Shape Memory Polymer Composites for Long-Term Exposure to Space Environment

Fabrizio Quadrini*, Denise Bellisario, Giovanni Matteo Tedde, Loredana Santo

Department of Industrial Engineering, University of Rome "Tor Vergata", Via del Politecnico 1, 00133, Rome, Italy

*Corresponding author: E-mail: fabrizio.quadrini@uniroma2.it

Received: 13 February 2019, Revised: 08 May 2019 and Accepted: 14 May 2019

DOI: 10.5185/amlett.2019.0007
www.vbripress.com/aml

Abstract

Shape memory polymer composite (SMPC) samples for long-term exposure in Space environment have been designed and tested. SMPC laminates consisted of two carbon fiber reinforced (CFR) plies and a SMP interlayer. Samples were manufactured by prepreg lamination and molding with subsequent thermomechanical processing for shape change. Commercial raw materials were selected both for CFR plies and SMP interlayer. Differential scanning calorimetry and dynamic mechanical analysis have been used to evaluate the thermo-mechanical behavior of the SMPC laminate in comparison with the neat CFR laminate and the SM epoxy resin of the interlayer. Results show that the hybrid nature of the SMPC laminate is responsible for their good shape memory behavior. A small disk with a simple shape change has been prepared to be integrated in the MISSE-FF platform for long-term exposure to Space environment. Recovery tests under IR light exposure highlighted the optimal functional behavior of this kind of sample. Copyright © VBRI Press.

Keywords: Shape memory, shape recovery, composite materials, space environment.

Introduction

Shape memory polymer composites (SMPCs) are smart materials which combine structural properties of fiber reinforced laminates with functional behavior of shape memory polymers. Thanks to their hybrid nature, SMPCs are optimal candidates to develop new concept structures for Space application from deploying systems (such as solar sails, panels, shields, booms and antennas) to grabbing devices [**1**]. For this aim, many efforts have been made recently in manufacturing and testing new SMPCs. The basic idea is starting from SM polymers with the addition of structural fibers SM epoxy resins have the highest potential [**2**] as they are typically used as matrix of carbon fiber reinforced (CFR) composites. By this solution, unidirectional [**3**] and 0/90 woven [**4**] CFR-SMPCs have been successfully prototyped also with the ability of shape recovery under light exposure. In most recent contributions, single-ply weave-reinforced shape memory polymer composites have been prototyped [**5**] for deployable Space structures as well as 0/90 woven carbon fibre reinforced SMPC made out of prepreg material [**6**]. Therefore, the debate on the best composite structure and manufacturing is still active.

A valuable technical alternative for CFR-SMPC manufacturing is using commercial CFR prepregs with the addition of SM interlayers during lamination. This interlayer can be foam in SMPC sandwiches [**7**] or thin film (100-150 µm) in SMPC laminates [**8**]. Laminates are particularly easy to manufacture as the resin interlayer polymerizes together with the prepreg matrix during composite curing. In laboratory, CFR-SMPC laminates have been used to produce small-scale prototypes of Space deployable structures [**1**] and antennas [**9**]. SMPCs have not been validated in Space environment yet, but recovery tests were carried out in micro-gravity on SMP foams [**10, 11**] and a small CFR-SMPC laminate [**12**]. In the FOAM2 experiment which was performed on 20th of April 2013 during the BION-M1 mission of the Soyuz spacecraft, shape recovery of 24×10×0.4 mm^3 bent laminate was successfully achieved. However, results from long-term exposure to Space environment are still missing. Apart from microgravity, the Space environment is a very hard place which strongly affects durability and performance of materials. Even if some components of this environment can be reproduced on the Earth, the unique combination of sun exposure, atmosphere and physical composition cannot be fully simulated. For this reason, experiments have been carried out to evaluate the behavior of material in Space environment. Environmental threats in LEO include atomic oxygen, photon radiation, charged particle radiation, temperature effects and thermal cycling, impacts from micrometeoroids and debris, and contamination. However, atomic oxygen seems to be the most predominant, even if the mutual interaction with other environmental factors is difficult to evaluate.

Several facilities have been used for exposure tests of technical materials in Space environment. NASA has designed its own platform named Materials International Space Station Experiment (MISSE) which is located on the exterior of the International Space Station (ISS) [**13**]. Up to now, over 540 samples have been tested in 8 different experimental campaigns to address long duration environmental durability of spacecraft materials in low-Earth orbit (LEO). Flight experiments consist of passive exposure to the environmental threats in LEO, including atomic oxygen, photon radiation, temperature effects and thermal cycling, impacts from micrometeoroids and debris, and contamination. At present, a new MISSE-9 experiment is running with a fully automated MISSE-FF module.

The goal of this study was manufacturing SMPC samples which are able to collect information from passive exposure in LEO in the MISSE-FF platform. Weight loss, material degradation, surface state are the typical data which can be analyzed on samples after their retrieval. Being SMPCs, it has been decided to find a way to measure the effect of Space exposure on their shape memory properties as well. Due to Space exposure, shape recovery could be avoided by matrix crosslinking or damaged by atomic oxygen erosion. Moreover, SMPCs could also be subjected to temperatures enough high to activate the shape change. Information about the effect of LEO exposure is fundamental for correct design and operation of future SMPC structures for Space applications. At present, there is no way to predict how the Space environment could interact with the SMP behavior of composite laminates. Unfortunately, this fundamental goal has to face with strong limitations coming from the MISSE-FF platform use, such as the small allowable size and thickness of the samples. For the first time, a solution has been found in this study by using SMPC samples which are externally similar to typical samples used in MISSE passive tests but with the addition of a shape change in the central part.

Materials and methods

The typical shape of a sample to be exposed in the MISSE-FF facility is a disk with a maximum diameter of 1 inch (25.4 mm). Design and manufacturing of the SMPC samples is shown in **Fig. 1**. The SMPC laminate consisted of 2 plies of CFR prepreg with 100 µm of SM epoxy resin interlayer. Two disks were trimmed from the prepreg (HexPly M49/42%/200T2X2/CHS-3K supplied by Hexcel) and some cuts were made to allow successive opening of a window into the composite laminate. The SM epoxy resin (3M Scotchkote 206 N) was deposited as free powder during lamination and co-cured with the CFR plies in a metallic mold. Commercial materials have been used to manufacture the samples. Aeronautical prepregs show very low SM behavior as they are typically designed for other aims. Therefore, the SMP interlayer is fundamental to give expected functional properties. In the scientific literature, most of the studies refer to SMPCs which are manufactured by impregnating fibers with SM matrices [**14**]. However, this solution is very complex because of the impregnation process, and the difficulty to reach the quality of commercial aeronautical products. The current solution seems to be a good compromise between the quality and traceability of used materials and final SM performances.

Laminate cure was performed on a heat plate at a temperature of 150°C for 30 min with applied pressure of 70 kPa. The internal window was opened by means of a successive thermo-mechanical cycle with a proper shaping mold (**Fig. 1**). The sample was heated over 150°C and a punch was used to open the window. Subsequently the entire assembly was left to cool in air, and the deformed SMPC sample was extracted. The shape of the SMPC sample has been designed mainly to provide information on the effect of Space environment on SM properties of laminates. The small window allows having two different movements on the same sample and to match the strong size restrictions of the MISSE-FF platform. Nevertheless, this SMPC configuration could also represent, in small scale, the closing window of a grabbing device. After Space debris grabbing, the window is closed to avoid its exit.

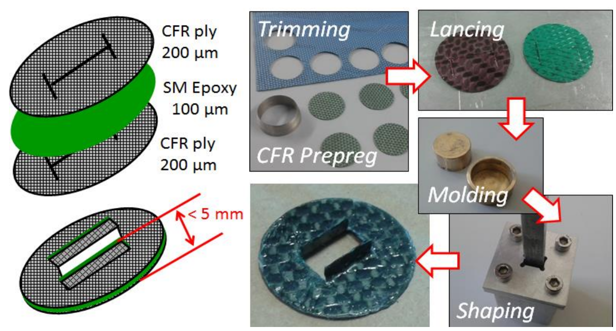

Fig. 1. Design and manufacturing of SMPC samples for long-term exposure to Space environment in LEO.

The thermo-mechanical cycle to freeze the non-equilibrium shape in the composite sample is better described in **Fig. 2**. The sample is clamped between two aluminum plates with rectangular holes so as to avoid warpage during deformation. The full mold is put in oven at 150°C for 30 min and, subsequently, is extracted to apply the deformation by means of a punch. The punch is left in contact with the SMPC up to its cooling down to room temperature at which the deformed samples is extracted. This procedure has been selected to minimize damages in the SMPC sample but made difficult a precise estimation of applied shape fixity. By a rough estimation, it was about 95%.

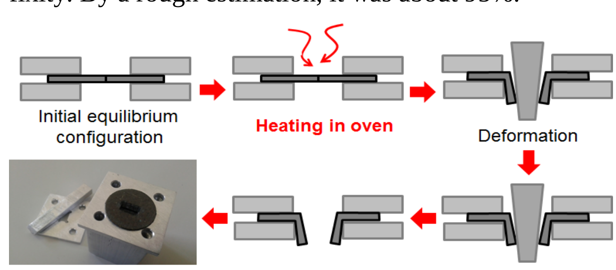

Fig. 2. Thermo-mechanical cycle for shape change.

Two flat laminates (45x7x0.5 mm^3) were also molded with and without SM interlayer for dynamic mechanical analysis (by Netzsch DMA 242 C) in bending configuration. Moreover, a thin specimen of cured SM epoxy resin (20x5x0.3) was tested in tensile configuration. All DMA tests were carried out at 10 Hz from room temperature to 200°C. Small samples of uncured specimens were also used for differential scanning calorimetry (by Perkin Elmer DSC7) which is a useful technique to investigate thermal behavior of SM composites [**15**]. Double scans were carried out from 10 to 250°C at 10 °C/min.

In order to evaluate the ability of the SMPC in recovering the original shape under light exposure, a recovery test has been performed by using a 75 W IR lamp. A thermocouple was inserted at the bottom of the sample to measure the temperature during recovery. During the irradiation test, the sample was located at very short distance from the lamp (about 50 mm) to reduce the time for shape recovery. The goal of the test was not to reproduce the solar exposure environment but understanding if manufacturing errors could affect shape change during heating. In fact, the sample was exposed in air at atmospheric pressure and standard environmental conditions.

Results and discussion

The hybrid nature of the manufactured SMPC samples is a consequence of the use of commercial materials for the CFR plies. Having weak SM properties, it is necessary that other materials provide this behavior. From a conceptual point of view, single CFR plies are able to elastically deform under bending and this deformation is particularly large if the resin matrix is in the soft state. However, CFR plies are not able to fix the shape during cooling. In multi-ply laminates elastic deformation is strongly reduced also at high temperature because of the interaction between adjacent plies and the low resin matrix ductility. Adding a SMP interlayer, it is possible to provide a soft cushion where single composite plies can deform during heating. This cushion is also able to freeze the shape during cooling. During the thermo-mechanical cycle for shape change, it is necessary that both the resin matrix of the CFR plies and the SMP interlayer exceed their glass transition temperature. In this condition, CFR plies reduce their stiffness and can be easily elastically deformed meanwhile the SMP interlayer can work as a cushion. During cooling, most of the elastic deformation of the CFR plies will be residual because of the SMP freezing.

DSC curves of the composite laminate with and without SM interlayer are reported in **Fig. 3a** together with scans for the uncured SM epoxy resin. The reaction peak is evident for all the samples by the peak in the first scan whereas glass transition of the cured samples is clearly visible by the inflection point in the second scans. The SMPC curve is the combination of the CFR and SM epoxy resin curves. In fact, the glass transition of the uncured epoxy powder is visible about 75°C whereas the polymerization peak is similar to CFR because of the small amount of SM resin interlayer. After polymerization, a single glass transition temperature is observed due to the superposition between the prepreg matrix and the SM resin softening. DMA results of **Fig. 3b** confirm this strong interaction. Small differences may be observed at low temperature for storage modulus (E') and loss factor (tg δ) values of the composite laminates with and without SM interlayer. However, during glass transition, lower stiffness and higher damping is shown by the SMPC because of the SM resin. Moreover, a small evidence of a double damping-peak is visible as the damping peak of the SM resin is anticipated in comparison with the stiffer CFR laminate.

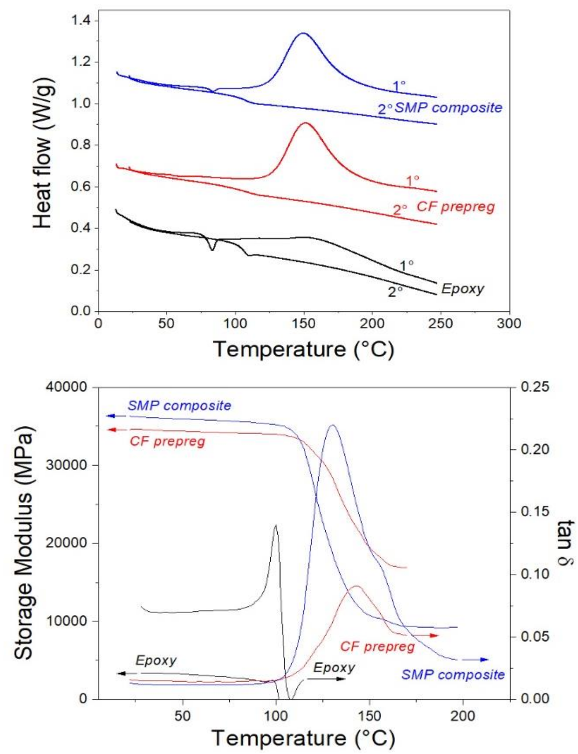

Fig. 3. DSC (a) and DMA (b) results from testing CFR laminate, CFR-SMPC laminate and SM epoxy resin.

The hybrid nature of the CFR-SMPC laminate is responsible for its optimal shape memory behavior. In fact, the SMPC laminate preserve the structural stiffness of the CFR laminate close to the glass transition of the SM resin. After transition, the material is very soft to easily change its shape. Data extracted from curves of **Fig. 3** are reported in **Table 1**. The reaction peak temperatures of the CFR prepreg and the SM resin are similar and therefore co-curing is possible. After cure, the glass transition temperature T_g can be extracted by the inflection point of the second scan of DSC or of the storage modulus of DMA, or by the peak of the loss factor of DMA. For the inflection points, the maximum of the curve derivative was used. In DSC scans, the T_g of the cured SM epoxy is very close to the T_g of the CF prepreg, being 2°C lower. Instead the SMP composite exhibits the same T_g of the neat composite probably due to the lower thermal contribution of the epoxy resin.

Table 1. Data extracted from DSC and DMA tests.

	DSC results		
	First scan		*Second scan*
Sample	***Peak Temperature***	***Peak Area***	***Glass Transition***
	(°C)	*(J/g)*	*(°C)*
Epoxy	159.83	27.502	106.0
CF prepreg	151.73	64.47	108.3
SMP composite	149.39	65.48	108.5
	DMA results		
Sample	***Glass Transition, tan δ***	***Glass Transition, E'***	
	(°C)	*(°C)*	
Epoxy	99.8	102.2	
CF prepreg	142.7	124.6	
SMP composite	131.3	114.9	

As expected, DMA results can better identify the effect of the SM resin on the SMPC glass transition. In fact, DMA tests measure the mechanical effect of the glass transition which is always strong even if related thermal effects can be weak. Nevertheless, mechanical effects need time to occur and T_g values are generally shifted toward higher values in comparison with DSC. Due to the soft resin interlayer, the glass transition of the composite laminate reduces about 10°C. By considering loss factor data, a processing temperature over 120°C is sufficient to change the shape of the SMPC sample.

Shape-recovery of the SMPC sample is shown in **Fig. 4**. After 20 s of irradiation, most of recovery is achieved with the temperature of 90°C at the bottom of the sample. A small residual strain is due to frozen internal stresses during cure. Because of these stresses is difficult to quantify precisely the final shape recovery which rounded about 95%, equal to the shape fixity. Recovery time is in agreement with other shape recovery tests of SMPC structures [**6, 10**] where high thermal input was used. It is not sure that Space exposure in the MISSE-FF platform is able to provide sufficient energy for shape change. However, if it would happen, the effect is clearly visible after sample retrieval.

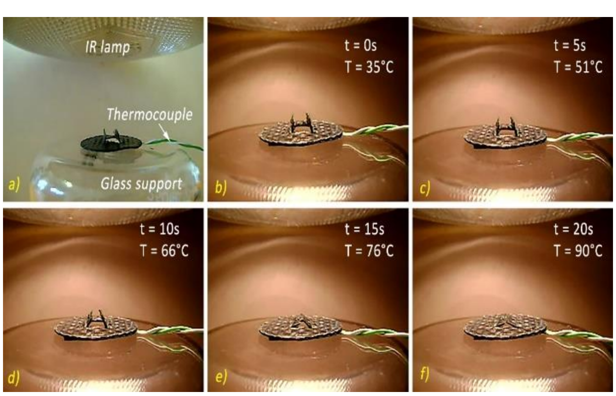

Fig. 4. On-Earth Shape recovery of the SMPC samples designed for long-term exposure to Space environment in LEO.

Conclusion

Some SMPC samples have been prepared to be exposed in Space environment. Tests have shown that a hybrid composite is made by combining the rigid behavior of the carbon fiber plies and the soft SMP interlayer. At room temperature this mismatch is low but it increases approaching the glass transition temperature of the hybrid system. SMPC samples have been already memorized on Earth, and now are exposed on the exterior of the ISS. Laboratory tests showed that irradiation is able to produce shape recovery. The experiment will show if sample recovery is possible in orbit as well because of sun irradiation or heat transfer from the surrounding platform. After sample retrieval, another goal will be estimating some aging effects of Space exposure in terms of mass loss, material degradation (cross-linking, chain polymer break, delamination, and embrittlement) and loss of performances. Cross-linking could stop shape recovery in Space and, in that case, shape recovery will be avoided also on Earth after sample return.

Acknowledgements

Authors want to acknowledge Kim de Groh of NASA Glenn Research Center for the support given in the design and development of composite samples.

References

1. Santo, L.; Quadrini, F.; Accettura, A.G.; Villadei, W.; *Procedia Engineering,* **2014**, *88C,* 42.
2. Wang, Z.; Song, W.; Ke, L.; Wang, Y.; *Materials Letters,* **2012**, *89,* 216.
3. Li, F.; Scarpa, F.; Lan, X.; Liu, L.; Liu, Y.; *Composites Part A: Applied Science and Manufacturing,* **2019**, *116,* 169.
4. Herath, H.M.C.M.; Epaarachchi, J.A.; Islam, M.M.; Al-Azzawi, W.; Leng, J.; Zhang, F.; *Composites Science and Technology,* **2018**, *167,* 206.
5. Gao, J.; Chen, W.; B. Yu, B.c, Fan, P.; Zhao, B.; Hu, J.; Zhang, D.; Fang, G.; Peng, F.; *Composites Part B: Engineering*, **2019**, 159, 336.
6. Herath, H.M.C.M.; Epaarachchi, J.A.; Islam, M.M.; Al-Azzawi, W.; Leng, J.; Zhang, F.; *Composites Science and Technology*, **2018**, *167,* 206.
7. Santo, L.; Quadrini, F.; De Chiffre, L.; *Key Engineering Materials,* **2013**, *554,* 1930.
8. Quadrini, F.; *Advanced Materials Research,* **2014**, *783,* 2509.
9. Santo, L.; Quadrini, F.; Bellisario, D.; Shape memory composite antennas for space applications, IOP Conference Series: Materials Science and Engineering, **2016**, *161,* 012066.
10. Santo, L.; Quadrini, F.; Squeo, E.A.; Dolce, F.; Mascetti, G.; Bertolotto, D.; Villadei, W.; Ganga, P.L.; Zolesi, V.; *Microgravity Science and Technology*, **2012**, *24,* 287.
11. Quadrini, F.; Santo L, L.; Squeo, E. A.; *Materials Letters,* **2012**, *69,* 20.
12. Santo, L.; Quadrini, F.; Ganga, P. L.; Zolesi, V.; *Aerospace Science and Technology*, **2015**, *40,* 109.
13. de Groh, K.K.; Bruce, A.; Joyce, A.; Miller, S.K.; NASA Glenn Research Center's Materials International Space Station Experiments (**2008**) NASA/TM-2008-215482.
14. Li, F.; Scarpa, F.; Lan, X.; Liu, L.; Liu, Y.; Leng J, J.; *Composite Part A-Applied Science,* **2019**, *116,* 169.
15. Sattar, R.; Kausar, A.; Siddiq, M.; *Advanced Materials Letters,* **2016**, *7,* 282.