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Novel timed and self-resistive heating shape memory polymer hybrid for large area and energy efficient application

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ABSTRACT

Shape memory polymers (SMPs) are a polymeric smart material that can register two or more temporary shapes and transform to one another through an external stimulus. Despite their compactness and customizability, SMPs haven't been able to be adopted for mainstream applications. Since the majority of SMPs are triggered by heat, and SMPs have a very poor thermal conductivity, large thermal gradients within the polymer appear which cause slow response, inhomogeneous heat distribution and thus non-uniform transformation of shapes and cracks. Many have attempted to improve their thermal performance through the incorporation of filler-based nanomaterials. However, the outcome is ineffective as the spatial dispersion of fillers within the SMP is inhomogeneous and leads to performance loss. Contrastingly, the herein presented new class of nanocomposite-SMP, composed by 3D-foam fillers, showcase a much more efficient SMP adaptable to larger area with faster transformation speed and without any performance loss. Furthermore, the improved thermal properties lead to a decrease in required input energy, as well as render the SMP a self-heating capability which can be further designed into timed multi-step SMP behavior.

1. Introduction

Shape memory polymer (SMP) is a special type of polymer defined as a polymeric smart material that can alter its shape from a deformed shape (temporary shape) back to its original shape (permanent shape) induced by an external stimulus (trigger) [1–3], such as external heating [4,5], electro-activated [6], light-induced [5,7], solution-responsive [8], magnetic-responsive [9], and microwave-induced [10]. The advantages of SMPs over traditional mechanical actuators and other shape memory materials such as shape memory alloys (SMAs) include lower density, lower weight, lower production cost, easier processing, and larger recoverable strains comparable to that of SMAs [2,11]. These advantages make SMPs an attractive solution suitable for many industries, such as in biomedical surgery [12], smart fabrics/wearable technology [13], automobile industry [14], and aerospace engineering [15].

The major drawbacks of SMPs are their relatively low modulus that results in their lower recovery stress/forces, their long response time, their lower cycle life, and their weak material stability [2,16]. Additionally, similar to other polymers, SMP is a poor conductor for heat with low operational frequency and narrow bandwidth. This hinders its use as a large area actuator due to the high potential of cracking and damage to the structure. The high cracking potential is a result of the non-uniformity of heat spread caused by the polymer low thermal conductivity. This non-uniformity in the SMP temperature will cause internal strains on the structure during the activation heating process, as parts of it will reach temperatures lower than the polymer glass transition temperatures (T_g) while other parts will reach higher temperatures.

In order to address these issues, many have incorporated fillers, i.e. alumina, aluminum, brass, glass, graphite, magnesium oxide, stainless steel, calcium carbonate, acetylene black [17]. These fillers

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may enhance the mechanical properties of the SMP and increase the speed and stability of its heat transmission. However, part of the fillers tend to agglomerate and bundle with one another through Van der Waals forces, making it difficult to obtain highly homogenously dispersed filler infused SMP, which, in addition to the filler itself, can cause shape memory loss [18].

Recently, the development of 3D interconnected 2D-materials network (such as graphene into 3D-C [19], h-BN into 3D-BN [20] and a combined h-BN and graphene into BNC [21]) have been reported. These 3D-materials are highly flexible, of ultra-light weight (1–5 mg cm^{-3}) with controllable porosity and pore sizes (typical diameter of these pores ~100–200 μm, and porosity of 99.7%). Both h-BN and graphene have shown to possess remarkable thermal conductivities with graphene reaching ~3000 W m^{-1}K^{-1} [22] and h-BN reaching ~2000 W m^{-1}K^{-1} [23]. Contrastingly, their electrical behavior is drastically different. Graphene is a highly electrically conductive material [24] while h-BN is electrically insulating with a wide bandgap of ~5.8 eV [25]. BNC hybridized both characteristics and renders a tunable electrically conductive material, while maintaining the high thermal conductivity. Furthermore, unlike typical nano-fillers, the entire structure of 3D-BN/3D-BNC/3D-C is fully interconnected and can be synthesized in a large scale [21]. As such, it is expected to have a better overall thermal conductivity than most of the polymeric nanocomposite films reported until now, and the capacity of providing an effective electron and phonon distributing channel within the SMP matrix [26]. In this work, the thermal and electrical conductivity of epoxy-based SMP are enhanced by incorporating minimum loading fractions of 0.3 vol% of 3D-foams into the SMP matrix. This improves the response of SMP shape transformation and increases the speed of the shape changing process three-fold, without loss of shape memory effect. All variations of 3D-foams, 3D-C, 3D-BN, and 3D-BNC, were tested for this purpose and infused with an epoxy SMP. Their thermal conductivity, switching speed, mechanical strength, and energy requirements for transformation were measured. The incorporation of the 3D-foams into the epoxy SMP lead to a more efficient transfer of heat, which enables an increase in the total shape memory active area, the reduction of the input power by 20% and additionally, through the use of 3D-BNC, to add a self-resistive heating capability to the SMP. Through precisely tuning the concentration of BN and C, different switching temperatures can be catered for, as well as tailored switching times, which allows designing SMPs with timed actuation.

2. Results and discussion

2.1. Material characterization of 3D-foam filled SMP

3D-foams were fabricated using a previously reported CVD growth technique [21]. Fig. S1a shows optical images of the three types of foam used for infiltration with SMP: black foam corresponds to 3D-C, white foam to 3D-BN, and 3D-BNC is a hybrid of both, a composite foam of h-BN and graphene. Fig. S1b shows the Raman spectroscopy results of the 3D-foams, with pure 3D-C on top, pure 3D-BN in the bottom and an example of 3D-BNC (50:50 by atomic %) in the center. The absence of D peak (1350 cm^{-1}) and presence of sharp G (1580 cm^{-1}) and 2D (2700 cm^{-1}) peaks in the pure 3D-C sample indicates the presence of high quality pristine graphene [27]. The sharp peak at ~1370 cm^{-1} for the 3D-BN sample indicates the presence of the E_{2g} phonon mode of h-BN which stands for high quality pristine h-BN [28]. The Raman spectrum of 3D-BNC shows three distinct peaks corresponding to D, G, and 2D band of graphene, respectively, whereby the D peak shifted to ~1360 cm^{-1}, as a combination of defect peak of graphene (D peak ~1350 cm^{-1}) and h-BN E_{2g} phonon peak [21,29,30]. Fig. S1c shows a scanning electron microscopy (SEM) image of a typical cross-sectional view of the 3D-foams. The interconnected structure can be clearly seen, with a pore diameter of typically ~100–200 μm. In Fig. S1d a cross-sectional SEM view of foam infused with SMP is shown. It can be seen that the process yields bubble free samples. The shadowed structures inside the polymer block correspond to parts of the foam. It can be seen that the foam spreads homogenously throughout the entire cross-sectional area of the SMP. It is worth mentioning that even though the foam expands uniformly throughout the entire structure, it requires only a volume (weight) fraction of 0.3 vol% (0.35 wt%) and due to the ultra-light density of the foams (1–5 mg cm^{-3}), the overall material does not change in weight or original density through the infusion step. These small filling fractions are also orders of magnitude smaller than current fillers used (such as talc with 30 vol% filling factor, carbon nanotubes with 2 vol%, and aluminum nitride with 40 wt%) [18].

Since the infusion with 3D-foams can alter the polymer's intrinsic properties (such as reported by Jia et al. [31] where the glass transition temperature of epoxy was affected after infiltration with 3D-C) and could thus affect the shape memory performance, it is necessary to first determine whether the intrinsic properties (i.e. decomposition temperature and glass transition temperature, T_g) of the SMP remain the same after infusion with 3D-foams. For this, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were respectively used to study the decomposition profile and determine the T_g of bare SMP and 3D-foam infused SMPs. Fig. S2 shows the decomposition profile of bare SMP and 3D-C, 3D-BN and 3D-BNC infused SMP. The temperature at the point of 5% mass loss determines the decomposition temperature [32]. It can be seen that all results show identical curves and the point of 5% mass loss is in a similar range of 283 ± 3.5 °C for all four materials. This indicates that the infusion of 3D-foam does not affect the structure of the cured SMP. For DSC, a temperature sweep up to 150 °C was carried out and results are shown in Fig. S3. It can be seen that glass transition temperatures of 58.4 °C, 56.7 °C, 50.6 °C, and 52.6 °C were obtained for bare SMP, 3D-C/SMP, 3D-BN/SMP, and 3D-BNC/SMP, respectively. Taking into consideration possible experimental error, it can be thus stated that the infusion with 3D-foams has no effect on the T_g of SMP. This non-invasiveness of the 3D-foams is owed to the sequence of preparation. Since the Ni template is etched off prior to infusion with the SMP [33], direct bonds between polymer resin and 3D-foam become unlikely. This is an important characteristic, since any structural changes within the polymer would also affect the shape memory performance of the SMP.

The use of 3D foams is expected to improve the thermal and electrical properties of the SMP. The thermal conductivity values of the bare epoxy SMP and the 3D-foam SMP composites were measured using the laser flash technique at room temperature (RT) and above the glass transition temperature of the SMPs at 60 °C [34]. The electrical conductivity measurements were obtained using the 4-point probe Van-der-Pauw method [35]. The thermal conductivity of bare SMP was found to be 0.09 Wm^{-1}K^{-1} at RT and 0.103 Wm^{-1}K^{-1} at 60 °C, while the 3D-C/SMP was measured to be 0.361 Wm^{-1}K^{-1} and 0.341 Wm^{-1}K^{-1} respectively, which represent an improvement of 4 to 3-times. For 3D-BN/SMP, the thermal conductivity was measured to be 0.157 Wm^{-1}K^{-1} at RT and 0.145 Wm^{-1}K^{-1} at 60 °C, a ~1.5-times improvement over the bare SMP. The thermal conductivity measured for 3D-BNC/SMP (50:50) was 0.21 Wm^{-1}K^{-1} at RT and 0.17 Wm^{-1}K^{-1} at 60 °C, which is a 2.3 to 1.6-times improvement over bare SMP. The slightly higher results of 3D-C/SMP over 3D-BN/SMP and 3D-BNC/SMP are in agreement with previous reports [21,36]. Electrical conductivity measurements showed a low sheet resistance of 40 $\Omega\square^{-1}$ for 3D-C/SMP, preserved complete insulating behavior (20000 T $\Omega\square^{-1}$) of bare