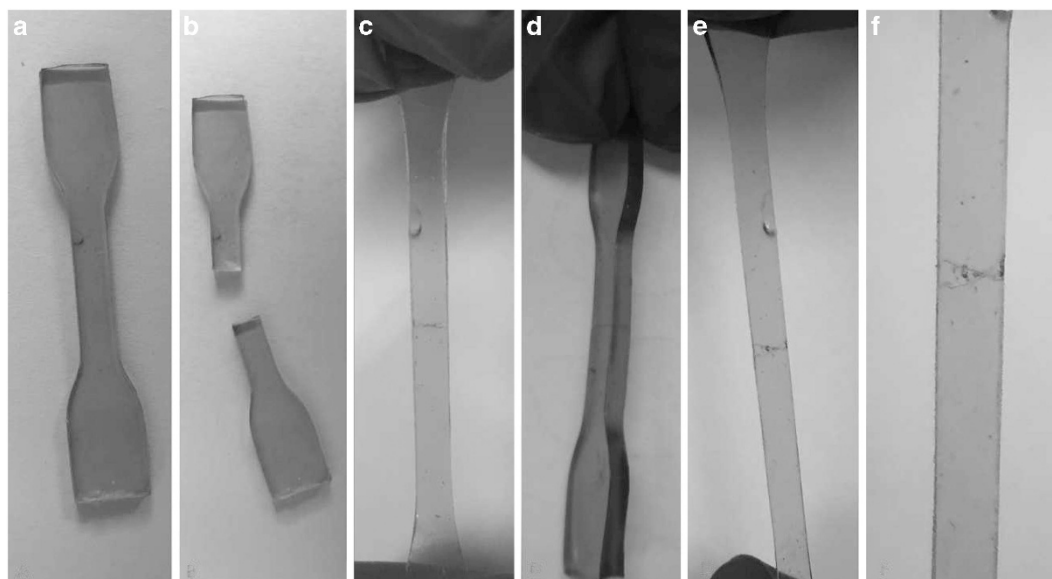

Figure 5 Storage modulus and tanδ profiles of the PU sample measured using DMA.

Figure 6 Variable-temperature FT-IR spectroscopy of the polymer.

Figure 7 (**a**) The original specimen. (**b**) The sample cut with scissors. (**c**) The two cut surfaces in contact with each other for 8 h at 120 °C. (**d**) The side view of the self-healing specimen. (**e**, **f**) The enlarged view of the location of self-healing. A full colour version of this figure is available at the *Polymer Journal* journal online.
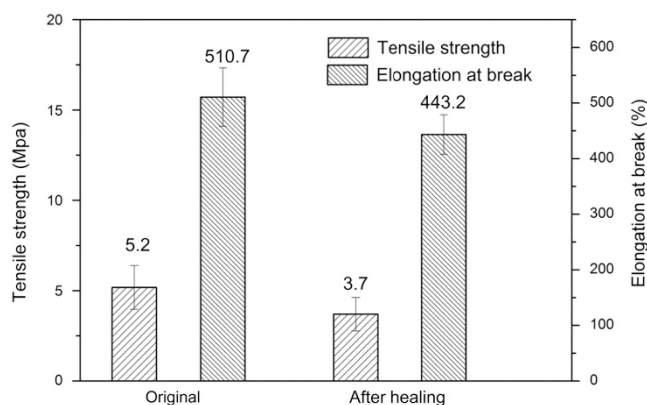
Figure 8 Tensile strength and elongation at break of the original and self-healed samples.
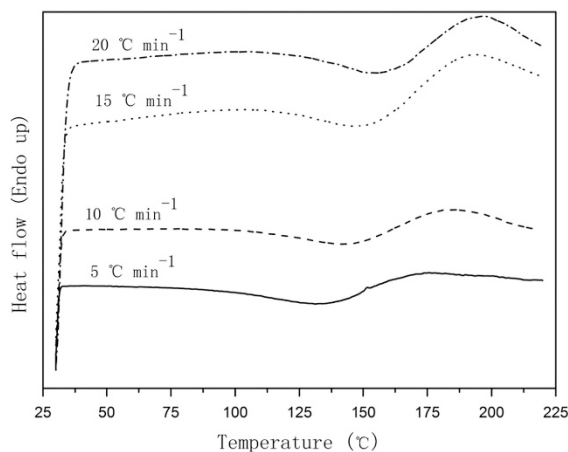
Figure 9 DSC curves of the curing and depolymerization reactions of the polymer at different heating rates. DSC, differential scanning calorimeter.

Therefore, a dry environment is favorable for self-healing. When the fractured surfaces were exposed to the moisture in the air for a long time, they displayed very poor self-healing ability. However, when the healed samples were broken at a new location, they were effectively repaired, and they displayed comparable mechanical properties compared with those after the first self-healing process.

Kinetics of the polymerization and depolymerization

Figure 9 shows the differential scanning calorimeter curves scanned at heating rates of 5, 10, 15 and 20 °C min^{-1}. Clearly, each curve exhibits an exothermic peak and an endothermic peak, which indicates that an exothermal curing reaction and urethane disassociation (depolymerization) occurred, respectively. With the increase in the heating rate, the exothermic peak temperature (T_{p1}) and the endothermic peak temperature (T_{p2}) both increased, and the shape of each peak gradually sharpened, which indicated that the high heating rate was conducive to the heat release of the curing reaction or the heat absorption during depolymerization.

The effective activation energy (E_a) is an important kinetic parameter that determines whether curing and depolymerization reactions can occur or not and it can be calculated from the Kissinger equation[37] as follows:

$$\ln\left(\beta/T_p{}^2\right) = \ln(AR/E_a) - E_a/RT_p \tag{1}$$

where β and A are the heating rate and the preexponential factor, respectively, and E_a can be determined from the slope (L) and intercept (d) from the curve of $\ln(\beta/T_p{}^2)$ versus $(1/T_p) \times 10^3$.

$$E_a = -LR \tag{2}$$

As shown in Table 1 and Figure 10, the values of E_a for the curing and depolymerization reactions are 81.28 and 95.69 kJ mol^{-1}, respectively.

To estimate the relatively ideal curing and depolymerization temperatures, we display the temperature versus heating rates in Figure 11, with the linear fitting of the curing peak temperature (T_{p1}) and depolymerization temperature (T_{p2}) at the near-zero heating rate

Table 1 Kinetic parameters of the curing and depolymerization reactions at different heating rates

β ($K\,min^{-1}$)	Curing reaction				Depolymerization reaction			
	T_p/K	$ln\beta$	$(1/T_p) \times 10^3/K^{-1}$	$ln(\beta/T_p^2)$	T_p/K	$ln\beta$	$(1/T_p) \times 10^3/K^{-1}$	$ln(\beta/T_p^2)$
5	411.18	1.609	2.43	−10.43	448.15	1.609	2.23	−10.60
10	420.71	2.303	2.38	−9.78	457.15	2.303	2.19	−9.94
15	430.87	2.996	2.32	−9.42	466.15	2.996	2.15	−9.58
20	431.64	3.401	2.31	−9.14	470.15	3.401	2.12	−9.31
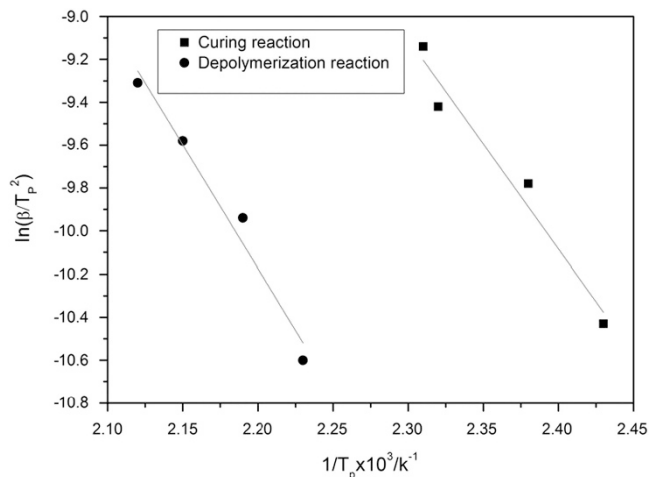
Figure 10 Linear fitting line of $T_p^{-1} \times 10^3$ and $ln(\beta/T_p^2)$. A full colour version of this figure is available at the *Polymer Journal* journal online.
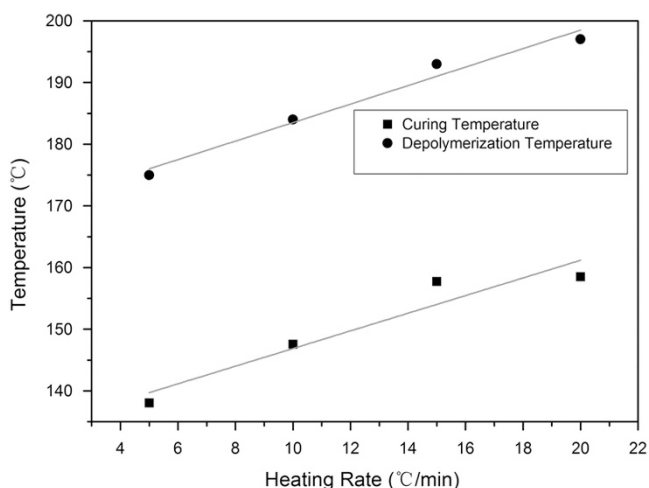
Figure 11 Curves of the curing temperature and depolymerization temperature versus the heating rate. A full colour version of this figure is available at the *Polymer Journal* journal online.

used as a reference. The T_{p1} and T_{p2} values at the zero heating rate indicate the relatively ideal curing and depolymerization temperatures, respectively, under isothermal conditions, which are 132.6 and 168.5 °C, respectively (Figure 11). We did not choose the ideal curing temperature of 132.6 °C as the practical curing temperature. Since PG is a good antioxidant, using an exceedingly high temperature makes the polyurethane darker. After the PG was oxidized, it could no longer participate in the self-healing process. Therefore, we set the initial curing temperature of 120 °C as the practical curing temperature.

CONCLUSION

We designed and prepared a self-healing thermosetting polyurethane. The concept was to develop reversible urethane bonds formed from phenol hydroxyls and isocyanates that could thermally disconnect and reconnect upon cooling. These reversible urethane bonds enabled the thermosetting polyurethane network to self-repair via temperature variations. The material was an elastomer and organic-insoluble below 120 °C. Compared to the original material, the self-healed thermoset achieved approximately 70% of its tensile strength and 86% of its elongation at break. This interesting thermosetting polyurethane can be applied in self-healing coatings or adhesives.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

1 Adhikari, B., De, D. & Maiti, S. Reclamation and recycling of waste rubber. *Progr. Polym. Sci.* **25**, 909 (2000).
2 Montarnal, D., Capelot, M., Tournilhac, F. & Leibler, L. Silica-like malleable materials from permanent organic networks. *Science* **334**, 965 (2011).
3 Grubbs, R. B., Dean, J. M., Broz, M. E. & Bates, F. S. Reactive block copolymers for modification of thermosetting epoxy. *Macromolecules* **33**, 9522 (2000).
4 Sperling, L. H. & Mishra, V. The current status of interpenetrating polymer networks. *Pol. Adv. Tech.* **7**, 197–208 (1996).
5 Trotignon, J. P., Verdu, J., Martin, C. & Morel, E. Fatigue behaviour of some temperature-resistant polymers. *Mater. Sci.* **28**, 2207–2213 (1993).
6 White, S. R., Sottos, N. R., Geubelle, P. H., Moore, J. S., Kessler, M. R., Sriram, S. R., Brown, E. N. & Viswanathan, S. Autonomic healing of polymer composites. *Nature* **409**, 794–797 (2001).
7 Brown, E. N., White, S. R. & Sottos, N. R. Microcapsule induced toughening in a self-healing polymer composite. *J. Mater. Sci.* **39**, 1703–1710 (2004).
8 Rule, J. D., Brown, E. N., Sottos, N. R., White, S. R. & Moore, J. S. Wax-protected catalyst microspheres for efficient self-healing materials. *Adv. Mater.* **17**, 205–208 (2005).
9 Shchukin, D. G. & Mohwald, H. Self-repairing coatings containing active nanoreservoirs. *Small* **3**, 926–943 (2007).
10 Yuan, Y. C., Rong, M. Z., Zhang, M. Q., Chen, J., Yang, G. C. & Li, X. M. Self-healing polymeric materials using epoxy/mercaptan as the healant. *Macromolecules* **41**, 5197–5202 (2008).
11 Sijbesma, R. P., Beijer, F. H., Brunsveld, L., Folmer, B. J. B., Hirschberg, J. H. K. K., Lange, R. F. M., Lowe, J. K. L. & Meijer, E. W. Reversible polymers formed from self-complementary monomers using quadruple hydrogen bonding. *Science* **278**, 1601–1604 (1997).
12 Cordier, P., Tournilhac, F., Ziakovic, C. S. & Leibler, L. Self-healing and thermo-reversible rubber from supramolecular assembly. *Nature* **451**, 977–980 (2008).
13 Woodward, P., Clarke, A., Greenland, B. W., Hermida Merino, D., Yates, L., Slark, A. T., Miravet, J. F. & Hayes, W. Facile bisurethane supramolecular polymers containing flexible alicyclicreceptor units. *Soft Matter* **5**, 2000–2010 (2009).
14 Wietor, J. L., Dimopoulos, A., Govaert, L. E., van Benthem, R. A. T. M., de With, G. & Sijbesma, R. P. Preemptive healing through supramolecular cross-links. *Macromolecules* **42**, 6640–6646 (2009).

15 Noro, A., Matsushita, Y. & Lodge, T. P. Gelation mechanism of thermoreversible supramacromolecular ion gels via hydrogen bonding. *Macromolecules* **42**, 5802–5810 (2009).

16 Beck, J. B. & Rowan, S. J. Multistimuli, multiresponsive metallo-supramocular polymers. *J. Am. Chem. Soc.* **125**, 13922–13923 (2003).

17 Weng, W., Beck, J. B., Jamieson, A. M. & Rowan, S. J. Understanding the mechanism of gelation and stimuli-responsive nature of a class of metallo-superamolecular gels. *J. Am. Chem. Soc.* **128**, 11663–11672 (2006).

18 Wang, F., Zhang, J., Ding, X., Dong, S., Liu, M., Zheng, B., Li, S., Wu, L., Yu, Y., Gibson, H. W. & Huang, F. Metal coordination mediated reversible conversion between linear and cross-linked superamolecular polymers. *Angew. Chem. Int. Ed.* **49**, 1090–1094 (2010).

19 Tobolsky, A. V., Macknight, W. J. & Takahashi, M. Relaxation of disulfide and tetrasulfide polymers. *J. Phys. Chem. C* **68**, 787–790 (1964).

20 Owen, G. D. T., Mcknight, W. J. & Tobolsky, A. V. Urethane elastomers containing disulfide and tetrasulfide linkages. *J. Phys. Chem. C* **68**, 784–786 (1964).

21 Deng, G. H., Tang, C. M., Li, H. Y., Jiang, H. F. & Chen, Y. M. Covalent cross-linked polymer gels with reversible sol-gel transition and self-healing properties. *Macromolecules* **43**, 1191–1194 (2010).

22 Yuan, C. E., Rong, M. Z., Zhang, M. Q., Zhang, Z. P. & Yuan, Y. C. Self-healing of polymers via synchronous covalent bond fisson/radical recombination. *Chem. Mater.* **23**, 5076 (2011).

23 Chen, X., Dam, M. A., Ono, K., Mal, A., Shen, H., Nutt, S. R., Sheran, K. & Wudl, F. A thermally re-mendable cross-linked polymeric material. *Science* **295**, 1698–1702 (2002).

24 Chen, X., Wudl, F., Mal, A. k., Shen, H. & Nut, S. R. New thermally remendable highly cross-linked polymeric materials. *Macromolecules* **36**, 1802–1807 (2003).

25 Yoon, J. A., Kamada, J., Koynov, k., Mohin, J., Nicolay, R., Zhang, Y. Z., Balazs, A. C., Kowalewski, T. & Matyjaszewski, K. Self-healing polymer films based on thiol-disulfide exchange reactions and self-healing kinetics measured using atomic force microscopy. *Macromolecules* **45**, 142–149 (2012).

26 Canadell, J., Goossens, H. & Klumperman, B. Self-healing materials based on disulfide links. *Macromolecules* **44**, 2536–2541 (2011).

27 Amamoto, Y., Otsuka, H., Takahara, A. & Matyjaszewski, K. Self-healing of covalently cross-linked polymers by reshuffling thiuram disulfide moieties in air under visible light. *Adv. Mater.* **24**, 3975–3980 (2010).

28 Amamoto, Y., Kamada, J., Otsuka, H., Takahara, A. & Matyjaszewski, k. Repeatable photoinduced self-healing of covalent cross-linked polymers through reshuffling of trithiocarbonate units. *Angew. Chem. Int. Ed.* **123**, 1698–1701 (2011).

29 Yuan, C. E., Rong, M. Z. & Zhang, M. Q. Self-healing polyurethane elastomer with thermally reversible alkoxyamines as crosslinkages. *Polymer* **55**, 1782–1791 (2014).

30 Kuhl, N., Bode, S., Bose, R. K., Vitz, J., Seifert, A., Hoeppener, S., Garcia, S. J., Spange, S., van der Zwaag, S., Hager, M. D. & Schubert, U. S. Acylhydrazones as reversible covalent crosslinkers for self-healing polymers. *Adv. Funct. Mater.* **25**, 3295–3301 (2015).

31 Yu, S., Zhang, R. C., Wu, Q., Chen, T. H. & Sun, P. C. Bio-inspired high-performance and recyclable cross-linked polymers. *Adv. Mater.* **25**, 4912–4917 (2013).

32 Tian, Q., Yuan, Y. C., Rong, M. Z. & Zhang, M. Q. A thermally remendable epoxy resin. *J. Mater. Chem.* **19**, 1289–1296 (2009).

33 Ying, H., Zhang, Y. & Cheng, J. J. Dynamic urea bond for the design of reversible and self-healing polymers. *Nat. Commun.* **5**, 3218 (2014).

34 Sultan Nasar, A., Shrinivas, V., Shanmugam, T. & Raghavan, A. Synthesis and deblocking of cardanol- and anacardate blocked toluene diisocyanates. *J. Polym. Sci. Pol. Chem.* **42**, 4047–4055 (2004).

35 Sudipta, M. & Krishnamurti, N. Synthesis and thermal deblocking of blocked diisocyanate adducts. *Eur. Polym. J.* **34**, 77–83 (1998).

36 Wang, S. K. & Sung, C. S. P. Spectroscopic characterization of model urea, urethane compound, and diamine extender for polyurethane-urea. *Macromolecules* **35**, 877 (2002).

37 Sabzevari, S. M., Alavi-Soltani, S. & Minaie, B. Effect of thermoplastic toughening agent on glass transition temperature and cure kinetics of an epoxy prepreg. *J Therm Anal Calorim* **106**, 905–911 (2011).