Carbon / Epoxy Resin Based Elastic Memory Composites

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Abstract

Elastic memory composites were processed from shape memory epoxy resins and carbon fabric reinforcements. Three different types of epoxies (diglycidyl ether of bisphenol-A, tris(4-glycidyloxy phenyl)methane, and epoxy novolac) were used as matrices. Developed composites were evaluated for flexural strength and analyzed by Dynamic Mechanical Thermal analysis. Of the three different epoxy systems with carbon: resin ratio of 50:50, the composite with diepoxy system exhibited maximum glass transition value of 119°C, epoxy novalac system exhibited a low glass transition value of 54°C and the tris epoxy system exhibited a glass transition of 100°C respectively. The flexural strength and modulus of the composites were optimised at a concentration of 40 wt.%. The transition temperature also showed a maximum at around this composition. Bending test was adopted for the shape memory evaluation. All the developed composites exhibited more than 90% shape recovery. The diepoxy resin series of composites exhibited the maximum shape recovery of 97%. The shape recovery properties of the tris epoxy and epoxy novolac-based composites were inferior. For the diepoxy resin-based system, the shape recovery time was proportional to the resin content. The shape recovery of composite with 80% resin was demonstrated experimentally. The properties of the composites show that these systems have the required elastic memory characteristics for possible use in thermo-responsive self-deployable applications.

Symbols and Abbreviations

Elastic Memory Composite	EMC
Poly(tetramethyleneoxide)	PTMO
Diglycidyl ether of bisphenol A	GY-250
Novalac epoxy	EPN-1179
Triphenylolmethane triglycidylether	TRI
Ethyl methyl ketone	MEK
Span length	L
Width of the specimen	b
Thickness of the specimen	d
Deformed angle	θ_f
Change in angle	θ_i
Glass transition	T_g
GY-250 / carbon composites	GY/C
EPN / carbon composites	EPN/C
TRI / carbon composites	TRI/C
Melting	T_C
Transition temperature	T_{trans}

Introduction

There is a need for deployable structures in space applications when the physical dimensions of the spacecraft's operational configuration are larger than the launch vehicle fairing dimensions, thus requiring reconfiguration of structural systems for stowage and on-orbit deployment. Deployable instrument masts, antenna, solar arrays, radiators and sunshields are some examples of deployable space structures currently in operation. Elastic memory composites (EMC) are increasingly preferred for self-deployable mechanical structures and systems for such missions. EMC materials are a newly developed class of materials hosting an ideal combination of properties required for deployable space structures. EMC materials retain the structural properties of traditional fiber-reinforced composites while also functioning as shape memory materials. These properties enable the creation of structurally efficient, controllable, deployable space structures and deployment mechanisms with no

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moving parts [1]. An EMC material is composed of a fiber-reinforced shape memory polymer. Shape memory polymers are a sub-set of the broad class of “smart” materials known as shape memory materials [2]. An EMC structure is fabricated using traditional composite fabrication methods, and is fully cured before entering service. Furthermore, an EMC structure behaves the same as conventional composites in stiffness and strength after deployment. EMCs have several advantages over traditional fibre composites. Elastic memory composite mechanisms can remove the need for mechanical latch and remove the post deployed microdynamic instabilities associated with them while providing a low shock, controlled deployment [3]. Additionally, elastic memory composite mechanisms are lighter, and have a lower coefficient of thermal expansion than shape memory alloys, which are desirable properties for space deployable systems. They also have a low processing cost [4, 5, 6].

Designing an EMC structure, in some ways, is very different from designing traditional structural materials [7]. In particular, the adequate design of a deployable EMC structure requires consideration of the non-linear constitutive behavior of the EMC material during packaging and deployment. Elastic memory self-locking hinges have been reported [3].

EMC systems have been developed and tested for large space structural applications [8]. These composite material systems were primarily based on single glass transition temperature systems with T_g ranging from 50°C to 95°C. Once the EMC is completely cured, it can be heated to the folding temperature (above the T_g) where it becomes flexible and can be tightly packed (folded and/or rolled). The flexibility of the SMP composite material at the folding temperature depends strongly on both the resin and fiber properties.

Several studies on EMC for deployable devices have been reported [3, 9]. Majority of the work focuses on epoxy resin or cyanate ester – based composites. The matrix resins constituting the composites are mostly epoxy resin or cyanate ester resin. Almost all the published reports refer to processing of EMC from proprietary shape memory resins. The synthesis and shape memory characteristics of these resin systems are scarcely reported. We reported the synthesis, curing and shape memory property of a polyether-epoxy resin system. [10]. Shape memory composites based on glass fibre reinforced polyethylene like polymers were developed and evaluated for their thermo-mechanical and shape memory properties [11]. Developed glass reinforced composites exhibited excellent shape memory properties same as the unreinforced polymer except insignificant changes in the shape recovery and shape fixing rates. Toughness of the shape memory epoxy was enhanced by polypropylene glycol diglycidyl ether as the toughening agent studied for the mechanical and shape memory properties. The shape memory evaluation exhibited the strain fixity ratio as high as 98.9% for the addition of 7, 9, 11, 13 and 15 weight % of toughening agent [12]. Epoxy resins are observed as an ideal thermosetting matrix for SMP due to their brilliant properties such as specific elastic modulus, high fracture stress, and good thermal stabilities [13, 14]. Epoxy resins are ideal for processing composites. In this paper we studied the processing and shape memory properties of EMC derived from carbon fabric reinforced epoxy resins. Thermo-mechanical and shape memory properties were evaluated and correlated to the epoxy: resin compositions.

Experimental

Materials and Method

Amine terminated poly(tetramethyleneoxide) (PTMO) was synthesized in our laboratory by a reported procedure [10], Epoxy (GY-250, diglycidyl ether of bisphenol A with epoxy value 5.4 eq/kg, Ciba Geigy, India), EPN-1179 (Novalac epoxy, Ciba Geigy, India, epoxy value 5.6 eq/kg), triphenylolmethane triglycidylether (TRI, Aldrich Chemicals, epoxy value, 5.6 eq/kg). AR grade ethyl methyl ketone (MEK, SRL, India) was used as solvent. Carbon fabric T-300 was used as received.

Preparation of Composites

Composites of three different epoxy systems were prepared by using epoxy resin in combination with amine terminated PTMO. Amine: epoxy equivalent ratio was taken as 1:1. The resin mixture was dissolved in MEK (70% by wt) at room temperature. Carbon prefabrics were prepared by dipping the fabric in the resin solution and drying for 2 h at room temperature. These prefabrics (3 Nos) of thickness 2 mm were stacked and moulded in a hydraulic press between two metallic plates. The cure reaction was carried out by slowly heating the system to its cure temperature (cure temperature was determined from DSC [10]) and maintaining it at this temperature for 3 h. Contact pressure was applied during the curing process.

Characterization of Composites

Flexural Strength

The flexural strength of the composites was determined using rectangular specimens of dimensions 56 × 25 × 2 (mm). The testing was done at room temperature (25 ±1 ^{o}C) by a three-point bend testing as per the standard ASTM procedure D790. The test was carried out using a span length of 32 mm at a crosshead speed of 0.85 mm/min. The break point (P) at maximum load was taken. At least three specimens were tested and the average value was taken.

$$\text{Flexural strength} = 3PL/2bd^2$$

Where L is the span length and b and d are width and thickness of the specimen in mm.

Dynamic-Mechanical and Shape Memory Properties

Dynamic mechanical properties were determined in Rheometrics Scientific Model Mark IV (UK) analyzer in the tensile mode at a frequency of 1 Hz. The specimens were heated from – 100°C to 150°C at a heating rate of 5°C/min.

Bending test [15] was adopted for evaluation of shape memory property as shown in Fig. 1. A straight rectangular strip of polymer of dimension 100 mm × 10 mm × 2 mm was used for the tests. The polymer was heated to a temperature T_{trans}+20^{o}C and deformed to an angle (θ_i) and then cooled to ambient temperature to fix the deformation. The deformed angle was 90°. Then the deformed polymer was heated to T_{trans}+20^{o}C, and the change in angle (θ_f) was recorded. The ratio of recovery was found as (θ_i -θ_f) /θ_i. The samples were subjected to bending test for five times and the value of fifth run was taken.

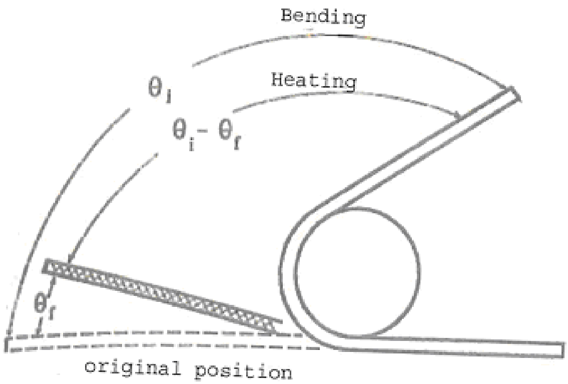

Fig. 1. Schematic representation of bending test.

Results and Discussions

Formulations of Composites

For the preparation of laminates, amine terminated PTMO was used to cure three different epoxies. The compositions giving the optimum mechanical and shape memory characteristics were chosen for making the composites [10]. Table 1 shows the formulations of composites. The compositions of the shape memory resin of GY-250 were varied from 80 to 50 wt.% as given in Table.1. The transition temperature, which was taken from DMTA (tan δ maximum) increased with carbon content. A high glass transition (T_g) value of 119°C was observed for a 50:50 composition. Comparing the three different epoxy systems with carbon: resin ratio of 50:50, the composite with GY-250 system exhibited maximum T_g value. EPN system exhibited a low T_g value of 54°C and TRI system exhibited a T_g of 100°C. Among the GY-250 / carbon composites (GY/C), the T_g increased with the reinforcement content. Normally the T_g of a composite is decided by the T_g of the matrix. However, an increase in T_g by increasing the reinforcement content implies that the resin at the interphase contribute to the overall T_g. Normally the resin at the interphase has a different composition than the bulk matrix. For the 50:50 composition, the difunctional epoxy based composite showed the highest T_g and the EPN system the lowest T_g.

Table 1.

Formulations and properties of carbon composites

Epoxy resin	Resin: carbon (Weight ratio)	T_g (°C) (obtained from DMA)	Flexural Strength (MPa)
GY-250	80:20	97	90
	70:30	108	130
	60:40	118	260
	50:50	119	150
EPN	50:50	54	10
TRI	50:50	100	40

Flexural Strength

Table 1 compiles the flexural properties of the composites. Flexural strength is a measure of the tensile and the compressive strength of the material. Generally, flexural strength of a material is in line with its tensile strength (transverse) rather than its compressive strength. This is because the compressive strength in the direction perpendicular to the reinforcement's plane is several times higher than the tensile strength in the transverse direction. For GY-250 system, with increase in carbon fabric content, flexural strength increases and attains an optimum of 264 MPa for 40% carbon fabric content. The initial reinforcement by the fabric gives way to the fibre fracture at high carbon loading. In comparison to GY system, the flexural strength of the EPN and TRI systems decreases tremendously due to the more rigid nature of these matrices.

Dynamic Mechanical Thermal Analysis

Figure 2 shows the storage modulus versus temperature properties of the GY-250 reinforced with carbon fabric at different resin/ reinforcement ratio. Generally the glassy modulus increases with reinforcement content. However, the maximum value was observed for 60/40 resin/reinforcement composition. A large difference in modulus between the glassy and rubbery states is conducive to a better shape memory property. A close observation shows that, the modulus tends to increase marginally at ~25°C due to the recrystallisation of the PTMO segments in the matrix. This is followed by a two-stage decrease in modulus. The modulus diminution at around 35°C is due to the melting (T_C) of the PTMO crystallites. The change in modulus at this stage is very benign. A sharp decrease in modulus is observed at the glass transition of the matrix. This is considered as the transition temperature (T_{trans}) or the switching temperature of the shape memory composites. The glass transition temperature rather than T_C is considered as the transition temperature as the modulus change is significant in the former case. For GY series, with increase in carbon content, tan δ curve shifted to higher temperature region and attains a maximum temperature of 119°C for a 50:50 shape memory resin: carbon fabric composition as shown in Fig. 3.

Comparing the storage modulus versus temperature plots for the various composites of 50/50 composition (Fig. 4) GY/C & EPN / carbon composites (EPN/C) have more or less similar glassy modulus value. TRI / carbon composites (TRI/C) processed inferior glassy modulus. The PTMO crystallization was seen at ~0°C for EPN as against 25°C for GY. The melting temperature of the soft segment was also seen to differ with matrix (10°C for EPN, 37°C for GY-250). The PTMO moiety could be detected at ~25°C for TRI/C. The modulus decrease at T_C not being significant, the T_g was considered as the T_{trans} for the purpose of shape memory property evaluation. T_{trans} were drawn from the tan δ maximum in the tanδ-versus temperature plot shown in Fig. 5. The values are shown in Table 1. The T_{trans} increased in the order GY/C > TRI/C > EPN/C. The temperatures obtained from tan delta maxim were used reference temperature for shape memory evaluation.

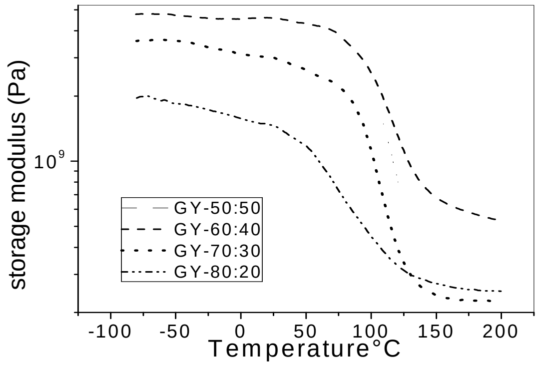

Fig. 2. Variation of storage modulus with temperature for the GY/ carbon composites.

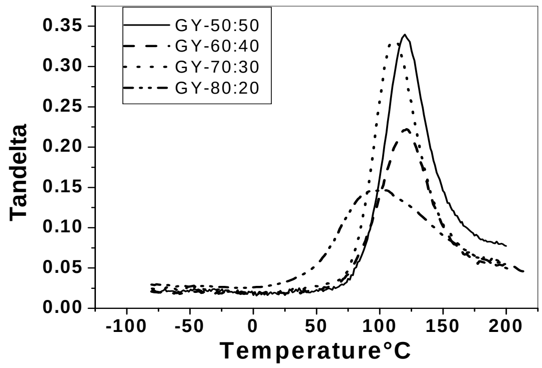

Fig. 3. Variation of tan δ vs temperatures for GY/carbon composites.

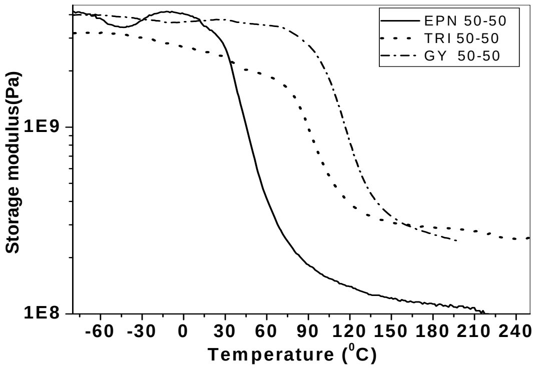

Fig. 4. DMA of different epoxy composites with 50/50 compositions; Variation of storage modulus with temperature.

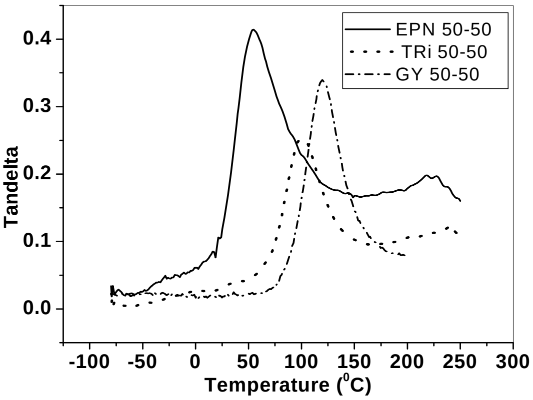

Fig. 5. DMA of different epoxy composites with 50/50 compositions-Variation of tan δ with temperatures.

Shape Memory Test

During the bending test, the deformed shapes were cooled below the crystallization temperature so that the shape gets locked by way of glassy transformation and recrystallization of PTMO. However for recovering the shape, the system was heated at a temperature 20^{o}C more than T_g (T_g+20^{o}C). Shape recovery of composites was determined using bending test. Shape recovery for all the GY-250 composites was independent of the composition and remained constant at 97%. However, the time for shape recovery increased with carbon content. Variation of recovery time for composites with different resin content is shown in Table 2. For robotic application of such composites, a fast recovery time is advisable. However for space deployment of stowed structures, a slow recovery is recommended to avoid damage to the structures arising from sudden deployment.

The shape recovery of composite with 80% resin content was demonstrated experimentally. Demonstration was done by processing a rectangular strip of 100 mm × 50 mm × 2 mm. It was heated at 120°C (above T_g), distorted and frozen in ice bath. The distorted shape was maintained at ambient. When the deformed composite was again heated to 120°C, the original shape was recovered in about 20 s. Different stages of shape recovery are shown in Fig. 6.

Table 2.

Shape memory properties of various composite systems

Epoxy resin	Wt% of Resin	Percentage of shape recovery	Recovery time (Seconds)
GY-250	80	97	20
	70	97	25
	60	97	30
	50	97	40
EPN	50	90	45
TRI	50	94	40

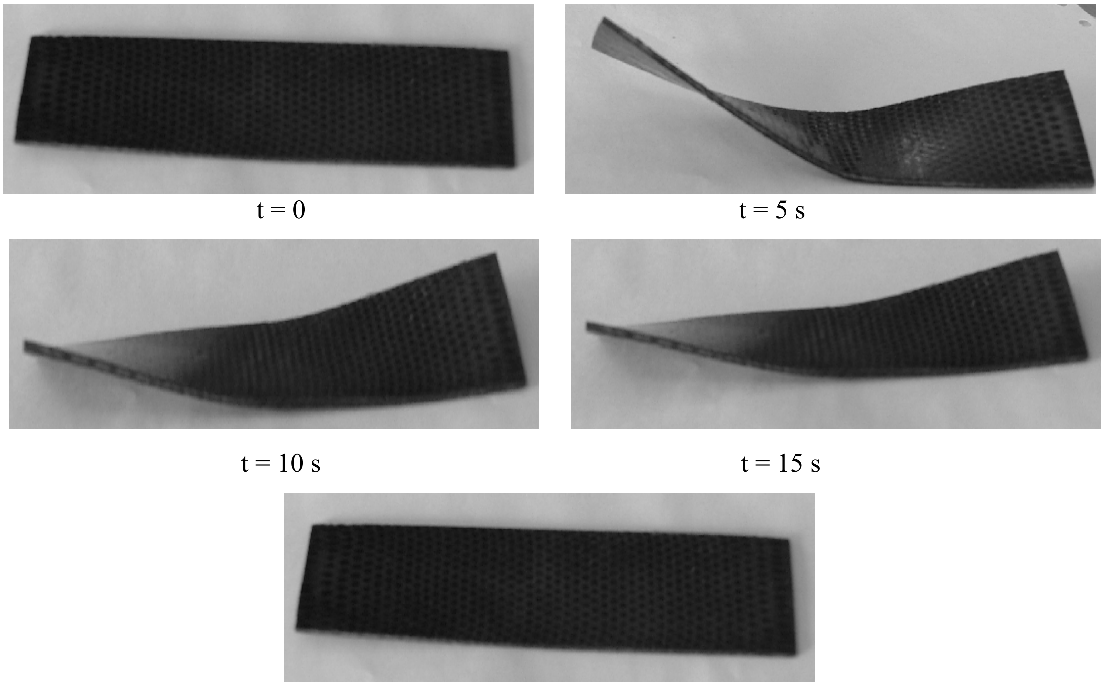
t = 0
t = 5 s
t = 10 s
t = 15 s
t = 20 s

Fig. 6. Shape recovery of composite with 80% resin content at different time interval at 120°C.

For composites of different epoxy systems, EPN and TRI exhibited 90 and 94% shape recovery with a recovery time of 45 and 40 seconds respectively. Comparing the shape recovery properties of three different epoxy composite systems (GY-250, EPN and TRI) with 50:50 epoxy: carbon content, GY-250 exhibited the maximum shape recovery characteristics. Comparing the shape recovery properties of the three different epoxy composites with the neat resin [10], epoxy composites exhibited the best shape recovery properties.

Conclusions

Elastic memory composites with varying shape memory characteristics were derived from shape memory epoxy resin reinforced with T-300 carbon fabric. For GY-250 / carbon composites the transition temperature increased with carbon content. Comparing the three different epoxy systems with carbon: resin ratio of 50:50 compositions, composite with GY-250 exhibited the highest T_g value of 119°C. Flexural properties of GY-250 composites also increased with carbon fabric content, and attained the optimum value for 40 wt.% carbon fabric content. EPN and TRI systems exhibited poor flexural properties. All the developed composites exhibited more than 90% shape recovery. The GY series of composites exhibited the maximum shape recovery of 97%. However, the recovery time was directly proportional to the shape memory resin-content of the composite. The composites have the required strength and shape memory properties for possible use in the development of temperature responsive self-deployable systems.

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