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Thermomechanical performance and shape recovery behaviour of shape memory polymer nanocomposite incorporated with hexagonal boron nitride

Purpose – The purpose of the study reported in this paper was to develop an effective approach to significantly improve the thermomechanical properties of shape memory polymer (SMP) nanocomposites that show fast thermally responsive shape recovery.

Design/methodology/approach – Hexagonal boron nitrides (h-BNs) were incorporated into polymer matrix in an attempt to improve the thermal conductivity and thermally responsive shape recovery behaviour of SMP, respectively. Thermally actuated shape recovery behaviour was recorded and monitored instrumentally.

Findings – The results show that both glass transition temperature (T_g) and thermomechanical properties of the SMP nanocomposites have been progressively improved with increasing concentration of h-BNs. Analytical results also suggest that the fast responsive recovery behaviour of the SMP nanocomposite incorporated with h-BNs was due to the increased thermal conductivity.

Research implications – A simple way for fabricating SMP nanocomposites with enhanced thermally responsive shape recovery based on the incorporation of hexagonal boron nitrides was developed.

Originality/value – The outcome of this study may help fabrication of SMP nanocomposites with fast responsive recovery behaviour.

Keywords: Shape memory polymer; Nanocomposite; Responsive material; Boron nitride; Thermomechanical property

Paper type Research paper

Introduction

Stimuli-responsive polymers are one of the smart materials that could show noticeable changes in their properties continuously with varying environmental conditions (Hu *et al.*, 2012). Such responsive polymers can adapt to surrounding environments, thus altering colour or transparency, changing shape (shape memory polymers, SMPs), regulating transport of ions and molecules, or converting chemical and biochemical signals into optical, electrical, thermal and mechanical signals, and vice versa (Hu *et al*., 2012; Zhao *et al*., 2013; Rousseau, 2008; Xie 2011; Hu *et al*., 2012; Yao *et al*., 2015; Lu *et al*., 2015a; Lu *et al*., 2015b). In recent years, as a smart material, SMPs have attracted increasing attention from the scientific community due to their abundant advantages over their metallic counterpart, namely shape memory alloys (SMAs) (Liu *et al*., 2007). Low cost, light weight, a broad range of transformation temperature, high durability and high recoverable strain (up to 200% in many cases) are some of the important advantages among others (Rousseau *et al*., 2008). With so much effort being made, many emerging applications of stimuli-responsive polymers have been explored, such as drug delivery, diagnostics, tissue engineering and optical systems, as well as biosensors, microelectromechanical systems, coatings and textiles (Hu *et al*., 2012; Zhao *et al*., 2013; Rousseau *et al*., 2008; Xie 2011; Hu *et al*., 2012; Yao *et al*., 2015; Lu *et al*., 2015a; Lu *et al*., 2015b; Xie and Rousseau, 2009; Wei *et al*., 2014). Despite tremendous progress in synthesis, analysis, characterisation, actuation methods and modelling enables us to develop SMPs through a knowledge based approach (Serrano and Ameer, 2012; Koerner *et al*., 2004; Huang *et al*., 2005). Fundamental research that concerned stimuli other than heat (e.g. light, electric current or alternating magnetic fields) and enabling the materials to possess more desirable properties-on-demand had been reported elsewhere (Lu *et al*., 2011a; Mohr *et al*., 2006; Li *et al*., 2012; Cho *et al*., 2005; Lu and Huang, 2013). Due to their practical and potential applications, SMP composites have been found to be highly desirable due to their tailorable properties after reinforcement. Currently, more attractive and critical research studies on SMP composites concern the creation of SMP composites for indirect heat actuation by incorporating conductive particles, including conductive hybrid fibres (Leng *et al*., 2008), carbon black (Le *et al*., 2010), carbon nanofibres (Lu *et al*., 2010a), carbon nanotubes (Lu *et al*., 2011b; Lu *et al*., 2015c), nickel nanostrand (Lu *et al*., 2011c), graphene (Lu and Gou, 2012) etc. However, this approach inevitably requires a high level loading of conductive fillers to achieve desirable efficiency of actuation. The high loading of filler tends to result in a high viscosity and strong interactions between the SMP resin and the conductive filler, which hinders the efficient manifestation of properties of the filler through to the matrix (Lu *et al*., 2010b).

Hexagonal boron nitride (h-BN) is the most stable crystalline form, which is the equivalent in structure of graphite (shown in Figure 1). Similar to graphite, in h-BN, boron and nitrogen atoms are bound by strong covalent bonds within each layer, whereas the layers are held together by weak van der Waals forces. Compared with graphite, the theoretical thermal conductivity of hexagonal boron nitride nanoribbons is of the same order of magnitude as the experimentally measured thermal conductivity of graphene (Tao *et al.*, 2010). Boron nitride is traditionally used as an additive in high-temperature equipment and electronics field due to its excellent thermal, dielectric and chemical stability. For example, plastics filled with BN have less thermal expansion as well as higher thermal conductivity and electrical resistivity (Davis, 1991).

(Insert Figure 1)

In this study, we developed an effective approach to significantly improve the thermomechanical properties of SMP. Thus, hexagonal boron nitrides (h-BNs) were incorporated into polymer matrix in an attempt to improve the thermal conductivity and thermally responsive shape recovery behaviour of the polymer matrix. It was found that both glass transition temperature (T_g) and thermomechanical properties of the resulting SMP nanocomposites improved with the increase of the concentration of h-BNs.

Experimental

Materials and nanocomposite preparation

h-BNs were synthesised by reacting boron trioxide (B_2O_3) with urea ($CO(NH_2)_2$) in a nitrogen atmosphere at a temperature of 1600°C (h-BN concentration >98%). The obtained h-BN is isoelectronic to a similarly structured carbon lattice. The thermal conductivity and thermal expansion coefficient of h-BN is 600 W/m·K and -2.7×10^{-6}/°C, respectively. The SMP is an epoxy-based fully thermosetting resin, which is a two-part system having a rigid part and a soft part. The h-BNs were blended into the SMP resin at weight fractions of 0, 2, 4, 6, 8 and 10 wt.%, respectively. Each of the resulting mixtures was mechanically stirred at a high speed of 600 rad/min. The resulting mixture was degasified in a vacuum oven to completely remove air bubbles. In this study, a resin transfer moulding process was used to create the SMP nanocomposite. The applied pressure during the resin transfer moulding process was kept constant. After the mould filling, the composite was cured at a temperature ramp of approximately 1°C/min from ambient temperature to 100°C and kept for 5 hours before being ramped to 120°C at 20°C per 180 minutes. Finally, the temperature was ramped to 150°C at 30°C per 120 minutes to obtain the final SMP nanocomposite.

Methods of characterisation

Field emission scanning electron microscopy (FESEM) was used to study the morphology of h-BN in SMP nanocomposite. The functional groups determination of the h-BN enabled SMP nanocomposite was performed on the Fourier transform infrared (FTIR) spectroscopy (Nicolet AVATAR 360) in a transmittance mode in the range of 4000 to 600 cm^{-1}. Differential scanning calorimetry (DSC) experiments were conducted on the DSC 204F1, Netzsch, Germany. All experiments were performed at a constant heating rate of 10°C min^{-1}. The tested samples were investigated in the temperature range of 25 to 200°C. Dynamic mechanical analysis (DMA) was employed in this study to measure the dynamic mechanical performance and T_g of amorphous polymers. All measurements were performed in the single cantilever mode at a constant heating rate of 10°C/min. The oscillation frequency was 1.0 Hz and temperature interval ranged from 25 to 180°C. The flexural strength of SMP composites was measured via three-point bending using a Zwick/Roell servo-mechanical testing frame with a series of digital controllers. An Instron clip-on extensometer was used for strain measurement (engineering strain) in three-point bending mode and a forced air convective environmental chamber was used for elevated temperature tests. The static bending tests were performed at a loading speed of 2 $mm \cdot min^{-1}$ with a support span of 30 mm. The dependence of flexural strength on fibrous filler content was investigated at a test temperature of 25°C.

Results and discussion

Morphology of h-BN in SMP nanocomposite

The morphology of the h-BNs were characterised using FESEM. Figures 2(a) and (b) show the morphology of shape memory composited based on h-BNs filler with a constant scale of 20 μm. The white dots are h-BN particles. As can be seen from Figure 2, there are present a significant number of h-BN particles, of which the aggregates could influence the thermal conductive property of the insulating polymer. A matrix structure was formed by the individual particle. Such a matrix made of individual h-BN acts as a conductive path for heating, which improves the thermal conductivity of the polymer. The nature of the matrix structure is highly dependent on the quality of the dispersion of h-BNs. Such a thermally conductive matrix is expected to improve the thermal conductivity and facilitate heat transfer from the nanopaper to the polymer matrix.

(Insert Figure 2)

Structural confirmation via Fourier Transform Infrared (FTIR) spectroscopy

Figure 3 shows comparative FTIR data of the nanocomposites containing 2, 6 and 10 wt.% of the h-BNs. There are three major peaks at 2929 cm^{-1}, 1384 cm^{-1} and 1153 cm^{-1}. The frequencies at around 1153 cm^{-1} and 2929 cm^{-1} corresponds to the aliphatic ether (C–O–C) bonding, $–C–H_3$ and $–CH_2–$ bonding, respectively. The characteristic peak for h-BNs bending vibration is observed at about 1384 cm^{-1} for the stretching mode.

(Insert Figure 3)

Thermomechanical properties

In the thermosetting epoxy-based SMP, the T_g plays a critical role in influencing the SME. Exceeding the T_g enables the mobility of the polymer segments and thereby allowing the material to regain its original form. Therefore, the T_g is a critical parameter and is necessary for characterising the shape recovery performance of SMPs. The change in T_g as a function of the temperature for the SMP nanocomposites incorporated with different weight concentrations of h-BNs is presented in Figure 4. T_g is determined as 72.7, 77.5, 79.6 and 82.3°C for the pristine SMP and SMP composite with 2, 6 and 10 wt.% h-BNs, respectively. The glass transition in tested samples occurs within a temperature range of 70 to 90°C. The experimental results thus indicate that h-BNs enhance the thermal properties of the SMP matrix.

(Insert Figure 4)

The storage modulus, tangent delta and T_g of the SMP nanocomposites incorporated with 2, 6 and 10 wt.% h-BNs were determined in this manner. The storage modulus and tangent delta data were recorded as a function of temperature. As shown in Figure 5, the T_g is defined as the intersection point of storage modulus and the tangent delta curves, the T_g of SMP composites incorporated were 73.1°C, 77.5°C and 80.5°C, respectively, while that of pristine SMP was 73.4°C. Experimental results could be attained from the h-BNs that enhanced the thermomechanical properties of SMP matrix, resulting in improved thermomechanical properties. Meanwhile, the dispersion and bonding of CNTs with both SMP and carbon fibre also play a critical role in influencing the dynamic mechanical behaviour of the composites.

(Insert Figure 5)

Mechanical properties

In general, it can be seen that the flexural strength of SMP composites increases with the increase of h-BN content, as shown in Figure 6, the flexural stress of the SMP composites with 2, 4, 6, 8 and 10 wt% h-BN is 25.31, 26.19, 26.56, 27.25 and 29.07 N, respectively. These results suggest that the mechanical strength of the composite specimens is proportionally improved with the increase of h-BN content. On the other hand, the deformation of the composites might be contributed to the occurrence and propagation of cracks initiated by the debonding between matrix resin and filler, which is the major failure characteristic of the composite specimens. Also, the cracks may not propagate easily since the viscous matrix resin may become difficult to flow and the composite materials brittle. However, it can also be seen that with the h-BN content further increased, the maximum fractures strains of the nanocomposites are not always increased due to the contingency factors of cracks propagate.

(Insert Figure 6)

Thermally responsive shape recovery behaviour

The tested SMP composites that were incorporated with a 2, 4 and 10wt.% h-BNs and originally had a flat shape. After the sample was heated above 110°C, it could be deformed into a desirable shape upon applying a 10N of external force. Cooling back to room temperature, the SMP composites with a deformed shape could subsequently be fixed. The thermal actuation was studied on a "Π" shaped sample. Thus, the flat sample with a dimension of 80×10×4 mm^3 was bent into a "U" shape at 110°C. Images were taken of the sample with a digital camera at a constant frame rate of 30 Hz, and with an appropriate visual range to detect the sample's curvature. Snapshots of the shape recovery sequence of the SMP composite sample that was incorporated with 10 wt.% h-BNs is shown in Figure 7. When the SMP composite was placed in a heating oven at 120°C, it took 50 seconds for the sample to complete the shape recovery. It showed very small recovery ratio during the first 10 seconds, but then exhibited a faster recovery speed until 40 seconds. Finally, the SMP composite sample regained its original shape.

(Insert Figure 7)

Simultaneously, thermally responsive shape recovery behaviour of pristine SMP was recorded and compared with that of SMP composites. Seven relevant snap-shots of the tested samples are presented in Figure 8. A faster shape recovery of SMP composites incorporated with h-BNs than pristine SMP was found under the same condition. Thus, the SMP composites completed the thermally induced shape recovery in 50 seconds, while the pristine SMP did in 60 s. The effectiveness of the h-BNs to accelerate the shape recovery of the SMP is thus clearly shown. This, as mentioned before, is due to the h-BNs in the polymer matrix improving the thermal conductivity and helping to conduct the heating from external environment to the SMP.

(Insert Figure 8)

Conclusions

A series of experiments were conducted to study the h-BN enabled SMP composite, of which the thermomechanical properties and shape recovery were improved by the heating.

The inclusion of the h-BN improved the thermal conductive property and helped to conduct the thermal heating for the SMP matrix. Both T_g and dynamic mechanical performance of the composites were improved by the addition of h-BNs. Furthermore, the thermally induced shape recovery of the pristine SMP and SMP composites was recorded and compared in the recovery process. The authors demonstrated a simple way to improve the thermomechanical performance of thermally responsive SMP composite and to accelerate the recovery behaviour in response to external stimulus by the incorporation of h-BN in the polymer matrix concerned.

Acknowledgments

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Conflict of interest

The authors declare that there is no conflict of interest.

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Figure 1 Illustration of the structure of hexagonal boron nitride

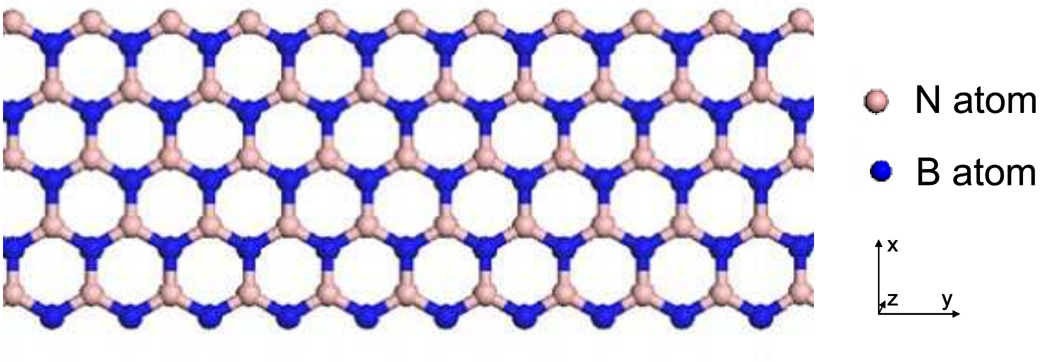

Figure 2 (a) and (b) the morphology and structure of h-BNs in the SMP composite at a scale of 20 µm

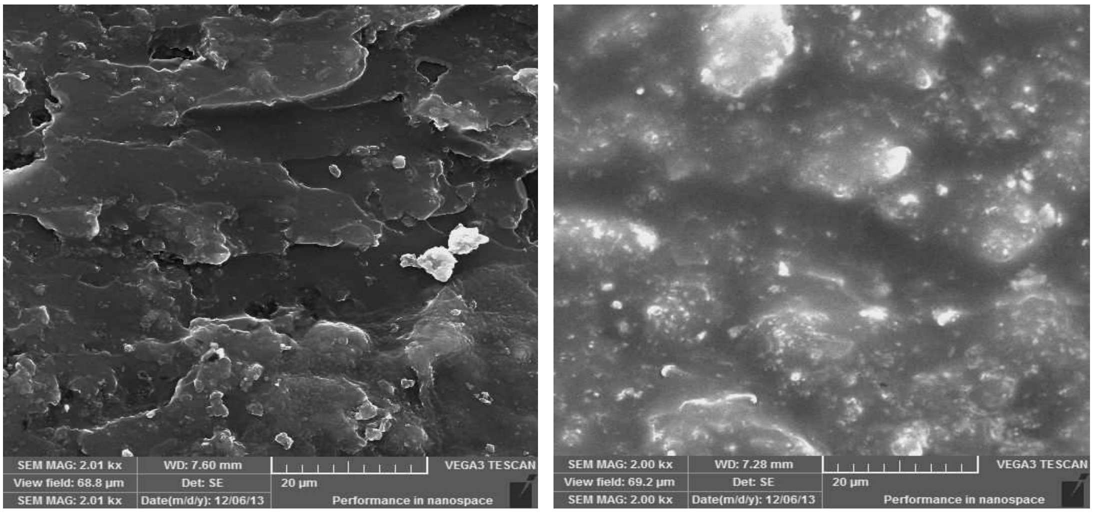

Figure 3 FTIR spectra of the h-BN enabled SMP composites at weight concentrations of 2, 6 and 10 wt.%

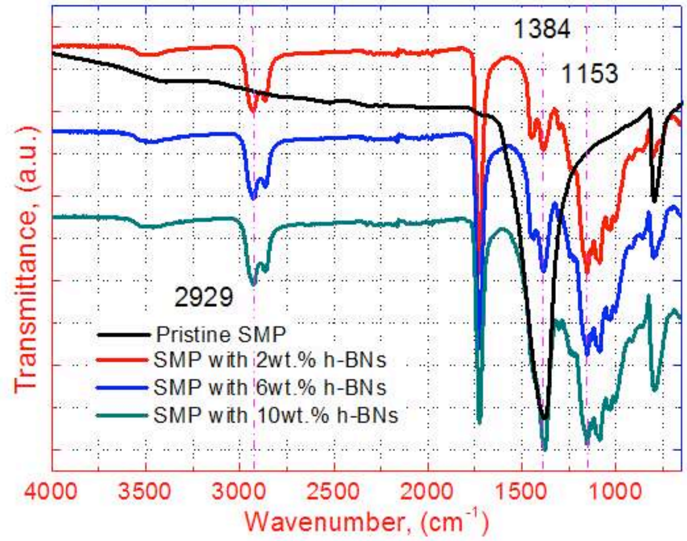

Figure 4 The T_g determined by the DSC measurement for the SMP and SMP composites incorporated with 2, 6 and 10 wt.% of h-BNs, respectively

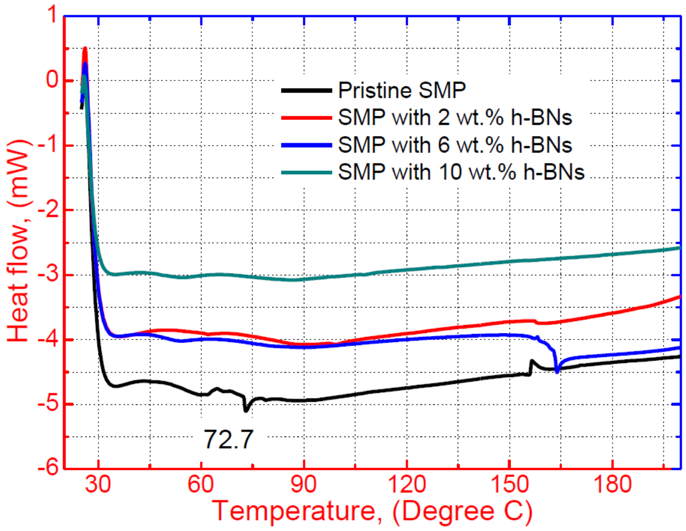

Figure 5 Storage modulus and tangent delta of SMP and SMP composites incorporated with 2, 6 and 10 wt.% of h-BN determined by DMA measurement

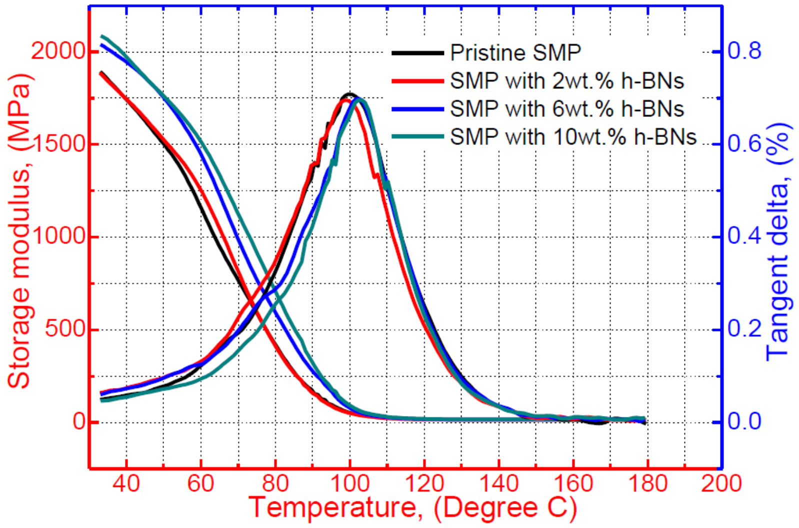

Figure 6 Stress–strain curves of SMP nanocomposites filled with various weight concentrations of boron nitride and CNT in a tensile mode

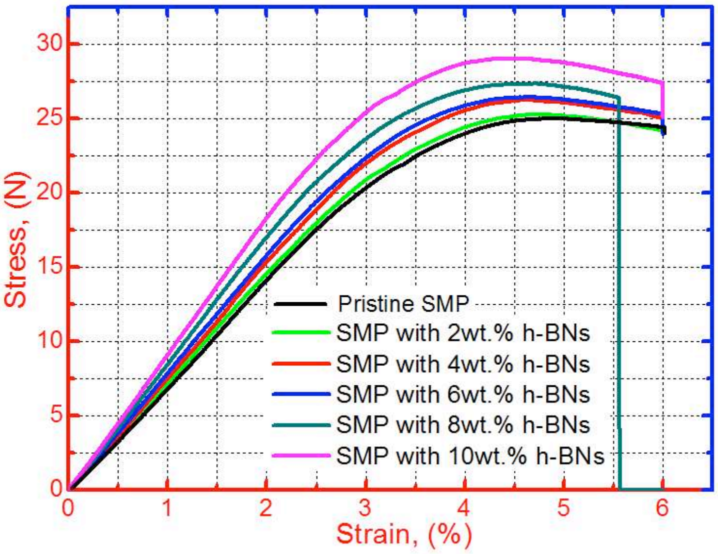

Figure 7 Snap shots of thermally responsive shape recovery of SMP nanocomposite incorporated with 10 wt.% of h-BNs

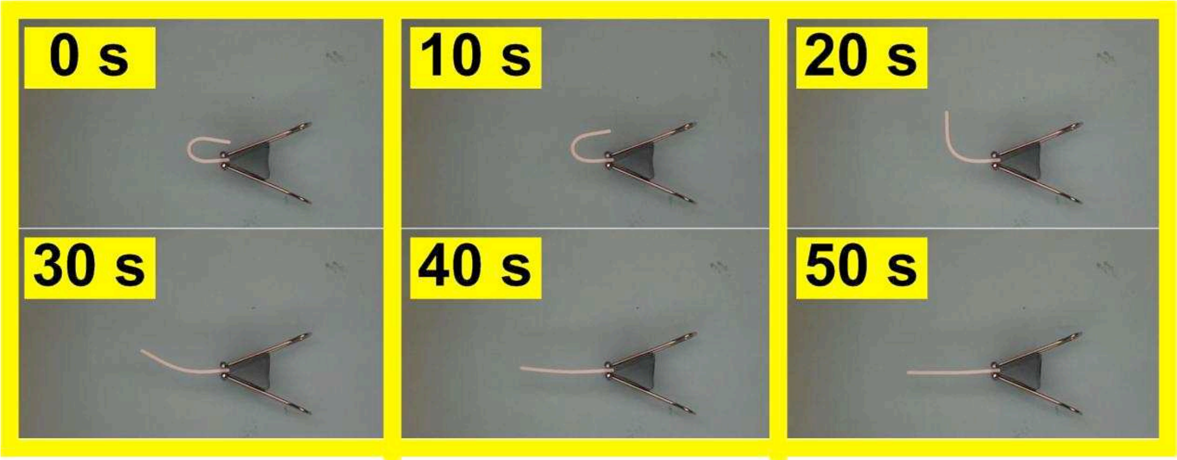

Figure 8 A comparison in thermal recovery performance of the SMP composites incorporated with 2, 4 and 10 wt.% of h-BNs with that of pristine SMP