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Significantly improving infrared light-induced shape recovery behavior of shape memory polymeric nanocomposite via a synergistic effect of carbon nanotube and boron nitride

Haibao Lu [a,*], Yongtao Yao [a], Wei Min Huang [b,*], Jinsong Leng [a], David Hui [c]

[a] Science and Technology on Advanced Composites in Special Environments Laboratory, Harbin Institute of Technology, Harbin 150080, China
[b] School of Mechanical and Aerospace Engineering, Nanyang Technological University, Singapore 639798, Singapore
[c] Composite Material Research Laboratory, Department of Mechanical Engineering, University of New Orleans, LA 70148, USA

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ABSTRACT

The present work studies the thermomechanical properties and infrared light-induced shape memory effect (SME) in shape memory polymer (SMP) nanocomposite incorporated with carbon nanotube (CNT) and boron nitride. The combination of CNT and boron nitride results in higher glass transition temperature, mechanical strength and thermomechanical strength. While CNTs are employed to improve the absorption of infrared light and thermally conductive property of SMP, boron nitrides facilitate heat transfer from CNTs to the polymer matrix and thus to enable fast response. A unique synergistic effect of CNT and boron nitride was explored to facilitate the heat transfer and accelerate the infrared light-induced shape recovery behavior of the shape memory polymeric nanocomposite.

1. Introduction

Shape memory polymers (SMPs) have the ability to "remember" their permanent shapes [1,2]. Unlike that of shape memory alloys (SMAs), the shape memory effect (SME) in SMPs is predominantly an entropic phenomenon [3,4]. Essentially a kind of dual-component structure is required to enable the SME in these polymers in most cases [5–9]. One component (or segment or netpoint) is always hard, which controls the configuration of polymer molecules, while the other is able to switch between soft and hard in response to the applied external stimulus [10–13]. Due to their great potentials in a range of applications to change shape, stiffness, position, etc. [14–25]. SMPs have become an interesting research topic at present. Light weight, ease in manufacturing and tailoring properties to precisely meet the needs of a particular application are advantages of SMPs among others [15,26–32].

Despite the tremendous progress in synthesis, analysis, characterization, actuation approaches, theoretical modeling and application exploration for SMPs [33–38], fundamental research works are currently ongoing aiming to for alternative stimuli other than direct heating and enabling higher performance [10–13,39–43]. It should be pointed out that a specified actuation approach for a SMP may not be applicable in a real practice [15,27,28,31,41]. For example, it is normally difficult to immerse structural components into a solvent for the chemo-responsive SME. Induction heating, resulted by applying an alternating magnetic field, is convenient for remote and wireless activation, but a magnetic field is requires a bulk system to produce. Infrared light possesses wide emission spectra and unique heating effect in a noncontact manner [34], so that this approach might be a good alternative to induction heating. The present work employs carbon nanotube (CNT) and boron nitride (BN) to enhance the strength of SMP nanocomposites and in the mean time, to achieve infrared light-induced actuation. The embedded CNTs are able to improve the absorption of infrared light and improve thermally conductive property of SMP. On the other hand, boron nitrides facilitate heat transfer from CNTs to the polymer matrix. Such a synergistic effect of CNTs and boron nitrides is designed to significantly improve the infrared light-induced shape recovery of SMP with faster response and higher mechanical strength.

2. Experimental details

CNTs were synthesized by chemical vapor deposition (CVD) and have a purity of 97%. Typical nanotubes have an out diameter of 50–100 nm and a length of 5–15 μm. The non-ionic surfactant (Triton X-100, $C_{14}H_{22}O(C_2H_4O)_n$), has a hydrophilic polyethylene

* Corresponding authors. Tel.: +86 45186412259 (H. Lu).
E-mail addresses: luhb@hit.edu.cn (H. Lu), mwmhuang@ntu.edu.sg (W.M. Huang).

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oxide group and a hydrophobic group. The hydrophobic group of surfactant backbone is closely in contact with CNTs, resulting in a hydrophilic polyethylene oxide group. Therefore, 2 ml surfactant was introduced to aid the dispersion of CNTs in the distilled water. CNT suspension was sonicated with a high-intensity sonicator at room temperature of 22 °C for 40 min at an ultrasound power level of 300 W. Boron nitrides were synthesized by reacting boron trioxide (B_2O_3) with urea ($CO(NH_2)_2$) in a nitrogen atmosphere. The resulting amorphous boron nitrides were converted into the crystalline structure at 1600 °C within an environment of nitrogen flow to achieve a higher concentration of boron nitride (>98%). The thermal conductivity of boron nitride is measured as 600 W/m K. As produced boron nitride particles were also dispersed into distilled water and then sonicated by an high-intensity sonicator for 30 min at an ultrasound power level of 300 W.

The epoxy-based SMP used in the course of this study is a two-part (a hard part and a soft part) thermosetting resin. The treated boron nitrides were blended into the SMP resin with a constant weight fraction of 4 wt.%. The mixture was mechanically stirred at a speed of 600 rad/min for 30 min. After that the treated CNTs were blended into the SMP resin with weight fractions of 0, 2, 4, 6, 8 and 10 wt.%, respectively, followed by mechanical stirring for another 30 min. The resulting mixture was then degasified in a vacuum oven to completely remove air bubbles. A resin transfer molding process was used to make the SMP nanocomposite samples under a constant pressure of 6 bar. After the mold was filled, curing was done upon heating from room temperature to 100 °C at a ramp of approximately 1 °C/min and then kept for 5 h before being ramped to 120 °C at a heating speed of 20 °C per 180 min. Finally, it was ramped to 150 °C at 30 °C per 120 min to make the final SMP nanocomposite.

3. Results and discussion

3.1. Morphology and structure of CNTs and BNs

Scanning electron microscopy (SEM) was used to characterize the morphology and structure of CNTs and boron nitrides. Fig. 1(a and b) shows the typical morphologies of CNT and boron nitride hybrid at an accelerating voltage of 20.00 keV. As we can see, the CNTs have a diameter ranging from 50 to 100 nm, and are entangled with each other. No large aggregates of nanotubes are found. On the other hand, there are many boron nitride particles and their aggregates entangle with CNTs to form many continuous paths. It is expected to endow the insulating polymer matrix with high thermally conductive property. Such hybrid fillers of CNT and boron nitride could play an important role in enhancing thermal conductivity of polymer composites.

3.2. Fourier transform infrared (FTIR) spectroscopy

The chemical structures of SMP nanocomposites were determined by the Fourier transform infrared (FTIR) spectroscopy (Nicolet AVATAR 360) in a transmittance mode from 4000 to 600 cm^{-1}. Fig. 2(a and b) compares FTIR results of nanocomposites with 0, 2, 4, 6 and 10 wt.% of CNTs. Two peaks at 2929 cm^{-1} and 1153 cm^{-1} correspond to aliphatic ether (C–O–C) bonding and as for $–C–H_3$ and $–CH_2–$ bonding, respectively. It is found that there is no remarkable chemical interaction between polymer matrix and fillers (both boron nitride and CNT).

Fig. 2(b) reveals the difference of infrared absorbing efficiency between pristine SMP and SMP nanocomposite from 4000 to 400 cm^{-1} in wavenumber. Pure SMP has lower absorption (less than 10%) within the whole wavenumber range, while SMP/BN/CNT nanocomposite shows continuum stronger (from 10% to 80%) absorption against all the tested wavenumber range. It is concluded that the presence of both CNT and boron nitride particles significantly increases the capability of nanocomposites to absorb infrared light energy. The reason is largely due to that most of the emitted energy is transmitted by SMP which is transparent, while most of the emitted infrared light is absorbed by the nanocomposite since it is black and opaque.

3.3. Differential scanning calorimetry

The temperature at which a polymer transforms from the glassy state to the rubbery state is called the glass transition temperature (T_g). Similar to other amorphous SMPs, T_g also plays an essential role in influencing the shape recovery behavior of the epoxy-based SMP. Therefore, it is necessary to confirm T_g prior to the investigation of the shape recovery behavior of this epoxy-based SMP. Differential scanning calorimetry (DSC) is routinely used to determine the T_g of polymers, including SMPs.

DSC (DSC 204F1, Netzsch, Germany) experiments were conducted in a nitrogen environment within a temperature range from 25 to 120 °C at a constant heating rate of 10 °C min^{-1}. Since the glass transition always occurs within a temperature range, the midpoint of the temperature range revealed in the scanning curve was defined as the T_g of a tested SMP sample in this study. The change in heat flow as a function of temperature is presented in Fig. 3(a). *Tg* is determined as 73.25, 94.80 and 107.8 °C for the pristine SMP and SMP nanocomposites, respectively. It can be seen that the glass transition is shifted to a higher temperature range

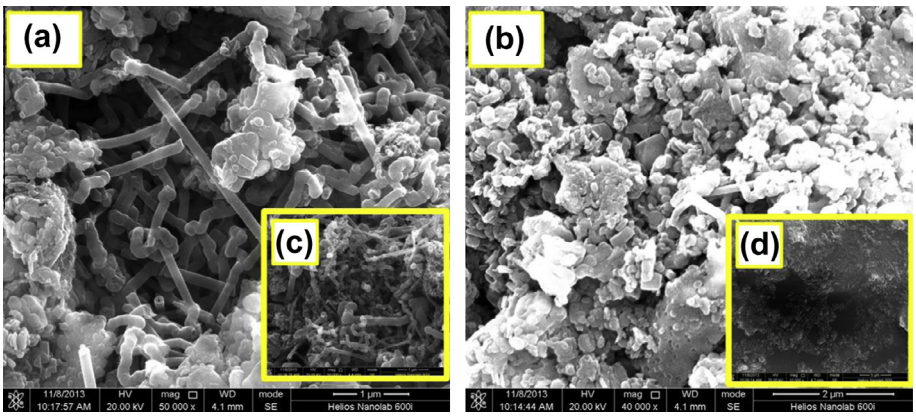

Fig. 1. (a and b) The morphology and structure of CNTs and boron nitrides at a scale of 1 μm and 2 μm, respectively. Inset image (c) presents the morphology and structure of the CNTs and inset image (d) presents the morphology and structure of the boron nitrides in SMP nanocomposite.