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A facile method for imparting sunlight driven catalyst-free self-healability and recyclability to commercial silicone elastomer

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ABSTRACT

A crosslinked silicone elastomer is prepared by utilizing polydimethylsiloxane as the host material and disulfide bond-containing silane as the crosslinking agent. By taking advantage of the sunlight activated metathesis of the included disulfide bonds, the crosslinked silicone elastomer can be self-healed and recycled for multiple times without any catalyst under sunshine. A series of verification experiments are carried out to reveal the underlying mechanism and the dynamicity of the silicone. Because the key raw materials are commercially available and the manufacturing follows common industrial procedures, the outcomes of this proof-of-concept study may be easily applied in practice. The simple and eco-friendly method would help to increase reliability and durability of silicone products and minimize wasting of resources.

1. Introduction

Silicone elastomer is known for its high chemical stability and good environmental adaptivity within wide temperature range [1]. Accordingly, it has been found in a wide variety of products, like automobiles, electronics, medical implants, housewares, sportswear, shoes and sealants. It would be meaningful if silicone elastomer possesses self-healability to autonomously repair the internal damages created during service, as well as recyclability to renew the wastes. The life circle of the material would thus be greatly extended.

So far, there have been some attempts to provide self-healing ability to silicone elastomer by means of extrinsic and intrinsic approaches [2,3]. Microcontainers like microcapsules [4] or glass capillaries [5] containing fluidic healing agents, for example, were respectively embedded in poly(dimethyl siloxane) (PDMS). Upon cracking of the composites, hydrosilylation reaction [4] or thiol-alkyne click chemistry [5] of the released healing agents took place at the damage sites, helping to re-bond the fracture surfaces. Besides, self-healing PDMS elastomeric coatings based on silicone chemistry from broken microcapsules [6] or core-shell nanofibers [7] for anti-corrosive protection were also fabricated.

Compared to extrinsic self-healing, intrinsic self-healing is more attractive as it enables multiple rehabilitation of the same place. To this end, a living silicone rubber was synthesized [8] and the living reactive anionic species produced during ring-opening polymerization of cyclosiloxane maintain reactivity to siloxane equilibration among different network isomers and cyclic oligomers, which can restore the original strength of broken samples. Furthermore, reversible Diels-Alder (DA) bonds were incorporated to crosslink polysiloxane elastomer, so that the latter was coupled with thermal remendability and remolding performance at elevated temperature [9]. Boroxine is another dynamic-covalent bond suitable for self-healing. The PDMS crosslinked by boroxine units can be healed by the reversible dehydration and hydrolysis of boroxine [10]. On the other hand, coordination complexes between the ligands in PDMS and Fe(III) centers were managed to be established, leading to self-healing of a silicone elastomer with properties close to biological muscles [11]. Similarly, dynamic complexation between thiol groups in modified silicone-oils and silver nanoparticles was applied for self-healing of fragmented silicone elastomer [12]. As

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for non-covalent interaction, a tris-urea motif giving six available hydrogen bonding sites was introduced into PDMS chains, so that the elastomer can self-repair the damaged surface via hydrogen bonds [13]. In addition, because the carboxyl end groups in linear carboxyl-terminated PDMS oligomers can react with diethylenetriamine and urea, supramolecular silicone elastomer with self-healing capacity was obtained [14]. Diffusion of polymer chains can also be utilized for self-healing of PDMS [15].

It is worth noting that silicone elastomers have to be crosslinked in practice by radical polymerization, hydrosilylation or condensation for turning them into solids with enough strength [16]. The irreversible covalent crosslinked networks do not allow for either self-healing or reprocessing [17–19]. Accordingly, the state-of-the-art recycling technology for the end-of-life irreversible silicones lies in the environmentally unfriendly conversion into low-molecular weight commodities or monomers with the aid of depolymerization agents, such as boron trifluoride diethyl etherate [7,18], and zinc salts [19]. Therefore, people had to design and prepare specific silicone containing reversible bonds as mentioned above to acquire intrinsic self-healability and reprocessing properties. Evidently, the method is not suitable for the commercial silicone elastomers, which are being used every day and hard to change their molecular structure.

For solving the problem, here we propose a facile route to prepare reversibly cured silicone elastomer from α,ω-dihydroxyl polydimethylsiloxane through condensation reaction with disulfide bond-containing silane coupling agent as crosslinker, which is similar to the industrial curing process of dealcoholized silicone rubber [16]. Disulfide bond belongs to dynamic reversible covalent bonds, and metathesis of disulfide bonds has successfully realized self-healing and recycling of cured epoxy [20–23], polyurethane [24–26] and vulcanized rubbers [27–29] via networks rearrangement. What we do is to find out the conditions under which exchange reaction of the disulfide bonds included in the cured silicone elastomer can effectively proceed. Compared to the existing works in this aspect, the key innovative part of the present investigation is that both the PDMS and silane curing agent are not tailor-made in laboratory but market available, which is conducive to the industrialization of the outcomes.

Meanwhile, the cured PDMS elastomers for practical usage have to be strengthened by other polymer resins or inorganic fillers. Since the introduction of inorganic fillers greatly reduces transparency of the materials, addition of polymer resins is a common measure. The mostly used resins are MQ and MTQ resins derived from hydrolysis-condensation between different silanes [16], which consist of end-capping agent (M unit, mono-functionality, refer to Fig. S1) and three-dimensional crosslinking segment (T unit, bis-tri-functionality, or Q unit, quadri-functionality, refer to Fig. S1). To improve both mechanical strength and reversibility of the PDMS elastomer, a new MTQ resin is synthesized hereinafter, in which the silane part of the T unit is substituted by the disulfide bond-containing silane coupling agent used for curing PDMS. The SS-MTQ resin (Fig. S1) is expected to behave like commercial MTQ resin in the case of reinforcing PDMS elastomer, and enhance self-healing and recycling abilities of the elastomer due to the increased amount of reversible disulfide bonds.

After many trials, we find out that the silane crosslinked silicone elastomer exhibits dynamicity under sunlight. Unconscious self-healing of cracks and reprocessing of silicone elastomer with the aid of sun shine is naturally attractive because solar energy is green and limitless. In the following, the smart stimulus-response performance and the underlying mechanism are analyzed, with the objective of forming a solid knowledge basis for the development of a technology having practical value.

2. Experimental

2.1. Materials

Three kinds of α,ω-dihydroxyl polydimethylsiloxane (HO-PDMS-OH, industrial grade) with different viscosities of 1500, 3000 and 5000 cSt purchased from Blue Star Chemical New Material Co., China were used as the matrix materials. Diethyl disulfide (DEDS) and dipropyl disulfide (DPDS) were supplied by Aldrich and used as received. Bis(triethoxysilylpropyl) disulfide (Si75) was purchased from Guangzhou Ecopower Chemical Co., Ltd., China (industrial grade) and Aldrich (chemical pure), respectively. Hexamethyldisiloxane (MM), tetraethyl orthosilicate (TEOS) and dibutyltin dilaurate (DBTDL) were industrial grade and purchased from Guangzhou Juchenzhaoye Silicone Co., Ltd., China.

2.2. Light sources

Two types of light source were employed: the sun and xenon lamp. The power intensity of sunlight on the midday of summer of Guangzhou is up to 90 mW/cm^2 (60–90 mW/cm^2 from 10:00 a.m. to 4:00 p.m.), and that of UVA and UVB is 2.5 mW/cm^2 (0.5–2.5 mW/cm^2 from 10:00 a.m. to 4:00 p.m.) [26].

To maintain the stability of light intensity for the model experiments, a xenon lamp equipped with cooling system was utilized to simulate natural sunlight. The distance between samples and the xenon lamp was about 30 cm. The light intensity of the xenon lamp radiation, unless otherwise noted, was 100 mW/cm^2, and that of UVA and UVB was about 0.8 mW/cm^2. Surface temperature of the specimens exposed to the xenon lamp with intensity of 100 mW/cm^2 was about 45 °C.

2.3. Model disulfide metathesis reaction

To verify whether disulfide metathesis can be effectively activated by sunlight in nonpolar solvent, a model exchange reaction between equimolar DEDS (1.2 g, 10 mmol) and DPDS (1.5 g, 10 mmol) in *n*-hexane (20 mL) was carried out under the xenon lamp light. The reaction progress was monitored by gas chromatography-mass spectrometry (GC-MS) analysis.

2.4. Preparation of disulfide containing-silicone resin (SS-MTQ, Fig. S1)

Hexamethyldisiloxane (MM, 40 g, 0.25 mol), ethyl alcohol (50 g), deionized water (90 g), and hydrochloric acid (8 g) were successively added into a 500 mL three necked round bottom flask. Next, the mixture was stirred at 25 °C for 30 min with the protection of nitrogen. Afterwards, the mixed solution of bis(triethoxysilylpropyl) disulfide (Si75, 75 g, 0.16 mol, made by Guangzhou or Aldrich for different tests) and tetraethyl orthosilicate (TEOS, 40 g, 0.19 mol) was dropwise added to the flask, and the reaction mixtures were further stirred at 65 °C for 4 h. When the system was cooled to room temperature, the organic layer was separated by a separatory funnel and rewashed with 75% ethyl alcohol for three times. A viscous light yellow liquid was obtained (Fig. S2) as the residual water and ethanol were removed by vacuum distillation at 130 °C for 1.5 h. The end groups in SS-MTQ are mainly methyl and hydroxyl groups. The latter would interact with PDMS as reinforcement when they are compounded together. By using back titration method, the hydroxyl content in SS-MTQ was found to be about 1.56 wt%.