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Shape Memory-Enhanced Electrical Self-Healing of Stretchable Electrodes

Hongsheng Luo [1,*], Huaquan Wang [1], Huankai Zhou [1], Xingdong Zhou [1], Jinlian Hu [2,*], Guobin Yi [1], Zhifeng Hao [1] and Wenjing Lin [1]

1 School of Chemical Engineering and Light Industry, Guangdong University of Technology, Guangzhou 510006, China; whq931@163.com (H.W.); zhouhk816@163.com; (H.Z.); zxd52013149898@163.com (X.Z); ygb702@163.com (G.Y.); haozhifeng3377@163.com (Z.H.); jingjingfable@126.com (W.L.)

2 Institute of Textiles and Clothing, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong, China

* Correspondence: hongshengluo@163.com (H.-S.L.); tchujl@polyu.edu.hk (J.-L.H.); Tel.: +86-20-3932-2231 (H.-S.L.)

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Abstract: A novel shape memory-based self-healable stretchable electrode was explored by embedding the silver nanowires (AgNWs) network into a healable polymer matrix. Unlike the traditional shape memory-assisted self-healing, pre-stretching to the temporary shapes, which was fixed in a typical shape, memory thermo-mechanical programming significantly enhanced the thermo-triggered healing performance. The morphological as well as conduction variations during the healing process were investigated. The enhancing effect of the pre-stretching on the healing efficiency was emphasized, which was expected to attribute to the release of the pre-stored strain energy driving the closure of the scratch. The findings disclosed how to utilize the shape memory effect to improve the biomimetic properties for the stretchable electrodes, which may greatly benefit the application of the intelligent polymers in the field of multi-functional flexible electronics.

Keywords: shape memory polymers; conductive; self-healing; stretching; enhanced

1. Introduction

Self-healing polymers are one set of very important bio-mimetic materials, which have been catching increasing academic and industrial interests over the recent years. The underlying mechanisms towards heal-ability in the polymeric systems included various types of reversible bonding, such as hydrogen and disulfide bonding [1,2]. Unlike the previous reports on the self-healable polymers commonly requiring complex macro-molecular design and synthesis, shape memory-assisted self-healing was explored for a thermoplastic shape memory polymers matrix containing the healing reagent [3]. In this shape memory-assisted self-healing polymeric systems, the polycaprolactone (PCL) was chosen as the healing reagent due to the programmable crystallization/melting transitions, compatibility with the polymer matrix and the moving ability of the molecules in the melted states [4]. For instance, the PCL was integrated into an epoxy or polyurethane polymeric matrix via direct physical blending or electro-spinning to nonwoven meshes [5]. The reversible thermal transitions at the aid of the shape memory effect enabled the scratches on the surfaces even in the scale of several micro-meters to heal under thermal stimulations. Furthermore, the integration of the conductive nano networks with intelligent polymers lead to flexible and stretchable electronics possessing multi-functionalities. For instance, P.S. Lee et al. explored a dynamic cross-linked hydrogel featuring the stain-dependent conduction and the high stretch-ability, which was applied to detect human-motion. The conductive networks were constructed by carbon nanotubes (CNTs) and the strain sensing properties were capable of self-healing [6]. X. X. Zhang et al. demonstrated a multiple hydrogen bonding network with the CNTs which exhibited extremely fast and repeatable self-healing ability with high healing efficiency of 93% [7]. Particularly, a multi-layer structure shape memory strain sensor was reported comprising a polyurethane fiber core, interconnected CNTs filament, and a polypyrrole cladding layer. The microcracks generated under strain endowed this fibriform sensor with the superior sensitivity, a wide detectable range and the ability to detect multimodal deformation and human motions [8]. Y.T. Yao et al. designed a two-way composite, which was comprised of an electroactive polymer providing actuation force and a traditional shape memory polymer to fix the temporary shapes due to the modulus changing abilities.

Although shape memory assisted self-healing has been developed for several years, there are few reports on the heal-ability of the conductivity for the shape memory-based conductive composites. We embedded the AgNWs into an epoxy shape memory matrix and achieved multi-stimuli triggered self-healing effect, i.e., healing the surface cracks under electrical and thermal stimulations [9]. Herein, a novel shape memory-based stretchable healable electrode was explored. The resultant composites were capable of healing the damaged conduction as exposed upon the scratch under thermal stimulation. To be interested, we pre-stored the strain energy perpendicular to that of the scratch by taking advantage of the stretch-ability and shape memory effect. The healing efficiency was greatly enhanced due to the closure of the crack surfaces driven by the release of the strain energy. We called the "pre-stored and release of the strain energy in order to improve the self-healing" as the shape memory-enhanced self-healing. The studies provided a facial physical programming to optimize the behaviors of shape memory conductive composites and may greatly benefit the application of intelligent polymers in the field of functional flexible electronics.

2. Materials and Methods

The bi-layer structure conductive composites were fabricated via the transfer process. Briefly speaking, the conductive network was firstly dip-coated onto a release substrate, followed by transferring into the shape memory polymer matrix [10,11]. The AgNWs were in the size of 25 μm length and 80–120 nm diameter. The resultant electrodes were cut into the average size of 75 × 25 × 0.05 mm (length× width× thickness). The shape memory polymers utilized in this study were synthesized with the PCL as the soft segment and the diphenyl-methane-diisocyanate as the hard segment. Additionally, 1,4-butylene glycol (BDO) was utilized as the extender. According to our previous study [11], the melting transition temperature of the PCL was determined to be around 58 °C by the Differential Scanning Calorimetry (DSC) measurements and 40 wt. % of the PCL content was arbitrarily chosen in order to obtain the optimized shape memory effect and healable performance. What's more, undesirable electrical-thermal effect due to the Joule heat should be avoided in the measurements. Based upon our previous infrared thermography study [9], the temperature of the AgNW-containing electrodes kept at the ambient temperature till the applied voltages was up to 1–3 V. Thus, the voltages utilized in this study were limited to be 0.1V, aiming at avoiding any phase transitions due to the Joule heating. In the electromechanical testing, the samples were extended to the temporary shapes at the rate of 10 mm/min, whose current was monitored with a constant voltage of 0.1V via the platform composedofan electrochemical workstation and a tensile machine(CHI800D, CH Instruments Ins, Shanghai, China). The samples were labeled as CSHP-5, CSHP-10, CSHP-15 and CSHP-20 where the numbers stood for the per-stretching percentages. The cracks were made by razor, followed by the investigations of Scanning Electron Microscope (Zeiss Evo 18 Special Edition SEM, Germany) with accelerating voltage of 15kV) and UV Laser Raman Spectroscopy(LabRAM HR 800, HORIBA Jobin Yvon, France).

3. Results and Discussion

3.1.Fabricationof the Healable Stretchable Electrodes

The traditional shape memory-assisted self-healing typically involved a two-step procedure, i.e., exposure upon the cracks in the original state and thermal-triggered self-healing [3]. Except for the crack areas, there were not visible macro-scale shape changes during the healing process. Unlike the traditional procedure, the explored shape memory-enhanced self-healing contained three steps, which are illustrated in Figure 1a. The samples were firstly pre-stretched and fixed into the temporary shapes via a typical shape memory thermo-mechanical programming. Afterwards, scratch in the direction perpendicular to the pre-stretching destroyed the conductive networks. Thirdly, heating was applied to trigger the heal-ability, meanwhile the shape recovery was simultaneously occurred. The pre-stretching and creation of the surface scratches meant that changes in the shape and length of the electrode caused resistance variation. Furthermore, the release of the strain energy along with the shape recovery dramatically improved the recovery of the conductivity. Compared with the conductions in the cracked and thermally-triggered recovered states, the electrodes exhibited better reconstruction of the conductive networks as well as enhanced heal-ability of the conduction. Figure 1b shows SEM image of the resultant electrodes in bi-layer structure. The conductive AgNWs network was embedded into the healable matrix, constructing pathways for the electrons transportation. On the other hand, the polymer matrix exhibited well compatibility due to the PCL segments in the compositions. The resistance of the electrodes significantly decreased as the increase of the AgNWs loads, the plot of which is shown in Figure 1c.The weight amounts of the AgNWs utilized for one time ranged 0.8 and 4 mg. Correspondingly, the area densities of the AgNWs were calculated ranged 0.43 and 2.12 $\mu g/mm^2$.According to the percolating theory, the conduction approached to constant once the content of the conductive nano-fillers reached threshold value. The threshold value for the AgNWs network was determined to be around 2.8 mg·(1.49 $\mu g/mm^2$). Thus, the samples containing 3.0 mg of the AgNWs were utilized in this study. The conduction could be seriously damaged by the cracks in the conductive surface layer. Figure 1d shows a representative scratch in the width of dozens of micrometers. The gap made the AgNWs separated in the local area. As a result, the conductive network was temporarily damaged.

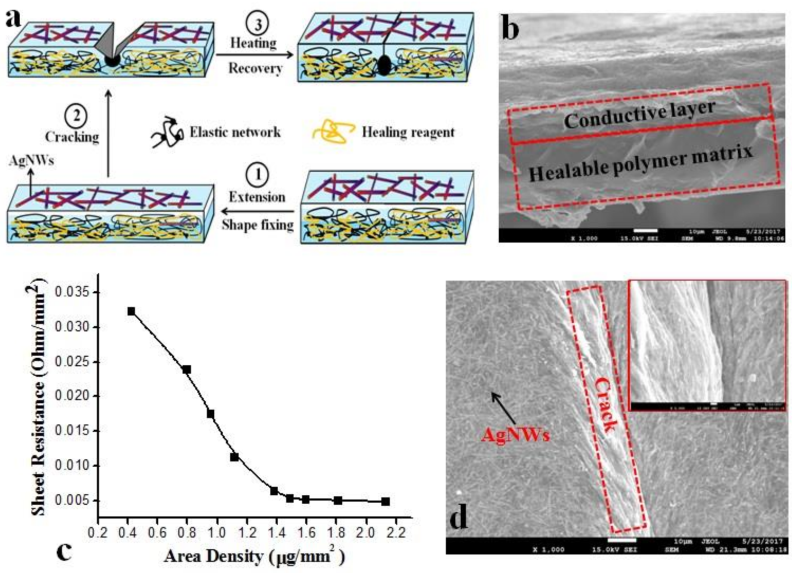

Figure 1. (**a**) Schematic illustration of the shape memory-enhanced self-healable electrode; (**b**) Scanning Electron Microscope (SEM) image of the electrode cross section; (**c**) The plot of the sheet resistance against the AgNWs loads. (**d**) SEM image of the surface morphology with micro-scale scratch.

3.1. Shape Memory-Enhanced Self-Healing with Pre-Stretching

In order to evaluate the reversibility and stretch-ability, the electromechanical measurements for the crack-free samples were performed firstly. The conduction–strain relationship was disclosed under constant voltage of 0.1 V and strain speed of 10 mm/min. Figure 2a shows the current variation which was monitored in the overall shape memory programming. After a slight drop as heated at 80 °C, the current dramatically decreased and stabilized as the samples were extended to the temporary shapes. After cooling down to fix the temporary shapes, heating again allowed the shape recovery along with the recovery of the current. The conduction could partially recover under the heat stimulations, depending on the extension percentages. The recovery ratio was calculated according to the ratios of the recovered and pristine currents, which was determined to be 99%, 70% and 40% as the pre-stretching percentage was 20%, 40% and 60%, respectively. Too large extension may result into the irreversibility associating with plastic deformation of the polymer matrix, permanent break of the conductive Ag network and local movement of the AgNWs [11]. Thus, the pre-stretching was limited to within 20% in the next electromechanical measurements, ensuring that it was in the reversible region for the study on the shape memory-enhanced self-healable conductions. Furthermore, as for the samples exposed upon the scratch in the temporary shapes (shown in Figure 2b), pre-stretching with four different percentages ranging from 0 to 20% led to dramatic decrease in the current. The cracks were made in the temporary shapes, enabling the currents to approach zero. Afterwards, the self-healing was triggered at 80 °C for several seconds, which was above the T_m of the PCL. The healing efficiency (η) was calculated by the following equation:

$$\eta = (I_o - I_c)/(I_h - I_c) \quad (1)$$

where I_o, I_c, I_h were the currents as the sample was in the states of original, cracked and healed states. Generally speaking, the healing efficiency could also be determined according to the variation in mechanics of the samples in the pristine, cracked and healed states. We once compared the heal-ability of the conductive shape memory composites with respect to the conduction and the mechanical properties. It was found that the healing efficiency of the mechanics was less than 50% which was lower than that of other healable polymeric systems based on reversible chemical bonding [9]. Considering that the emphasis of this study was put on the healable conductivity of the polymeric electrodes, herein the healing efficiency was chosen to calculate by the currents rather than the peak stress in the tensile tests. The dependence of the healing efficiency against the pre-stretching percentages is demonstrated in Figure 2c. The efficiency was calculated to be 13.4%, 18.1%, 47%, 63% and 60% as the pre-stretching percentage was 0%, 5%, 10%, 15% and 20%, respectively. The results suggested obvious enhancing effect of the pre-stretching on the healing behaviors. According to the previous report on the self-healing improved by the shape memory pre-stretching, the enhancement may attribute to the release of the strain energy driving the local shape recovery and favoring the closure of the scratch and its complete healing [12,13]. The SEM images, shown in Figure 2d–f, clearly disclosed that the thermal stimulation made the scratch gap closer and reconstructed the conductive pathways of the AgNWs. Comparatively, the sample with 20% of the pre-stretching had the best morphology in the healed state. The SEM investigations were consistent with the above current monitoring results, providing with the evidence that the shape memory pre-stretching significantly enhanced the healing performance in both the structure and the conduction recovery.

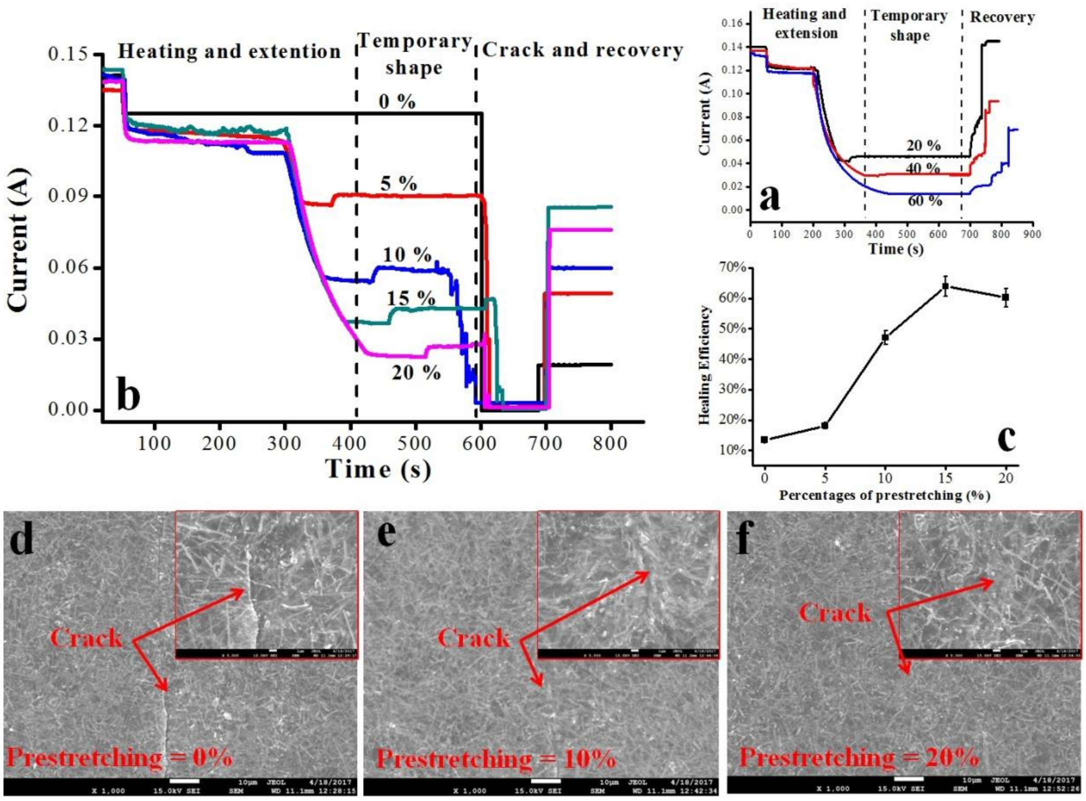

Figure 2. The plots of the current against time for the crack-free samples (**a**) and those exposed upon scratch (**b**) in the healing process; (**c**) The plot of healing efficiency against the pre-stretching percentages; (**d**–**f**) SEM images for the healed surface morphologies (triggered at 80 °C for 10 min) with different pre-stretching percentages.

3.2. Raman Spectra Investigations on the Microstructure Evolution

The samples in different states of the stretched, cracked and healed were measured by Raman spectra which are shown Figure 3a–c. The dominant peaks, mainly distributing in the ranges, i.e., 1335–1390 cm^{-1}, 1551–1597 cm^{-1} and 2417–2934 cm^{-1}, were assigned as the deformation or stretching of –CH_2 groups, aromatic hard segment as well as the –NH–C=O and –CH_3 groups in the polyurethane matrix. The peaks locating at 1597 cm^{-1} shifted downwards to 1563 and 1559 cm^{-1} in sequence as the crack-free sample was stretched by 10% and 20%, being indicative of the pre-storage of the strain energy in the composites. Furthermore, as for the samples without pre-stretching, the absorption intensities in the local cracked area dramatically reduced, which may result from the absence of the AgNWs in the scratch gap. The changes in Raman absorptions before and after the healing process were greatly magnified for the samples with the shape memory pre-stretching. For instance, the sample CSHP-15 had depressed adsorptions as scratched. By contrast, it significantly increased the intensities of the peaks distributing in the range 1182 and 1559 cm^{-1} astransferred into the healed state from the cracked state. The spectra results indicated that the release of the strain energy magnified micro-structural variations in the shape memory-enhanced self-healing process. The internal stress and stored mechanical energy were found to be correlated to the shape/temperature memory behavior below and above the transition temperature [14]. It is well known that the T_m-type shape memory polymers, exhibited the so called stress-memory effect [15,16]. The extended samples after the thermo-mechanical programming to fix in the temporary states reversibly generated stress in the contraction directions as the macro-scale shape was constrained. Given that the shape memory-assisted self-healing involved closure of the crack surfaces driven by the shape memory recovery, the release of the strain energy improved the closure and the reconstruction of the conductive networks. Meanwhile, thermal stimulation allowed the healing reagent PCL to melt, which tended to move and enrich in the crack interfaces. The re-crystallization transition of the PCL in the crack area led to heal-ability of the electrode in micro-structures. The shape memory-enhanced self-healing of the stretchable electrodes is photographically demonstrated in Figure 3d. The sample was connected into a circuit with 1 V of voltage. Pre-stretching by 20% into the temporary shape made the LED lamp darken. Subsequently, exposure upon the crack led to complete loss of the conduction. Heating at 80 °C for several minutes triggered obvious shape recovery, along with the process of which the stretchable electrode was capable of healing the conductive pathways, enabling the lamp to enlighten again.

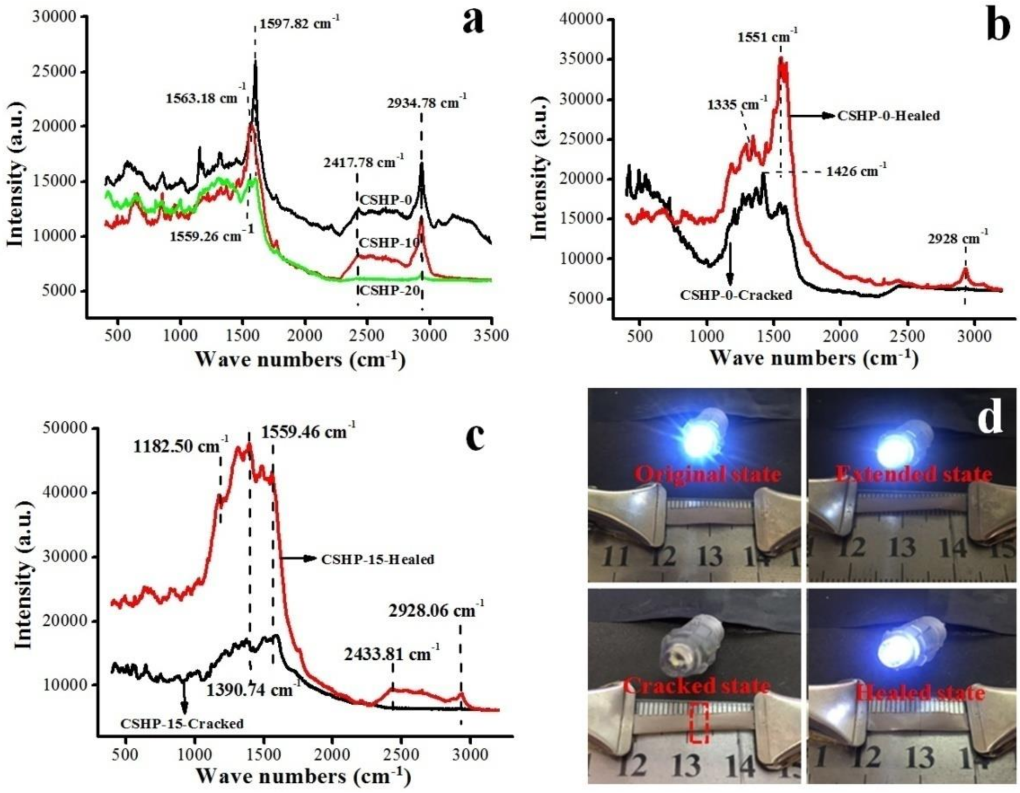

Figure 3. Raman spectra of the crack-free sample in different pre-stretched states (**a**), the local area in the cracked and healed states without (**b**) and with the pre-stretching(**c**); (**d**) Photographical demonstration of the shape memory-enhanced self-healing.

4. Conclusions

A novel stretchable AgNW-containing electrode was fabricated, whose heal-ability was greatly improved by pre-stretching in a shape memory thermo-mechanical programming. The healing efficiency was enhanced to around 63% from 13.4% as the sample was pre-stretched to 15% before exposure upon the scratches. The release of the strain energy under thermal stimulation favored the closure of the scratch and the complete healing, contributing to the enhancing effect.

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Conflicts of Interest: The founding sponsors had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, and in the decision to publish the results.

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