



Preparation of amorphous nanocomposites with quick heat triggered shape memory behavior



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ABSTRACT

The aim of this work was to prepare shape memory materials from poly(vinyl acetate) (PVAc), a low-cost commercial polymer, through the simple solution mixing method without need for complex synthetic routes. However, neat PVAc with inherent low strength and modulus exhibited inappropriate shape memory behavior. Therefore, stiff graphene nanoplatelets were incorporated within the PVAc matrix to improve its thermomechanical properties. Transmission electron microscopy (TEM) observations showed that graphene nanoplatelets built up a dense 3D network throughout PVAc. Furthermore, tensile and dynamic mechanical analysis (DMA) results demonstrated that the strength and modulus of PVAc were noticeably enhanced by introducing graphene nanoplatelets. DMA revealed that the PVAc/graphene nanocomposites possess excellent shape memory properties, as the fixation ratio (R_f) and recovery ratio (R_r) could be as high as 99.8 and 98.2%, respectively, and the original shape recovery time was ~5 s. The remarkable improvement in the shape memory properties of nanocomposites was correlated to great stored elastic strain energy in nanocomposites providing a high driving force for subsequent quick and almost complete shape recovery. In addition, enhanced heat transfer rate in the presence of graphene network can also account for high speed thermal actuation of the developed nanocomposites.

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1. Introduction

Shape-memory polymers (SMPs) are materials that have the ability to switch from an applied temporary shape to a permanent shape when an external stimulus, such as heat [1–7], electricity [8], alternating magnetic field [9], solvent [10], light radiation [11] or pH [12] is applied. Thermal induced shape memory behavior is the most facile and common method in triggering SMPs. Generally, two structural elements are required for an SMP; netpoints and switch segments that provide permanent shape fixation and shape recovery, respectively. The netpoints can be created with either chemical covalent bonds or physical interactions, such as glassy hard domains and crystallites [13,14]. Polymers containing physical netpoints can be reprocessed into various permanent shapes. However, most of the SMPs comprising physical netpoints display low stiffness as compared to those with chemical netpoints. This

leads to quite low shape fixation, inadequate shape recovery force and thereby incomplete shape recovery behavior [13].

On the other hand, switch segments are mostly based on reversible thermal phase transitions of melting-crystallization and glass transition. Unlike the melting temperature (T_m)-type SMPs, a large amount of rubbery modulus can usually maintain above the glass transition temperature (T_g) in the T_g -type SMPs [15]. However, the T_g -type SMPs usually indicate slow shape recovery process as compared to the T_m -type ones because of their broad glass transition interval [15–17], which limits their use in many applications that require sudden shape recovery. Totally, a main concern in the designing SMPs is fabricating shape memory devices that demonstrate simultaneous high recovery force and fast recovery response [18]. The most straightforward strategy for the raising recovery stress as well as recovery speed is strengthening of the amorphous polymeric matrixes with nanofillers [19–21]. Because percolated network of nano fillers can be served as second netpoints in conjunction with the physical entanglement netpoints of polymer matrix. To achieve stiff SMPs, various fillers were embedded into

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the polymer matrixes [17,22,23]. Among them, graphene based nanoparticles are effective reinforcing fillers for enhancing shape recovery force and shape recovery speed due to their ultra-high strength, excellent elastic modulus, high aspect ratio and surface area as well as high thermal conductivity [6,7,19,22–25].

In this study, PVAc, a commercial polymer, was used to prepare smart nanocomposite materials demonstrating shape memory behavior without need for complex synthetic routes. To the best of our knowledge, up to now, the application of PVAc nanocomposites as thermal induced shape memory materials hasn't been reported. Only few qualitative studies were reported regarding the shape memory behavior of neat PVAc [26,27]. However, due to the low strength and modulus of neat PVAc, it exhibited inadequate shape memory properties. This is the first report of how a nanofiller affects the thermomechanical properties of PVAc matrix and, as a result, improves its shape memory performance. Herein, we expect that the stiff and conductive graphene nanoplatelets will build up a strong 3D network throughout the PVAc matrix, and provide a high driving force as well as high thermal conductivity for nanocomposites that are necessary for the subsequent quick and complete shape recovery.

2. Materials and methods

2.1. Materials

poly(vinyl acetate) (PVAc) with $M_w = 125,000\text{--}175,000$ g/mol was purchased from Wacker Chemie AG. Chloroform with purity of $\geq 99.8\%$ was prepared from Merck Co. The commercially available graphene nanoplatelets, N002-PDR (with average number of graphene layers < 3 , average X & Y dimensions ≤ 10 μm , specific surface area = $400\text{--}800$ g/m^2 , true density ≥ 2.2 g/cm^3 , carbon content $\geq 95.0\%$, oxygen content $\leq 2.5\%$, hydrogen content $\leq 2.0\%$ and nitrogen content $\leq 0.5\%$) prepared by chemical exfoliation and thermal reduction from natural graphite [28] were obtained from Angstrom Materials, Inc.

2.2. Preparation of nanocomposites

The solution mixing method was used to prepare PVAc/graphene nanocomposites. Desired amounts of graphene powder were added into 100 mL chloroform and stirred for 8 h with aid of a magnetic stirrer at room temperature, followed by more dispersing of nanoparticles in the solvent through sonication for 5 min. Then, PVAc was poured into the graphene suspension and allowed to completely dissolve by stirring for 8 h at room temperature and sonication for 5 min. Afterward, the solution was poured into a silicon mold with a specific dimension and dried at room temperature for at least 24 h. It was then further dried in a vacuum oven at 90 $^\circ\text{C}$ for 12 h. Finally, the sheet of samples with thickness of ~ 0.5 mm was fabricated using a hot press operating at 120 $^\circ\text{C}$. PVAc/graphene nanocomposites with 3 and 4.5 wt% graphene nanoplatelets were designated as PVAc-G3 and PVAc-G4.5, respectively.

2.3. Characterization

For Fourier transform infrared spectroscopy analysis, FTIR (Perkin Elmer Spectrum 1), the dried samples were milled and mixed with dried KBr powder to prepare pellets. Then, the FTIR spectra of samples were obtained with the subtraction of KBr background to investigate possible molecular interactions between PVAc and graphene.

Wide angle X-ray diffraction (WAXRD) spectra of powdered samples were obtained using a JEOL X-ray diffractometer (JDX-8030) operating at a voltage of 40 kV and current of 44 mA under

CuK α radiation.

For transmission electron microscopy (TEM) observations, the prepared films were embedded in epoxy (Epon/Araldite) and cut into thin slices ($70\text{--}90$ nm) via diamond knife of an ultramicrotome apparatus. The obtained sections were then put on 2×1 mm^2 carbon-formvar coated copper grids. The micrographs were obtained through a JEOL 2100 LaB6 TEM operating at a voltage of 200 kV.

The mechanical properties of rectangular samples ($60 \times 10 \times 0.5$ mm^3) were measured by a Zwick Roell universal tensile testing machine at room temperature (23 ± 2 $^\circ\text{C}$). All mechanical tests were conducted at a crosshead speed of 20 mm/min using a 10 kN load cell. For reproducibility, at least 3 specimens were tested for each sample, and the average was reported.

Differential scanning calorimetry (DSC) was conducted using a DSC200F3 (Netzsch Instruments, Germany) under nitrogen atmosphere. All the samples were first heated from -20 to 120 $^\circ\text{C}$ with heating rate of 10 $^\circ\text{C}/\text{min}$ followed by keeping isothermally at 120 $^\circ\text{C}$ for 3 min to erase their previous thermal history. They were then cooled to -20 $^\circ\text{C}$ at 10 $^\circ\text{C}/\text{min}$, and subsequently scanned from -20 to 120 $^\circ\text{C}$ with the same rate. The T_g was chosen as the middle point of the step transition peak, and associated transition width (ΔT_g) was determined thanks to the standard tangential method.

For thermal conductivity analysis, samples were first prepared in disc-shaped forms, with diameter of ~ 10 mm and a thickness of ~ 0.5 mm, and then their thermal conductivity was measured using laser flash technique (LFA447-Nanoflash, NETZSCH) at room temperature.

Dynamic mechanical analysis (DMA) was performed via Triton (Tritec 2000 DMA) instrument in tensile mode with a dynamic strain of 0.1%. DMA was conducted on rectangular specimens ($25 \times 10 \times 0.5$ mm^3) in a temperature range of $5\text{--}90$ $^\circ\text{C}$ and heating rate of 3 $^\circ\text{C}/\text{min}$ at frequency of 1 Hz.

Quantitative measurements of dual-shape memory properties were performed using the same DMA instrument under controlled force mode as follows [29,30] (Scheme 1): (i) heating with a rate of 3 $^\circ\text{C}/\text{min}$ and equilibrating at 70 $^\circ\text{C}$, above the switching temperature of samples, (ii) ramping the force at 0.05 N min^{-1} until a strain of $\sim 40\%$ was achieved, (iii) cooling to -20 $^\circ\text{C}$ at 3 $^\circ\text{C}/\text{min}$, and isothermal holding at -20 $^\circ\text{C}$ for 60 min while keeping the external force constant, (iv) fixing the temporary shape by releasing the external load by unloading the force back to 0.001 N (a small pre-load), and (v) recovering the permanent shape with heating to 70 $^\circ\text{C}$ at 3 $^\circ\text{C}/\text{min}$. This cycle was then conducted consecutively for two more times on the same sample. The dual-shape memory properties of samples were quantified by calculating the fixing ratios (R_f) and recovery ratios (R_r) through the following equations [30]:

$$R_f(N)\% = \frac{\varepsilon_u(N)}{\varepsilon_m(N)} \times 100 \quad R_r(N)\% = \frac{\varepsilon_u(N) - \varepsilon_p(N)}{\varepsilon_u(N) - \varepsilon_p(N-1)} \times 100$$

where ε_m , ε_u , ε_p , and N represent the maximum strain before unloading, the strain upon unloading, the permanent (residual) strain after heat induced shape recovery, and the cycle number, respectively.

3. Results and discussion

3.1. Microstructure analysis

The FTIR spectra of the pristine graphene power, pure PVAc and its corresponding nanocomposites are shown in Fig. 1. The typical

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