

SHAPE MEMORY EFFECT OF A THERMOSET POLYMER AND ITS FIBER REINFORCED COMPOSITES

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1 Introduction

In the last few decades researchers have developed special polymers that exhibit shape memory effects that are referred to as Shape Memory Polymers (SMPs), and concentrated on characterizing these polymers [1, 2]. However, it has been long known that many of the existing polymers can change shape upon application of an external stimuli such as heat [3]. Understanding and utilizing the shape memory effect (SME) of these conventional polymers may present great advantages. Unfortunately very limited data is available in the open literature on this topic.

2 Motivation

SMPs have been shown to be promising materials for some applications such as medical devices and textile structures [3]. It is believed that broader utilization of these SMPs will be realized if the inherently low mechanical properties and low recovery forces can be improved. Some possible applications being considered include deployable space structures and micro aerial vehicles. It is our objective in this study to examine the role of fiber reinforcement architecture influencing the thermal - mechanical properties of SMPs.

Specially developed SMPs can be divided into two main categories, namely: thermoplastics (TP) and thermosets (TS). Due to the high melt viscosity of TP-SMPs, homogeneous and thorough impregnation of continuous fibers using this material is challenging. On the other hand, most of the TS-SMPs are still at the development stage and they are unavailable commercially even for research purposes. Hence, using commercially available ordinary TS polymers for shape memory applications may be a strong alternative to the specially designed SMPs.

This paper reports on initial SME characterization of a thermoset epoxy resin/hardener system and its fiber reinforced composites.

3 Methodology

3.1 Materials and Manufacturing

This study was conducted using a commercially available TS epoxy system composed of EPON 828 resin and EPIKURE 3055 hardener. This epoxy system is widely used in the fiber-composites industry and it is commercially available. A woven carbon mat was used as the reinforcing material to form 0/90 degree and +45/-45 degree reinforced specimens to study the effect of reinforcement and reinforcement direction on the thermo-mechanical and SME properties of the prepared samples.

Pure resin and reinforced composite systems were prepared using a multi-channel Aluminum mold. Teflon[®] mold release agent was applied to the molds before casting for easy removal of the cured specimens. The specimens were prepared and cured in the oven at 60 degrees Celsius for 15 hours following a degassing procedure to obtain void-free specimens.

3.2 Experimental Procedure

3.2.1 Glass Transition Temperature

Glass transition temperature (T_g) is one of the most crucial properties that need to be determined for SME applications. Hence, the effect of hardener content of the epoxy system on the glass transition temperature was investigated by changing the resin-to-hardener content of the epoxy system. The T_g of the specimens was obtained using both Differential Scanning Calorimetry (DSC) and Dynamic Mechanical Analyzer (DMA) that are available in the Advanced Materials Processing Engineering Laboratory (AMPEL) at the University of British

Columbia, Canada. The specimens that were used for the DMA experiments had average dimensions of 1.7 mm thickness, 13.1 mm width and 55 mm length. The DMA machine was TA Instruments DMA Q800 model that was used with a 3 point bend module.

3.2.2 Shape Recovery Force and Shape Recovery Characteristics

Shape recovery force and shape recovery properties of the three types of specimens (pure resin, 0/90 degree and +45/-45 degree reinforced specimens) were determined using three-point-bending tests. A tensile testing machine and a customized three-point-bending test jig (with a span length of 40 mm) were used along with a temperature controller to conduct the tests. The schematic illustration of the test protocol is shown in Fig. 1. This protocol was partially adapted from Tobushi et al. [4]. The specimens were heated to temperatures above their T_g using the temperature chamber (Fig. 1 (a)). Then an external force was applied to assign a temporary shape, (Fig. 1(b)), and the specimens were cooled down to a temperature below T_g while maintaining the applied deformation (Fig. 1(c)).

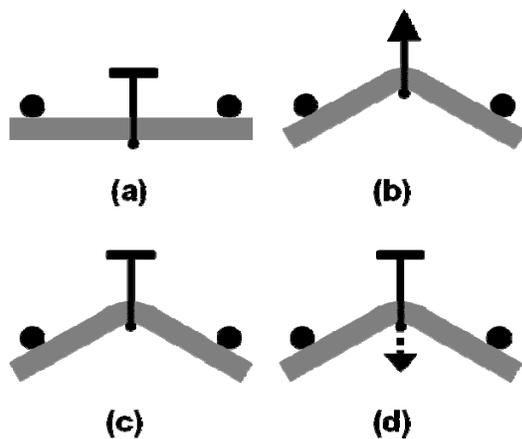


Fig. 1. The schematic illustration of the shape recovery test protocol (partially adopted from [4]).

The force was removed once the specimen was below the T_g . Activation of the SME was done by applying heat to the specimens to bring the temperature above the T_g . During this process the applied deformation was maintained constant and the force applied by the specimen (shape recovery

force) was measured as the temperature was increased. The specimens prepared for the shape recovery and recovery force experiments had average dimensions of 6.1 mm thickness, 13.1 mm width and 70 mm length. Fig. 2 shows a picture of a specimen during a test in the temperature chamber in a deformed state (Fig. 1 (c)).



Fig. 2. Picture of a specimen during a shape recovery test in the environmental chamber in a deformed state (Fig. 1 (c)).

Understanding and characterizing the forces required to store a temporary shape in a system and the recovery forces that those systems will exert during activation is crucial. The systems that are designed to be activated under full or semi-constrained applications will particularly benefit from this understanding. An example of these systems may be Micro Aerial Vehicles (MAVs). One may consider an MAV that is dropped in the air at an elevated height with temporarily bent (closed) wings. If the wings need to be activated to obtain the permanent straight shape, while the vehicle is free-falling towards the earth, the recovery force of the wings need to over-come the drag force for successful shape activation.

4 Results and Discussions

4.1 Glass Transition Temperature (T_g)

Specimens with three different hardener-to-resin weight ratios were prepared and analyzed using the DSC to understand the effect of hardener on the glass transition temperature. Fig. 3 shows the findings.

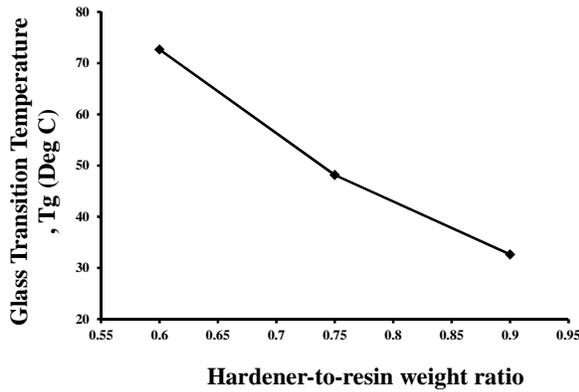
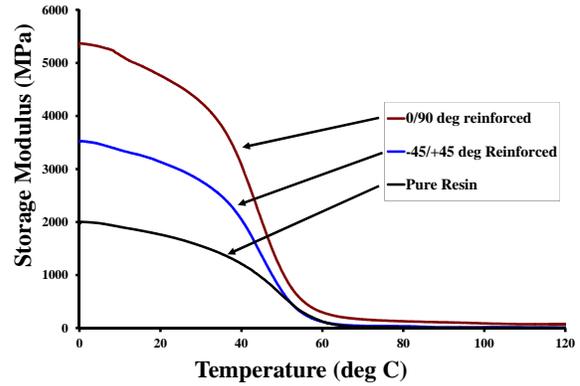


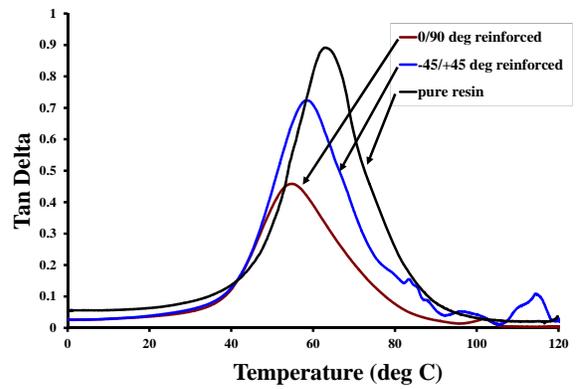
Fig. 3. Change of glass transition temperature as a function of hardener-to-resin ratio.

An increase in hardener content resulted in a decrease in Tg. This finding is crucial for tailoring the properties of the resin for specific applications. Wu et al [5] has previously published results with the same resin but for a different hardener and they reported less pronounced changes in Tg. The more pronounced effect of the ratio on Tg in this study may be due to the different types of hardener used. For the remainder of the specimens prepared in this study, the resin-to-weight ratio was selected as 0.75. This gives a glass transition temperature of approximately 48°C.

Fig. 4 (a) and (b) shows the results obtained by the DMA analysis of the pure resin, +45/-45 degree and 0/90 degree reinforced specimens. As can be seen from Fig. 4 (a), the temperature dependent storage modulus is a strong function of fiber orientation with 0/90 degree specimen being the highest and that of pure resin being the lowest. The Tan-δ versus temperature graph, Fig. 4 (b), shows the slight increase in the Tg as reinforcement is added to the pure resin. Zhang and Ni [6] have reported that addition of reinforcements to a shape memory polymer changes the storage modulus and the Tg; however, the effect of the direction of reinforcement has not been reported in the literature. This study was an initial attempt to outline the effect of the orientation of the reinforcements on shape memory effect of ordinary composite systems.



(a)



(b)

Fig. 4. (a) Storage modulus (b) Tan(delta) versus temperature of pure resin, +45/-45 degree and 0/90 degree reinforced specimens.

4.2 Shape Recovery Force and Shape Recovery Characteristics

Fig. 5 shows the responses of the three types of specimens, at 65°C, during initial loading and recovery with respect to time. The initial loading responses that were followed by a relaxation due to the constant deformation for all three types of specimens were plotted using solid lines. All three types of specimens were deformed 5mm (mid-point deformation). The maximum load required for this deformation was 7.1 N, 20.25 N, and 48.04 N for the pure resin, +45/-45 degree and 0/90 degree reinforced specimens, respectively. The specimens were relaxed (stress relaxation) down to 6.9 N, 16.8N, and 41.5N, respectively, this corresponds to a decrease of 2.8%, 7.4%, and 13.5%.

Shape recovery forces applied by the specimens were plotted by dashed legends in Fig. 5. The maximum recovery forces obtained from the samples were 6.34 N, 16.84 N, and 35.3 N, respectively. This corresponds to a drop of 10.7 %, 16.8 % and 26 % from the peak of the applied loads during temporary shape storage.

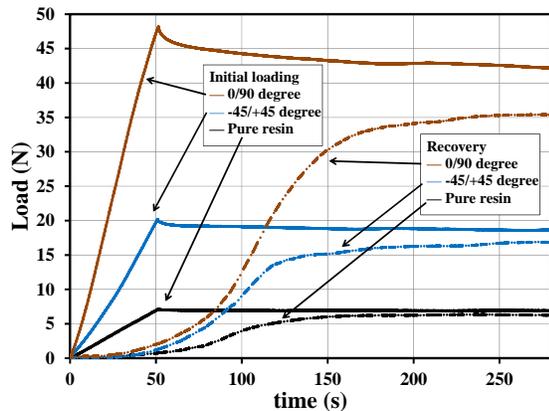


Fig. 5. Initial loading and shape recovery forces of the three types of specimens.

It is particularly important to notice the effect of reinforcement in recovery forces. The experiments showed that by adding +45/-45 degree reinforcement to the resin the recovery forces can be increased dramatically (in this case an increase of 2.7 times from 6.34N to 16.84N). The experiments also showed that by changing the reinforcements' placement from +45/-45 degree to 0/90 degree, the recovery force can be increased more than 2 times (16.84 N versus 35.3 N). This is an important consideration for design of functional shape memory composite structures.

Fig. 6 shows the initial loading response and shape recovery force response for +45/-45 degree specimens for different temperatures. This experiment was conducted at 65°C, 75°C, 85°C, and 95°C using the same specimen. As can be seen from the figure neither multiple loadings of the same specimen nor change in temperature have a significant effect on the measured properties. It may be beneficial to conduct more tests for temperatures closer to the glass transition temperature for future studies.

Finally, all three types of specimens used in this study showed excellent shape recovery properties upon activation of the shape memory effect.

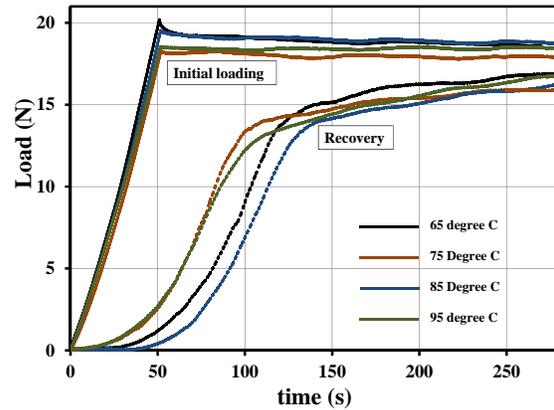


Fig. 6. Effect of temperature on the response of -45/+45 degree specimen.

5 Conclusions and Recommendations

This paper reports on the initial investigation of the shape memory effect (SME) characterization of a commercially available ordinary thermoset polymer epoxy resin/hardener system and its fiber reinforced composites. The effect of reinforcement angle on SME characteristics was of particular interest during the study.

Conclusions and recommendations of the study can be listed as follows:

1- In addition to the specifically designed shape memory polymers (SMPs), some of the ordinary thermoset polymer epoxy resin/hardener systems and their fiber reinforced composites can be used for some shape memory effect applications.

2- One of the crucial parameters used in design of structures with shape memory effect (SME) is the glass transition temperature, T_g . T_g of these polymers are proven to be easily tailorable by changing the resin-to-hardener ratio.

3- These ordinary polymers do retain their shape memory effect properties even when they are reinforced with advanced high strength continuous fibers. This reinforcing provides stiffened and

strengthened structures as well as causes changes in SME characteristics.

4- DMA experiments showed slight changes in the T_g values of unreinforced and reinforced specimens. The T_g was also found to be affected by the orientation of the reinforcing fibers.

5- The addition of small amounts of carbon fiber reinforcement increased the shape recovery force obtained from the specimens more than five times.

6- Use of same amount of reinforcement in different orientation (0/90 degree versus +45/-45 degree) resulted in more than two times increase in recovery forces.

7- Further characterization of these materials with a controlled experimental procedure is currently being conducted by the authors.

8- Design curves of recovery forces versus amount and orientation of fibers is necessary for broader use of fiber reinforced composites with shape memory effect.

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References

- [1] C. Liu, H. Qin, P.T. Mather, "Review of progress in shape-memory polymers", *Journal of Materials Chemistry*, v 17, n 16, p 1543-1558, 2007.
- [2] A. Lendlein, S. Kelch, "Shape-memory polymers", *Angewandte Chemie - International Edition*, v 41, n 12, p 2035-2057, June 17, 2002.
- [3] J. Hu, "Shape memory polymers and textiles", Woodhead Publishing Limited, CRC Press LLC, 2007.
- [4] H. Tobushi, S. Hayashi, K. Hoshio, Y. Makino, N. Miwa, "Bending actuation characteristics of shape memory composites with SMA and SMP", *Journal of Intelligent Material Systems and Structures*, v17, 1075 – 1081, 2006.
- [5] L. Wu, S.V. Hoa, Minh-Tan; Ton-That, "Effects of composition of hardener on the curing

and aging for an epoxy resin system", *Journal of Applied Polymer Science*, Vol. 99, 580–588 (2006).

[6] C.-S. Zhang , Q.-Q. Ni, "Bending behavior of shape memory polymer based laminates", *Composite Structures*, 78, 153–161, 2007.