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Qualitative separation of the physical swelling effect on the recovery behavior of shape memory polymer

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ABSTRACT

The physical swelling effect-induced shape recovery is studied in a thermo-responsive styrene-based shape memory polymer (SMP). Fourier transform-infrared (FTIR) test reveals no apparent change in the characteristic polar bonds of C=O and O–H after immersing the SMP into toluene solvent. Based on the rubber elastic and relaxation theory, the decrease in internal energy is identified as the driving force for the shape recovery. Subsequently, the rubber elastic theory is further applied to investigate the swelling-induced free/constraint shape recovery in this SMP, and the free-energy function is utilized to analyze the swelling-induced homogenous/inhomogeneous deformation. This study provides a framework to study both the swelling effect-induced shape recovery and complex shape memory behavior in solvent-responsive SMPs.

1. Introduction

As a high performance shape memory material, shape memory polymer (SMP) has attracted more attention in recent years, largely due to its advantages and variety when compared with its metallic counterpart, namely shape memory alloys (SMAs) [1,2]. Different from SMAs [3], all SMPs are based on a dual-segment system, in which one segment is always elastic, while the other is able to remarkably reduce its stiffness when a particular stimulus is presented. The shape memory effect, i.e., the ability to return the original shape after being seemingly plastically deformed, in SMPs is resulted by the change of stiffness in the latter segment, i.e., transition segment, by means of either molecular switch or stimulus-sensitive domain [4,5]. As compared with other shape memory materials, SMPs have much higher shape recovery strain (up to 400%) and lower density, and in addition, they are more convenience in processing, lower cost, easier to achieve tailored properties, potential biocompatibility and biodegradability [1–5]. Atop of these, perhaps the most notable feature of SMPs is the variety in stimuli for actuation. Taking thermo-responsive SMPs as an example, in addition to direct-thermo-heating, light-heating [6–9], joule heating [10–15] and induction heating [16–18] are possible.

Instead of heating thermo-responsive SMPs for shape recovery, recently, an alternative approach through decreasing the activation temperature of SMPs has been demonstrated [19–24]. Lower transition or switching temperature is achieved by diffusion of solvent molecules into the polymer network. The absorbed solvent molecules work as a plasticizer [25]. Meanwhile, the effect of physical ageing on a polyurethane SMP is also reported [26]. These insightful research works are expected to significantly widen the potential applications of SMPs. As well known, when a polymer is brought into contact with a solvent, polymer network imbibes solvent molecules progressively and swells, resulting in aggregation of solvent molecules, known as gel [27,28]. A gel can undergo large deformation due to the long-range migration of the solvent molecules, causing both shape and volume of the polymer changed, until an equilibrium condition within a particular

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environment is reached. In this process, a great change in transition/switching temperature in SMPs is expected. The change in transition/switching temperature will affect the relative motion of transition segments, which is the primary mechanism of the shape memory effect in SMPs. This approach demonstrates that the shape memory effect in thermally responsive SMPs can be triggered not only by heating, but also by lowering the transition/switching temperature of polymers.

This paper explores a novel activation approach for shape recovery in a styrene-based SMP by the physical swelling effect upon immersion into toluene solvent. Dynamic mechanical analysis (DMA) and Fourier transform-infrared (FTIR) tests are conducted to characterize the thermomechanical properties and chemical structures of this SMP after different immersion times, in order to identify the underline mechanism behind the physical swelling-induced shape recovery. A framework based on the rubber elastic theory is proposed for theoretical investigation of this feature in this type of SMP.

2. Experiments, results and discussions

2.1. Sample preparation

The styrene-based SMP resin (Veriflex®S, VF62) used in the course of this study was bought from Cornerstone Research Group, Inc., Dayton, Ohio, USA. The Veriflex VF62 is a two-part, fully formable thermoset resin system. The resin is engineered with a glass transition temperature (T_g) of 62 °C. The resin mixture is polymerized with dibenzoyl peroxide (as a paste) at a fixed proportion of 24:1 (in weight). The cured Veriflex VF62 resin has the "shape memory" properties. When heated above its switching temperature (T_g), it changes from rigid plastic state to elastic rubber state and thus it can be twisted, compressed, bent, and/or stretched easily.

The SMP resin was mixed with curing agent using a high shear mixer and filled with 0.5 wt.% thermo-responsive dye that changes its color from purple to pink at 45 °C. It was aimed to demonstrate that during shape recovery no heat was involved in the SMP. The resulting mixture was degasified in a vacuum oven to remove air bubbles. The SMP resin mixture was then injected into a mold and cured with a ramp of approximate 1 °C/min from room temperature to 75 °C. The sample was then held at 75 °C for 3 h before being ramped to 90 °C at 15 °C/180 min. Finally, it was ramped to 110 °C at 20 °C/120 min.

2.2. Demonstration of shape recovery upon immersing into toluene

Fig. 1 shows the shape change of a piece of styrene-based SMP upon immersing into toluene solvent. The flat (original shape) specimen with dimensions of 72 × 5 × 5 mm was bent into "U"-like shape (temporary shape) at 75 °C. This shape was held until the specimen was cooled back to room temperature. No apparent shape recovery was observed even after the deformed specimen was left in air for 4 h until it was immersed into 35 °C toluene. The recovery behavior of the SMP sample was

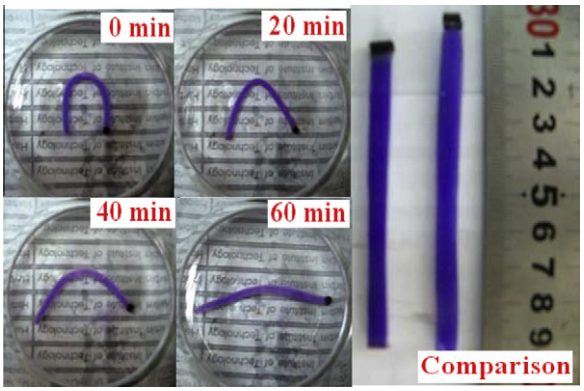

Fig. 1. A series photos of shape recovery of rectangle SMP sample (bent into "n" like shape) in Toluene; comparison of length change between unswollen and swollen samples.

recorded by a camera. As we can see, in the first 20 min, the recovery was small and it became significant afterward. One hundred percent of recovery was not achieved even after 60 min of immersion, i.e., the SMP could not fully regain its original flat shape, due to that the plasticizing effect between solvent molecules and polymer molecules caused the recovery force of polymer seriously reduced. Here, the polymer can not provide enough mechanical loading to resist conditioned pressure of toluene solvent. On the other hand, after being immersed into the toluene solvent for 60 min at 35 °C, a noticeable change in volume was found along with the shape change in SMP. Finally, the dimensions of the SMP were stretched from 72 × 5 × 5 mm to 90 × 8 × 10 mm.

2.3. Dynamic mechanical analysis

Dynamic mechanical properties of SMP samples (25 × 10 × 3 mm) with different immersion time were tested using a Netzsch DMA 242C (Netzsch, Germany) in three-point bending mode at an oscillation frequency of 1.0 Hz and a constant heating rate of 10.0 °C min^{-1} from 0 to 100 °C. Storage modulus and tangent delta curves were recorded as a function of temperature. Fig. 2(a) reveals that the storage modulus of SMP samples decreases from 1204 to 434 MPa with an increase in immersion time from 0 to 60 min. And the T_g of the SMP samples with an immersion time of 0, 20 and 60 min is 55.77, 44.86 and 35.82 °C, respectively, where the T_g is defined as the point of intersection between the storage modulus and the tangent delta curves, as shown in Fig. 2(b). These results indicate that both the storage modulus and T_g of SMP samples are depressed with an increase immersion time.

From these DMA results, it reveals that the T_g of the immersed samples is lowered. With an increase in immersion time, the decrease in T_g becomes more significant. A lowered T_g causes the shape recovery in the pre-deformed SMP.

2.4. FTIR measurement

To better validate and qualitatively identify the mechanism of shape recovery in SMPs induced by the physical