

Solution-responsive Shape-Memory Polymer Driven by Forming Hydrogen Bonding

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Abstract. Recently, there is interest in triggering shape recovery of shape-memory polymers(SMPs) by novel non-external heating. In this paper, many hard works have been carried out to make SMP induced by solution. The main challenge in the development of such polymer systems is the conversion of solution-induced effects at the molecular level to macroscopic movement of working pieces. This paper presents a systematic study on the effects of solution on the glass transition temperature (T_g). The results reveal that the hydrogen bonding of shape memory polymer (SMP) was aroused by the absorbed solution that significantly reduces T_g of polymer. The mechanism behind it is solution firstly intenerates polymeric materials till the T_g of polymer lowered down to the temperature of ambient, then hydrogen bonding interaction improves the flexibility of polymeric macro-molecular chains. Thus, the shape memory effect (SME) can undergo solution-driven shape recovery. In addition, it provides a new approach that the SMP can be induced by applying non-energy stimulus. The Dynamic Mechanical Analyzer (DMA) results reveal that the modulus of polymer was softened gradually with immersion time increasing. The experimental result is approximate to the theory.

Introduction

Shape memory polymers (SMPs) derive their name from their inherent ability to return to their original "memorized" shape after undergoing a shape deformation [1]. SMPs that have been performed can be deformed to any desired shape above its transition temperature. And they must remain below, or be quenched to below, the glass transition temperature (T_g) while maintained in the desired thermoformed shape to "lock" in the deformation. Once the deformation is locked in, the polymer network cannot return to a relaxed state due to thermal barriers. The polymer will hold its deformed shape indefinitely until it is heated above its T_g , whereat it stored mechanical strain is released and returns to its performed state [2,3]. SMPs have a number of advantages over shape memory alloys (SMAs) for some particular applications. Ease in transforming into another shape and control of recovery temperature, and more importantly, low cost [4-6].

Stimuli-sensitive materials are able to change certain properties in response to specific external stimuli such as heat [1,2,5], light [7,8], electricity [9-11], Magnetic field [12] or moisture [3]. Among them, the thermo-responsive SMPs have been the major focus under investigation in the past years. Although they have found a few applications, they have not fully reached their technological potential. Largely due to that the actuation of shape recovery in thermal-responsive SMP is normally only driven by external heat.

It is well known that phase transition often accompanies great changes in physical properties of polymeric materials, like a large decrease of modulus, on which solution-responsive SMP is based.

The mechanism behind it is that the interaction between polymeric macromolecule with micro-molecule of absorbed solution. There are three major reasons maybe can be used to explain it. Firstly, the hydrogen bonding enlarges the flexibility of polymeric chains [3,5]. Secondly, the interaction resulting in volume change of polymer that destroys the modulus of the polymer explained by continuum theories of rubber elasticity, the Mooney-Rivlin Equation and volume change refinement theory. Thirdly, when the temperature of solution (or the ambient) is lower than the T_g of the polymer, the solution firstly intenerates the polymer till the T_g is lowered down to the temperature of solution, followed the solution has other effects on polymer. Thus, the actuation of the SMPs can be triggered by their solutions. The styrene-based thermosetting SMP can recover from the pre-deformed ‘n’ shape sequentially after being immersed in N,N-Dimethylformamide (DMF) for forming the hydrogen bonding shown in Fig. 1.

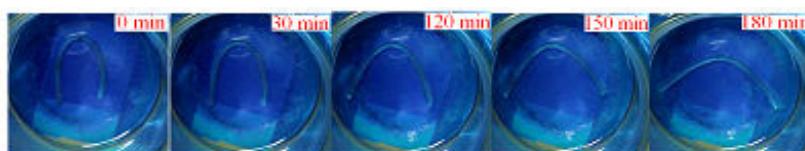


Fig. 1. Shape recovery of a 2.88 mm diameter SMP wire in DMF.
The wire was bent into “n” like shape

2. Results and Discussion

2.1. Effect of Solution on the Modulus

Dynamic mechanical analysis (DMA) test was carried out at a constant frequency of 1 Hz on a DMA Q800 (TA Instruments). After different immersion minutes in DMF at room temperature, the rectangular samples were heated at a rate of 5°C/min.

Typical results of storage modulus, the loss modulus and tangent delta as a function of temperature are plotted in Fig. 2. The storage modulus is the modulus of elastic portion of material; it reveals the transition velocity from glass state to rubber state. Figure 2 (A) shows, upon gradually absorbing solution, the storage modulus decreased from 1475 MPa (0 min) to 604 MPa (after 120 min immersion) at the temperature of 25°C; and the transition temperature determined by storage modulus curves reveal that it decreased gradually with immersion time increasing. At last, the transition temperature determined from storage modulus curves decreased with immersion time increasing.

Tangent delta is defined as the ratio of the loss modulus over the storage modulus, and the temperature corresponding to the peaks of tangent delta is an alternative T_g . T_g defined in such a way is determined as 84.29, 74.04, 65.30, 60.72 and 55.05°C for immersion time 0, 10, 30, 60 and 120 minutes respectively. As shown in Fig. 2 (B), upon gradually absorbing solution, the maximum peaks of tangent delta curves decrease obviously. It reveals that the tangent delta curves reach their maximum at lower temperature with the immersion time increasing.

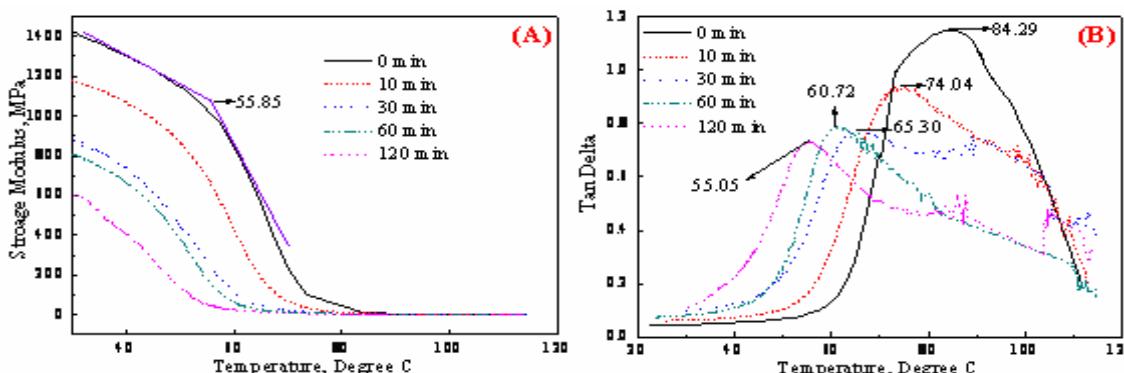


Fig. 2. Storage modulus, loss modulus and tangent delta curves of samples with different immersion times at the oscillation frequency of 1 Hz

The DMA results show that the mechanical properties of styrene-based SMP are destroyed by its solution for forming hydrogen bonding. That's because the bonded hydrogen between polymer and solution results in improving the flexibility of polymeric molecular, which has a negative role on polymeric mechanical properties. All above mentioned can be cited from physics of polymer.

2.2. Interactions between Solution and Polymer

On above tests, we have demonstrated that the solution DMF has a strong influence on the glass transition temperature and the dynamic mechanical properties of styrene-based SMP. However, the mechanism behind these phenomenons remains unknown.

In this study, FTIR spectroscopy was used to study the interaction between the SMP and the DMF solution and identify possible factors. The samples used for FTIR test were thin rectangle sheets with a thickness of 1.0 mm. FTIR spectra were collected by averaging 128 scans at a 4 cm^{-1} in a reflection mode from a FTIR spectrometer (AVATAR 360, Nicolet).

The full FTIR spectra of the SMPs (at the temperature of 20°C) after different immersion minutes in DMF are presented in Fig. 3. The peak of bonded C=O that is relevant to this study has been marked out and identified according to some references [13,14]. The infrared band of free C=O stretching at 1724 cm^{-1} shifts to that of the bonded one at 1740 cm^{-1} . As such, the hydrogen bonding in the SMP is apparent.

Figure 3 (A) shows that after immersion the infrared band of the hydrogen-bonded C=O stretching shifts slightly to a lower frequency. Furthermore, with the increase of immersion time the infrared band intensity of the bonded C=O stretching becomes more striking compared with that of free C=O stretching, which indicates that a longer immersion time triggers more C=O groups in hydrogen bonding.

Figure 3 (B) presents the FTIR spectra in the C=O stretching regions in samples after different immersion hours, respectively. It shows that after immersion the infrared band of the hydrogen-bonded C=O stretching shifts slight to a higher frequency. Moreover, with the immersion time increasing, the intensity of the bonded C=O stretching becomes more inapparent, which indicates that a longer immersion time triggers more C=O groups involved in hydrogen bonding [15].

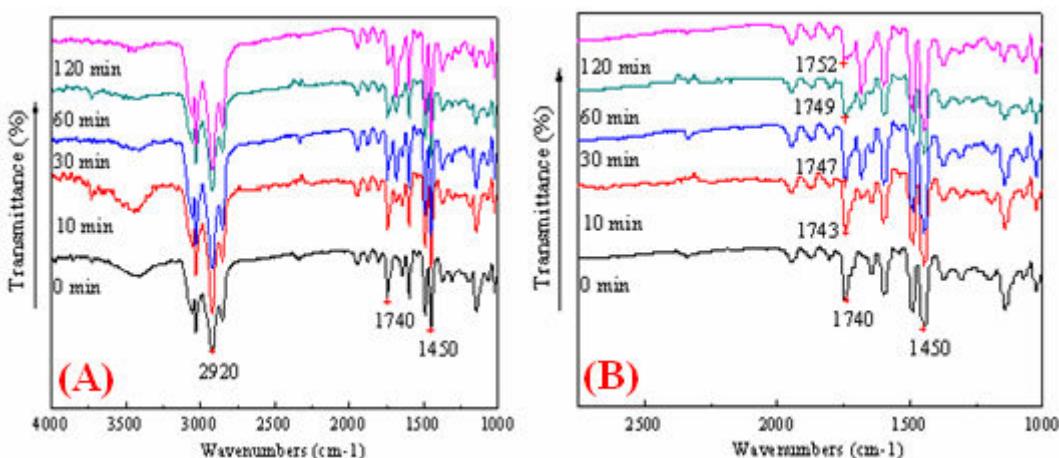


Fig. 3. FTIR spectra of styrene-based SMP after different immersion minute, (A) for full spectra; (B) for C=O stretching region

3. Conclusions

Solution-driven SMP provides an alternative approach, so that heating becomes unnecessary. The actuation can be triggered upon immersing the material into solution. That is to say, instead of heating the material to above its T_g , shape recovery can be achieved by means of reducing the T_g of the material itself upon immersing the SMP into solution that is the same as water driven PU SMP in principle. Three main conclusions followed as: (1) A variety of polymer architectures and

functionalization processes have been discovered, enabling solution-activate shape change in polymers. Thus, shape recovery of SMP can be triggered not only by applying energy, but also by non-energy. (2) Micro molecular of solution absorbing in the SMP weakens the elasticity modulus, which causes a significant decrease in the T_g , which has a direct influence on the shape recovery of SMP. This obvious decrease can be obtained by DSC and DMA tests easily. (3) This mechanism may be applicable for all the SMPs that have the capability of forming hydrogen with their special solution. Though the hydrogen has a slight effect on the structure of SMP, it has an obvious influence on the T_g . Moreover, solution-induced shape-memory operates over a wide temperature range.

4. Experimental

Styrene-based shape-memory thermosetting resin and its cured agent bought from Cornerstone Research Group (CRG) Inc. were used in this study. According to the data provided by CRG, the resin has a T_g of 65°C and a density of 0.88-0.92 g/cm³. In the process of fabrication, the polymer was prepared by mixing resin with the crosslink agent in a proper proportion at room temperature. Then, the mixture was followed by mechanical stirring for more than 15 minutes. A vacuum pump was used to dispose air bubble for more than 90 minutes. At last, the mixture was poured into a close-mould made of glass, and cured at the temperature of 75°C in oven for more than 12 hours. Several rectangle sheets were prepared in the course of this study. In the immersion test, the samples were thrown into the 100 ml DMF solution at the temperature of 22°C. And after immersion, the samples were dried till its weight unchanged at the temperature of 40°C. The appearance of the samples changed from clarity to opacity (showing ivory-white).

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