A Highly Stretchable Polymer that Can Be Thermally Healed at Mild Temperature

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Combining stretchability and self-healing properties in a man-made material is a challenging task. For an efficient self-healing material, weaker dynamic or reversible bonds should be presented as crosslinks so that they will first break upon damage and then reform after healing, which is not favorable when developing elastic materials. In this work, by incorporating dynamic Fe(III)-triazole coordination bonds into polydimethylsiloxane (PDMS) backbone, a highly elastic polymer is obtained that can be thermally healed at mild temperature. The as-prepared polymer can be stretched to 3400% strain at low loading speed (1 mm min⁻¹). When damaged, the polymer can be thermally healed at 60 °C for 20 h with a healing efficiency of over 90%. The good mechanical and healable properties of this polymer can be ascribed to the unique coordination bond strength and coordination conformation of Fe(III)-triazole coordination complex.

1. Introduction

Self-healing materials have been the subject of intense investigation over past decades as they can prolong the lifetime of products and reduce waste.[1–6] Recently, efforts in this research field have been made to develop materials that show high stretchability as well as self-healing properties. However, there are fundamental challenges when combining stretchability and self-healing properties in the same material. For stretchable polymers, the crosslinks between the long chains should be as strong as possible, otherwise they will be disassociated upon tension, resulting in a permanent deformation.[7] However, for a self-healing material, weak dynamic bonds should be present as crosslinks so that they will first break upon damage and then reform after healing.[8–11] Therefore, self-healing materials based on strong reversible covalent bonds (such as alkoxyamine,[12] disulfide,[13,14] and boronic ester)[15,16] or crosslinking reactions (such as Diels-Alder reaction,[17,18] radical dimerization reaction,[19] or cycloadDITION reaction)[20] are stretchable but can only be healed upon external stimulus (such as heat, light irradiation, or the addition of catalyst, reducing, or oxidizing species), while those based on weak dynamic van der Waals’ interactions (such as hydrogen bonds,[21–23] π–π stacking interactions,[24–26] and host-guest interactions)[27,28] can ensure autonomous self-healing, but are soft and poorly elastic. Materials that simultaneously exhibit high elasticity and autonomous self-healing properties are scarce in the literature.[29–36]

Recently, coordination bonds have been demonstrated to be advantageous for constructing self-healing materials.[37–44] The strength of coordination bonds is between that of covalent bonds and van der Waals’ interactions and, most importantly, it can be tuned. By careful selection of the combination of ligand and metal ion, it is possible to design a crosslink with appropriate bond strength to derive simultaneously high stretchability and excellent self-healing properties.

1,2,4-Triazoles have been frequently shown to act as bridging ligands to form linear polymeric metal...
complexes. In our previous work, we demonstrated a novel metallopolymer based on PDMS and Co(II)-triazole complexes (Co-TIA-PDMS), which shows healable and solvatochromic properties. However, the healing temperature of Co-TIA-PDMS was quite high (120 °C) while the healing efficiency was quite low, which is not desirable for self-healing materials. It is important to make metallo-polymers that can be healed at mild temperatures through adjusting the strength of the metal-triazole coordination bonds. In this work, by substitution of Co(II) with Fe(III), which was expected to form weaker coordination bonds with triazole ligands (Figure 1), a highly stretchable polymer can be obtained (it can be stretched to over 3400% strain) that can also be thermally healed at mild temperature (60 °C).

2. Results and Discussion

The synthesis of the polymer TIA-PDMS was described in our previous work. The TIA-PDMS polymers were coordinated to Fe(III) by a ligand substitution reaction with FeCl₃. Evidence of the coordination was found by comparing the UV-vis spectra before and after the coordination reaction. New absorption bands at 313 nm and 363 nm were attributed to ligand-to-metal charge transfer. A ligand to metal molar ratio of 3:1 was used based on the literature and UV-vis titration results (see Figure S1 in the Supporting Information). After reaction, the solution was poured into a polytetrafluoroethylene (PTFE) mould and dried at room temperature for 1 d, followed by drying at 80 °C for 24 h. The as-prepared film had a size of 75 × 14 × 1.0 mm³ (see Figure S2 in the Supporting Information). DSC measurements showed that the Tg was below −90 °C. An exothermal peak at −74.03 °C and an endothermic peak at −40.98 °C corresponded to crystallization and melting respectively (see Figure S3 in the Supporting Information). A rheological study showed that the storage modulus G’ decreased while the loss modulus G” increased with increasing temperature (see Figure S4 in the Supporting Information). Therefore, the polymer became softer upon heating, which is favorable for thermal healing.

Mechanical tensile-stress experiments were performed using an Instron 5848 Microtester. Tensile experiments were performed at room temperature (25°C) at different sample sizes and strain rates when evaluating the stretchability. This Fe-TIA-PDMS polymer showed excellent mechanical properties (Figure 2). The Young’s modulus of the film was calculated to be 0.46 ± 0.1 MPa from the low strain region (<20% strain) of the stress-strain curve. Surprisingly, Fe-TIA-PDMS was highly stretchable. The stretchability was dependent on sample thickness, width, gage length, and loading speed. Such phenomena are typical of elastic polymers. There were more defects in samples with larger dimensions, which made the polymer break easily through defect propagation upon tension. Therefore, decreasing the sample dimensions led to higher stretchability. On the other hand, when the loading speed increased, less time was allowed for the displacement, re-orientation, and re-configuration of polymer chain segments, reducing the fracture tolerance, and leading to higher tensile stress and lower stretchability. A maximum stretchability up to 3400% could be achieved for a sample of 1 mm thickness, 2 mm gage length, and 7 mm width at a loading rate of 1 mm min⁻¹ (Figure 2a). In the literature, different loading speeds have been used to characterize the stretchability of different polymers. Therefore, it is hard to compare our results with other reported highly stretchable self-healing polymers. However, we noted that the poly(N,N-dimethylacrylamide) hydrogels developed by Okay et al. could be stretched to 4200% with a loading speed of 5 mm min⁻¹ [14]. At that loading speed, our polymer could be stretched to over 26 times its initial length, which is very impressive among the reported stretchable self-healing polymers. Cyclic stress-strain tests showed small hysteresis at low strain (from 50% to 200%) and it could recover fully (Figure 2c). However, as the strain increased...
from 300% to 2000%, the hysteresis became more and more pronounced (Figure 2d). Therefore, the polymer was elastic at low strain (< 200%) but started to deform plastically at strains higher than 200%. After resting for 1 h, the film was observed to almost fully self-recover to its original stress-strain behaviors (Figure 2e).

The stretchable Fe-TIA-PDMS films also showed thermal healing properties. In a typical healing experiment, a film was cut into two pieces and then put together to heal itself at different temperatures for different times. The healing properties of PDMS polymer films are illustrated in Figure 3. The notch on the film almost disappeared after healing treatment, although an indistinct healed scar was still visible under the microscope (Figure 3a). The healing efficiencies were quantitatively evaluated from the toughness of the polymers (see Table S1 in the Supporting Information).

A longer healing time and higher healing temperature resulted in higher healing efficiencies (Figure 3b). A higher healing temperature also accelerated the healing process (see Figure S5 in the Supporting Information). The polymer film could be almost completely healed upon heating at 60°C for 20 h with a healing efficiency of 94.3% (see Table S1 and Figure S6 in the Supporting Information). Such a highly efficient healing under mild temperatures has been rarely reported for self-healing polymers based on coordination bonds.

In order to make the self-healing region more distinguishable, a small amount of methylene blue was doped into a film before putting it together with another undoped film. The integrated film was then healed at 60°C for 20 h. The healed film showed similar mechanical properties to the undoped and uncut film. Interestingly, the fracture incision was not the cutting point (Figure 3d).

Figure 2. The mechanical properties of the Fe-TIA-PDMS film (1 mm in thickness and 7 mm in width). a) Stress-strain curves at different loading speeds (gage length: 2 mm). b) Stress-strain curves with different gage length (loading speed: 5 mm min⁻¹). c) Cyclic stress-strain tests of the film for different strains (from 300% to 2000%; gage length: 2 mm; loading speed: 5 mm min⁻¹). d) Cyclic stress-strain tests of the film for different strains (from 300% to 2000%; gage length: 2 mm; loading speed: 5 mm min⁻¹). e) The stress-strain curves of the film in cyclic stress-strain tests (up to 2000% strain) in successive stretching and stretching after relaxation for 1 h (gage length: 2 mm; loading speed: 5 mm min⁻¹). f) Photographs of the stretching of the pristine film (up to 2000%, gage length: 2 mm; loading speed: 5 mm min⁻¹).
It is noteworthy that distinct differences were observed between polymers of Co-TIA-PDMS and Fe-TIA-PDMS. The Young's modulus of Fe-TIA-PDMS is much lower than that of Co-TIA-PDMS (1.12 MPa). However, Fe-TIA-PDMS is much more stretchable than Co-TIA-PDMS (with a maximum extensibility of 560%). The elastic regime of Co-TIA-PDMS is 300% (see Figure S7 in the Supporting Information) while that of Fe-TIA-PDMS is 200% (Figure 2c), after which the both polymers deform plastically. Moreover, Fe-TIA-PDMS can be healed at 60 °C with a high healing efficiency while Co-TIA-PDMS can only be partially healed at 120 °C. These differences can be rationalized from their different coordination bond strengths and coordination conformations. According to hard-soft-acid-base theory, triazole is a mediate base and has stronger coordination bond strength toward a mediate acid like Co$^{2+}$ as compared to a hard acid like Fe$^{3+}$. Therefore, Co-TIA-PDMS has a higher Young's modulus due to the stronger crosslinking interactions. Consequently, higher energy will be necessary to break such crosslinking sites, leading to higher Young's modulus and healing temperature. On the other hand, Co$^{2+}$ is four-coordinated while Fe$^{3+}$ is six-coordinated, as evidenced by UV-vis spectroscopy. As shown in Figure 4, three-coordination Co$^{2+}$ complex and five-coordinated Fe$^{3+}$ complex will be formed upon stretching of the polymer. It is known that three-coordination Co$^{3+}$ complex is highly unstable. Therefore, the three-coordination Co$^{2+}$ structure will quickly dissociate, leading to the fracture of the polymer film. In contrast, a five-coordinated Fe$^{3+}$ complex is meta-stable, as evidenced by the literature. Such a meta-stable complex can sustain a short period without full dissociation. If there is a free triazole ligand nearby, the five-coordinated Fe$^{3+}$ complex can bind to the free triazole ligand to reform the stable six-coordinated Fe$^{3+}$ complex. Meanwhile, the dynamic rupture and reconstruction of the Fe-triazole bonding configurations during chain unfolding and sliding will dissipate the strain energy and therefore lead to high stretchability.
3. Conclusion

In summary, we have developed a highly stretchable and self-healing PDMS film by incorporating dynamic coordination bonds. The as-prepared film can be stretched to over 30 times its initial length. The film displays excellent self-healing properties and can be healed completely at mild temperatures. This kind of material could find applications in a wide range of fields, such as protective coatings, sealing agents, electronic skins, and artificial muscles.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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