Self-healable Hydroxyl-terminated Polybutadiene based Polyurethane for Sustainable Development

Yahao Liu1, Jian Zheng1,*, Xiao Zhang2, Yu Zhang1, Guibo Yu1, Yunfei Jia1
1Shijiazhuang Campus, Army Engineering University, Shijiazhuang 050003, China
2Engineering University of PAP, Xi’an 710086, China

*E-mail: zhengj2020@163.com

Abstract. Self-healing technology provides a promising road for the sustainable development of the environment, which can extend the service life of materials, thereby reducing the waste of natural resources. As is known to all, it is difficult to obtain a polymer with fast room-temperature self-healing properties without any external stimuli. In this work, a series of polyurethanes with fast room-temperature self-healing capability were designed and prepared by combining the hydrogen bonds and the aromatic disulfide bonds. Owing to their synergistic effect, the obtained polyurethane exhibited high self-healing efficiency of 95.2% for SPU-1, and 98.4% for SPU-2. It is excepted that this design strategy may be potential applications in sustainable development for applied materials.

1. Introduction

As is known to all, polyurethane (PU) has extensively aroused many attentions in numerous fields, such as adhesives, coating, etc.[1], owing to its excellent properties. Given it outstanding properties like excellent elasticity, relatively low glass transition temperature(Tg), and low viscosity[2], hydroxyl-terminated polybutadiene (HTPB)-based PU has become more and more popular as promising material for many devices[3]. Nevertheless, PU usually suffer from various environmental influences during its service life, resulting in the generation of cracks and defects. As a kind of thermosetting material, it cannot be repaired conveniently once damaged, which shorten its service life and cause huge material waste.

Recently, self-healing technology have been regarded as a practicable method to solve the above problems[4-6]. Generally, self-healing polymer are mainly achieved through the reconstruction of reversible dynamic bonds[7-9]. Nevertheless, some external stimuli, e.g. heat, and light are demanded during the self-healing process, which also leads to a waste of resources[10]. Therefore, it is hard to obtain polymer with fast room-temperature self-healing performances without any external stimuli. Nowadays, aromatic disulfide bonds have aroused many attentions in self-healing fields. Besides, some reports have also indicated that there are synergistic effects between hydrogen bonds disulfide exchange reactions[11]. Herein, based on the above viewpoints, it is believed that polymer with fast room-temperature self-healing performances can be prepared via combining aromatic disulfide bonds and hydrogen bonds together.

In this work, a kind of PU with fast room-temperature self-healing capabilities were designed and fabricated. In this system, the hydrogen bonds formed and the disulfide bonds work together to achieve its self-healing capabilities. Then, the self-healing properties of PU were measured, and its self-healing mechanism was analysed based on the literature to further studied its self-healing properties.
2. Materials and tests

2.1. Raw materials in this work
Hydroxyl-terminated polybutadiene (HTPB, 99.9%) was provided by Liming Research & Design Institute of Chemical Industry Co., Ltd., Luoyang, China. Isophorone diisocyanate (IPDI, 99%), dibutyltin dilaurate (DBTDL), tetrahydrofuran (THF, ≥99.5%), dopamine hydrochloride (DA, 98%) and 2-aminophenyl disulfide (APD, 98%) were provided by Aladdin Co., Shanghai, China.

2.2. Preparation of self-healing polyurethane
Firstly, 3g HTPB (1.25mmol) was poured into a three-necked flask and dried under 60°C for 24h to remove moisture. Secondly, IPDI (2.25mmol) and DBTDL (3mg) in THF (5ml) were poured into the flask. The mixture reacted for 3h under 70°C. Thereafter, APD (1.0125mmol) was added and reacted for another 2h at 50°C. Next, 0.225mmol of DA was added and reacted under 40°C for 3h. All steps were carried out under nitrogen protection. Finally, the obtained mixture were pouring into polytetrafluoroethylene molds and curing under 60°C for 36h. Additionally, PU with different ratios of 2-aminophenyl disulfide and dopamine were also fabricated with the same steps and their names and formula are listed in Table 1.

| Reagent | SPU-1 | SPU-2 | SPU-3 | PU  |
|---------|-------|-------|-------|-----|
| HTPB    | 1.25  | 1.25  | 1.25  | 1.25|
| IPDI    | 2.25  | 2.25  | 2.25  | 2.25|
| APD     | 1.0125| 0.9   | 0.7875| 0   |
| DA      | 0.225 | 0.45  | 0.675 | 0   |

2.3. Self-healing efficiency
The self-healing efficiency ($\eta$) was defined as[10]:

$$\eta = \frac{\sigma_{healed}}{\sigma_{original}} \times 100\%$$

where $\sigma_{healed}$ is the tensile strength of the healed samples, and $\sigma_{original}$ is the tensile strength of the original samples.

3. Results and discussion

3.1. Materials preparation
In our paper, a kind of self-healing PU was prepared through a facile strategy, and the reaction steps are displayed in Figure 1. At first, the -NCO groups-terminal prepolymer was fabricated via adding double equivalent of IPDI. Secondly, 2-aminophenyl disulfide was added to react with partial -NCO groups, introducing the aromatic disulfide bonds. Finally, dopamine was used to react with the residual -NCO groups, which can introduce catechol groups to provide hydrogen bonds. Then, a series of self-healing PU can be obtained through changing their ratios. In this PU system, aromatic disulfide reaction can achieve under room temperature, which is beneficial to realize the room-temperature self-healing properties of PU. On the other hand, the catechol groups of dopamine can be grafted onto the molecular chain of HTPB to form hydrogen bonds which can promote the self-healing process.
3.2. Self-healing tests

Figure 2. (a-c) The tensile stress-strain curves of different PU after various healing time. (d) The calculated $\eta$ value of different PU

To demonstrate the outstanding self-healing capabilities, all the prepared PU were cut into two separate parts and brought into together for some time under room temperature. After that, the tensile tests were conducted on them and the results are shown in Figure 2 (a). Obviously, the PU presented almost no self-healing properties, even after healing for 12h. On the contrary, after introducing 2-aminophenyl disulfide and dopamine, the self-healing properties were improved significantly.
Specifically, after healing for 6h, both SPU-1 and SPU-2 could be almost stretched to the same elongation as the original ones, especially SPU-1. Quantitatively, the $\eta$ value of PU is only 16.9%, while SPU-1 and SPU-2 are 95.2% and 98.3%, respectively. The excellent self-healing properties may be assigned to the synergistic effect of aromatic disulfide bonds and hydrogen bonds formed by catechol groups as analysed in last section.

4. Conclusions
In conclusion, in order to address the problem of resources wasting, a kind of self-healing PU were designed and prepared in this work. Owing to the synergistic effect of aromatic disulfide bonds and hydrogen bonds, the self-healable HTPB-based PU exhibited satisfactory $\eta$ value of 95.2% for SPU-1 and 98.4% for SPU-2. It is excepted that this design strategy may be potential applications in sustainable development for applied materials.

References
[1] Chattopadhyay D K and Raju K V S N 2007 Structural Engineering of Polyurethane Coatings for High Performance Applications Prog. Polym. Sci. 32 352-418
[2] Liu Y, Zheng J, Zhang X, Du Y, Yu G, Li K, Jia Y and Zhang Y 2021 Hyperbranched polyamide modified graphene oxide-reinforced polyurethane nanocomposites with enhanced mechanical properties RSC Advances 11 14484-94
[3] Liu Y, Zheng J, Zhang X, Du Y, Li K, Yu G, Jia Y and Zhang Y 2021 Mussel-inspired and aromatic disulfide-mediated polyurea-urethane with rapid self-healing performance and water-resistance J. Colloid Interface Sci. 593 105-15
[4] Wu D Y, Meure S and Solomon D 2008 Self-Healing Polymeric Materials: A Review of Recent Developments Prog. Polym. Sci. 33 479-522
[5] Michael P, Döhler D and Binder W H 2015 Improving Autonomous Self Healing via Combined Chemical/Physical Principles Polymer 69 216-27
[6] Huynh T-P, Sonar P and Haick H 2017 Advanced Materials for Use in Soft Self-Healing Devices Adv. Mater. 29 1604973
[7] Zhang L, Wang D, Xu L, Zhang X, Zhang A and Xu Y 2020 A highly Stretchable, Transparent, Notch-Insensitive Self-Healing Elastomer for Coating Journal of Materials Chemistry C 8 2043-53
[8] Prado-Audelo M L D, Caballero-Florán I H, Mendoza-Muñoz N, Giraldo-Gómez D, Sharifi-Rad J, Patra J K, González-Torres M, Florán B, Cortes H and Leyva-Gómez G 2021 Current progress of self-healing polymers for medical applications in tissue engineering Iranian Polymer Journal
[9] Seongwoo G, Eunjong A and Myoungsu S 2020 Water permeability and rapid self-healing of sustainable sulfur composites using superabsorbent polymer and binary cement Construction and Building Materials 265
[10] Liu Y, Zheng J, Zhang X, Du Y, Yu G, Li K, Jia Y and Zhang Y 2021 Bioinspired modified graphene oxide/polyurethane composites with rapid self-healing performance and excellent mechanical properties RSC Advances 11 14665-77
[11] Matxain J M, Asua J M and Ruipérez F 2016 Design of New Disulfide-Based Organic Compounds for the Improvement of Self-Healing Materials Phys. Chem. Chem. Phys. 18 1758-70