EFFECT OF GRAPHENE ADDITION ON SHAPE MEMORY BEHAVIOR OF EPOXY RESINS

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ABSTRACT

Shape memory polymers (SMPs) and composites are a special class of smart materials known for their ability to change size and shape upon exposure to an external stimulus (e.g. light, heat, pH, or magnetic field). These materials are commonly used for biomedical applications; however, recent attempts have been made towards developing SMPs and composites for use in aircraft and space applications. Implementing SMPs and composites to create a shape change effect in some aircraft structures could potentially reduce drag, decrease fuel consumption, and improve engine performance. This paper discusses the development of suitable materials to use in morphing aircraft structures. Thermally responsive epoxy SMPs and nanocomposites were developed and the shape memory behavior and thermo-mechanical properties were studied. Overall, preliminary results from dynamic mechanical analysis (DMA) showed that thermally actuated shape memory epoxies and nanocomposites possessed T_gs near ~168°C. When graphene nanofiller was added, the storage modulus and crosslinking density decreased. On the other hand, the addition of graphene enhanced the recovery behavior of the shape memory nanocomposites. It was assumed that the addition of graphene improved shape memory recovery by reducing the crosslinking density and increasing the elasticity of the nanocomposites.

1. INTRODUCTION

Smart materials are gaining a considerable amount of attention due to their versatility for use in areas, such as biomedical engineering, defense, automotive, and aerospace industries [1-5]. In aerospace applications, the use of adaptive materials in large area antennae and solar cell arrays is attractive because the materials could be stored in low volume and then self-deployed while in space [6, 7]. In aeronautics, some types of adaptive polymers and composites can display self-healing properties, which would help increase the longevity of materials and decrease maintenance costs over time [8].

Another aeronautics application for shape memory materials is the use of morphing aircraft structures to aid in improving flight performance. Many aircraft structures can benefit from undergoing shape change, which in turn could lead to reduced weight, noise, vibration, and costs [9, 10]. However, with prices of fuel on the rise, an item most often of particular interest to the aviation industry is reduced fuel burn.

1.1 Morphing aircraft structures

Employing the use of SMPs and composites in some structures, such as wings or airfoils, could lead to a decrease in fuel consumption and better engine performance [11]. Additionally,

these structures have the potential to change incidence angles and set optimum camber levels in a variety of in-flight conditions [12]. Previous reports with a shape changing airfoil showed that morphing airfoils could be set to a high camber position at max power during take-off and later transform to a low camber position at cruise to achieve better engine efficiency [11]. Preliminary studies with the shape memory alloy (SMA) airfoil design reported that even a 4° change in camber could lead to improved engine performance. Morphing to this extent was also estimated to lead to at least a 0.5-1.0% reduction in fuel consumption [11]. Unfortunately, concerns arose about the reliability of achieving controlled actuation, use of passive or active actuation, and power requirements needed to induce shape change.

1.2 Shape memory polymers

Shape memory polymers (SMPs) and composites are believed to be an ideal choice to create a shape memory effect in some aircraft structures. Unlike SMAs, SMPs and composites are lightweight, can be tailored to display high strength and thermal properties, and can achieve exceptionally high strain rates [13, 14]. Thermally responsive SMPs work by having the ability to return to their original rigid state after transitioning from a temporary deformed state following exposure to temperatures above the SMP's T_g. With the use of shape memory epoxies, the mechanical properties and thermal stability could be tailored to possess behavior very similar to those observed in traditional aeronautics grade epoxy matrix composites.

Shape memory epoxies have generally been prepared by curing a single epoxy monomer with a dual curing agent system or by curing a dual epoxy monomer system with a single curing agent [15-17]. Results from these studies showed that the T_gs of most thermally responsive epoxy SMPs ranged between 40-98°C [15, 17]. However, the T_gs for epoxy matrix composites used in aircraft are often observed to be on the range of 100-200°C [18]. Therefore, in order for epoxy SMPs to be compatible to use in aeronautics applications, the T_gs of these resins should be higher than the T_g values observed for previously reported shape memory epoxies.

1.3 Objective

This paper discusses the development of a thermally responsive SMP and nanocomposite with a T_g exceeding 130°C to create a shape change effect. A shape memory epoxy was used for this study since epoxies are commonly used in polymer matrix composite aircraft structures. The shape memory behavior of the nanocomposite was designed to be primarily driven through actuation of the polymer. Graphene was selected to increase the strength of the nanocomposite and allow the nanocomposite to reach higher levels of deformation without concerns for fiber breakage. The overall focus of this study is to determine the feasibility of using epoxy-based shape memory nanocomposites to endure repetitive cycling of controlled morphing events.

2. EXPERIMENTATION

2.1 Materials and Methods

Shape memory epoxy resins were made by curing a 1:1 ratio of Epon 862 *(Hexion Specialty Chemicals)* and Epon 828 *(Hexion Specialty Chemicals)* with Epikure W *(Hexion Specialty Chemicals)*. The curing agent made up approximately 20 wt% of the total resin concentration.

The neat epoxy SMPs were cured at 120°C for 8 hours, followed by post-curing at 150°C for 2.5 hours.

Graphene-reinforced shape memory polymers were made by adding 0.1 wt% of Vor-x™ graphene sheets (*Vorbeck Materials)* to Epon 862 and 828 monomers and magnetically stirring under low heat for 16 hours, followed by sonicating for 5 hours. Next, Epikure W was stirred into the mixture for 30 minutes and later transferred to a vacuum oven where the samples were degassed at room temperature for 45 minutes. The shape memory nanocomposite samples were cured and post-cured under the same conditions as the neat resin.

2.2 Characterization

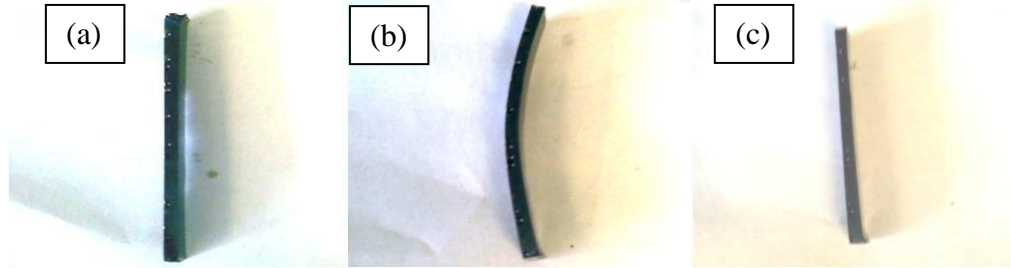### 2.2.1 Thermo-mechanical properties and shape recovery

Dynamic mechanical analysis (DMA) was used to determine the T_g and study the effect of graphene on the crosslinking density and shape memory performance of epoxy-based SMPs. All samples were run using a TA Instruments Q800 Dynamic Mechanical Analyzer with a dual cantilever accessory. The test was run in Multi-frequency Strain mode to obtain information about the T_g. To monitor actuation, the instrument was run using Controlled Force mode. Four continuous cycles of heating and cooling were carried out, and the stress and resulting deformation strains were measured from the SMPs and nanocomposites.

2.2.2 Thermal transitions of cured shape memory epoxies and nanocomposites

The thermal transitions of shape memory epoxies and graphene-epoxy nanocomposites were studied to determine if the samples were fully cured. A TA Instruments Q600 DSC analyzer was used with a 5°C/min ramp rate under nitrogen atmosphere. Approximately 7.0 mg of sample was weighed and studied for DSC analysis.

3. RESULTS

The effect of using graphene in epoxy-based shape memory polymers was studied using DMA and DSC analysis. Physical observations showed that when the neat epoxy SMP was heated above the T_g, the polymer was slightly flexible and could be deformed minimally by hand. When epoxy-graphene shape memory nanocomposites were heated above the T_g and deformation temperature (T_d), the samples were able to deform easier than the neat SMPs. Figures 1(a)-(c) show photographs of the graphene-epoxy shape memory nanocomposite before and after the heating, setting, and cooling transitions. Visually, Figure 1(c) revealed that the shape memory nanocomposites appeared to recover fully when heated to the deformation temperature (T_d) following "locking" the nanocomposite into its temporary shape.

Figures 1(a)-(c). (a) Original, (b) deformed, and (c) recovered states of graphene-epoxy shape memory nanocomposites

3.1 Effect of graphene on T_g of shape memory epoxy resins

Figures 2(a) and (b) illustrate changes in thermo-mechanical properties from adding 0.1 wt% graphene to epoxy SMPs. The plots show that the addition of 0.1 wt% graphene led to a 30% reduction in the storage modulus (E') (Figure 2(a)). The decrease in E' for graphene-epoxy SMP could have been the result of the shape memory nanocomposites possessing a lower crosslinking density compared to the neat epoxy SMPs.

Figures 2(a) and (b) also showed that the apex of the loss factor curve was lower for graphene-epoxy nanocomposites compared to the neat epoxy SMPs. A possible reason for the lower tan δ of graphene-epoxy shape memory nanocomposite is due to an increase in intermolecular friction between epoxy molecules from the addition of graphene. Because graphene reduced the mobility of epoxy SMP chains, the loss factor was lower, and the nanocomposite exhibited more elastic behavior than the neat epoxy SMP.

Additionally, information about the shape setting temperature (T_s), T_g, and T_d were gathered from DMA. The T_s and T_d were chosen by selecting a temperature in the plateau regions before and after the T_g [15]. The final T_s and T_d selected for shape memory cycling studies were based upon an approximation of the T_s and T_d values for all the samples.
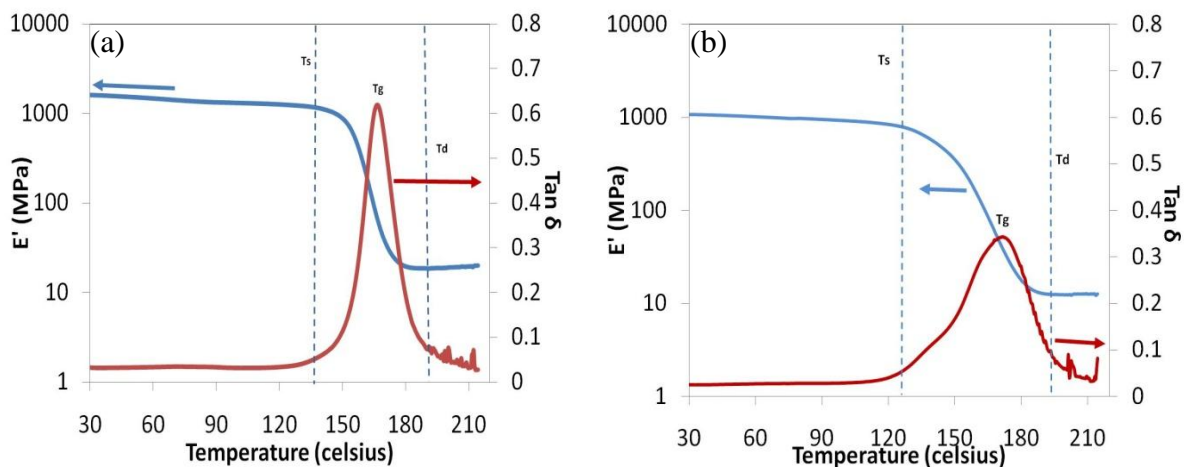
Figures 2 (a) and (b). Effect of graphene on thermo-mechanical properties

Table 1 shows the crosslinking densities for the neat epoxy SMP and graphene-epoxy shape memory nanocomposites. The crosslink molecular weight (M_c) and crosslinking density (ν) were calculated using the following equations:

$$E' = \frac{3\rho RT}{M_c} \tag{1}$$

$$\nu = \frac{\rho}{M_c} \tag{2}$$

where E' represents the storage modulus in the rubbery plateau region, R is the Boltzmann constant, T is the absolute temperature, and ρ is the sample density. Calculations showed that the M_c was higher for graphene-epoxy shape memory nanocomposites than the neat epoxy SMPs. Results also showed that the crosslinking density for the graphene-epoxy shape memory nanocomposites were lower than the neat epoxy SMP. Previous studies with nanotube fillers reported similar results and showed that the M_c may have been higher because of the nanofiller increasing the amount of spacing between crosslinks [19].

3.2 Thermal behavior of shape memory epoxy resins and nanocomposites

Figure 3 shows the DSC thermograms following cure and post-cure. The average DSC T_g values from neat epoxy were calculated to be 147.6°C, while the average T_g for 0.1 wt% graphene-epoxy was 141.6°C. Although a small decrease in T_g was observed for the nanocomposites, DMA results suggested that there was no significant difference in T_gs between neat epoxy SMP and 0.1 wt% graphene-epoxy shape memory nanocomposites. More importantly, DSC showed that the addition of 0.1 wt% graphene did not significantly alter the cure, and the lack of an exothermic peak in the curves implied that the epoxy SMPs and nanocomposites were fully cured.

Table 1. Thermo-mechanical properties of neat epoxy SMP and graphene-epoxy nanocomposites

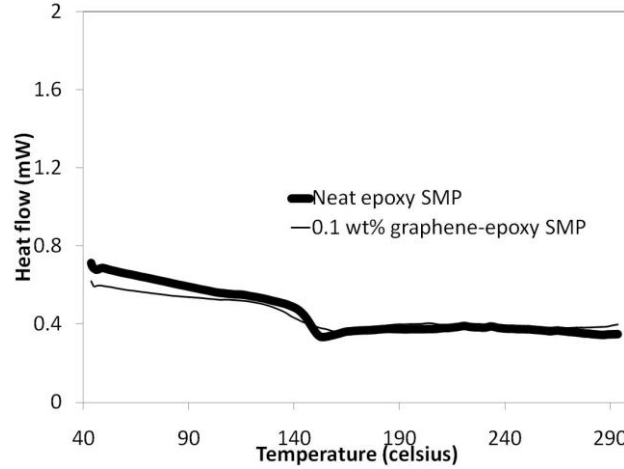|	Storage modulus @ 30°C (MPa)	T_g (°C)	Mc (g/mol)	Crosslinking density x10^{-3} (mol/cm^3)
Neat epoxy SMP	1671.0 ± 212.1	166.8 ± 1.71	622.5 ± 75	1.82
0.1 wt% graphene-epoxy	1181.5 ± 190.8	169.9 ± 1.15	824.4 ± 69	1.29

Figure 3. Effect of graphene on the cure of epoxy SMPs

3.3 Effect of graphene addition on shape memory behavior

The shape memory effects of thermally responsive epoxies and nanocomposites were quantitatively analyzed using DMA. Figure 4 showed the shape memory behavior of neat epoxy SMP undergoing four cycles of temperature changes above and below the transition temperatures. The graph displayed that the differences in deformation strains of the neat epoxy SMP were larger when heating between 150-185°C compared to the other temperature ranges. On the other hand, it was observed that the differences in deformation strain between 150-185°C became less noticeable as the neat epoxy SMP was exposed to more cycles.

Four cycles of shape memory behavior in graphene-epoxy shape memory nanocomposites are shown in Figure 5. The shape memory nanocomposite samples possessed a higher strain deformation and lower stress compared to the neat epoxy SMP. The higher strain and reduced stress values may have been attributed to graphene sheets serving more as a resin toughener rather than resin reinforcement.
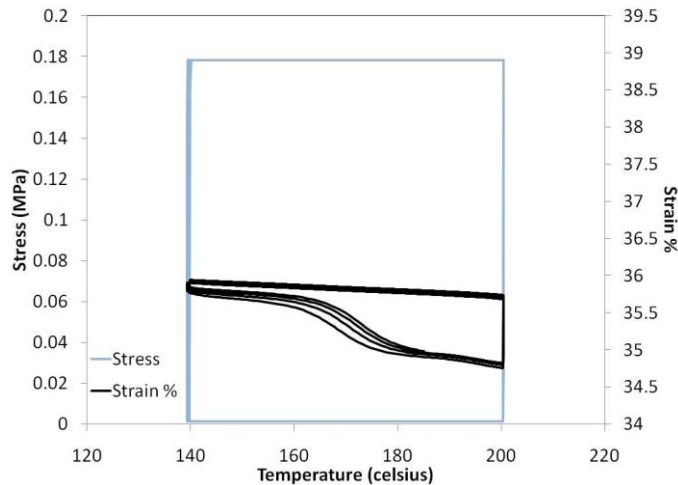

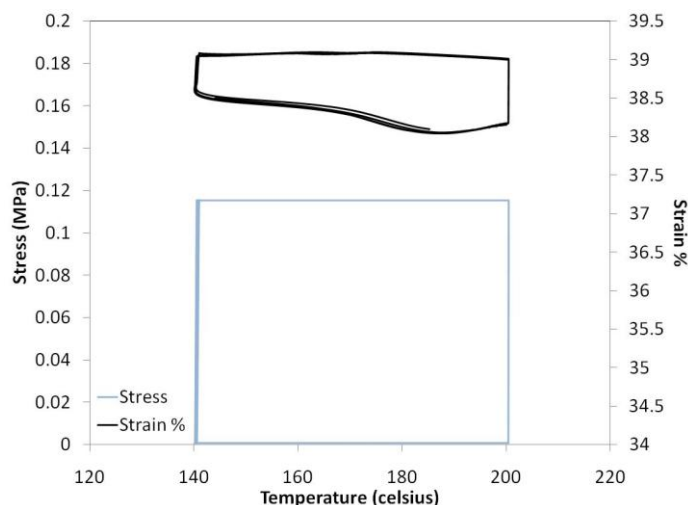Figure 4. Shape memory behavior and recovery of neat epoxy SMP

Figure 5. Shape memory behavior and recovery of 0.1 wt% graphene-epoxy shape memory nanocomposite

Figure 5 revealed that adding graphene had a positive effect on the performance of shape memory nanocomposites. The graphene-epoxy nanocomposite samples demonstrated that the trends in deformation strain and stress were more consistent between cycles compared to that of the neat epoxy SMP (Figure 4). This information is in agreement with the loss factor results illustrated in Figure 2(b) and may be related to the nanofiller increasing the elasticity of the shape memory nanocomposites. In other words, the higher elasticity in graphene-epoxy nanocomposites may have corresponded to the nanocomposites exhibiting a higher degree of recoverable energy, which led to an improvement in the recovery of shape memory nanocomposites.

4. CONCLUSIONS

Epoxy-based shape memory polymers and nanocomposites were prepared by use of commercial epoxy monomers, curing agents, and graphene. DMA and DSC analysis revealed that there were no significant differences in T_g when graphene was added. DSC analysis also supported that the samples were fully cured after adding graphene.

Calculations based on thermo-mechanical data showed that adding graphene decreased the crosslinking density, which more than likely increased the toughness of epoxy SMPs. The lower crosslink density in graphene-epoxy nanocomposites appeared to have a positive influence on the shape memory behavior because shape memory nanocomposites containing graphene were observed to display better shape memory recovery between cycling. On the other hand, the color of the shape memory polymer was darker after heating to 200°C. Therefore, it is essential to select an accurate T_d by locating the lowest temperature in the rubbery plateau region of the DMA curves to prevent discoloration.

Future studies in this area will include varying the loading of graphene to study the effect of concentration on shape memory recovery and thermo-mechanical properties, studying the mechanical properties of the epoxy SMPs and nanocomposites, and increasing the number of

cycles to better determine if the proposed materials are able to withstand numerous cycles of continuous morphing transitions.

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