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Shape memory effect and mechanical properties of carbon nanotube/shape memory polymer nanocomposites

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Abstract

Carbon nanotubes (CNT) have remarkable mechanical properties with very high elastic modulus and electrical conductivity. Shape memory polymer (SMP) as one of smart materials is characterized with its remarkable recoverability and shape memory effect, but its mechanical properties such as strength and elastic modulus is not high enough. In this study, CNT/SMP nanocomposites were developed with the typical CNTs of the vapor growth carbon fibers (VGCFs). A fine and homogeneous dispersion of VGCF throughout the SMP matrix is obtained. The specimens with different VGCF weight fraction, such as SMP bulk, 1.7 wt.%, 3.3 wt.% and 5.0 wt.%, were prepared, and their dynamic mechanical properties and shape recovery behavior were investigated. It was found that storage elastic modulus is improved obviously with increment of VGCF weight fraction, and the CNT/SMP nanocomposites showed a good shape memory effect. It is indicated that the recovery stress of CNT/SMP nanocomposites with only 3.3% weight fraction of carbon nanotubes will reach almost twice of that in SMP bulk.

Keywords: Carbon nanotube; Shape memory polymer; Nanocomposites; Shape memory effect; Shape recovery; Recovery stress

1. Introduction

Carbon nanotubes (CNTs) are seamlessly rolled sheets of hexagonal array of carbon atoms with diameter ranging from a few Angstroms to several tens of nanometers. Carbon nanotubes are receiving steadily increasing attention because of their unique structural and electrical characteristics. The tensile modulus and strength of CNTs reach 270 GPa to 1 TPa and 11–200 GPa, respectively [1–4]. The unusual electrical and mechanical properties of carbon nanotubes have motivated a flurry of interests to exploit their applications in advanced composite materials, particularly polymer based composites, to improve the performance of a matrix or to achieve new properties [5]. Polymer composites with CNTs were expected to improve the mechanical properties of the matrix polymer. Recently, because a large quantity composition technology was established, the cost of CNT decreased and then the applications to various fields became more and active. Many researches on mechanical, thermal and electric characterizations of CNT reinforced polymers are reported, such as CNT/polystyrene [6–8], CNT/PVA [9], CNT/PVDF [10], CNT/PP [11–17], CNT/nylon [18], and CNT/epoxy [19–21], etc.

One the other hand, shape memory polymers (SMPs) have the characteristics such as large recoverability, light-

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weight, superior molding property and lower cost. These advantages have resulted in that the SMPs become one of functional materials with much attention from many fields [22–24]. Fig. 1 shows the schematic representation of four steps of the shape memory effect in SMPs. This was based on thermo-elastic phase transformation and its reversal at the temperatures above and below T_g. When the SMPs were heated at fluxing temperature over T_g and formed into a specified shape by compression, extrusion or injection mouldings they memorized the formed shape (step 1). In this situation, it is considered that there exist two phases, stationary phase and reversible phase, which correspond to the crystal portion with bridging construction and the amorphous portion, respectively. The amorphous portion shows the rubber elasticity by heating above T_g, and is easy to be deformed into an arbitrary shape under an applied force (step 2). Then, the deformed shape is fixed by cooling below T_g (step 3). This was called shape fixity in shape memory behavior. To change the deformed shape, SMPs could recover the memorized shape by heating over glass transition temperature under a free load condition (step 4), and then go through the process again as above [25–29].

For shape memory polymer (SMP) of polyurethane series, its glass transfer temperature (T_g) may be set up around room temperature, and its characterizations such as shape recovery and/or shape fixation may appear to be quite different at the temperature above and below T_g [30–35]. Thus the polyurethane SMP will have wide applications in the field of industry as an actuation material. However, their lower mechanical properties such as strength and stiffness result in the current limited application. The low stiffness of SMP resins only produces a relatively small recovery force in a temperature change process. Thus, a few researches have studied adding reinforcement to SMP for improvement of mechanical property. Liang et al. [36] report that glass fiber and the Kevlar fiber reinforced SMP increased stiffness and Young's modulus, and decreased a recoverable strain. Ken Gall et al. [37] presented that SiC reinforced SMP nanocomposites increased elastic modulus by approximately a factor of 3 with the addition of 40 wt.% SiC, and permanent bend stain were discovered. The present authors group [38–41] demonstrated that the relationship between fiber weight fraction and recoverability for chopped strand glass fiber reinforced SMP composites by injection moulding. It is found that the composite stiffness and recoverable strain levels depend strongly on the fiber weight fraction. The material with 50 wt.% fraction of glass fiber will increase failure stress 140% and decrease recovery rate 62% compared with the bulk one.

The study of SMP nanocomposites with carbon nanotubes (CNTs) has not been reported. Using carbon nanotubes may obtain higher performance than usual reinforcement due to the large surface area of carbon nanotubes. In this paper, CNT/SMP nanocomposites were innovated with different CNT weight fractions. The fundamental mechanical properties and shape recovery behavior of CNT/SMP nanocomposite were examined. The tensile properties were evaluated at the temperature above and below T_g. The thermo-mechanical cycle tests were carried out for evaluating the influence of CNT weight fraction on shape memory effects. And the recovery stress test was also conducted in order to investigate the influence of CNT weight fraction on recovery stress.

2. Experimental

2.1. Material

Vapor grown carbon fibers (VGCFs) (Showa Denko K.K.), one of typical carbon nanotubes, is used. The diameter of VGCF is about 150 nm and length is 10–20 μm. The polyesterpolyol series of polyurethane SMP (Diary, MS4510) was used and its glass transition temperature T_g was about 45 °C. The raw material was liquid. The weight ratio of polymer to solvent is set to be 3:7.

2.2. Fabrication of specimens

VGCFs were put into the solvent little by little and dispersed for 3 h by ultrasonic vibration at 45 °C. The diluted SMP solution is gradually poured into the mixed-solution of VGCF and solvent, and then whole mixture was agi-

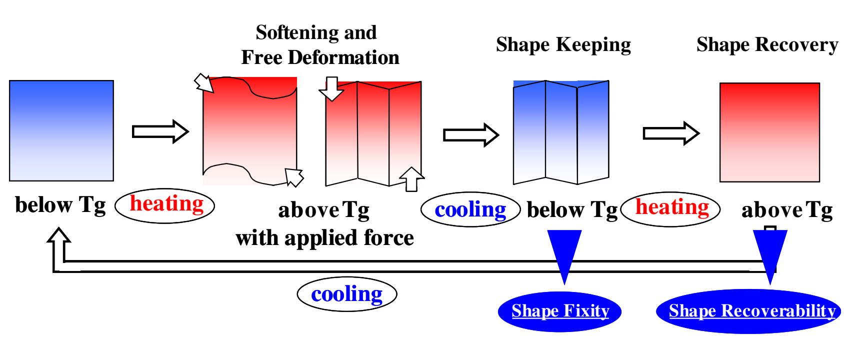

Fig. 1. Schematic representation of the shape memory effect with four steps: (1) memorized shape after molding and cooling; (2) free deformation due to the rubber elasticity of the amorphous portion by heating over T_g under an applied force; (3) shape fixity by cooling below T_g; and (4) shape recovery by heating over T_g under free load condition.