



A self-healing polysiloxane elastomer based on siloxane equilibration synthesized through amino-ene Michael addition reaction

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ABSTRACT

A facile approach to synthesize silicone elastomers with good mechanical properties as well as high self-healing efficiency is reported in the present research. The silicone elastomer is synthesized through amino-ene Michael addition reaction, with amino groups from aminopropyl-terminated polydimethylsiloxane and acrylate groups from multifunctional acrylate monomer. Meanwhile, basic catalyst tetramethylammonium hydroxide is added into the elastomer to derive a dynamically crosslinked network. Tensile strength and break elongation of the synthesized elastomers are 1.08 ± 0.06 MPa and $206.10 \pm 9.55\%$, respectively, indicating good mechanical properties of the elastomers. The fractured samples can recover 91% of their original strength after healing at 105 °C for 24 h. Moreover, the silicone elastomer in this work is recyclable due to the dynamic siloxane equilibration reaction.

1. Introduction

Self-healing polymer materials are polymers with the ability to recover their properties after damage to improve their durability and reliability during application [1–3]. They can be divided into two types, extrinsic and intrinsic types, according to different mechanisms of healing. Extrinsic type is to store the healing agents in microcapsules, nanotubes or other microcontainers, which will be released once the matrix is subjected to damage [4–7]. Intrinsic type is polymeric materials containing reversible bonds, including dynamic covalent or non-covalent bonds which are able to be activated by external stimuli once the materials are subjected to damage. Dynamic covalent bonds can be reversible Diels-Alder (DA) reaction [8], esterification [9], disulfide bonding [10] and so on, while non-covalent bonds can be introduced through hydrogen bonding [11,12], metal-ligand coordination [13,14]. A recently developed type of self-healing materials, vitrimers, which are derived from thermosetting polymers but can change their topology or shape by thermally activated bond-exchange reactions, is actually also belong to intrinsic self-healing materials [15,16].

Silicone elastomers have been widely applied in various areas, such as astronautics devices, automobiles, medical implants, soft robots due to their excellent properties of non-reactive and resistant to extreme environments as well as their ease of manufacturing [17–23]. Silicone elastomers are typically fabricated through platinum-catalyzed hydrosilylation, condensation or peroxide-initiated radical reactions. In

addition, silicone polymers with pendant polymerizable groups, such as epoxide, acrylate groups can also form silicone elastomers [24–26]. It would be meaningful if silicone elastomers possess the ability of self-healing during service.

Many efforts have been made by researchers to fabricate self-healable silicone elastomers. In 2007, Keller et al. fabricated self-healing silicone elastomers based on embedded healing materials containing vinyl-terminated polysiloxane, methylhydrosiloxane and platinum catalyst, which are separately microencapsulated in the matrix [27]. Afterwards, researchers tried to prepare intrinsic self-healing elastomers. In the past few years, Feng's group has done a lot of works on preparation of self-healing silicone elastomers. They fabricated self-healing silicone elastomers through “salt-forming vulcanization” [28], dynamic-covalent boronic ester linkage [29] and reversible DA reaction [30]. Xia et al. successfully prepared self-healing polysiloxane elastomer by crosslinking PDMS containing maleimide pendants with furan-end functionalized siloxane via DA reaction [8]. Skov et al. reported the synthesis of silicone elastomer through proton exchange between amines and acids [9]. Zhang et al. reported the commercially available silicone elastomer with self-healability and recyclability through crosslinking with disulfide bonds, which can be triggered by the low concentration of UV component in sunlight [10]. Non-covalent bonding like metal-ligand coordination has also been applied to prepare silicone elastomers [13,14,31,32].

MaCarthy et al. discovered a type of self-healing silicone elastomer

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based on publications from the 1950s [33–36]. Such polysiloxane network was synthesized through tetramethylammonium silanolate-initiated ring-opening polymerization of octamethylcyclotetrasiloxane (D_4) and bis(heptamethylcyclotetrasiloxanyl)-ethane (bis- D_4). The “living” reactive silanolate end groups can promote thermally activated equilibration among isomers and cyclic oligomers in the network [36]. Experiments show that objects cut into several pieces can be rejoined and healed to its original shape after heated in an oven at 90 °C for 24 h. Seiffert et al. refined the structure of the silicone elastomer by controlling the crosslinking density and the amount of ionic initiator and realized stress relaxation and self-healing of the material at room temperature on short time scale [37]. Since the healing process is based on anionic moieties initiated siloxane equilibration reaction, MaCarthy concluded that any cross-linked polydimethylsiloxane elastomer can be converted to a living one by the addition of basic catalysts. Silicon-oxygen bonds can be broken and reconstructed upon the basic catalysts, resulting in dynamically crosslinked silicone elastomers.

A variety of polydimethylsiloxane networks can be prepared through different routes. In our present research, a facile amino-ene Michael addition reaction is applied to get silicone elastomer. A type of aminopropyl terminated polydimethylsiloxane with high molecular weight is synthesized and multifunctional acrylate monomer is applied as crosslinker. Basic catalyst tetramethylammonium hydroxide (TMAH) is added to the system during the preparation of the silicone elastomer. Experiments reveal that samples cut into pieces can be rejoined and healed to their original shapes and the self-healing ability is proved to be quite high. Thus, our research result verifies the conclusion drawn by MaCarthy. Compared with existing reports concerning self-healing silicone elastomers, the elastomers in our present research show good mechanical properties and high self-healing ability and more importantly, the synthesis process is simple and easy.

2. Experimental part

2.1. Synthesis

2.1.1. Materials

Octamethylcyclotetrasiloxane (D_4) and 1,3-bis(3-aminopropyl)tetramethyldisiloxane were purchased from Energy Chemical Co., Ltd and used as received. Tetramethylammonium hydroxide (TMAH) and ethyl alcohol were obtained from Sinopharm Chemical Reagent Beijing Co., Ltd. Trimethylolpropane triacrylate (TMPTA) was purchased from Royal DSM. The treated fumed nanosilica (Aerosil R974) was supplied from Evonik Industries AG, Germany.

2.1.2. Synthesis of aminopropyl terminated polydimethylsiloxane (APT-PDMS)

A mixture of D_4 (135.00 g, 0.4551 mol) and TMAH (0.62 g, 0.0034 mol, 0.46 %wt of D_4) was added to a 250 ml four-necked round bottom flask equipped with a mechanical stirrer, a nitrogen inlet and a thermometer. Afterwards, the mixture was stirred for 0.5 h at 50 °C to remove trace water with N_2 . Then, the heating rate was controlled gently by raising 10 °C every 0.5 h and 1,3-bis(3-aminopropyl)tetramethyldisiloxane (1.54 g, 0.0062 mol) was injected into the flask when the viscosity of the system became high. The mixture was then heated to 105 °C and maintained at that temperature for 16 h to keep equilibrium reaction and after that the system was heated to 180 °C to decompose the catalyst for 1 h. At last, the residual D_4 and low-boiling components in the system were removed under vacuum of 80 mmHg. Finally, the APT-PDMS was obtained as a colorless viscous liquid (yield: 90.25%).

2.1.3. Preparation of polydimethylsiloxane elastomer

A mixture of APT-PDMS (13.50 g, 0.64 mmol), TMPTA (0.25 g, 0.85 mmol) (molar ratio of N-H and C=C is 1:2), TMAH (0.0138 g, 0.1 wt% of reactants) dissolved in 0.2 g absolute ethyl alcohol was

prepared. Fumed nanosilica (1.38 g, 10 wt% of the mixture) was added into the system to enhance the strength of the elastomers. The mixture was blended with a Planetary Centrifugal Mixer (Thinky Mixer ARE-30). It was set firstly in the mixing mode for 2 min at 2000 r/min and then in de-foaming mode for 2 min at 2200 r/min to get a homogeneous mixture. Afterwards, the mixture was poured into a PTFE mold, degassed under vacuum for 10 min, covered with a PET film and then put in an oven at 90 °C for 24 h for the curing process.

2.2. Characterization

FTIR spectroscopy was carried out with a Bruker Tensor-27 FTIR spectrometer. 1H NMR measurements were performed with a Bruker Advance 400 MHz NMR spectrophotometer. The fracture surface morphology of the samples was characterized by Olympus BX53 optical microscope and scanning electron microscopy (Hitachi S4800).

The mechanical properties of the elastomers were evaluated using an Instron 5567 Universal Tester in accordance with ASTM D68-14 at room temperature. Dumbbell-shaped samples (50 mm × 8 mm × 2 mm) were made for the tensile tests and a deformation speed of 200 mm min⁻¹ was employed in the test process. The mechanical property results were the average of at least five measurements.

Dynamic mechanical analysis (DMA) was carried out on a TA Q800 instrument. Measurements were done in shear sandwich mode at a frequency of 1 Hz at different temperatures. Two samples with the same size (10 mm × 10 mm × 2 mm) were put in the shear clamp and temperature is maintained at 40, 60, 80 and 105 °C for 10 h. The change of storage modulus of the elastomer samples at different temperatures with time was recorded.

3. Results and discussion

3.1. Synthesis of silicone elastomer

The synthetic strategy and structure of silicone elastomer is outlined in Scheme 1. Aminopropyl terminated polydimethylsiloxane (APT-PDMS) is synthesized through ring-opening reaction of D_4 and siloxane equilibration reaction with 1,3-bis(3-aminopropyl)tetramethyldisiloxane initiated by basic catalyst TMAH. Afterwards, silicone elastomer is prepared through Michael addition reaction of amino groups on APT-PDMS and acrylate groups on TMPTA. 1H NMR and FTIR measurements are applied to characterize the structure of the synthesized APT-PDMS and silicone elastomer and the results are shown in Fig. 1. The resonance peaks corresponding to the synthesized APT-PDMS are labeled clearly on the spectrum. 1H NMR (400 MHz, $CDCl_3$): Si-CH₃ (0.052–0.106 ppm), Si-CH₂-CH₂-CH₂-NH₂ (t, 0.52 ppm), Si-CH₂-CH₂-CH₂-NH₂ (m, 1.47 ppm), Si-CH₂-CH₂-CH₂-NH₂ (t, 2.68 ppm), Si-CH₂-CH₂-CH₂-NH₂ (s, 1.73 ppm). The resonance peaks at 3.49 and 2.36 ppm are related to residual methanol and trimethylamine, derived from the decomposition of TMAH at high temperature. Based on the integration of resonance peak at 2.68 ppm and peak at 0.052–0.106 ppm, the molar molecular weight of the synthesized APT-PDMS is calculated to be about 21,000 g/mol. Fig. 1b shows FTIR spectra of TMPTA, synthesized APT-PDMS and silicone elastomer. The characteristic absorption peaks of acrylate groups at 1636, 1619 cm⁻¹ and 1721 cm⁻¹ (corresponding to stretching vibration of C=C and carbonyl groups) are clearly shown on the spectrum of TMPTA. Comparison of the spectra of APT-PDMS and silicone elastomer, the absorption peak at 1721 cm⁻¹ corresponding to carbonyl groups can be detected clearly, but the peaks at 1636, 1619 cm⁻¹ due to unsaturated double bonds disappear on the spectrum of silicone elastomer, indicating complete conversion of acrylate groups. So, 1H NMR and FTIR results verify the successful synthesis of APT-PDMS and silicone elastomers.

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