

# INFLUENCE OF AMINE AND EPOXIDE POSS ON THE FUNCTIONALITY OF SHAPE MEMORY POLYMERS AND THEIR DURABILITY TO THE LOW-EARTH ORBIT SPACE ENVIRONMENT

**Avraham I. Bram**<sup>(1),(2)</sup>, **Eliana R. Wallach**<sup>(1)</sup>, **Asaf Bolker**<sup>(1)</sup>, **Irina Gouzman**<sup>(1)</sup>, **Eitan Grossman**<sup>(1)</sup>,

**Noam Eliaz**<sup>(3)</sup>, **Ronen Verker**<sup>(1)</sup>

<sup>(1)</sup> *Space Environment Department, Soreq Nuclear Research Center, Yavne, Israel, email:avrambram@gmail.com*

<sup>(2)</sup> *Licensing & Safety Office, Israel Atomic Energy Commission, Yavne, Israel*

<sup>(3)</sup> *Department of Materials Science and Engineering, Tel-Aviv University, Tel Aviv, Israel*

## ABSTRACT

Thermally activated shape memory polymers (SMPs) can memorize at low temperature a temporary shape and return at higher threshold temperature to their permanent shape. Due to their higher strength-to-weight ratio, SMPs' potential space application is to replace heavy metallic mechanisms that are used in spacecraft in the low Earth orbit (LEO) as well as in geosynchronous Earth orbit (GEO). One of the main hazards for organic materials, such as SMPs, in LEO is atomic oxygen (AO). In order to improve their durability to AO, varying amounts of polyhedral oligomeric silsesquioxane (POSS) molecules containing either amine or epoxied functional groups were incorporated into an epoxy-based SMP. Under the stringent conditions of a ground-based RF-oxygen plasma AO exposure test, POSS containing SMPs showed substantially lower erosion rate than pristine epoxy. Mechanical properties, such as storage modulus, measured using dynamic mechanical analysis (DMA). In case of amine-based epoxy-POSS were increased, implying on higher elasticity of this novel nanocomposite-based SMP. On the other hand, incorporation of epoxide-based POSS led to an opposite phenomenon, i.e. a decrease in the storage modulus, implying on lower elasticity.

In addition, incorporation of POSS led to reduction in the SMP's glass transition temperature for various amine and epoxide POSS contents. This additional feature of POSS may be used for tailoring a desired thermal transition temperature in future applications.

## 1. INTRODUCTION

The volume and mass budgets of spacecraft launched into low Earth orbit (LEO) and geosynchronous Earth orbit (GEO) are limited. Hence, it needs to be equipped with lightweight, compact, reliable built-in mechanisms for deployment of antennas, radiators, solar arrays, optical systems, and more. Large space deployment systems are usually classified into two different groups: mechanical mechanisms and inflatable system. Mechanical mechanisms have significant drawbacks such as large mass, complex assembled process, large volume, and undesired impact during deployment [1,2]. Inflatable systems on the other hand, have lower weight and better packing efficiency, but only few systems have

demonstrated the necessary deployment control [3]. A new class of materials that can be used for deployment mechanisms is based on SMPs.

SMPs are stimuli-responsive materials that, after being deformed, have the ability to return to their pre-deformed shape by external stimuli such as light, temperature, electric current, electromagnetism, pH, and ionic strength [4-6]. The SMPs are elastic polymer networks that underlie active movement. The SMP has a polymer network which consists of molecular switching segment and hard segment (netpoints) [7]. The molecular switches are able to reduce their stiffness upon a particular stimulus, allowing the polymer to be programmed into its temporary shape. Upon exposure to specific stimulus, the molecular switches are triggered, and strain energy stored in the temporary shape is released, which consequently results in the shape recovery [4,5] to the polymer's original permanent shape.

Thermally activated SMPs can memorize at low temperature a temporary shape and return at higher temperature to their permanent shape. The molecular switches are able to reduce their stiffness upon a particular stimulus, in this case, temperature, allowing the polymer to be programmed into its temporary shape and maintain this temporary shape as the SMP is cooled below a certain threshold temperature. The SMP can return to its permanent shape following sample heating above this threshold temperature. Usually, this threshold temperature is the SMP's glass transition temperature [5]. Among the main advantages of SMPs over metallic materials are higher strength-to-weight ratio, as well as great flexibility in terms of material design [8].

Due to these advantages, a potential application of SMPs is to replace metallic mechanisms that are used nowadays in spacecraft which operate in the LEO, as well as in GEO [9].

The LEO space environment extends from an altitude of 200 km to an altitude of 800 km. It is characterized by severe conditions such as hypervelocity micro-meteoroids and space debris, ultrahigh vacuum, ionizing radiation, ultraviolet (UV) and vacuum UV radiation, electrostatic discharge, and extreme thermal cycles from -100°C to +100°C [10-12]. The most destructive elements for organic materials, selected for LEO space application, are UV radiation and atomic oxygen (AO) [10-12].

AO attack of organic materials may result in surface chemical reactions [13]. These reactions can cause surface erosion, which results in mass loss, changes in surface morphology, chemical composition, and optical, as well as thermo-optical properties. The AO flux depends on the daytime, solar activity, orbit inclination, and the position of the material on the spacecraft [12]. The range of the AO density in LEO is  $10^4$ - $10^{10}$  O-atoms/cm<sup>3</sup> [14]. Unprotected polymers will erode in LEO by AO at an approximate rate of 100 μm/year. Due to these severe LEO conditions, polymers require AO protection. Usually, such protection is provided to the spacecraft outer layer by silicon dioxide (SiO<sub>2</sub>) or indium tin oxide (ITO). However, such protective layer can be damaged due to hypervelocity debris, as well as by ground-based handling [13].

A potential solution to this problem is to incorporate polyhedral oligomeric silsesquioxane (POSS) molecules into the polymer backbone. POSS is a cage-like silicon oxide-based molecule that can incorporate various organic functional groups. As such, POSS molecules are in a state between organic and ceramic material. Incorporation of POSS molecules having the right functional group to be physically incorporated or chemically react with a specific monomer can create a hybrid polymer-POSS material with improved mechanical properties and lower AO erosion yield. Polymers that contain POSS molecules have lower AO erosion yield due to the formation of a passivation layer as the AO oxidized the SiO<sub>1.5</sub> POSS into SiO<sub>2</sub> AO durable layer [15].

SMPs have a potential to replace metallic mechanisms but need AO protection. A potential solution is a hybrid organic-inorganic SMP which is based on an epoxy-POSS nanocomposite material system with improved AO durability.

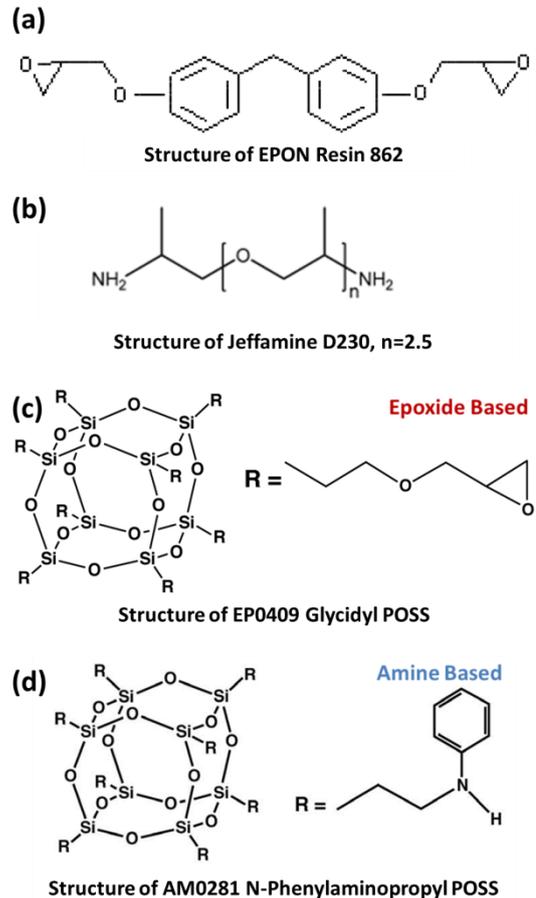
In this work, two types of SMPs were prepared; the first contained various amounts of POSS with amine functional groups. The second contained various amounts of epoxide-based functional groups. The effect of the POSS type on the shape memory effect (SME) was studied by bending rectangle SMP samples with various contents of POSS. The SME was studied in terms of deformability and deployment time. The mechanical and thermo-mechanical properties of the SMPs, such as storage modulus as well as their glass transition temperature, *T<sub>g</sub>*, were characterized using dynamic mechanical analysis (DMA). Durability to AO was studied by exposing the SMP samples to a ground-based AO simulation system, based on an oxygen RF-plasma system environment.

## 2. EXPERIMENTAL SECTION

### 2.1. MATERIALS

Diglycidyl ether of Bisphenol F (EPON 862, from Hexion [16]) was used as an epoxy monomer for the SMP. Poly(propylene glycol) bis (2-aminopropyl) ether

(Jeffamine D230 from Huntsman [17]), was used as a crosslinker agent. N-Phenylaminopropyl POSS<sup>®</sup> (AM0281 from Hybrid Plastics [18]), containing 8 secondary amine groups, or Glycidyl POSS<sup>®</sup> EP0409 from Hybrid Plastics [19]), containing 8 epoxide groups, were used as additives. The molecular structures of the various epoxy-POSS components are shown in Figure 1.



**Fig. 1:** Molecular structures of (a) EPON 862 epoxy resin monomer, (b) Jeffamine D230 crosslinker (c) EP0409 Glycidyl POSS, and (d) AM0281 N-Phenylaminopropyl POSS [16-19].

### 2.1. EPOXY AND EPOXY-POSS SYNTHESIS

The epoxy resin, crosslinker, and POSS additives were weighed and transferred into a glass vial, while maintaining a 1:1 molar ratio between amine and epoxide functional groups. For example, in order to preserve a 1:1 molar ratio, while adding amine-POSS, the amount of Jeffamine D230 crosslinker that contains amine functional group has been reduced accordingly. The vial was then heated to 50°C in order to reduce the epoxy resin viscosity, thus allowing efficient mixing, and was shaken vigorously by a vortex shaker for 1 minute at 3000 rpm. After mixing, the adhesive was placed into a vacuum oven, which was preheated to 50°C for degassing. The degassing was performed for 8 minutes at a pressure of

less than 10 Torr. The adhesive was then casted into aluminum molds having  $10 \times 70 \times 1$  mm cavities. The adhesive was thermally cured at  $100^\circ\text{C}$  for 1.5 h and post cured at  $130^\circ\text{C}$  for another 1 h [20]. Prepared epoxy-based SMP samples contained various amounts of POSS additives as summarized in Table 1. Since amine or epoxied POSS additives substituted the Jeffamine D230 crosslinker or the epoxy EPON 862 resin, respectively, a maximum content of the POSS additive was determined. As indicated earlier, this maximum POSS content maintains a 1:1 molar ratio between the amine and the epoxide functional groups. The difference between the maximum content of the amine (50 wt.%) and epoxide (75 wt.%) POSS is inherent from the difference between the amine and epoxide equivalent weight of the Jeffamine D230 [16] and epoxy EPON 862 resin [17].

**Table 1:** Composition of epoxy-POSS nano-composite samples.

wt.% POSS	Amine-based epoxy-POSS SMP	Epoxide-based epoxy-POSS SMP
0	Epoxy without POSS	
5	+	+
10	+	+
15	+	+
20	+	+
25	+	+
30	+	+
35	+	+
45	+	+
50	+	-
	Max. concentration	
65	-	-
75	-	Max. concentration

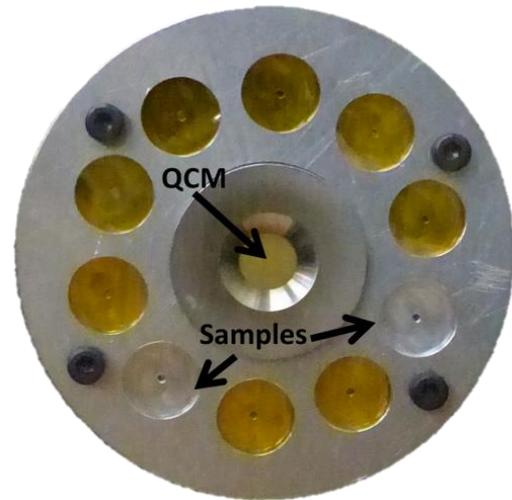
## 2.1. CHARACTERIZATION TECHNIQUES

The SME was studied by bending the epoxy samples to a U-like temporary shape, using a  $130^\circ\text{C}$  hot oil bath and a 45 mm in diameter aluminum cylinder, which was used as a mandrel. After bending, the samples were cooled while in their temporary shape in a cold bath being maintained at room temperature. Upon cooling, the samples were reheated in the oil bath above their  $T_g$  and eventually returned to their permanent shape. The SME was studied in terms of deployment time. The deployment time is defined as the time from the moment the U-like shape sample is immersed in the oil bath until the sample is returned to its permanent straight shape.

Mechanical and thermo-mechanical properties of the SMPs, such as storage modulus and  $T_g$ , were characterized using Q800 model DMA (from TA instrument). The experiments were performed at a constant strain of 0.1% using a single frequency of 1 Hz and a temperature ramp rate of  $3^\circ\text{C}/\text{min}$ , from  $30^\circ\text{C}$  to  $130^\circ\text{C}$ . The  $T_g$  was determined from the onset point of the storage modulus versus the temperature curve.

## 2.2. DURABILITY TO ATOMIC OXYGEN

Durability to AO was studied by exposing the SMP samples to a ground simulated AO environment based on RF-oxygen plasma source (LITMAS<sup>TM</sup> RPS, LB-1200), attached to a vacuum system. During the experiment, 1-mm thick disc-like samples, having 12 mm diameter, were placed on a holder in the vacuum chamber at a pressure of  $2.1 \times 10^{-2}$  Torr, down-stream from the plasma source. The AO equivalent flux was measured in-situ, by placing at the center of the sample holder a quartz crystal microbalance (QCM) coated with pyromellitic dianhydride-oxydianiline (PMDA-ODA) polyimide. The uniformity of the AO plasma source was confirmed by placing Kapton sample near each SMP sample. The mass loss of the Kapton samples was used for determining the AO fluence and for calculation of the erosion yield of the epoxy-POSS samples. Photograph of the sample holder containing the QCM, the Kapton samples, and the transparent pristine epoxy-POSS SMP samples is shown in Figure 2.



**Fig. 2:** Photograph of the sample holder, containing the QCM, SMP, and Kapton samples.

The samples were removed periodically from the system in order to measure their mass loss and evaluate the effect of the two types of POSS on their AO durability. Weight measurements were done using micro-balance, (SE2 model from Sartorius). The AO equivalent fluence was calculated using equation 1 [21]:

$$(1) E = \frac{\Delta m}{\rho A t F}$$

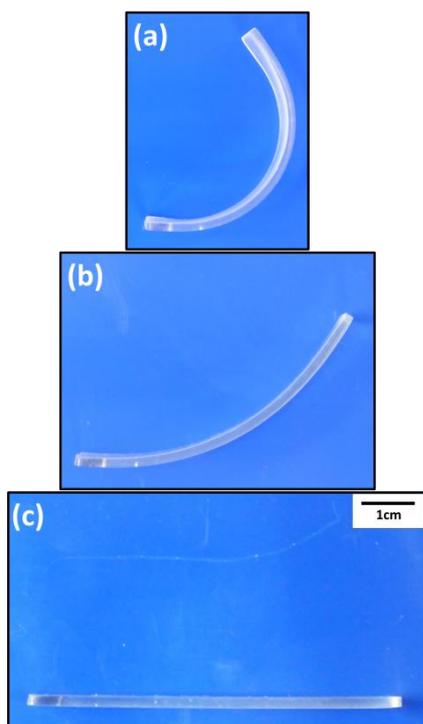
where  $E$  is the erosion yield ( $\text{cm}^3/\text{O-atom}$ ),  $\Delta m$  is the mass loss (g),  $A$  is the material's exposure area ( $\text{cm}^2$ ),  $\rho$  is the material's density ( $\text{g}/\text{cm}^3$ ) and  $F$  is the AO fluence ( $\text{atoms}/\text{cm}^2$ ).

### 3. RESULTS AND DISCUSSION

#### 3.1. SME PROPERTIES

Amine and epoxied based epoxy-POSS samples having different POSS contents, as per Table 1, were prepared. The maximum POSS loading that enabled both substantial deformation to a U-like shape with a radius of 22.5 mm and deployment back to the permanent shape was 50 wt.% in the case of amine-based epoxy-POSS. In the case of epoxide-based epoxy-POSS the maximum POSS content that enabled bending to the temporary shape and deployment to the permanent shape was 45 wt.%.

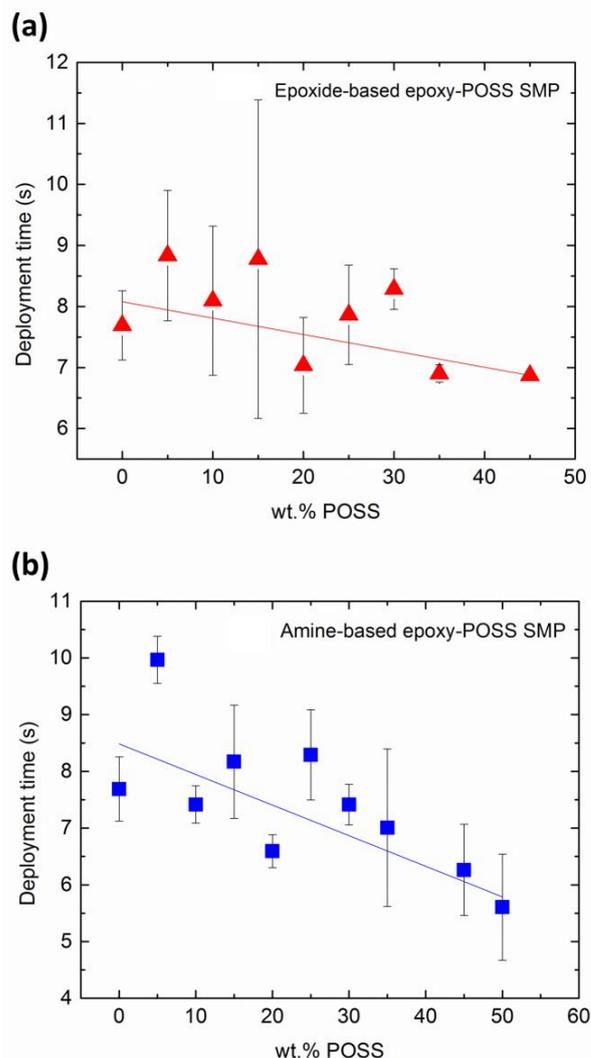
Photos of the U-like temporary shape, during the deployment and at the permanent shape state, are shown in Figure 3. The epoxy-POSS SMP samples that were deformed to a temporary shape and returned to their permanent shape are marked as "+" in Table 1. Epoxy-POSS SMPs that failed during deformation to the temporary state are marked as "-" in Table 1. The failure can be explained due to high amount of cross-linking, which makes the polymer brittle. Another possible explanation is aggregation of POSS molecules and coalescence of these aggregates into critical-size defects, which leads to premature failure during deformation [22].



**Fig. 3:** (a) U-like SMP's temporary shape, (b) during deployment, and (c) final permanent shape.

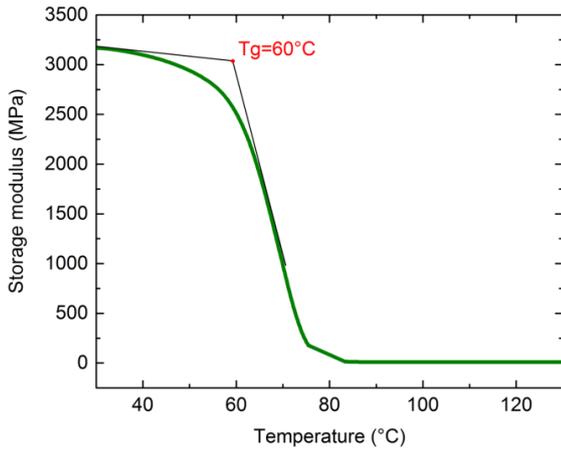
The SME was studied in terms of deployment time in the oil bath. Figure 4 presents the SMPs' deployment time versus POSS wt.% and type. In general, for both types of POSS, deployment times decreased while the POSS content was increased. However, the observed decrease

in the deployment time versus POSS content of the amine POSS based SMP is twice (-0.054 s/wt.%POSS) that for epoxide POSS based SMP (-0.026 s/wt.%POSS).

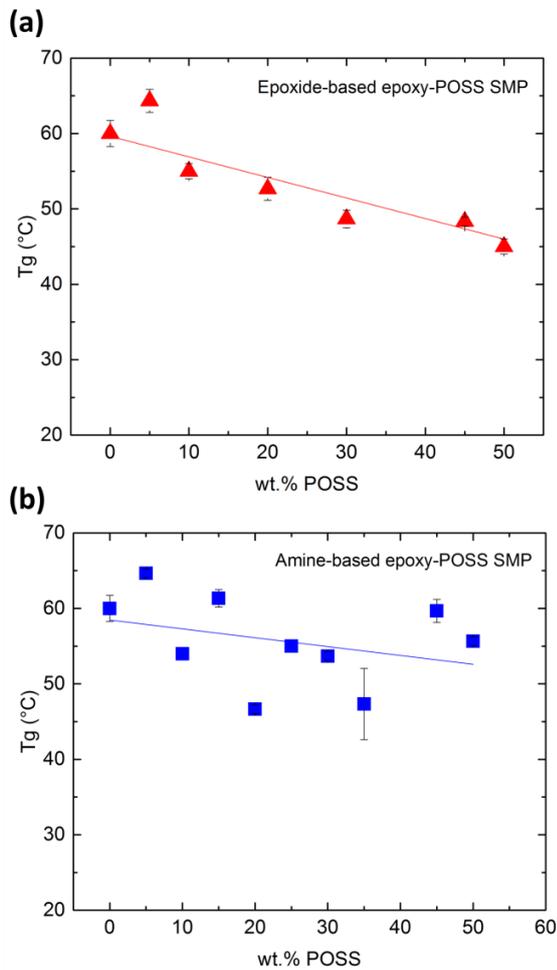


**Fig. 4:** Effect of POSS content on deployment time of (a) epoxide and (b) amine-based epoxy-POSS SMPs.

$T_g$  was determined from the onset point of the storage modulus versus the temperature curve, as demonstrated in Figure 5, for pristine epoxy, in this particular example. Figure 6 presents a summary of  $T_g$  measurements for the two types of epoxy-POSS samples at various POSS content.  $T_g$  decreases from 60°C to 45°C in the case of 50 wt.% epoxide-based epoxy-POSS and 56°C in the case of amine-based epoxy-POSS.  $T_g$  measurements support the result from deployment time measurements: for both types of POSS, while the POSS content increases, the  $T_g$  decreases. These results are complementary, because when  $T_g$  decreases, the heating time is shorter, in order for the samples to reach a temperature which triggers the SME.



**Fig. 5:** Storage modulus vs. temperature of pristine epoxy sample.



**Fig. 6:** Effect of POSS content on  $T_g$  of (a) epoxide, and (b) amine-based epoxy-POSS SMPs.

### 3.1. MECHANICAL PROPERTIES

The storage modulus at 30°C was studied for different amine and epoxide-based epoxy-POSS contents (Figure 7). The storage modulus is an indication of the ability of the epoxy-POSS SMP to store deformation energy in an elastic manner. It is directly related to the extent of cross-

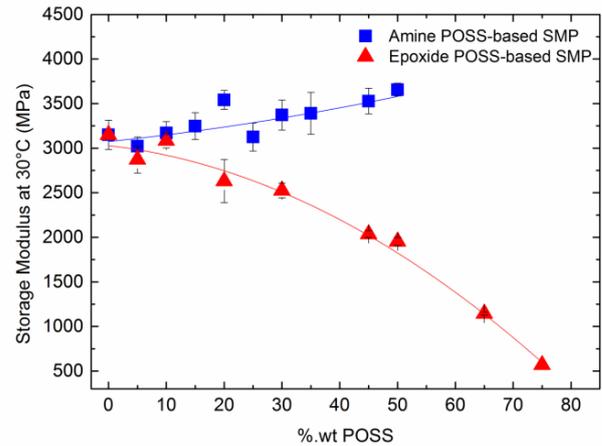
linking; the higher the degree of cross-linking, the greater the storage modulus [23].

In the case of amine-based epoxy-POSS SMP, increasing the POSS content led to an increase in the storage modulus. This means an increase in the material's elasticity. On the other hand, increasing the epoxide-based POSS content led to an opposite phenomenon (i.e. a decrease in the storage modulus), reflecting a decrease in the material's elasticity.

From the storage modulus measurement, we can assume that the epoxide-based epoxy-POSS-SMP has lower crosslinking degree than the amine-based epoxy-POSS-SMP. It is possible that the epoxide POSS molecule has a lower ability to move and react with the crosslinker's amine groups compared the EPON 862 epoxy resin monomer.

However, in the case of the amine POSS, the opposite occurs. This may lead to a conclusion that the amine POSS serves as a more efficient crosslinker than the Jeffamine D230 crosslinker when reacting with the EPON 862 monomers.

Moreover, since the storage modulus of the epoxide-based epoxy-POSS SMP decreases as the POSS content increases, the early failure during the bending test which was discussed in Section 3.1, is probably due to the agglomeration of POSS, which leads to formation of critical size defects during deformation and consequentially to an early failure [22].

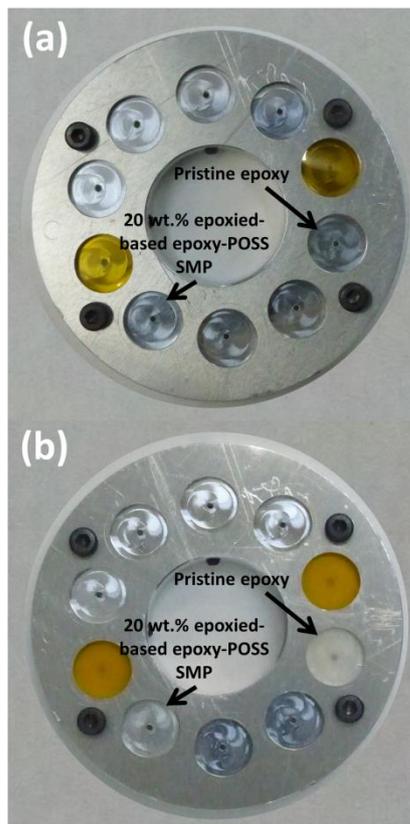


**Fig. 7:** DMA measurements of storage modulus at 30°C of epoxy-POSS SMP samples.

### 3.1. DURABILIRY TO AO

Pristine and 20 wt.% amine and epoxide-based epoxy-POSS disc-like samples were exposed to the RF- oxygen plasma. After 3 days of exposure, which are equivalent to an AO fluence of  $5 \times 10^{22}$  O-atoms/cm<sup>2</sup>, the samples were removed from the system and their mass loss was measured. Photos of pristine epoxy and 20 wt.% epoxide-based epoxy-POSS samples before (a) and after (b) AO ground-based irradiation are shown in Figure 8. While the surface of the pristine epoxy became rough and the sample became semi-opaque, the 20 wt.% epoxide-based

epoxy-POSS SMP sample remained smooth and transparent. The amine-based epoxy-POSS SMP sample (not shown) also remained smooth. The erosion yields of the three types of samples are given in Table 2. It can be seen that the erosion yield of the pristine epoxy is 2 orders of magnitude higher than the amine and epoxied based epoxy-POSS SMPs. The lower AO erosion yield of the POSS containing samples can be explained by formation of a passivation layer of SiO<sub>2</sub> AO-durable layer [15]. The buildup of this layer and its morphology will be verified in future work.



**Fig. 8:** Photos of the pristine epoxy and 20 wt.% epoxied-based epoxy-POSS samples (a) before and (b) after the AO-irradiation. Arrows mark the samples.

**Table 2:** Erosion yield of pristine epoxy versus 20 wt.% epoxy-POSS SMP.

Sample	Erosion yield [cm <sup>3</sup> /O-atom]
Pristine epoxy	$1.10 \times 10^{-24}$
20 wt.% amine-based epoxy-POSS SMP	$3.32 \times 10^{-26}$
20 wt.% epoxied-based epoxy-POSS SMP	$1.16 \times 10^{-26}$

#### 4. SUMMARY AND CONCLUSIONS

Amine and epoxide-based epoxy-POSS SMP samples were prepared with various POSS contents. The effect of the POSS type and content on the samples' SME and mechanical and thermo-mechanical properties were studied. The  $T_g$  of the epoxy-POSS at various amine and

epoxide contents was measured using DMA. As the POSS content was increased,  $T_g$ , and as a result – the deployment time, decreased for both types of POSS. However, the effect of the POSS type on the SMPs' mechanical properties was quite different. In the case of amine-based epoxy-POSS SMP, increasing the POSS content led to an increase in the storage modulus, meaning an increase in the material's elasticity. On the other hand, in the case of epoxide-based epoxy-POSS SMP, increasing the POSS content led to decrease in the storage modulus, meaning a decrease in the material's elasticity. The epoxy-POSS SMPs exhibited also higher durability to AO compared to pristine epoxy. Under the stringent conditions of the RF-plasma source, 20 wt.% amine and epoxied-based epoxy-POSS SMPs showed an erosion rate of 1-3% the erosion rate of pristine epoxy. The decreased erosion rate may be attributed to the formation of a passivation layer, where the AO oxidized the SiO<sub>1.5</sub> POSS into SiO<sub>2</sub> [15].

This work presents novel nanocomposite materials and the benefit of incorporating POSS into the backbone of epoxy-POSS SMPs for increasing their durability to AO. It also presents the effect of POSS type on the SME and offers means to tailor the SMPs' mechanical properties and tune the temperature to the desired value.

#### REFERENCES

1. J.K. H. Lin, C.F. Knoll and C.E. Willey, Shape memory rigidizable inflatable (RI) structures for large space systems applications, 47<sup>th</sup> Structures, Structural Dynamics and Materials Conf., 2003.
2. J. Leng and S. Du, Shape Memory Polymers and multifunctional composites, CRC Press; 2010.
3. D.P. Cadogan and M.S. Grahne, Deployment control mechanisms for inflatable Space structures, 33<sup>rd</sup> Aerospace Mechanisms Conf., 1999.
4. W.D. Callister and D.G. Rethwisch, Materials Science and Engineering: An Introduction, 7<sup>th</sup> edition, pp. 348-350, 2007.
5. H. Tobushi, S. Hayashi, Y. Sugimoto and K. Date, Two-way bending properties of shape memory composite with SMA and SMP, *Materials* (Basel) **2**, 1180–1192, 2009.
6. X. Zheng, S. Zhou, X. Li and J. Weng, Shape memory properties of poly(d,l-lactide)/hydroxyapatite composites, *Biomaterials* **27**, 4288–4295, 2006.
7. T. Liu, T. Zhou, Y. Yao, F. Zhang, L. Liu, Y. Liu and J. Leng, Stimulus methods of multi-functional shape memory polymer nanocomposites: A review, *Composites: Part A* **100**, 20–30, 2017.
8. A. Lendlein and S. Kelch, Shape-memory polymers, *Angew. Chem.* **41**, 2034–2057, 2002.
9. Y. Liu, H. Du, L. Liu and J. Leng, Shape memory polymers and their composites in aerospace applications: a review, *Smart Mater. Struct.* **23**, 23001, 2014.
10. A. Laikhtman, I. Gouzman, R. Verker, E. Grossman and H.G. Pippin, Atomic oxygen and UV irradiation

- effects on fluorosilicone rubber: comparison of RF plasma and in-flight exposure. *High Perform. Polymers* **20**, 447–460, 2008.
11. X. Wang, X. Zhao, M. Wang and Z. Shen, An experimental study on improving the atomic oxygen resistance of epoxy resin/silica nanocomposites, *Polymer Eng. Sci.* **47**, 1156–1162, 2007.
  12. E. Grossman and I. Gouzman, Space environment effects on polymers in low earth orbit, *Nucl. Instrum. Methods Phys. Res. Section B: Beam Interactions Mater. Atoms* **208**, 48–57, 2003.
  13. S. Packirisamy, D. Schwam and M.H. Litt, Atomic oxygen resistant coatings for low earth orbit space structures, *J. Mater. Sci.* **30**, 308–320, 1995.
  14. S.W. Samwel, Low Earth orbital atomic oxygen erosion effect on spacecraft material, *Space Res. J.* **7**, 1–13, 2014.
  15. A.L. Brunsvold, T.K. Minton, I. Gouzman, E. Grossman and R. Gonzalez, An investigation of the resistance of polyhedral oligomeric silsesquioxane polyimide to atomic-oxygen attack, *High Perf. Polymers* **16**, 303–318, 2004.
  16. A.K. Rai, A. Porwal and S.B. Mishra, Investigation of mechanical properties of Epoxy EPON 862 cured With TETA by molecular dynamics, *S-JPSET* **4**, 81–86, 2013.
  17. Huntsman Corporation, JEFFAMINE® D-230 Polyetheramine - Technical Bulletin, 2008.
  18. V. Pistor, B.G. Soares and R.S. Mauler, Influence of the polyhedral oligomeric silsesquioxane n-phenylaminopropyl-POSS in the thermal stability and the glass transition temperature of epoxy resin, *Polímeros* **23**, 331–338, 2012.
  19. Hybrid Plastics, Safety Data Sheet, Glycidyl POSS® Cage Mixture, v 1.2.
  20. T. Xie and I.A. Rousseau, Facile tailoring of thermal transition temperatures of epoxy shape memory polymers, *Polymer* **50**, 1852–1856, 2009.
  21. S.K. Rutledge, B.A. Banks and M. Cales, A comparison of atomic oxygen erosion yields of carbon and selected polymers exposed in ground based facilities and in low Earth orbit, NASA Technical Memorandum 106622, AIAA-94-2628, 1994.
  22. R. Verker, E. Grossman, I. Gouzman, N. Eliaz, The effect of POSS-polyimide film's nanostructure on its mechanical properties, *Composites Sci. Technol.* **69**, 2178–2184, 2009.
  23. S.F. Edwards, H. Takano and E.M. Terentjev, Dynamic mechanical response of polymer networks, *J. Chem. Phys.* **113**, 5531–5538 2000.