

Various Kinds of Self-Healing Elastomer Materials for 3D Printing

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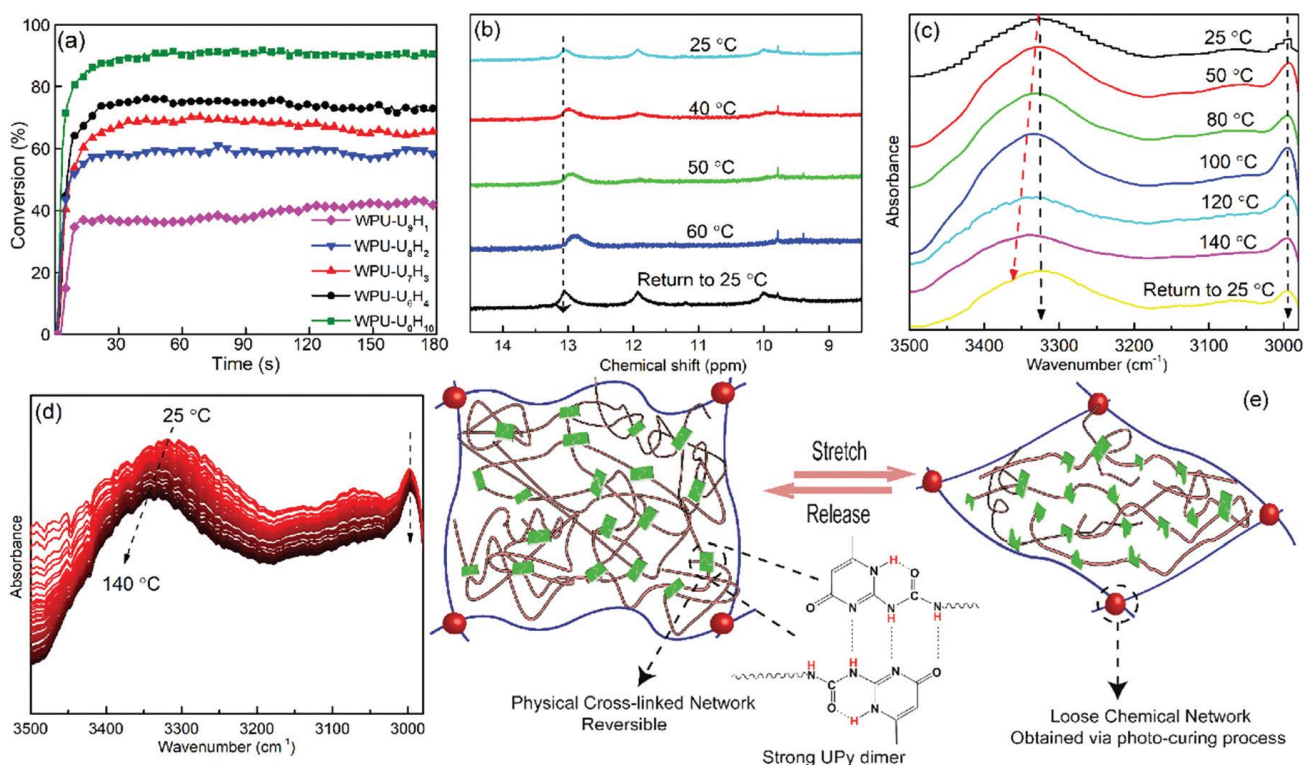
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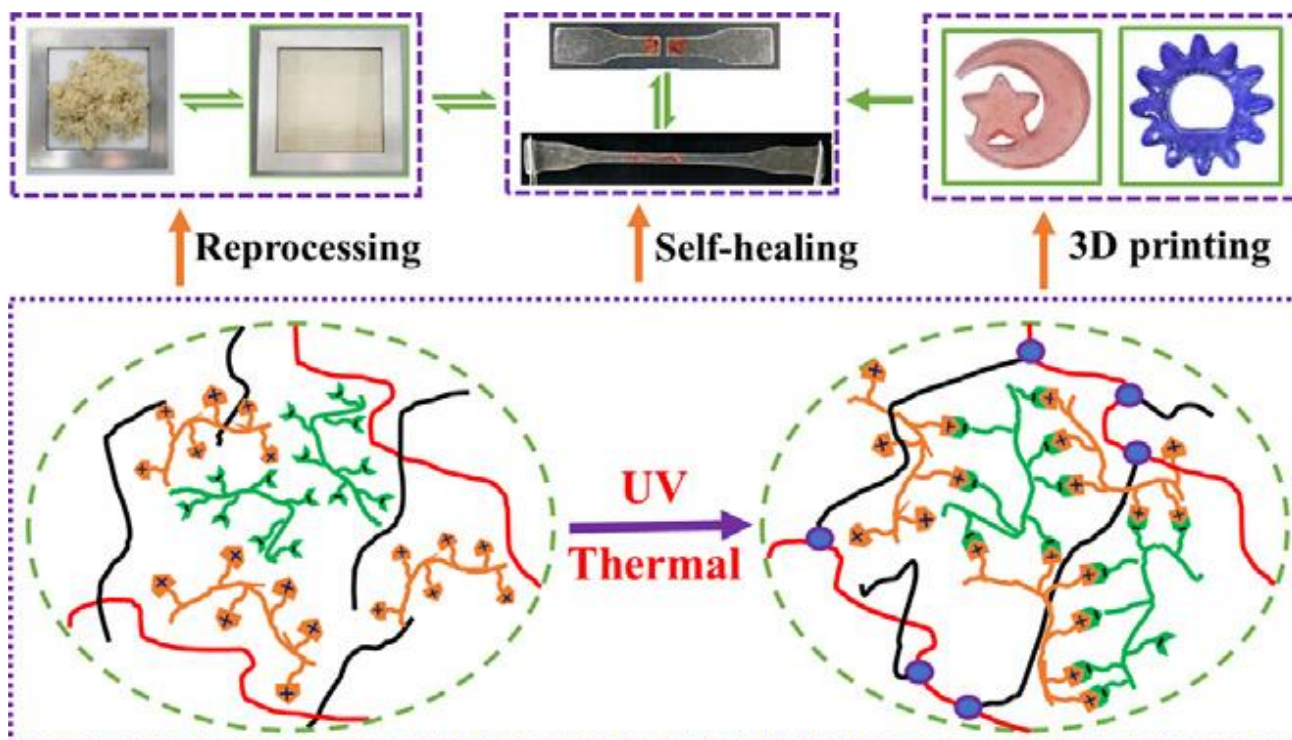
Graphical Abstract

Herein, a novel healable polyurethane elastomer was developed using a double-network (DN) structure system. In the DN system, a loosely cross-linked chemical network was obtained via a photo-curable acrylic double bond, acting as a robust molecular framework and maintaining the elasticity of the polymer. Simultaneously, the physical cross-linked network produced by quadruple H-bonds of ureidopyrimidinone (UPy) units can not only achieve rapid reformation after fracture but also dissipate strain energy as a weak dynamic bond, endowing the elastomer with excellent self-healing ability and high stretchability.



Highlights

- A self-healable and recyclable silicone elastomer realized by UV/thermos-curing.
- Self-healing and recycling abilities derived from reversible ionic crosslinks.
- The silicone elastomer was transparent and hydrolysis-resistant.
- The silicone elastomer could be 3D printed into self-healable soft devices.



Abstract

Elastomer materials integrated with high mechanical strength and excellent self-healing ability can be used as substrates in electronic skins, soft robots, and electrical devices. However, simultaneously enhancing the mechanical and self-healing properties of elastomers is still a great challenge because the self-healing ability of polymer materials is usually antagonistic to its mechanical strength. Herein, the two kinds of novel self-healable elastomers was developed using different crosslinking mechanisms, such as the double-network (DN) structure system and the thiol-ene UV-curing between thiol and vinyl functionalized polysiloxanes, and thermos-curing between carboxyl and amido functionalized polysiloxanes. We have successively fabricated a self-healable waterborne polyurethane composite conductor and a transparent and hydrolysis resistant silicone elastomer. In the DN system, a loosely cross-linked chemical network was obtained via a photo-curable acrylic double bond, acting as a robust molecular framework and maintaining the elasticity of the polymer. Simultaneously, the physical cross-linked network produced by quadruple H-bonds of ureidopyrimidinone (UPy) units can not only achieve rapid reformation after fracture but also dissipate strain energy as a weak dynamic bond, endowing the elastomer with excellent self-healing ability and high stretch ability. Owing to the accurate design, the synthesized elastomer exhibits

excellent properties, including high tensile stress (13.71 MPa), high stretch ability (B500%), exceptional resilience and self-healing ability (90%). The robust healable elastomer enables the easy fabrication of composite conductors, which the prominent performance suggests as a great potential of the healable flexible sensor in next-generation wearable stretchable electronic devices, soft robots, and strain sensors. Various intrinsic self-healing silicone elastomers have been developed by incorporating different dynamic noncovalent or covalent bonds into elastomeric crosslinked networks. However, these silicone elastomers are either non-transparent or non-resistant to hydrolysis. In this study, a transparent and hydrolysis resistant silicone elastomer with self-healing ability, reprocess ability and 3D printability is facilely prepared the elastomer show an excellent healing efficiency of 97%, and the healing processes are repeatable for many times. Moreover, these elastomers can be repeatedly reprocessed with a recovery of 90% of virgin mechanical strengths, and the reprocessed elastomers can still repair damages with efficiency over 90%. These self-healing and reprocessing behaviours mainly derive from the rearrangement of crosslinked networks via reversible breakage and reformation of ionic bonds. Importantly, the silicone elastomers are transparent with a transmittance of over 90% in visible light and hydrolysis-resistant to hydro-thermal treatment. Besides, the silicone elastomers can be fabricated into various self-healable architectures via 3D printing. Therefore, a feasible approach is provided to impart reversible ionic association induced self-healing and reprocessing to 3D printable silicone elastomers.

Keywords: Self-healable, transparent silicone elastomers, polyurethane composite conductor, thiol-ene UV-curing, double-network structure, 3D printing.

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Biography of Presenting Author



Xiaoxuan Liu, obtained Bachelor degree from Dalian University of Technology in 1982. From 1983 to 1985, He was a postgraduate student in Shanghai Institute of Optics and Fine Mechanics, Chinese Academy of Sciences with a master's degree and the same time he worked in Changchun Institute of Optics and Mechanics. From 1986 to 2006, he started as a professional faculty in Shantou University, and promoted to an associate professor in 1995. During 1997 to 2001, he studied at Institute of Polymer Science, Sun Yat-sen University, and obtained his Ph.D. in Polymer Photochemistry. In 2004, he was promoted to a professor in Shantou University. From 2006 to present, he has been a professor, supervisor for Ph.D. postgraduates, and dean of Department of Polymeric Materials and Engineering, School of Materials and Energy, Guangdong University of Technology, and dean of Guangdong Province R&D center of UV-curing Advanced Materials. His main professional works are in polymer photochemistry, functional photopolymer materials and UV-curing technology. He has completed five projects of National Natural Science Foundation of China (NSFC, No. 20274023, 20474036, 20874022, 51641302 and 51873043). Around 137 research papers and 59 presentations have been published on the academic journal for polymer science. Beside the topics mentioned above, his team have also developed many new technologies such as UV-curable dry film of the transfer printing by cast & cure (C2) technique, and UV-curing resin of the vacuum metallization on the surface of plastics, and special developed the multifunctional water-borne polyurethane-acrylate (PUA) and application to UV-curing coatings for wood, glass and 3C products. Recently, his research is focusing on the photosensitive resin and the self-healing elastomer applied in 3D printing, from which 19 patents have been authorized.

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