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A Stiff and Healable Polymer Based on Dynamic-Covalent Boroxine Bonds

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The ability to spontaneously repair damage, which is termed as self-healing, is an important survival feature in nature. Synthetic self-healing materials are highly desirable because this can lead to extension of materials' lifetime and reduction of waste.[1] So far, two types of self-healing materials have been reported: (i) extrinsic self-healing materials in which a healing agent has to be pre-embedded (in microcapsules[2] or microvascular[3] networks), and (ii) intrinsic self-healing materials that are able to heal cracks by utilizing reversible covalent bonds (such as alkoxyamine,[4] disulfide,[5] Diels–Alder reaction,[6] radical dimerization reaction,[7] and cycloaddition reaction[8]) or dynamic interactions (such as hydrogen bonds,[9] π–π stacking interactions,[10] host–guest interactions,[11] and metal–ligand interactions[12]).

Polymer chain mobility is a key factor to facilitate self-healing. The polymer matrix will be healed only when polymer chains can diffuse along the polymer/polymer interface.[1a] Therefore, it is a challenge to realize self-healing in stiff polymers (with reduced mobility of the molecular segments).[13] Most of the present self-healing materials are soft and/or stretchable due to sufficient polymer chain mobility. However, a stiff self-healing polymer is needed as they can be used as strong and light weight material for building industry, aerospace engineering, and protective coatings.

Boroxines have been frequently employed to prepare a number of dynamic-covalent assemblies.[14] The boroxine/boronic acid equilibrium can be readily shifted by temperature or the addition/removal of Lewis bases or water, thus providing a mechanism for self-healing.[14a,15] Herein, we report a boroxine-containing polymer exhibiting simultaneously strong (with tensile Young's module up to 182 ± 15.8 MPa and compressive Young's module up to 142 ± 9.8 MPa), stiff (with elongation and compressibility less than 10% at 10 MPa stress) and water-assisted self-healing properties. Specifically, we use dynamic-covalent boroxine bond to crosslink the poly(dimethylsiloxane) (PDMS) chain into 3D networks. The as-prepared sample is very strong and stiff, and can bear a load of more than 450 times of its weight. Upon wetting, the equilibrium of surface-exposed boroxine was shifted toward the disassociated state so that abundant free boronic acid were generated and the PDMS chains were decrosslinked, resulting in increased molecular segments mobility (**Figure 1**). This process was reversed by removing water. Therefore, the polymer can be completely healed upon heating after wetting. Such stiff and healable property combined into a synthetic polymer has never been realized before. Moreover, we demonstrated that our polymer can be used both as healable adhesives and in fabricating healable semi-transparent conductors.

The boroxine-containing PDMS networks (**PDMS-Boroxine**) were prepared according to Scheme S1 (Supporting Information). The Aryl-Boroxine was synthesized according to previous report with little modification.[16] As shown in Figure S1 (Supporting Information), the formation of the expected boron-based ring of boroxine was evidenced in the ^{1}H NMR, ^{11}B NMR, and fourier transform infrared (FT-IR) spectra.[14a,15c] The **PDMS-Boroxine** polymer was prepared by crosslinking between Aryl-Boroxine and bis(3-aminopropyl) terminated poly(dimethylsiloxane) (H_2N-PDMS-NH_2) via amidation reaction. The FT-IR spectrum revealed that the amide I (C=O stretching) bands shifted to lower wavenumbers and a new weak band appeared at 759 and 684 cm^{-1}(Figure S2, Supporting Information), which is characteristic for boroxine formation.[14a,15c] The as-prepared film has a size of 75 × 14 × 1.0 mm^3. Differential scanning calorimetry (DSC) measurement shows that the T_g is about 65 °C (Figure S3, Supporting Information).

The mechanical properties of **PDMS-Boroxine** were characterized via static uniaxial tensile test, compressive test, and stress-relaxation test[17] at ambient air (20 °C, 35 H%, H% means percent of humidity.). The tensile and compressive tests were carried out by measuring four equal samples at a rate of 10 mm min^{-1}. The key mechanical properties of tensile testing are summarized in Table S1 (Supporting Information). The static tensile and compressive stress–strain curves are reproducible and resemble those of typical stiff polymers (**Figure 2**a; Figure S4, Supporting Information). Polymer **PDMS-Boroxine** has a high Young's modulus (tensile 182 ± 15.8 MPa; compressive 142 ± 9.8 MPa, the inconsistency between the tensile modulus and compressive modulus should be due to the different sample dimensions and measurement conditions.), which is about two orders of magnitude higher than the previously reported self-healing PDMS-containing polymer system.[1,12]

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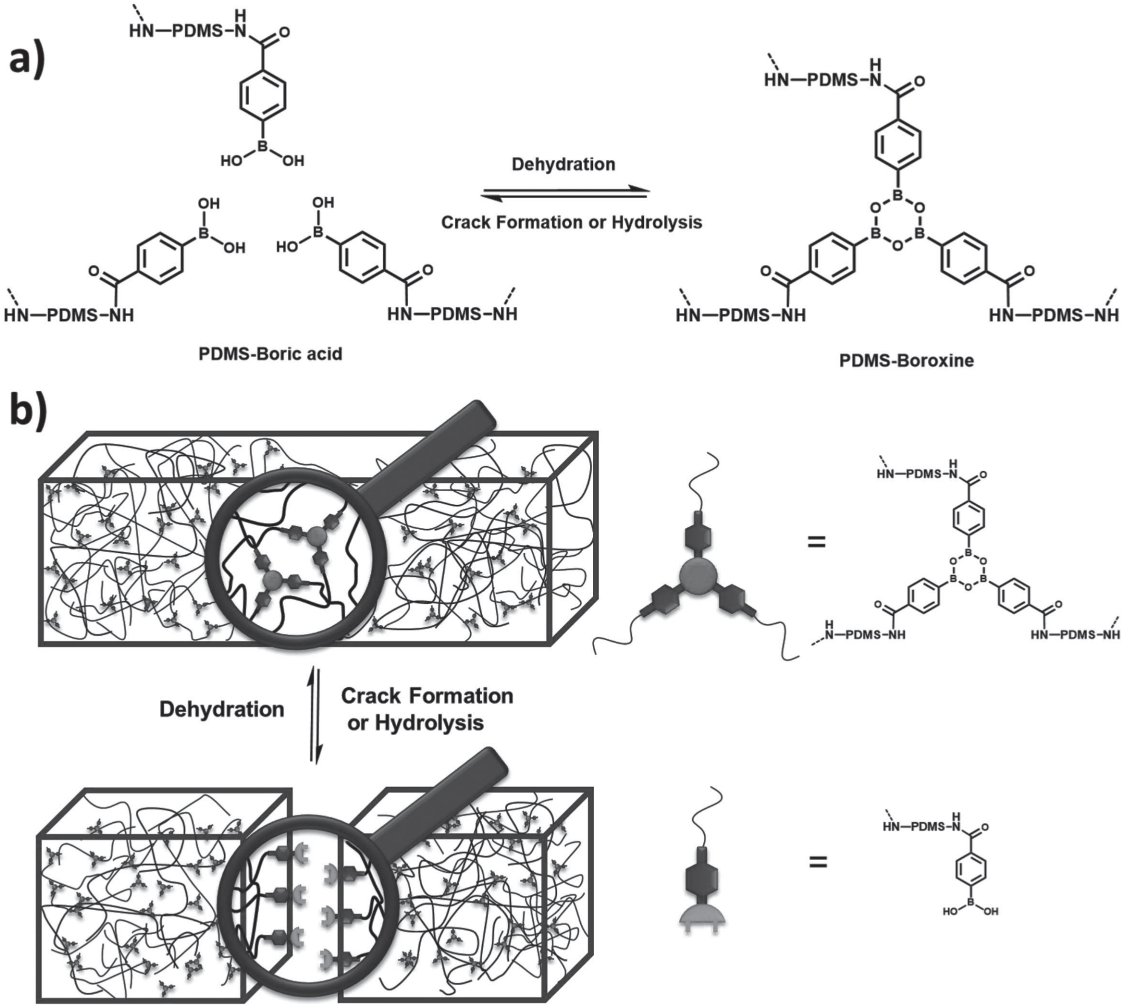

Figure 1. a) The structure and the dynamic process of PDMS-Boroxine; b) The mechanism for the water-enabled healing process.

Such a high Young's modulus is attributed to the strong and 3D network crosslinked through boroxine unit. However, only slight elongation (<10% before fracturing) was observed upon applying a tensile strength of 9.46 MPa. Stress-relaxation experiments showed that the samples undergo substantial stress-relaxation with time. However, the residual stress (1.82 MPa at 20 °C) was still quite high after 20 min (Figure S8, Supporting Information). Such features indicate that our new material is a stiff and strong polymer with very poor molecular segment mobility, which is unfavorable for self-healing.

However, the **PDMS-Boroxine** polymer exhibited water-enabled healing properties as demonstrated in Figure 2 and Figure S5 (Supporting Information). The films were cut into two completely separate pieces with a razor blade (Figure S5a,b, Supporting Information). For making the self-healing effects more obvious, one piece of sample was colored into yellow and the other was colored into dark green. The two half films were wetted with water and then brought back into contact (Figure S5c, Supporting Information). After healing for several seconds at room temperature, we observed that the two pieces healed and could withstand their own weight (Figure S5d, Supporting Information). We further investigated the effect of healing time and healing temperature on the recovery of mechanical properties of the testing sample. The results showed that the healing efficiency increases by prolonging healing times and increasing the healing temperature (Figure 2b; Tables S2 and S3 and Figure S6, Supporting Information). Heating to 70 °C significantly accelerated the healing process, which agrees well with the T_g of **PDMS-Boroxine**. At 70 °C, the healing efficiencies were over 50% for 30 min and reached 95% for 5 h. When healed at 70 °C for 12 h, the breaking strain and maximal strength were completely recovered as compared to the original sample (Figure 2b). The notch on the film almost disappeared after healing treatment although an indistinct healed scar was still visible under the microscope (Figure 2c). The cycle of breaking and healing can be repeated many times. Such complete healing ability for stiff and strong polymers has never been reported before.

The mechanism for the water-enabled healing process was elucidated in Figure 1b. The PDMS chains were crosslinked by boroxine unit in a 3D manner. When the film was cut and water was added to the freshly cleaved surfaces, the equilibrium of surface-exposed boroxine was shifted toward the disassociated state so that abundant free boronic acid was generated.

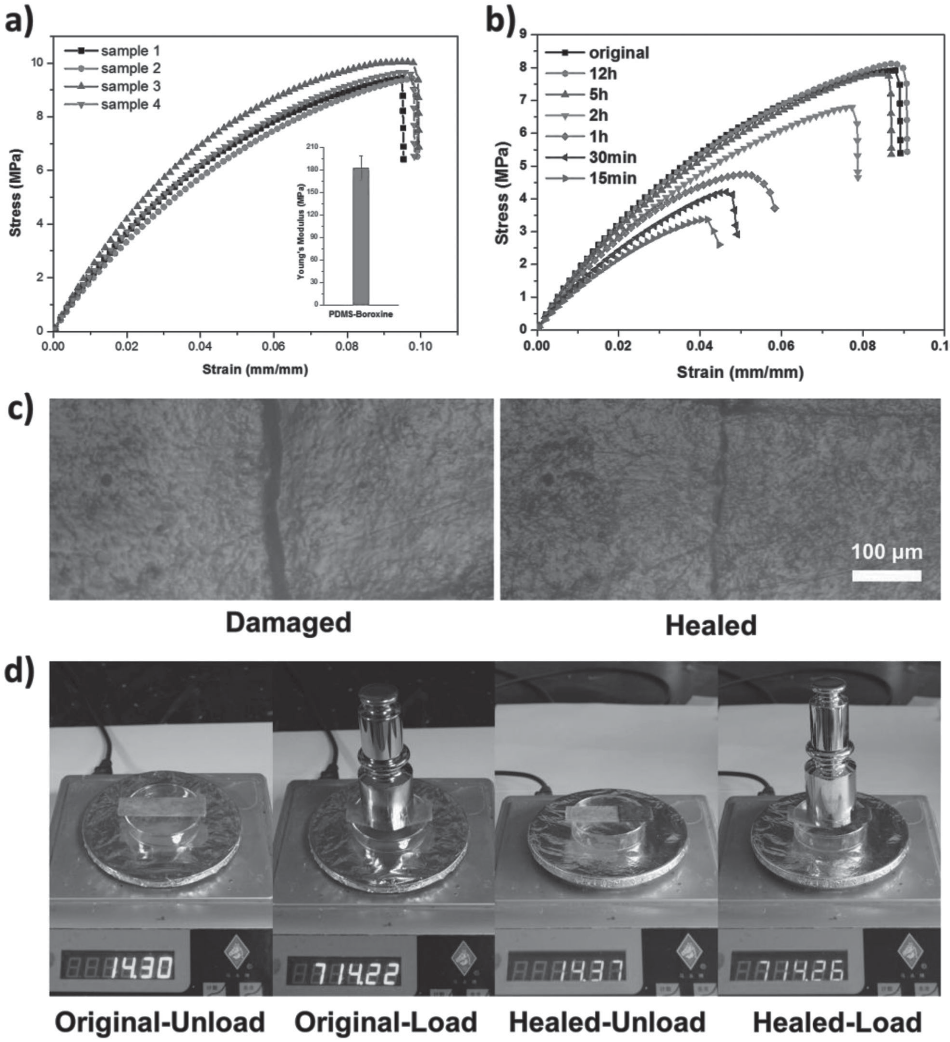

Figure 2. The mechanical and healing properties of PDMS-Boroxine. a) Tensile stress–strain curve of PDMS-Boroxine. Data for four samples are shown to illustrate the reproducibility. The inset shows the average Young's modulus of the four testing samples with error bar. b) Stress–strain curve of healed PDMS-Boroxine at 70 °C for various healing times. c) Microscopic images of a film before (left) and after (right) healing at 70 °C for 5 h. d) The weight-bearing test of PDMS-Boroxine film before (left) and after (right) healing at 70 °C for 5 h. The weight of petri dish is 12.77 g as shown in Figure S9, Supporting Information).

The resulting free boronic acid on each surface could readily form bridges via boroxine bond formation across the fracture after drying.[14a,15] Additionally, heating will lead to softening of the materials, thus increases the chain mobility and facilitates the healing process. We performed variable temperature tensile-stress and stress-relaxation tests to study the effect of temperature on the mechanical properties. Results from these tests showed that the Young's modulus, maximum strength, and residual loading stress all decreased upon increasing the temperature (Figures S7 and S8, Supporting Information), indicating that the polymer was softened at high temperature. However, at 70 °C, the Young's modulus, maximum strength, and residual loading stress after 20 min of the material were 124.8, 3.68, and 0.40 MPa, respectively, which indicates that the materials were still quite stiff at the healing temperature.

The stiff nature of **PDMS-Boroxine** was also determined by a weight-bearing test (Figure 2d). The testing sample (70 mm × 40 mm × 2 mm, 1.53 g) was colored yellow and placed on a petri dish (with the diameter of 50 mm, weight of 12.77 g, Figure S9, Supporting Information). The weights were then added on the testing sample one by one. The results showed that the testing sample could withstand weight of 700 g without fracturing, which is more than 450 times of its own weight. The degrees of deformation will increase by increasing bearing weights and decrease by withdrawing the bearing weights, until the total recovery (Figure S10, Supporting Information). The healed samples were also able to sustain a weight of 700 g with little deformation and recover its shape without any crack when withdrawing the bearing weights. The process could be repeated many times (Figure S11, Supporting Information, Supplementary movie 1). The coexistence of excellent mechanical property and water-enabled healing behavior is very intriguing as they could be useful as strong, light-weight, and healable structural materials in some special situations.

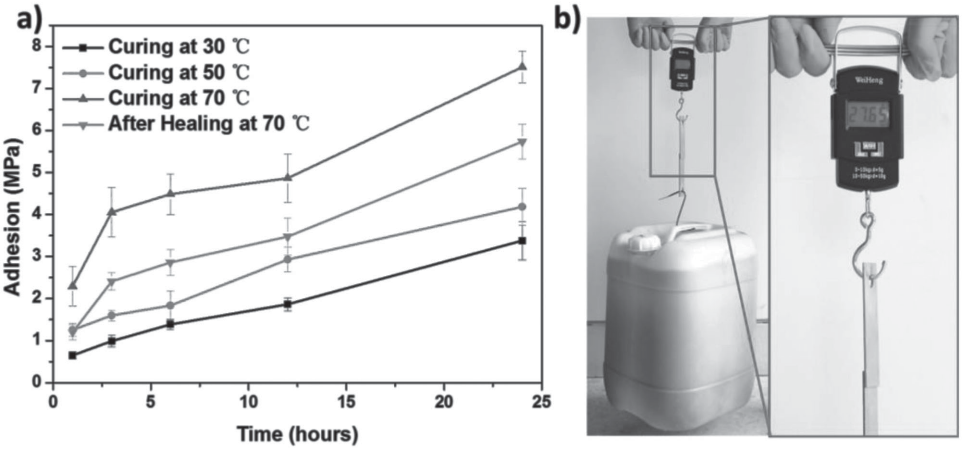

Figure 3. The performances of PDMS-Boroxine as adhesive. a) The effect of cure time and temperature upon lap shear adhesion of PDMS-Boroxine on sanded steel substrates. b) The image showing that two sanded steel substrates bonded by PDMS-Boroxine can withstand a full force of 27.65 kg (approximately equal to 271 N).

A unique property of boron compounds is their wide use in adhesives[18] as their surfaces are sticky upon wetting. Therefore, we envisage our new polymer might be useful as a reusable adhesive with healable property which has been rarely reported before.[19] As shown in **Figure 3**a, the adhesion values are dependent on the curing temperature and time. When cured at 70 °C for 24 h, the adhesion value reached a maximum of 7.5 MPa which rivals the commercial glues such as cyanoacrylate and epoxy.[20] Interestingly, our glue can be reused after damage. When two sanded steel substrates bonded by **PDMS-Boroxine** were separated, they can be rejoined by dipping the end with adhesive into water and then dried. After drying at 70 °C for 24 h, the adhesion value can be recovered to 5.7 MPa. Figure 3b shows that two sanded steel substrates bonded by **PDMS-Boroxine** can withstand a full force of 27.65 kg (approximately equal to 271 N, gravitational acceleration $g = 9.8$ N kg^{-1}).

Developing conductors that can repair themselves after experiencing damage is important as this can increase the lifetime and reliability of the devices and reduce the amount of electronic waste. In the past few years, much effort has been devoted to this topic by covering Ag nanowires (Ag-NWs) layer on top of self-healing polymer matrix.[21] Solution casting[21,22] and vacuum filtration process[23] are the two most frequently used methods for fabricating Ag-NWs transparent conductors. The vacuum filtration process can generally afford conductors with better transmittance. However, the Ag-NWs have weak adhesion to the substrates as they can't penetrate into the polymer matrix, so they can be easily removed. The surface of our polymer material can be softened by adding some water due to hydration of boroxine, thus can provide an effective way to fabricate healable conductors with strong adhesion through vacuum filtration process (**Figure 4**a). By covering Ag-NWs (432 mg m^{-2}) layer on top of the water-pretreated **PDMS-Boroxine** polymer matrix, we successfully obtained a healable semi-transparent conductor (sheet resistances of 12 Ω sq^{-1}) with enhanced adhesion between Ag-NWs and the polymer substrate (Figure 4b; Figure S12a,b, Supporting Information). The scanning electron microscope (SEM) images of the surface and cross-sections of the composite conductor are shown in Figure 4c. The cross-section image shows that many of the Ag-NWs are embedded in the stiff polymer substrate (Figure 4c, inset). Only a 5% decrease of conductivity was observed after 100 cycles of repeated adhesion and peeling test using 3M Scotch Tape (Figure 4d). The SEM images show that there are abundant Ag-NWs left in the polymer matrix after the repeated adhesion-peeling test, most of them are inserted into the polymer (as shown in the red frame) (Figure S12c, Supporting Information). Such a strong bonding with substrate polymer has only been realized in transparent conductors prepared by solution casting method.[22a] After cutting and healing the crack became invisible (Figure S12d,e, Supporting Information), the electric conductivity recovered with the sheet resistance remained almost unchanged at 15 Ω sq^{-1}.

Interestingly, the polymer **PDMS-Boroxine** is relatively nonhygroscopic although it shows water initiated hydration of **Boroxine** which facilitated the healing process and its utilization in adhesives and healable conductors. We performed tensile-stress and stress-relaxation at different moist conditions (Figures S13 and S14, Supporting Information). Before test, the samples were placed under the humidity of 35 H%, 50 H%, 65 H%, and 80 H%, respectively, for 3 d. The tensile-stress curves showed that the stress was decreased while the strain was increased when the humidity increased from 35 to 80 H%. The stress-relaxation curves also showed the decrease of residual loading stress upon increasing moisture. However, after exposure to moist environment (80 H%) for 3 d, the Young's modulus, maximum strength and residual loading stress of the materials remained 120.7, 3.69, and 0.72 MPa, respectively, indicating that the materials are relatively stable under moist conditions (Figure S14, Supporting Information).

In summary, we have designed and synthesized a PDMS polymer network crosslinked by dynamic-covalent boroxine bond. The as-prepared sample is strong and stiff due to poor molecular segment mobility. After wetting, the equilibrium of surface-exposed boroxine was shifted toward the disassociated state and therefore the polymer became sticky and soft, leading to a water-enabled healing ability. Moreover, we demonstrated that our polymer can be used as healable adhesive and to

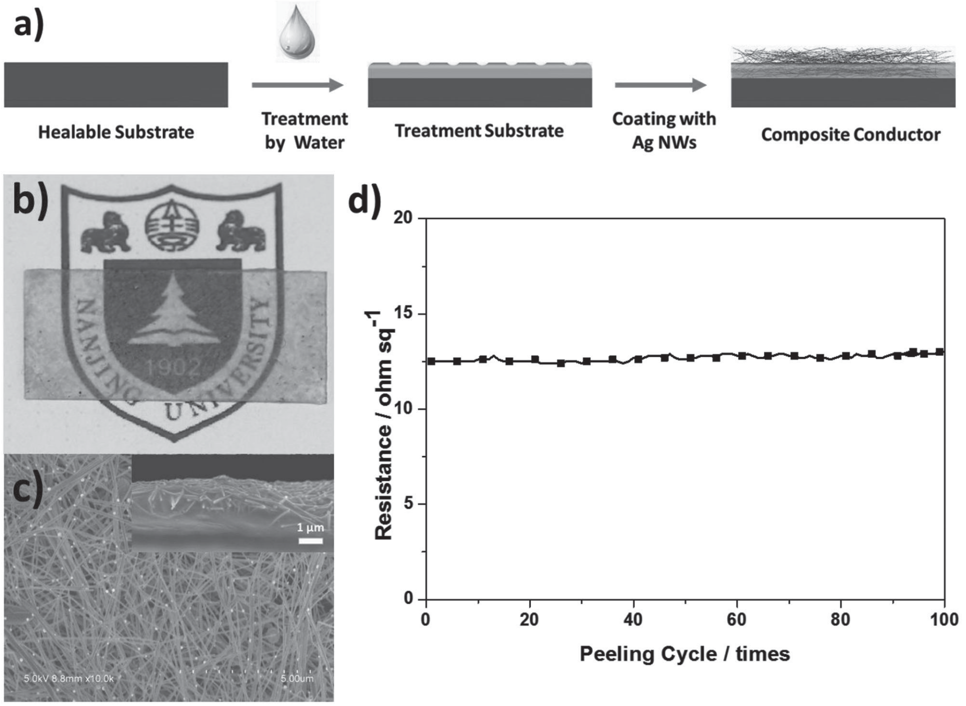

Figure 4. Healable semi-transparent conductors based on PDMS-Boroxine. a) The model and fabrication procedure of AgNW-polymer composite conductor. b) Photograph of the semitransparent composite polymer conductors with the sheet resistance of 12 Ω sq^{-1}. c) The scanning electron microscope (SEM) images of the surface and cross-sections (inset SEM image) of the composite conductor. d) Resistance changes of composite conductor with the cycles of adhesion and peeling with 3M Scotch Tape.

fabricate healable semi-transparent conductors with enhanced adhesion between Ag-NWs and the polymer substrate. Our results suggest that the stiffness and healable properties can be obtained simultaneously without conflict by utilizing specific dynamic-covalent chemical bonds.

Experimental Section

Mechanical and Healing Tests: Mechanical tensile-stress, compressive-stress, and stress-relaxation experiments were performed using an Instron 5944 Microtester. For mechanical tensile-stress and self-healing test, sample size of 40 mm length × 5 mm width × 2 mm height, gauge length of 10 mm, and strain rate of 10 mm min^{-1} were adopted. For mechanical compressive-stress test, sample size of 4 mm length × 3 mm width × 3 mm height, loading area of 12 mm^2, and strain rate of 10 mm min^{-1} were adopted. All samples were tested at ambient conditions (20 °C, 35 H%). For stress-relaxation experiments, the samples with dimensions of 40 mm length × 5 mm width × 2 mm height were held at 5% strain (gauge length of 10 mm) for 20 min and the decay of stress was monitored over time.[17] For the temperature- or humidity-dependent experiments, the samples were equilibrated for 15 min (for temperature-dependent experiments) or 3 d (for humidity-dependent experiments) at the corresponding temperature or humidity before testing. The temperature and humidity was controlled by self-made environment chamber. For self-healing tests, the sample was cut into two completely separate pieces with a razor blade. The two half films were wetted with water by dipping the cut end into water for 10 s and then brought back into contact for subsequent healing at different temperatures for different time (humidity of 35 H%). The healed films were then tested following the same procedure to obtain the stress–strain curves.

Adhesive Tests: The Lap shear testing experiments were performed using an Instron 4200 Microtester. Lap shear testing was used to evaluate the adhesion properties and all adhesive tests were carried out on steel substrates. The steel adherends (100 mm × 25 mm × 2 mm) were sanded with 50 grit sandpaper, then washed with soapy water, and rinsed with acetone.[24] The polymer (1.0 g) was swelled in DCM (5 mL) to obtain the glue, and then each glue (50 mg) was smeared on the testing sample to form the overlapped (12.5 mm × 25 mm) in a single lap-shear configuration.

Fabrication of Ag-NWs Composite Conductor: Ag-NWs networks were prepared by vacuum filtration of a dilute dispersion (1 mg mL^{-1}) through PTFE filter paper (Whatman, pore size 0.45 mm). The surface of polymer **PDMS-Boroxine** was pretreated by deionized water for 5 min. Then the **PDMS-Boroxine** substrate was placed on the top of deposited film with the pretreated side in contact with the Ag-NWs for several minutes, and then kept in vacuum for 2 h at 70 °C to remove the residual water and regenerate the boroxine. The PTFE filter paper was then peeled off from the substrate and the percolation networks were transferred onto the surface of the polymer to obtain composite conductor film.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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