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Room temperature self-healing power of silicone elastomers having silver nanoparticles as crosslinkers†

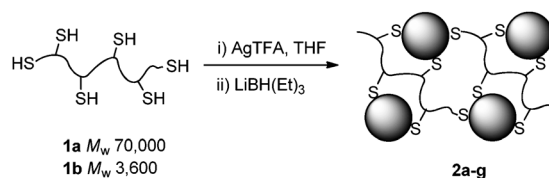
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Received 20th March 2012, Accepted 31st March 2012

DOI: 10.1039/c2cc32030d

Thiol-functionalised silicone-oils were crosslinked with silver nanoparticles to give mechanically consistent elastomers with high self-healing power. The materials were broken into small pieces and put together in intimate contact for 24 hours at room temperature, observing a complete macroscopic healing and a quantitative recovery of compression-stress and strain.

Self-healing materials have the ability to “autonomously” respond to damage inflicted on them. Recent years have witnessed a number of different approaches to address the challenge of fabricating materials that can fully or partially restore their physico-mechanical properties after suffering a fracture.¹ A particularly useful approach to generate self-healable polymers has been the introduction of reversible or dynamic bonds² (or crosslinks) into the polymer network. The idea is to reconnect the chemical crosslinks which are broken when a material fractures, restoring the integrity of the material. This dynamic crosslink-based self-healing approach has been carried out using both covalent chemistries and supramolecular interactions. With the exception of some organogels³ and hydrogels,⁴ in the vast majority of the self-healable polymer systems developed to date, this process usually requires the application of an external stimulus such as heat⁵ or UV light,⁶ and in many cases the presence of a catalyst or a radical initiator is needed. This is not ideal if we want a truly “autonomous” system, as the next generation of self-healing materials will be required to respond to damage with little or no human intervention. Furthermore, the description of elastomeric systems that self-heal without any external stimulus is very scarce.⁷ Here we describe a novel elastomeric system composed of a thiol-functionalised silicone polymer crosslinked by silver nanoparticles (Ag NPs), exhibiting high self-healing power. The new approach is based on the dynamic character of the crosslinks, e.g. thiolate bonds on the Ag NP surface, which are in constant exchange at room temperature.⁸



Scheme 1 Synthetic route followed for the preparation of self-healing silicone elastomers. Spheres represent Ag NPs.

The elastomers were prepared starting from two commercial silicone-oils, both functionalised with an average of 6 thiol groups per molecule (Genesee Polymers Corp., USA, average M_w 70 000 and 3600), using a very simple one pot procedure (Scheme 1). First, the silicone precursor **1a** was mixed with an appropriate amount of silver trifluoroacetate (1, 3, 5, 10 or 15 equivalents relative to –SH) in THF.[‡] Then the silver ions were reduced to Ag NPs by addition of lithium triethylborohydride (super-hydride®). Finally, the resulting black rubbery materials were transferred to a cylindrical mould and dried in air, to give the corresponding elastomers **2a–e** (Table 1).

The Ag/thiol molar ratio was found to be determinant in the macroscopic mechanical properties of the elastomers. Thus, when the ratio was too small (< 3) or too high (> 10) the materials obtained presented very low consistency and flowed in the form of fluids or “slimes”. The best elastic properties were achieved with systems having a Ag/SH molar ratio around 5 (Table 1).

Control material prepared by chemically cross-linking silicone oil resulted to be a dust-like (non-elastomeric) non-self-healable solid (see Fig. S1 and Scheme S2, ESI†). This kind of Ag/SH dependent behaviour has also been reported for other elastomeric materials crosslinked with Ag NPs.⁹

Table 1 Different elastomeric compositions prepared from **1a**, **1b** and AgTFA

Compound	Ag/thiol molar ratio	1a : 1b	Aspect
2a	1	1 : 0	Fluid
2b	3	1 : 0	Rubbery elastomer
2c^a	5	1 : 0	Rubbery elastomer
2d	10	1 : 0	Putty-like
2e	15	1 : 0	Slime-like
2f	5	0.9 : 0.1	Rubbery elastomer
2g	5	0.8 : 0.2	Rubbery elastomer

^a This is the best composition.

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† Electronic supplementary information (ESI) available: Synthetic procedures and characterization data, including TEM, UV/vis, TGA, FT-IR, SEM and DSC, and a short movie clip. See DOI: 10.1039/c2cc32030d

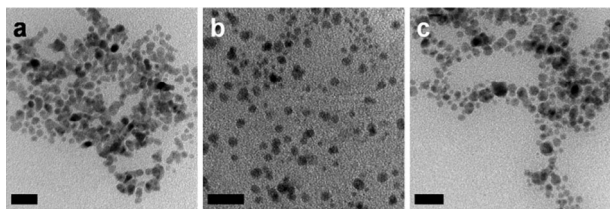


Fig. 1 TEM micrographs obtained for self-healing silicone elastomers **2c** (a), **2f** (b) and **2g** (c). Scale-bars correspond to 20 nm.

The presence of Ag NPs in the as-prepared silicone elastomers, even if the black colour of the material could certainly be a good visual indication of nanoparticle formation, was confirmed by different characterization techniques. UV-Vis spectra of the samples showed the typical plasmon resonance absorbance band at 420–440 nm (see Fig. S5, ESI†). TEM images revealed the presence of quite uniformly distributed Ag nanoparticles with an average diameter of 5 nm (Fig. 1). The ash residue observed in TGA analyses was in good agreement with the theoretical silver amount in each sample (see Fig. S6 and Table S1, ESI†). FT-IR spectra showed the disappearance of the –SH symmetrical stretching vibration, which appeared in the silicone precursor at 2490 cm^{-1} thus corroborating the formation of thiolate–silver bonds (Fig. S7, ESI†).

These singular silicone rubbers, when solid, presented high self-healing ability at room temperature. Thus, when a sample which was fragmented into small pieces was placed inside a syringe equipped with 2 pistons and allowed to stand at room temperature for 24 hours, the material restored into one single cylindrical piece with no observable cracks (Fig. 2a–d). This process could be repeated at will, without observing any loss of such self-healing power. SEM images of freshly cut surfaces of healed samples showed quite smooth surfaces, along with the complete absence of scars (Fig. S8, ESI†).

Compression test assays were performed in order to assess the mechanical properties of **2c**. In a typical experiment, a sample moulded in the form of a cylinder ($12\text{ }\varnothing \times 17\text{ mm}$ long) was compressed until failure (Fig. 2e–g). Sample **2c** presented a maximum compression stress close to 0.3 MPa, which represents a considerable pressure for nanoparticle-cross-linked elastomers. The elastomeric nature of **2c** allowed it to be compressed to more than 6.5 times its original length before failure

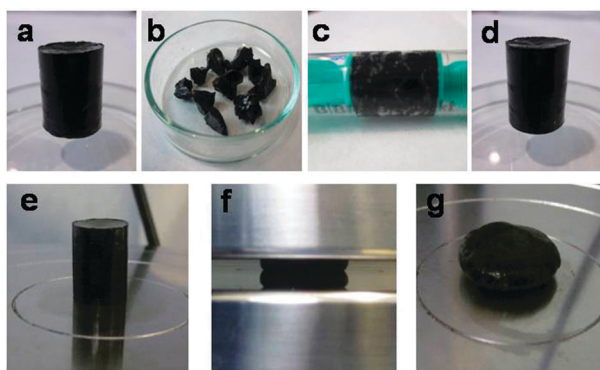


Fig. 2 Top: typical self-healing cycle for **2c**—pristine material (a), cut into small fragments (b), re-moulding (c) and healed material (d). Bottom: pictures of elastomer **2c** prior to axial-compression test (e), during compression (f) and after rupture (g).

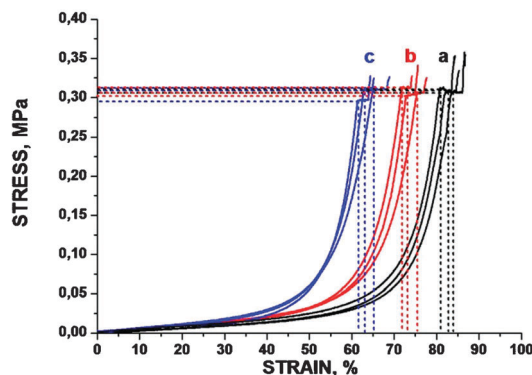


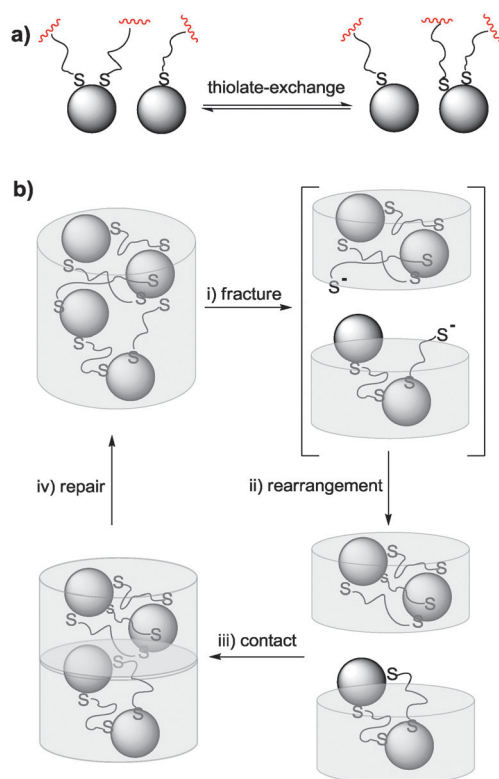
Fig. 3 Stress vs. strain curves determined for **2c** (a), **2f** (b) and **2g** (c). Different traces were recorded after each healing cycle, consisting of breaking and healing at r.t. for 24 h. Curves of each series have been slightly shifted on the *x*-axis for clarity.

(80–85% compression-strain). After the experiment, the sample was cut into small pieces, placed inside a cylindrical mould consisting of a plastic syringe equipped with 2 pistons, and allowed to stand at room temperature for 24 h. Then, the repaired cylinder was re-subjected to a new compression test. The compression-stress and strain recovery resulted to be quantitative. Fig. 3a shows almost identical stress vs. strain curves performed for a sample subjected to 3 breaking/healing cycles, where each healing process was carried out at r.t. for 24 h.

In order to study the effect of the crosslinking density on the mechanical properties of these materials, 2 different mixtures of thiolated silicones **1a** and **1b** (0.9:0.1 and 0.8:0.2 weight ratios, respectively) were crosslinked with 5 equivalents of AgTFA (compounds **2f** and **2g**, Table 1). It was expected that the lower molecular weight, and thus, the higher thiol density of **1b** would confer stronger mechanical properties to the final elastomer. Interestingly, samples **2f** and **2g** both withstood a maximum compression-stress of 0.3 MPa, identical to that observed for **2c**. However, a diminution of the compression-strain (70–75 and 60–65%, respectively) was observed along with the increase in the **1a**:**1b** ratio, as shown in Fig. 3 (traces b and c). Materials made from mixtures containing higher **1a**:**1b** ratios were more brittle and did not present proper elastomeric behaviour.

The mechanism involved in the healing-process described here is attributed to the dynamic character of the thiolate–silver interaction.¹⁰ It is well known that thiolate ligands can exchange over gold or silver surfaces.⁸ Such bonds are in constant exchange under equilibrium conditions, the system behaving as a dynamic network (Scheme 2a). It is precisely such exchange that makes our system to self-heal. Thus, the healing mechanism could occur as depicted in Scheme 2b: a fracture causes the dissociation of the weaker thiolate–silver bonds (i), which then immediately would rearrange and associate with neighbouring Ag NPs (ii); when the fragment surfaces are put in contact together (iii), the thiolate exchange between neighbouring Ag NPs results in the complete reparation of the network (iv).

Concerning thermal stability, an important softening was observed for **2c**, **2f** and **2g** when they were heated for a few minutes approximately above 105, 122 and 135 °C, respectively. After cooling down the materials recovered their initial aspect. Nevertheless, no DSC signal was observed in the 25–250 °C



Scheme 2 (a) Reversible thiolate exchange over Ag nanoparticles; (b) proposed self-healing mechanism for Ag-crosslinked silicone elastomers described herein. Spheres represent Ag nanoparticles.

range by DSC (Fig. S5, ESI[†]), showing that such a phase transition process undergoes gradually over a wide temperature range.⁹ However, after prolonged heating at lower temperatures (8 h at 80 °C) an irreversible transition from rubbery-like to pasty-like materials was observed. This structural change could be attributed to nanoparticle aggregation and subsequent decrease in crosslinking density, as such aggregation phenomena are common and well documented in the metallic nanoparticle-related literature.¹¹

In summary, we have developed a new type of self-healing silicone elastomer which is easily prepared from readily available starting materials. This new healing concept *via* thiol–silver exchange could be applied for the synthesis of other elastomeric systems with enhanced durability and performance. In addition, the known antibacterial properties of silver-containing elastomers⁹ could further encourage the use of these systems in applications in which hygienic materials are desirable, such as drinking water tanks and pipelines or food and beverage industry.

This work was partially financed by the Basque Government, through the i-Nanogune Ertortek Program. We thank A. Ochoa de Eribe, E. Elorza and S. Montes for assistance with TGA and DSC experiments.

Notes and references

[†] According to our previous experience, the addition of 1 equivalent of Ag is enough to guarantee conversion of all thiols to silver thiolates.¹²
[§] The syringe pistons were pushed until all the fragments make a good contact and air did not remain in between the fragments. Then it was allowed to stand without any applied pressure.

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