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Repeated Instant Self-healing Shape Memory Composites

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We present a shape memory composite which is made of two types of shape memory materials, namely shape memory alloy (SMA) and shape memory hybrid. This composite has repeated instant self-healing function by means of not only shape recovery but also strength recovery (over 80%). The activation of the self-healing function is triggered by joule heating the embedded SMA.

Keywords Joule heating, self-healing, shape memory alloy, shape memory hybrid, shape memory material

1. Introduction

As presented in the movie series, Terminator, future robots with not only shape recovery (to return the original shape) and strength recovery but also repeated and instant self-healing function, even after being torn into parts, become virtually almost undefeatable. This is scientific fiction based on a material which does not exist at all, at least at this moment.

We have seen good progress, in particular in recent days, in developing self-healing materials based on some different working mechanisms, such as healing agent (embedded in micro-capsules or delivered through micro-channels), Brownian motion, Diels-Alder reaction, hydrogen bonding, polymer melting, etc. (Ref 1, 2). However, a close-look reveals that all of them fail to provide a realistic solution to simultaneously meet the needs of not only both shape and strength recovery but also repeated and instant healing in the case of very large cracks and even fractured into parts as in those future robots (Ref 1).

After being severely and quasi-plastically distorted, shape memory materials (SMMs) are able to recover their original shape at the presence of the right stimulus, which can be heat, moisture, light, etc. (Ref 3). Because of this ability to return to their original shape, i.e., the shape memory effect (SME), all SMMs are naturally suitable for repeated and instant shape recovery. Recently, we have seen efforts toward integrating self-healing function into SMMs, in particular, in shape memory polymers (SMPs) (e.g., Ref 4, 5).

In this article, as a small step, we demonstrate a composite, made of shape memory hybrid (SMH) and shape memory alloy (SMA), which simultaneously meets all above-mentioned requirements in future robots.

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2. SMA for Shape Recovery and Crack Closure (Fig. 1)

Upon stretching at room temperature to 10% strain, a residual strain of over 8% was observed in a piece of 0.5 mm diameter NiTi SMA wire. Different from conventional metals/alloys, upon heating to above 60 °C, most of the residual strain disappears. More importantly, it is still able to recover even against a tensile stress of 500 MPa upon heating (Ref 6). It proves that as-received wire has excellent SME.

Utilizing the significant recovery stress/strain in SMAs, at least as early as 1997, embedded NiTi SMA wire has been proposed for crack closure in a Sn-Bi composite (Ref 7).

This concept is further extended and demonstrated in Fig. 2, in which an externally attached 0.5 mm diameter NiTi wire was joule heated not only to close the crack in a silicone/clay composite beam but also to restore the original straight shape of the beam against a constant working load, i.e., instant in situ crack closure and shape restoration under working conditions. The required heating temperature was only about 60 °C. Depending on the applied electrical power, recovery could be achieved within 1 or 2 s (Ref 8).

3. Rubber-Like SMH with Repeated Healing Function

Despite SMAs are able to provide significant force for crack closure and shape recovery even under loading conditions, Joule heating must be applied continuously, which is not practically acceptable in many applications. Instead, it is more realistic to heal the cracks within a short period of time, so that both shape and strength are recovered *instantly.*

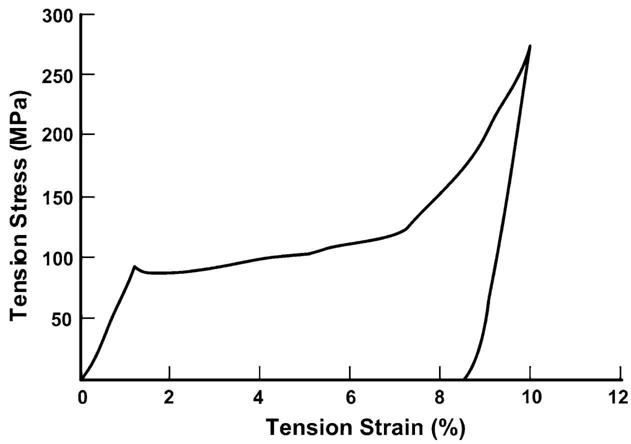

Fig. 1 Typical stress versus strain curve of NiTi SMA wire in uniaxial tension at room temperature

This may be achieved by embedding SMA components into a material which when heated, has the ability of not only shape recovery (i.e., like a thermo-responsive SMM) but also self-healing (i.e., a thermo-responsive self-healing material as reported in Ref 4, 5).

A polymeric material with such features has been found in a silicone/melting glue (MG) hybrid (Ref 3, 8, 9). Here, the silicone (S) is Sylgard® 184 silicone elastomer (from Dow Corning Corporation, Midland, MI) and the MG is Sellery® 96-802 glue stick, which is ethylene vinyl acetate (EVA) based, and bought from Centenary Materials Co., Ltd., Hsin-Chu City, Taiwan. The melting temperature of this MG is about 70 °C, while S is elastic and stable within the whole temperature range of our interest (i.e., from −50 to 150 °C). The densities of two materials (S and MG) are about the same. The detailed fabrication procedure of the hybrid can be found in Ref 9.

Silicone/MG (SMG) samples with different volume fractions of MG were fabricated. Stress-strain relationships under cyclic uniaxial tension at room temperature (about 22 °C) were obtained. Typical results of some samples, namely, S, SMG-25 (with 25% volume fraction of MG), SMG-40 (40% of MG) and MG, are plotted in Fig. 3. Unless otherwise stated, hereinafter, the stress/strain is engineering stress/strain.

Apparently, SMG is even more elastic than S, while MG is harder and appears to be elastic-plastic with some large residual strain after unloading. A close-look reveals that SMG actually becomes softer and more elastic with the increase of MG content.

The SME in SMGs was investigated. A typical example (SMG-30, i.e., with 30% volume fraction of MG) is presented in Fig. 4. The sample, which was straight as fabricated, was pre-bent at 90 °C, which is above the melting temperature of MG, and then cooled back to room temperature. Upon heating atop a hot plate, full shape recovery was observed. As a matter of fact, all SMG samples that we have fabricated are able to fully recover their original straight shape.

Shape fixity ratio and shape recovery ratio are two important parameters to evaluate a SMM (Ref 10). Shape fixity ratio is defined as the ratio between the maximum deformation during programming (i.e., the procedure to achieve the deformed/temporary shape) and the residual deformation after unloading (e.g., the maximum strain in stretching vs. residual strain after unloading). In fact, to achieve a higher shape fixity ratio, which

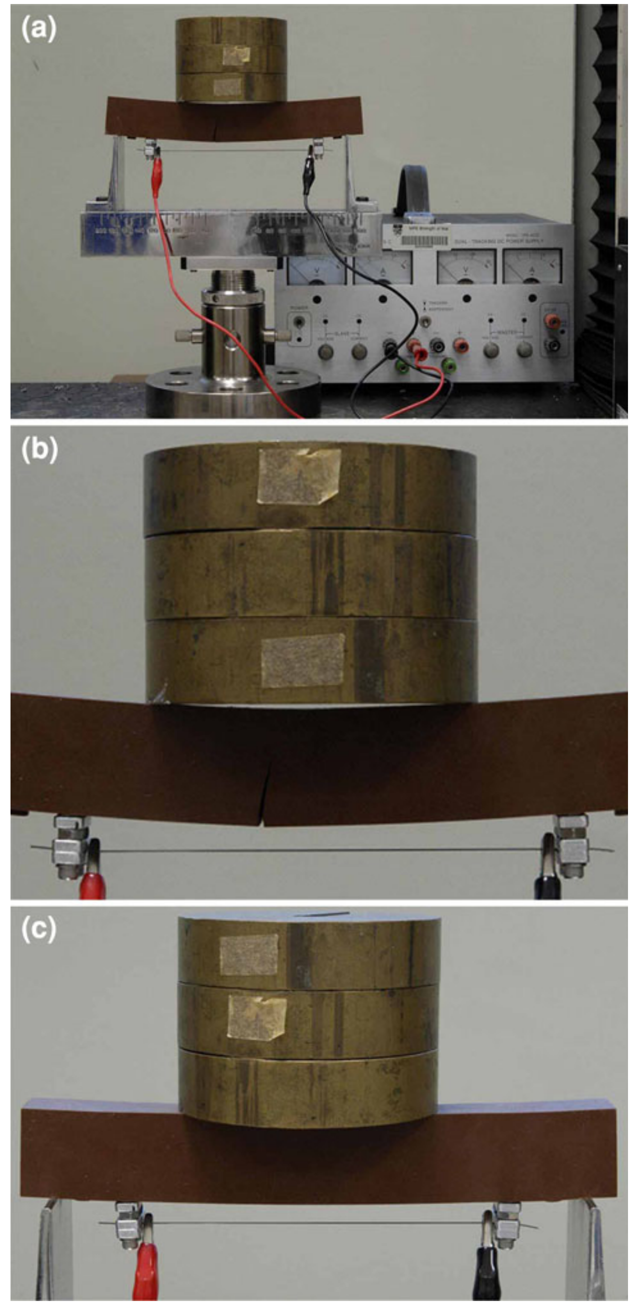

Fig. 2 (a) Experimental set-up, (b) zoom-in view of cracked beam upon loaded to 3 kg, (c) crack fully closed after SMA wire was joule heated (from Ref 8 with permission)

is preferred in many engineering applications, a commonly applied approach is to program a thermo-responsive SMM at above its recovery/transition temperature. In this part of study, the programming temperature was 90 °C, i.e., a SMG was deformed at 90 °C and then cooled back to room temperature before the constraint was removed. On the other hand, shape recovery ratio measures the ability of a SMM to recover its original shape. 100% shape recovery ratio is preferable in most applications, but in some others, partial recovery is also acceptable (e.g., in shrink-fitting type of active assembly and active disassembly).

Shape fixity ratio and shape recovery ratio of all samples were measured following the standard bending approach (by means of measuring two bending angles, one is after programming with 180° bending at 90 °C, and the other is after heating for shape recovery). The experimental results are summarized in Fig. 5.

The basic concept of SMH is actually an extension of SMP, in which a dual-component (that can be segment, domain, or a combination of both) system is the working mechanism behind the SME (Ref 3, 8). However, different from SMPs, the two basic components of a SMH (one is elastic component, which is always elastic within the whole working process; while the other is transition component, which is able to remarkably alter its stiffness depending on whether the right stimulus is present) can be selected virtually from any material, even including metal/alloy and inorganic (Ref 11). As such, we have a wider range of choice to design a SMM with the required properties and function(s) to meet the need(s) of a particular application.

In this study, S is the elastic component, while MG is the transition component. Hence, as expected, SMGs should have the SME. In fact, in this study, the reason of selecting MG as the transition component is more than using it as the transition segment as in a standard thermo-responsive SMH.

From engineering application point of view, MG is commonly used for its adhesion feature to bond two pieces of materials together. High bonding stress after solidification of MG may be utilized for healing in current SMGs. This is another reason of selecting MG as the transition component.

Furthermore, from chemistry point of view, there is no chemical interaction between S and this EVA-based MG. Consequently, we can well predict some important properties of the resultant SMGs, in particular, the transition temperature, from the very beginning. This is one of the advantages of SMHs, i.e., selecting materials and processing procedure to

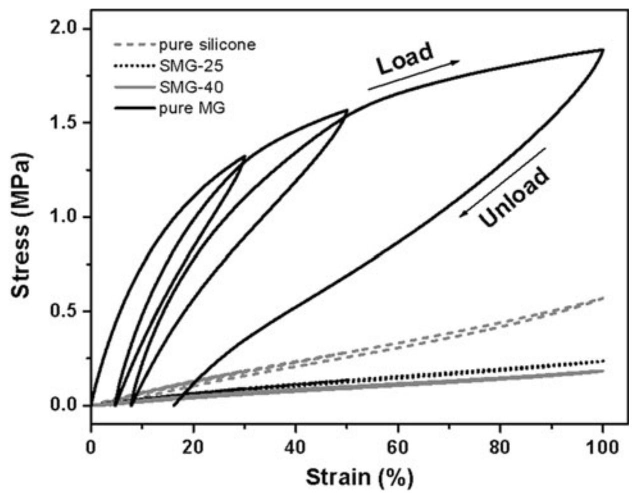

Fig. 3 Stress versus strain curves under cyclic uniaxial stretching at a strain rate of 10^{-3}/s at room temperature

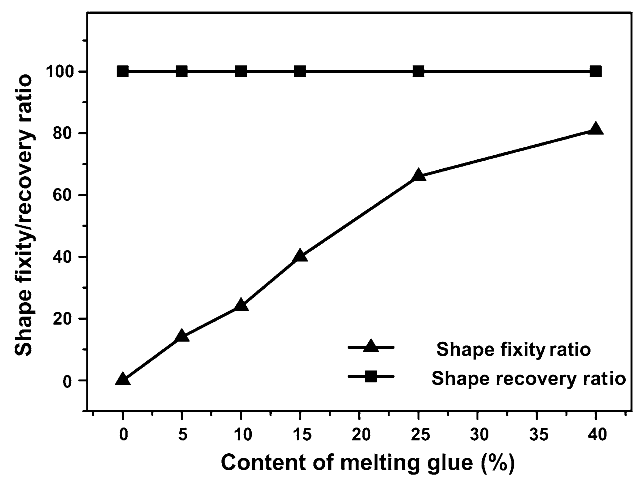

Fig. 5 Shape fixity/recovery ratios of SMGs with different MG contents (in terms of volume fraction)

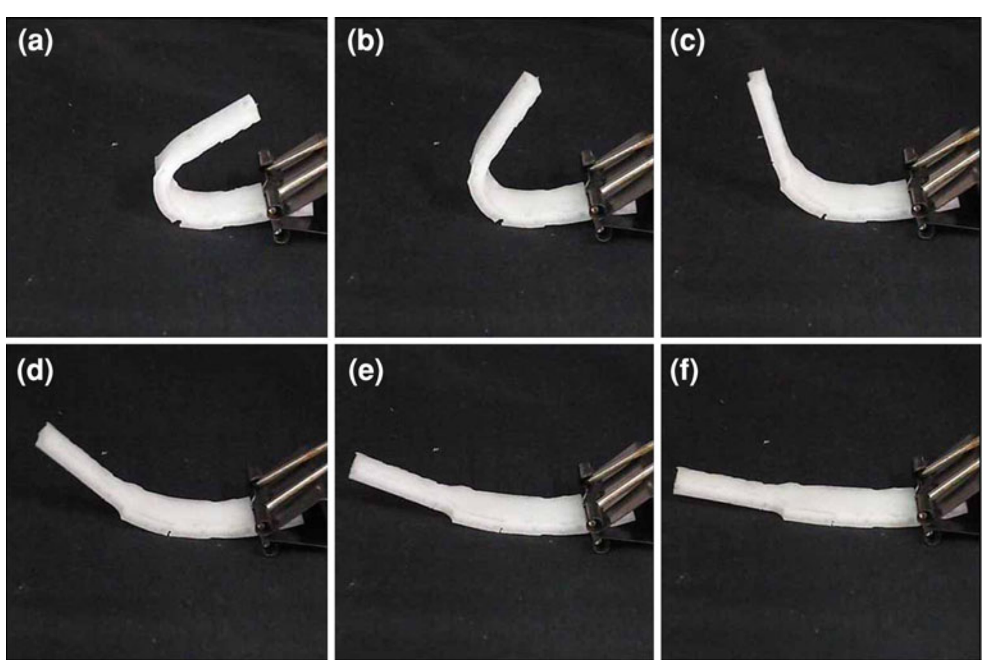

Fig. 4 Shape recovery in a SMG-30 hybrid upon heating (from the top-left to top-right, and then from bottom-left to bottom-right)

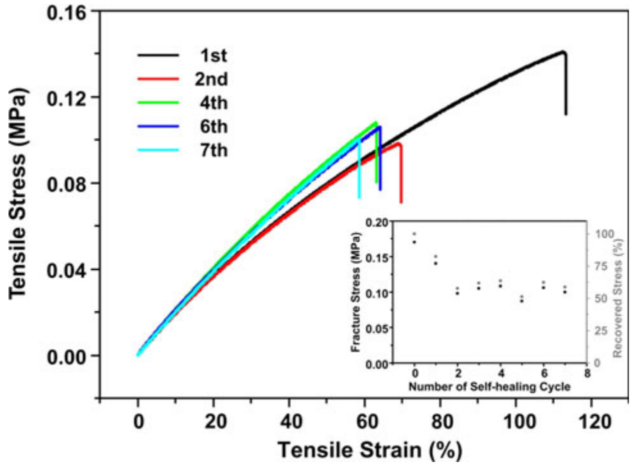

Fig. 6 Typical stress versus strain curves of SMG-40 at room temperature in repeated self-healing. Inset: evolution of actual fracture stress and recovered stress in %

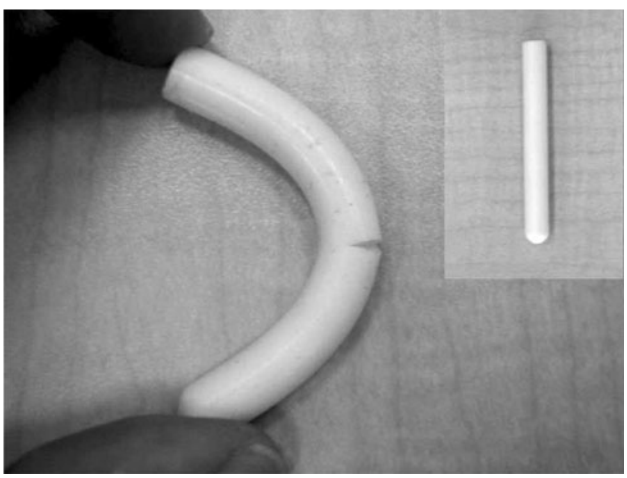

Fig. 7 Cylindrical SMG-40 (8 mm in diameter) with and without (inset) cutting

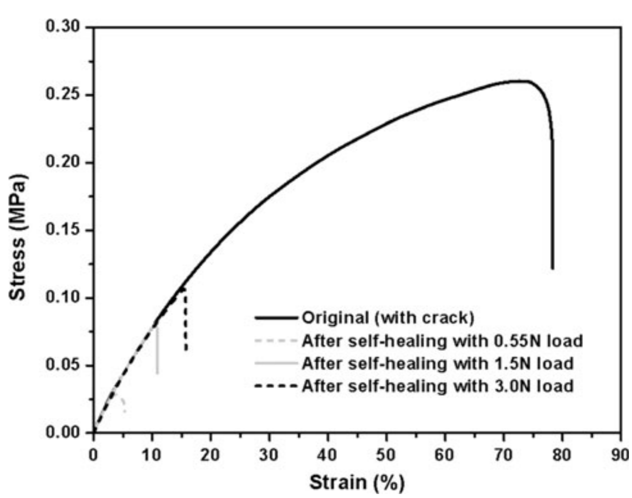

Fig. 8 Stress versus strain curves of SMG-40 after healing with different applied loads

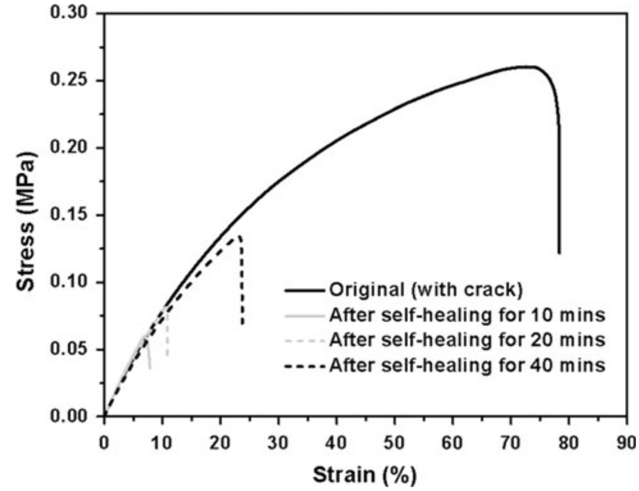

Fig. 9 Stress versus strain curves of SMG-40 after healing with different heating times

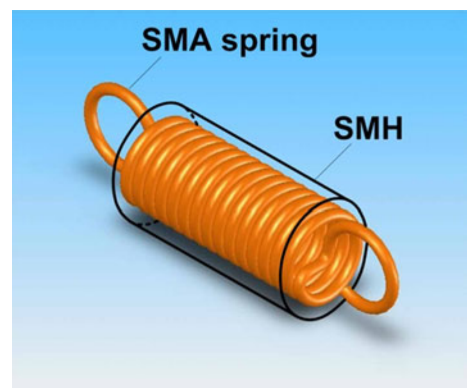

Fig. 10 Illustration of SMH/SMA composite (from Ref 3 with permission)

Fig. 11 Fabricated SMH/SMA samples

avoid interaction between the elastic component and transition component, so that the performance of the resultant hybrid can be more or less pre-determined, instead of tailoring the properties of a SMM through a time-consuming procedure of trial and error as in synthesis of SMPs.

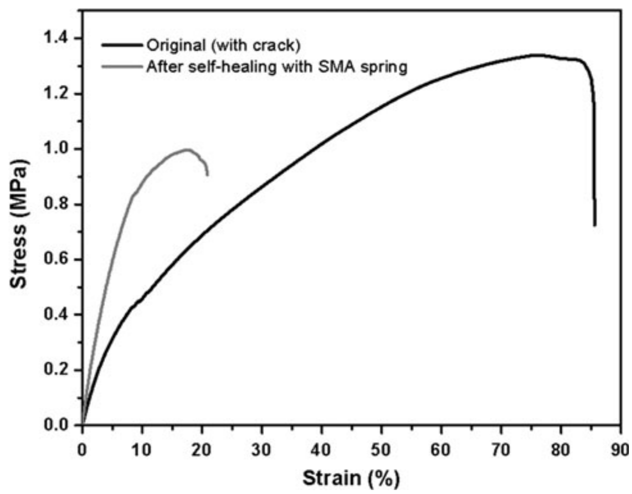

Fig. 12 Stress versus strain curves of SMG/SMA composite before and after healing

It should be pointed out that a number of tests (including differential scanning calorimeter, scanning electron microscope, Fourier transform infrared spectroscopy, Raman spectroscopy, surface fracture test, laser interferometer, etc., in Ref. 9) reveal that MG within S in current SMG samples exists in two forms, one is segment (chains, most likely tangling with S chains at submicron scale) and the other is domain (MG micro-inclusions in spherical shape).

Two pieces of cylindrical-shaped SMG-40, both with a diameter of 2.5 cm were fabricated and heated to 100 °C and then compressed together under a compressive stress of 20.0 kPa for 30 min. Subsequently, the sample, now bonded together as one piece, was stretched at a strain rate of 10^{-3}/s till fracture. This is cycle no. 0, and we take this result as the reference for comparison in subsequent analysis.

Such a healing/fracture test was repeated on the same sample for a few times. Typical stress versus strain curves are presented in Fig. 6, together with the evolution of fracture stress against cycle number (as inset). It is observed that in the first three cycles, the fracture stress decreases continuously due

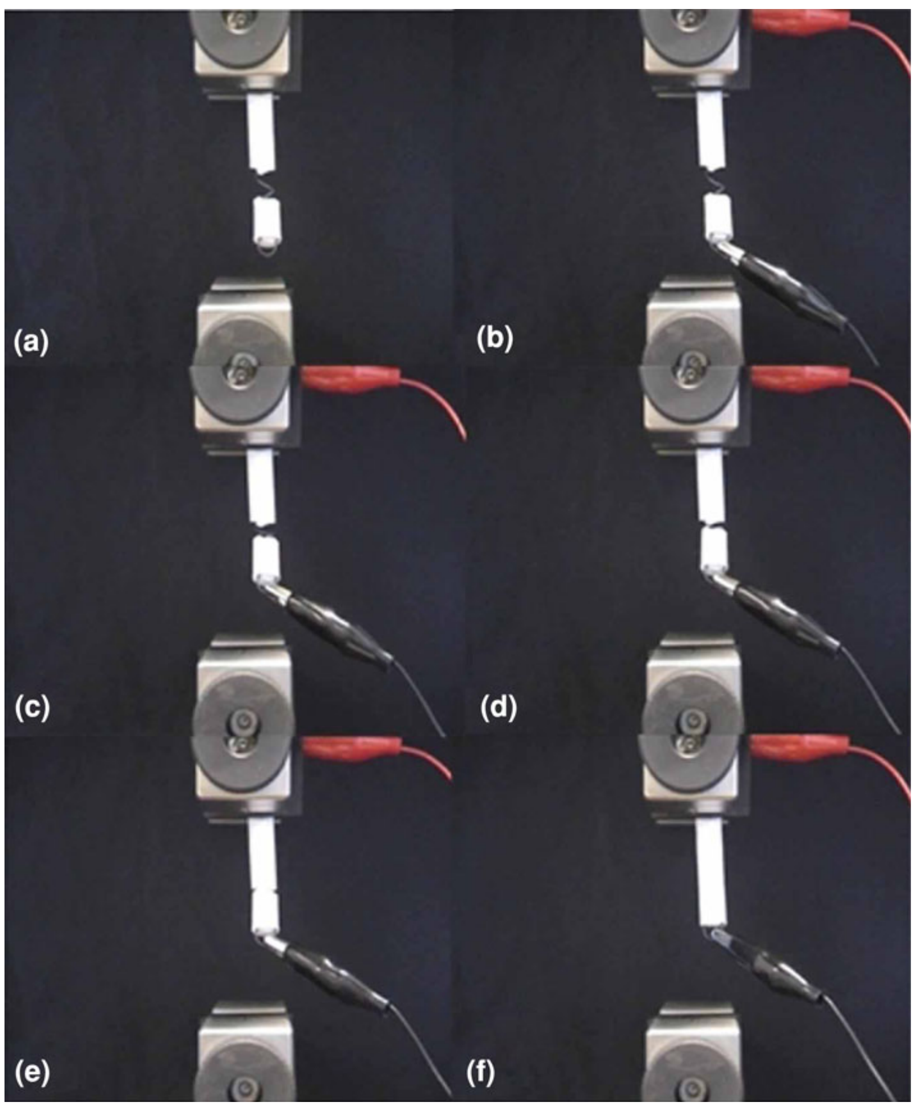

Fig. 13 Healing of SMH/SMA sample by means of Joule heating-embedded SMA spring

to the MG inclusions at the interface gradually pulled-out, so that in the subsequent cycles, only the segmented MG plays a dominant role and thus, the fracture stress becomes more or less stable.

It is apparent that both heating time and pressure during healing are two important parameters which control the effectiveness of the healing. A long cylindrical SMG-40 sample (8 mm in diameter) was prepared and cut slightly using a sharp knife in its middle part (refer to Fig. 7) to investigate the influence of both parameters.

The sample was first stretched at a strain rate of 10^{-3}/s till fracture (refer to Fig. 8, solid line, for stress vs. strain curve recorded). Subsequently, the two parts were heated at 100 °C for 20 min under three different constant compressive forces (namely from 0.55, 1.5 to 3.0 N, which correspond to compressive stresses of 11.0, 30.0, and 60.0 kPa, respectively) in three healing cycles. The stress versus strain curves of these tests are revealed in Fig. 8.

It is apparent that even without considering the influence of MG micro-inclusions at the healed interface, which should decrease with cycle number as discussed above, we can clearly see that a higher pressure applied during healing increases the fracture stress in the subsequent tensile test.

In the next round of tests, which were carried out continuously on the same sample, we investigated the influence of heating time. Three more cycles were conducted with a constant compressive force of 1.5 N (i.e., 30.0 kPa) at 100 °C but for different periods of time, from 10, 30 to 40 min. As we can see from Fig. 9, a longer heating time is better to achieve a higher fracture stress in the subsequent stretching test.

From application point of view, we should bear in mind that either a very high pressure or a prolonged healing time may not be practically feasible in many occasions.

4. SMH/SMA Composites for Repeated Instant Self-healing

It becomes logical and rather straight forward to come out with the idea of integrating SMG, as discussed above, and SMA together to achieve repeated instant self-healing in such SMH/SMA composites, as illustrated in Fig. 10. As SMA spring is able to stretch a significant amount to well match the remarkable deformation in SMHs, we used NiTi spring in the course of this study.

8 mm diameter composite samples, each with one NiTi SMA spring (wire diameter 0.75 mm, coil diameter 6 mm, bought from Images Scientific Instruments, USA) embedded in the middle, were fabricated (Fig. 11).

According to the supplier, the transition temperature of the SMA spring is about 44 °C. Hence, at room temperature, the spring can be quasi-plastically stretched with ease. The SMH was SMG-40, which was selected due to its high shape fixity ratio and good ability for healing. According to the experimental results (not reported here), at higher contents of MG (45% and above), the S and MG mixture becomes sticky and almost incurable.

We tested the self-healing ability of these composites. In order to ensure fracture happened only in the middle part, a small cut was introduced into one piece of as-fabricated sample using a sharp penknife. Consequently, upon stretching at a strain rate of 10^{-3}/s, the sample fractured into two parts at around 85% strain (refer to Fig. 12, black line), but still linked by the SMA spring (refer to Fig. 13a).

Joule heating of the SMA spring was conducted using a 6 V rechargeable battery in tapping mode. As revealed in Fig. 13, instantly the SMA spring shrank and pulled two fractured parts together. In the mean time, the SMG was simultaneously heated and compressed by SMA spring, and thus healing started. Tapping mode was applied to achieve a relatively longer heating time while avoiding over-heating, which may cause damage to both SMA and SMH.

The total healing time lasted for about 5 min. The healed sample, in which the healed line was not very much visible unless examined closely, was tested again. The result was then compared with the original one in Fig. 12. About 80% of strength recovery is observed.

Despite there is room for improvement for better performance, at this point in time, we may conclude that this approach is seemingly very much promising.

5. Conclusions

We demonstrate an approach to achieve repeated instant self-healing in a SMH/SMA composite for both shape and strength recovery. Preliminary results are reported in this article to verify the basic concept. The next step is to integrate sensing function into such composites to realize self-sensing/self-healing. In addition, a hard version instead of skin-like version in this study can be developed for structural materials, just like self-healing bones, using hard SMHs with the thermally induced self-healing function.

Acknowledgments

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