THERMOMECHANICAL PROPERTY OF EPOXY SHAPE MEMORY POLYMERS

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Epoxy shape memory polymers (SMPs) were preparation and their mechanical properties are focused on. Full shape recovery is observed at 150 °C for each polymer, and the SMP with lower hardener content shows a quicker shape recovery speed. In addition to a good thermal stability, glass transition temperature of the polymers increases with increasing hardener content. Of particular attention of DMA test is that the epoxy SMPs show a high storage modulus not only in glass state but also in rubber state. The tension test indicates that both stress at break and corresponding elastic modulus vary with a peak value for the polymers.

Keywords: Mechanical properties; shape memory polymer.

1. Introduction
Shape memory polymer (SMP) is a new class of smart material which attracts great interest in recent years. SMPs are defined by their capacity to recover inelastic strains by
the application of external stimuli such as light,\textsuperscript{1} electric current,\textsuperscript{2,4} magnetic field,\textsuperscript{5} or solution.\textsuperscript{6,7} SMPs possess higher recoverable strain levels (~400%), lower cost and weight, ease of manufacturing and great versatility.\textsuperscript{6} On basis of these unique characteristics, SMP materials can be used in many potential smart material applications, such as medical application\textsuperscript{6} and deployable space structures.\textsuperscript{10} The thermo-mechanical property of SMP is a strong factor for its applications. Epoxy SMP can supply excellent mechanical properties compared with that of other types of SMP,\textsuperscript{3,11-12} and it is also a good candidate material for further study because it can be easily chemically modified. However, few studies\textsuperscript{13-14} focused on the mechanical property of epoxy SMP. In this paper, a new system of epoxy SMP with various hardener contents is synthesized, and its thermo-mechanical property is focused on.

2. Experiments

Epoxy SMP was prepared by mixing epoxy resin and hardener. The hardener content was 27, 35 and 41 wt% for EP04, EP06 and EP08, respectively. The liquid mixture was degassed in a vacuum oven and cast into a glass mold to be cured at 80 °C for 2 h, and 150 °C for 5h. Finally, SMP sheets with a thickness of 3mm were obtained. DSC test was performed on an Instrument NETZSCH DSC 204F1 from 30 to 200 °C with a heating rate of 10 °C/min. Thermal Gravity Analyzer (TGA) was performed from 20 to 550 °C with a heating rate of 10 °C/min. Dynamic mechanical analysis (DMA) test was carried out at a constant frequency of 10 Hz on a DMA Q800 (NETZSCH DMA 242), with a three-point tensile mode at a heating rate of 5 °C/min. Isothermal quasi-static tension test was also conducted at 25 °C using an Instron-5569 instrument according to ASTM D638.

3. Results and Discussion

3.1. Shape memory behavior

Samples with size of 3×0.5×0.1 cm were used to investigate shape memory behavior of the polymers. The samples were heated up to 150 °C and deformed into a circular shape with external force, and the deformed samples were cooled to room temperature to keep the temporary shape. Finally, as shown in Fig.1, when the bent samples were heated at 150 °C again, they returned to the initial shape gradually with a shape recovery ratio of above 99%. Furthermore, it is obvious that the polymer with lower hardener content shows quicker shape recovery speed. The lower hardener content results in a lower cross-linking density, which leads to the reversible phase is less constrained by fixed phase in the network and then the SMP shows quicker shape recovery speed.
3.2. **DSC test**

The glass transition temperature, $T_g$, is the reference point for thermo-mechanical deformation and recovery. The full DSC term curves of the SMPs are plotted in Fig. 2. The result reveals that $T_g$ of epoxy SMPs vary from 75 to 114 °C, and shifts toward a higher temperature range with an increasing hardener content. The cross-linking density in network of each epoxy SMP varies according to hardener content which affect chemical reaction degree of epoxy resin and hardener. Therefore, the higher hardener content results in the higher cross-linking density in network and then $T_g$. 

![Fig. 1. Series images of shape recovery of epoxy SMPs at 150 °C](image)

![Fig. 2. DSC curves of epoxy SMPs.](image)
3.3. **TGA test**

Thermal stability of the epoxy SMPs is investigated by TGA test and Fig. 3 plots TGA diagrams of the epoxy SMPs. As shown in Fig.3, a line is drawn through the two points of 10 wt% and 50 wt% in weight loss in each TGA curve, and the decomposition temperature is defined as the intersection point of the line and baseline. It is clear the decomposition temperatures are higher than 300 °C for the polymers. It is obvious that each epoxy SMP has a good thermal stability basically. The possible explanation is that the component of the network structure of the polymer is stable because thermal stability of a polymer is determined by network structure mainly.

3.4 **DMA test**

Typical results of storage and loss modulus as functions of temperature respectively are plotted in Fig.4.. As shown in Fig. 4., the storage modulus decreases sharply from 110 to 140 °C and it is more than 2GPa higher than that in rubber state for each sample. Of particular attention is that the polymers show higher storage modulus not only in a glass state but also in a rubber state. The value of storage modulus of the epoxy SMPs at rubber state is equal to that of some SMPs at glass state\(^{13}\). It reveals that both excellent shape memory effect and better Load-bearing capacity of these epoxy SMPs can be found, and this novel characteristic makes it suitable for being used as structural material in many engineering fields.
3.5. Tension test

Fig. 5 presents the typical stress-strain curves of the polymers. The result indicates that both the stress at break and the elastic modulus increases and decreases with a peak value with increasing hardener content, respectively. The hardener content has an influence in the density of the cross-linking network and by this way the stress at break and elastic modulus. In addition, at the same temperature of 25 °C, the modulus of EP06 and EP08 from tension test (Fig. 5) are in accord with the storage modulus from the DMA test (Fig. 4). While, the elastic modulus of EP04 (2.7GPa) in the tension test is lower than the storage modulus (3.6GPa) from the DMA test. The difference is attributed to the higher viscous friction of EP04.
4. Conclusion

Epoxy SMPs were prepared. Each polymer shows full recovery and the lower hardener content increases the shape recovery speed. With increasing hardener content, $T_g$ increases while the decomposition temperature is stable, and both stress at break and elastic modulus vary for the polymers. Each polymer possesses a high modulus not only in glass state but also in rubber state. According to the above mechanical properties, the epoxy system is a good candidate material for many potential applications.

References
