ABSTRACT

Synthesized three-dimensional (3D) foam-like materials are a new way of building up normally 2D flat materials into 3D space, the so-called “3D interconnected 2D material networks”. These 3D porous materials retain many of the unique properties of their constituent 2D precursors while creating a low density, flexible, and ultralight version of their “bulk” form. These highly porous and interconnected materials can serve as effective fillers for creating composite materials with desirable properties, in combination with a selection of polymer matrices. These unique materials may be used in a variety of space related applications. This paper focuses on two examples; the first depicts 3D graphene (3D-C) incorporated into polyimide (PI) matrix, enhancing its thermal conductivity (one order of magnitude), electrical conductivity (10 orders of magnitude), and addresses its interaction with a space environment. The second example shows a new class of nanocomposite-shape memory polymer (SMP) which is composed of 3D-foam fillers and serves as an efficient, self-heated SMP adaptable to larger area with faster transformation speed and without any performance loss.

1. INTRODUCTION

Recent advances in the synthesis of two-dimensional (2D) materials, such as graphene and boron nitride (BN), have presented a way of building up these normally flat materials into a three-dimensional (3D) interconnected, flexible, ultralight (1–5 mg cm$^{-3}$), macro-porous foam like structures. One such method is template-directed chemical vapor deposition (CVD), in which the material produced retain the desirable properties of the 2D materials from which they are composed, while allowing the final shape and porosity to be determined by the substrate template used.

Multilayer graphene based foams, referred to as 3D graphene (3D-C), have the combined advantages of high specific surface area, ultra-light, strong mechanical strength, and excellent thermal and electrical conductivity. In contrast, hexagonal boron nitride (h-BN) foams, referred to as 3D h-BN (3D-BN), are electrically insulating while exhibiting similar thermal conductivity and mechanical strength to that of 3D-C. In addition, since both graphene and h-BN are grown using similar CVD process and have a lattice mismatch of about 1.5%, it is possible to create a hybrid material composed of both graphene and h-BN. Thus, allowing a controllable hybridization of 3D-C and 3D h-BN into a new 3D-BNC network with different C:BN composition. These 3D-BNC composites show a highly tunable electrical conductivity while maintaining a high thermal diffusivity. A typical example of the structure of these macroporous foams is shown in Figure 1a. In addition, the multilayer nature of the grown structure is shown in Figure 1b and c. The high quality of a CVD grown 3D-C can be seen in the STM images (Figure 1d and e).

Figure 1: (a) SEM image showing the top view of the foam-like architecture; (b, c) TEM images showing the layered structure of 3D-BN and 3D-C, respectively; (d) Inverse fast Fourier transform (FFT) of an atomic resolution image taken using STM showing the triangle lattice characteristic of the coupling between the upper graphene layer and the layer beneath (30mV, 2nA) of a 3D-C foam. In the inset, a line profile (indicated as a black dotted line at the main figure) shows the distance of 0.246nm between each individual atom. (e) Shows a superlattice with both triangular and hexagonal symmetry on a continuous graphene layer.

The mechanical, electrical, and thermal properties of these macro-porous foams make them highly suited to
serve as effective fillers for composite materials with a variety of polymer matrices. Their interconnected structure allows the composite material to retain the electrical and thermal properties of the bare foam with a much lower fill content than traditional fillers. In addition, the relatively large typical diameter of the foam pores (~100 – 200 μm), and a porosity of 99.7% \(^2,3\), make the infiltration of the polymer matrix into the structure a relatively easy process. The effectiveness of 3D-C as a filler material with epoxy matrix was demonstrated by Jia et al. The 3D-C epoxy composite conductivity was increased by 12 orders of magnitude, to 3 S cm\(^{-1}\)\(^5\). The 3D-C structure contained roughly four graphene layers, which is equivalent to 0.1 wt% filler content. In comparison, the maximum conductivity achieved by Yoonessi et al. \(^7\) for graphene–PI nanocomposite, containing well-dispersed graphene nano-sheets, was 0.96 S cm\(^{-1}\) at a filler content of 5 vol%. This value is three times lower than the conductivity achieved using 3D-C with similar and lower loading fractions\(^5,6\).

Therefore, these unique materials have potential use in a variety of space related applications, such as composite films for electrostatic discharge protection\(^5\), flexible electronic devices\(^8\), thermal interface material (TIM) \(^9\), thermally triggered shape memory polymer (SMP) actuators\(^10\), flexible antennas\(^11\), etc. This paper will review two of these potential space related applications. In the first example the incorporation of 3D-C into polyimide (PI) matrix will be addressed, including its interaction with a space environment. The results show a significant increase in the PI composite thermal and electrical conductivity with no weakening induced to the polymer structure. Moreover, space environment tests show that it is applicable for space vehicle protection. An additional example will show the enhancement of the thermal and electrical properties of epoxy-based SMP. SMP based actuators are a promising light weight alternative to bulky traditional mechanical actuators. The enhancement of the thermal properties is achieved by incorporating minimum loading fractions of 0.3 vol% of 3D-foams into the SMP matrix.

2. 3D-GRAPHENE INFUSED POLYIMIDE FOR SPACE APPLICATIONS

Polyimides (PIs) are known for their excellent mechanical properties and high thermal stability \(^12\). In addition, PIs are among the few polymers that are space qualified \(^13\). Thus, they are extensively used in various spacecraft systems. One of those is in thermal control blankets (multilayer insulator, MIL) for satellites and space exploration mission \(^14\). However, due to possible electrostatic discharge (ESD) issues there is a difficulty in implementing PI films in the outer layer of space thermal blankets \(^15,16\). The ESD problem exists as a result of the PI insulating nature, which causes different amount of charge to build up in different areas of the spacecraft surface in the presence of the plasma environment. This accumulated charge difference leads to electric potential differences that may cause ESD. The current solution to mitigate potential ESD is by coating the PI with indium tin oxide (ITO) conductive layer. However, ITO is brittle and susceptible to cracking which causes an immediate increase in sheet resistance;\(^17\) In addition, ITO coated PI cannot tolerate folding or bending\(^18\).

In our recent work a 3D-C/PI composite was developed, increasing the PI thermal conductivity by one order of magnitude and electrical conductivity by 10 orders of magnitude \(^5\). This material presents several advantages over traditional conductive coated PI, since due to the 3D-C interconnected structure it can tolerate local mechanical damage to the composite film without degradation of the overall electrical and thermal conductivity.

2.1 Preparation

3D-C/PI composites were prepared via a two-step process. In the first step the 3D-C foam was synthesized using CVD method \(^3\). In the second step the 3D-C was infiltrated with pyromellitic dianhydride-oxydianiline (PMDA-ODA) PI precursor. The infiltration process described in \(^5\) is composed of several steps with diluted polyamic acid solution, thus enabling enhanced penetration of the solution. This process prevents the build-up of strain within the film and at the interface between PI and 3D-C during the curing stage. The resulting film can be seen in Figure 2a, showing optical images of the bare 3D-C and 3D-C/PI composite, indicating a homogeneous distribution of PI along the 3D-C. In addition, Figure 2b shows the cross-section scanning electron microscope (SEM) image of both.

![Figure 2: (a) Optical images of the bare 3D-C and the nanocomposite film; (b) cross-section SEM images of bare 3D-C and 3D-C/PI film.](image-url)
3D-C increases the thermal conductivity by one order of magnitude. As seen in Figure 3a, the thermal conductivity increases from 0.15 Wm\(^{-1}\)K\(^{-1}\) for the bare PI to 1.7 Wm\(^{-1}\)K\(^{-1}\) for the composite film. The thermal conductivity enhancement was compared to that achieved by using other fillers such as carbon nano tubes, metal particles and graphene. The data was normalized by the filling fraction of each filler material in order to present a better comparison and is shown in Table I.

\[
R_s(T) = R_{00} T^{rac{1}{2}} \exp \left( \frac{T_0}{T} \right)^{1/d}
\]

Where \(R_{00}\) is the band tail's resistivity pre-factor, \(T_0\) is the temperature coefficient that contains the hopping parameters (localization length and density of states) and \(d\) is the dimensionality.

2.3 Space environment testing

In order to investigate the stability of the 3D-C PI based composite for space applications, the material was subjected to a set of tests that include outgassing, thermal cycles, thermos-optical characteristics, bending cycles, ionizing radiation exposure, and atomic oxygen exposure.

Figure 4 shows the results of aging studies of the 3D-C PI composite. The change in the sheet resistance (%) during thermal cycles between -100°C to 160°C for 30 repetitions is depicted in Figure 4a. The composite material shows only minor fluctuations (0.09%). Figure 4b shows the change in sheet resistance under repeated bending cycles. A bending diameter of 3.4 mm was used resulting in a 17.6% outer surface strain. After 260 cycles the sheet resistance increased to 9.37 \(\Omega\) with no obvious damage to the material.

The sheet resistance of the composite film and bare 3D-C foam was measured using the Van-der-Pauw method at a temperature range from -160 °C to +200 °C. As seen in Figure 3b, both measurements show a maximum of 4.8 \(\Omega\) at -160 °C and a minimum value of 3 \(\Omega\) at +200 °C. The average sheet resistance measured for ten different 3D-C/PI samples (thickness 218 ± 22 μm) at room temperature was 4.9 ± 1.16 \(\Omega\). The measured conductivity was found to fit the variable range hopping (VRH) model described by equation 1:

Figure 3: Thermal and electrical conductivity characterization. (a) Thermal conductivity characterization at a temperature range of 0°C – 200°C for 3D-C/PI film and bare PI, (b) Sheet resistance of bare 3D-C and 3D-C/PI at a temperature range of -160°C – 200°C (inset: fit of VRH model, that is ln(R×T\(^{-1/2}\)) vs. T\(^{-1/4}\) for both materials).

Figure 4: a) The change in sheet resistance after repeated thermal cycles; b) the sheet resistance of the composite film for 260 bending cycles (inset shows the start state and end state of the film at a bending cycle).

The 3D-C PI composite outgassing was measured according to the ECSS-Q-70-02A standard. The resulting residual mass loss (RML) and collected volatile condensable materials (CVCM) were 0.3% and 0.06% respectively. The values are similar to those of bare PI.
and satisfy the standard criterion of RML<1% and CVCM<0.1%.

The effect of exposure to ionizing particle radiation was simulated by exposing the 3D-C PI composite to a dose of up to 10 MGy of gamma radiation from a 60Co source (~15 years in GEO orbit). The exposure impact on the sheet resistance and electrical conductivity mechanism of the composite was examined. The results are displayed in Figure 5 and show that no change in the film sheet resistance and conductivity mechanism was detected after the exposure. In addition, no visible degradation of the material was observed.

Polyimide based films are susceptible to damage by the hyper-thermal atomic oxygen (AO) encountered by spacecraft at low earth orbits (LEO). In order to increase the durability of the 3D-C/PI composite to AO, the use of polyhedral oligomeric silsesquioxane (POSS) nano particles was examined. POSS monomers can be added to the PI matrix as well as deposited on the 3D-C scaffold. Four combinations of samples were prepared. The combinations includeaminopropylisobutyl POSS deposited on the 3D-C (may improve the attachment of the PI to the 3D-C) and 15 wt% trisilanolphenyl POSS incorporated into the polyimide matrix. The various samples and POSS combinations are described in Table II.

The electrical properties of the prepared samples were measured in order to identify whether the incorporation of POSS nano-particles has any effect on the electrical conductivity. All samples possess a low sheet resistance of 3 to 4 \( \Omega/\square \) at temperatures ranging from 25°C to 250°C, independent to POSS content.

In addition, all the measured samples exhibit the same variable range hopping conductivity mechanism as evident from the linear fit of the measurements to the \( T^{-1/4} \) model.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>3D-C POSS coating</th>
<th>Polyimide POSS content</th>
</tr>
</thead>
<tbody>
<tr>
<td>D15</td>
<td>No POSS</td>
<td>No POSS</td>
</tr>
<tr>
<td>D17</td>
<td>No POSS</td>
<td>15 wt% Trisilanolphenyl</td>
</tr>
<tr>
<td>D18</td>
<td>Aminopropylisobutyl</td>
<td>15 wt% Trisilanolphenyl</td>
</tr>
<tr>
<td>D19</td>
<td>Aminopropylisobutyl</td>
<td>No POSS</td>
</tr>
</tbody>
</table>

Table II: POSS content combinations on the 3D-C and in the polyimide that were examined.

**Table I: Comparison of the thermal conductivity of various reported filler-PI composite film**

<table>
<thead>
<tr>
<th>Filling Factor</th>
<th>Thermal Conductivity [W m(^{-1}) K(^{-1})]</th>
<th>Normalized increase per 0.1% filling factor*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Bare PI</td>
<td>Filled PI</td>
</tr>
<tr>
<td>SiC nanowires</td>
<td>7</td>
<td>0.25</td>
</tr>
<tr>
<td>on graphene</td>
<td>11</td>
<td>0.25</td>
</tr>
<tr>
<td>MWCNTs</td>
<td>3</td>
<td>0.18</td>
</tr>
<tr>
<td>BN-c-MWCNTs</td>
<td>3</td>
<td>0.18</td>
</tr>
<tr>
<td>Silver particles</td>
<td>45</td>
<td>0.2</td>
</tr>
<tr>
<td>BN</td>
<td>30</td>
<td>0.18</td>
</tr>
<tr>
<td>Aluminum nitride</td>
<td>30</td>
<td>0.22</td>
</tr>
<tr>
<td>Nanoparticles</td>
<td>10</td>
<td>0.26</td>
</tr>
<tr>
<td>3D-C</td>
<td>0.35</td>
<td>0.3</td>
</tr>
</tbody>
</table>

*Normalized increase per 0.1% filling factor = \( \frac{\text{Conductivity of Filled PI - Conductivity of Bare PI}}{0.1\%} \).
The samples were exposed to AO using a ground-based apparatus at Montana state university. A pulsed, hyperthermal, O-containing beam is produced with a laser detonation source, operating at a repetition rate of 2 Hz. The AO beam contains O atoms that are generated by the laser-induced breakdown of O₂ gas in a conical nozzle with the use of a 7-joule-per-pulse CO₂ laser. The samples were exposed to 5 eV atomic oxygen equivalent fluences of 7.2×10^{19} AO/cm² and 2.7×10^{20} AO/cm².

with pure PI matrix, showing values of ~5×10^{-25} cm³/AO and ~2.4×10^{-24} cm³/AO respectively. Additionally, it was noticed that the erosion yield of samples with 3D-C scaffolds without POSS is comparable to that of 3D-C POSS coated scaffolds. These results are expected as the PI matrix makes up the majority of the composite film mass; hence reducing its erosion yield will significantly reduce the erosion yield of the entire composite.

In conclusion, the infusion of 3D-C in PI has significantly increased its thermal and electrical conductivity with no weakening induced to its polymer structure and it is readily applicable for space applications and potentially for flexible electronics.

3. 3D-BNC COMPOSITE AS A SELF-RESISTIVE HEATING SHAPE MEMORY POLYMER

Shape memory polymer (SMP) is a special type of polymer defined as a smart material that can alter its shape from a deformed shape (temporary shape) back to its original shape (permanent shape) induced by an external stimulus (trigger). Unlike traditional mechanical actuators and other shape memory materials such as shape memory alloys (SMAs), SMP’s have a lower density, lower weight, lower production cost, are easier to process, and have larger recoverable strains comparable to that of SMAs.

SMPs are usually poor conductor for heat with low operational frequency and narrow bandwidth. This hinders their use as large area actuators due to the high potential of cracking and damage to the structure. The high cracking potential is a result of the non-uniformity of heat spread caused by the polymer low thermal conductivity. This non-uniformity in the SMP temperature will cause internal strains on the structure during the activation heating process, as parts of it will reach temperatures lower than the polymer glass transition temperatures (T_g) while other parts will reach higher temperatures.

A solution can be found in the use of 3D interconnected 2D-materials networks, such as 3D-C, BNC and a combined h-BN and graphene into BNC. As noted previously, h-BN and graphene possess high thermal conductivities, with graphene reaching ~3000 W/mK and h-BN reaching ~2000 W/mK. However, their electrical behavior is different. Graphene is a highly electrically conductive material while h-BN is electrically insulating with a wide bandgap of ~5.8 eV. BNC hybridized both characteristics and renders a tunable electrically conductive material.

In the presented example the thermal and electrical conductivity of epoxy-based SMP are enhanced by incorporating minimum loading fractions of 0.3 vol% of 3D-foams into the SMP matrix. The incorporation of
the 3D-foams into the epoxy SMP lead to a more efficient transfer of heat, which improves the response of SMP shape transformation, increases the speed of the shape changing process three-fold, enables an increase in the total shape memory active area, the reduction of the input power by 20% and additionally, through the use of 3D-BNC, to add a self-resistive heating capability to the SMP.

3.1 Characterization

Figure 7 depicts a cross-sectional SEM view of foam infused with SMP. The shadowed structures inside the polymer block correspond to parts of the foam. It can be seen that the foam spreads homogenously throughout the entire cross-sectional area of the SMP. The foam expands uniformly throughout the entire structure, however it requires only a volume (weight) fraction of 0.3 vol% (0.35 wt%) and due to the ultra-light density of the foams (1 – 5 mg cm⁻³), the overall material does not change in weight or original density through the infusion step. In addition, the incorporation of the 3D foams does not change the material’s glass transition temperature (T_g~60°C) ¹⁰.

The improvement in the thermal and electrical properties of the SMP was measured and compared to the values of the bare epoxy SMP. The thermal conductivity was measured using the laser flash technique at room temperature (RT) and above the glass transition temperature of the SMPs at 60°C. The electrical conductivity measurements were obtained using the 4-point probe Van-der-Pauw method. The results are summarized in Table III.

Table III: Summary of important characteristics of SMP and 3D-foam infused SMPs ¹⁰

<table>
<thead>
<tr>
<th></th>
<th>Bare SMP</th>
<th>SMP-C</th>
<th>SMP-BN</th>
<th>SMP-BNC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Filling factor</td>
<td>-</td>
<td>0.3 vol%</td>
<td>0.3 vol%</td>
<td>0.3 vol%</td>
</tr>
<tr>
<td>Decomposition temp.</td>
<td>280.7 °C</td>
<td>280.6 °C</td>
<td>282.3 °C</td>
<td>288.2 °C</td>
</tr>
<tr>
<td>Glass transition temp.</td>
<td>58.4 ±3 °C</td>
<td>56.7 ±3 °C</td>
<td>53.6 ±3 °C</td>
<td>52.6 ±3 °C</td>
</tr>
<tr>
<td>Thermal conductivity, RT</td>
<td>0.090 ±0.003 Wm⁻¹K⁻¹</td>
<td>0.361 ±0.017 Wm⁻¹K⁻¹</td>
<td>0.157 ±0.007 Wm⁻¹K⁻¹</td>
<td>0.21 ±0.010 Wm⁻¹K⁻¹</td>
</tr>
<tr>
<td>Thermal conductivity, 60 °C</td>
<td>0.103 ±0.006 Wm⁻¹K⁻¹</td>
<td>0.341 ±0.003 Wm⁻¹K⁻¹</td>
<td>0.145 ±0.016 Wm⁻¹K⁻¹</td>
<td>0.17 ±0.007 Wm⁻¹K⁻¹</td>
</tr>
<tr>
<td>Sheet resistance</td>
<td>20000 TΩcm⁻¹</td>
<td>40 TΩcm⁻¹ (bare 3D-C)</td>
<td>63.9 TΩcm⁻¹ (bare 3D-BN)</td>
<td>24580-230 TΩcm⁻¹ (bare 3D-BNC)</td>
</tr>
<tr>
<td>Strain recovery rate R_s</td>
<td>98 ±0.04%</td>
<td>97.1 ±0.03%</td>
<td>99.4 ±0.01%</td>
<td>94.6 ±0.06%</td>
</tr>
<tr>
<td>Shape fixity rate R_f</td>
<td>98.5 ±0.05%</td>
<td>98.6 ±0.01%</td>
<td>97.3 ±0.02%</td>
<td>97 ±0.05%</td>
</tr>
<tr>
<td>Tensile strength</td>
<td>31 MPa</td>
<td>30.6 MPa</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Elongation at break</td>
<td>26.2%</td>
<td>2.8%</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Young’s modulus</td>
<td>960.83 MPa</td>
<td>1176.98 MPa</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Figure 7: Cross-sectional SEM image of SMP infused with 3D-foam ¹⁰

The shape memory properties were examined through dynamic mechanical analysis (DMA) and are presented in Table III. During the experiment the DMA monitored the stress, strain, and displacement while the samples underwent temperature changes and force application. The test was repeated 4 times and 60°C was used as heating temperature, which is higher than the glass transition of all samples. The required force for inducing shape transformation was assessed prior to cyclic testing through a force ramp at 60°C inside the DMA. A final force of 2 N was chosen for all samples. These results are represented as three-dimensional stress-strain-temperature curves (“shape memory behaviour” curves) in Figure 8. The schematics in shown in Figure 8b explain the process of the testing: first, the sample is clamped and stabilized inside the DMA; afterwards the temperature is ramped up to 60°C.
After reaching 60°C, a force of 2 N is applied on the sample, which remains stable while the sample is subsequently cooled down (shape fixing). In the next step, the force is released, and the temperature is raised again to 60°C. This makes the SMP switch back to its original flat permanent shape (shape recovery). When the original shape is recovered and stable 60°C reached, the force is re-applied and the process is repeated. Through these cyclic tests, the strain fixity rate $R_f$ and the strain recovery rate $R_r$ can be determined.

For each number of cycles $N$, $R_r$ quantifies the ability of the material to recover its permanent shape; $R_f$ quantifies the ability to hold the applied mechanical deformation during the process. These parameters are calculated through the following ratios:

$$R_r(N) = \frac{\varepsilon_m - \varepsilon_p(N)}{\varepsilon_m - \varepsilon_p(N-1)} \times 100$$

$$R_f(N) = \frac{\varepsilon_p(N)}{\varepsilon_m} \times 100$$

Where $\varepsilon_m$ represents the temporary shape’s mechanical deformation, $\varepsilon_p(N)$ the permanent shape’s mechanical deformation after $N$ cycles and $\varepsilon_p(N-1)$ the residual of strain after retraction in the $N$th cycle. Ideally $R_f$ and $R_r$ should be 100%. The results are shown in Table III.

$R_r$ was found to be 98±0.04%, 97.1±0.03%, 99.4±0.01%, 94.6±0.06% for the bare SMP, SMP/3D-C, SMP/3D-BN and SMP/BNC respectively. In addition, $R_f$ was found to be 98.5±0.05%, 98.6±0.01%, 97.3±0.02%, 97±0.05% for the bare SMP, SMP/3D-C, SMP/3D-BN and SMP-BNC respectively. These results indicate that the incorporation of the 3D-foams into the epoxy SMP does not change or obstruct the shape memory performance of the polymer.

### 3.2 Shape memory performance improvements

In order to examine the thermal conductivity enhancement achieved by using 3D-fillers, two equally sized SMP pieces, one bare and one with 3D-C filler, were deformed into the same shape and placed simultaneously on a heating stage. This way, their temporary to permanent transition speed of transformation was compared. The 3D-C infused SMP returned to its original shape within 45 seconds while the bare epoxy SMP returned to its original shape after 2 minutes.

In order to quantify the uniformity of heat transfer of 3D-foam infused SMP, the thermographic image of a 3D-BN/SMP sample was compared to an image of the bare SMP. The samples used were SMP molded into two 1 cm × 7 cm slabs with carbon wires embedded in the sample edges as integrated resistive heating elements. One of the two samples includes a 1.1 cm × 2.4 cm (1.8 mm thick) 3D-BN embedded across the top part of the slab.

The 3D-BN is expected to serve as a heat conductor, transferring heat from the carbon fiber heaters embedded at the edges to the center of the SMP slab, potentially reducing the temperature gradient across the sample. Figure 9a shows the average temperature measured for...
each of the samples as a function of the power used for heating the carbon wires, normalized by the sample mass.

During the heating process, non-uniformities in temperature may cause parts of the material to have a temperature higher than the glass transition temperature while others remain below it. This will cause parts of the material to be in a rubbery state while other parts remain solid, giving rise to internal non-uniform strains that can produce mechanical failure in the form of cracks. The improvement in the uniformity was clearly seen in a test involving two larger pieces (7 cm x 1.5 cm) of bare SMP and 3D-C/SMP. The samples were deformed into the same shape and heated up by applying a constant current onto an embedded wire. The results of the experiment are depicted in Figure 10. The poor heat transfer in the bare SMP caused stress at the bent area, leading to a failure in the form of a crack spreading along the bend point. The 3D-C/SMP sample returned back to its permanent shape without any damage, clearly showing the advantage of the uniformity of the heat spread through the 3D-foam.

Normalizing by the sample mass is required to compare the results of the different samples, as heating a larger mass will require more energy and therefore result in higher power consumption. These measurements clearly show that heating the 3D-BN/SMP sample needs measurably less power than heating the reference SMP sample. The 3D-BN/SMP sample requires ~20% less power (4.89 W g\(^{-1}\)) than the reference sample (6.25 W g\(^{-1}\)) in order to reach an average temperature of 139°C. Moreover, the addition of 3D-BN to the SMP reduced the temperature gradient measured on the sample surface, thus making the temperature more uniform across the sample. This effect is observed in the reduced standard deviation measured for the 3D-BN/SMP sample, as seen in Figure 9b. 3D-BN not only significantly reduced the amount of power needed in order to heat the SMP up beyond its glass transition temperature, but also increased the temperature uniformity in the center of the SMP sample, minimizing the temperature gradient present in the sample, thus making the sample less susceptible to internal mechanical failure.

3.3 Joule heating capability

For most practical SMP applications, internal Joule heating (resistive heating) is necessary. This can be achieved through the use of materials such as 3D-C or 3D-BNC embedded in the polymer matrix. These 3D-fillers would not only render an internal resistive heating element, but as shown also improve the SMP’s overall performance.

The Joule heating properties of the 3D-BNC were demonstrated using an 85 at% BN 15 at% C sample before and after it was infused with SMP. The sample was connected to a Keithley source meter 2400 via two wires and simultaneously monitored under thermal camera. The current running through the samples was then gradually ramped up, while monitoring the heat distribution under thermal camera. Before taking the image, the temperature of the sample was measured with a thermocouple to ensure the accuracy of the measurement. Throughout the measurement, the sample was kept suspended with minimum thermal contact to other surfaces.
The results are shown in Figure 11(a,b). It can be seen that after the infusion of SMP, there is an increased in the measured resistance. It is likely that the infusion and curing process of the SMP produced some structural change to the 3D-BNC that caused this increase. In addition, the SMP infused sample reached similar temperatures to the bare sample for the same current. This may indicate that the effect of resistance increase and reduction of surface area in contact with air balanced off the effect of increased mass of the sample.

**Figure 11**: Temperature and voltage as a function of heating current and thermal image at 30 mA for (a) bare 85 at% BN 15 at% C and (b) SMP infused 85 at% BN 15 at% C sample. (c) Comparison of simulated results for BNC/SMP with measured results.10

A simulation using COMSOL® Multiphysics was implemented and its results were compared to the measured normalized results and are presented in Figure 11c. The comparison shows that the model used for the SMP infused 3D-BNC is in relatively good agreement with the experimental results for several foam compositions and applied power. Therefore, this model can be used to design self-resistive heating SMP for given dimensions temperature and electric input. Thus, those input parameters will determine the resistivity required for the 3D-BNC, which in turn determines the BN:C ratio.

Hence, the integration of 3D-Foam into SMP represents a new concept of combining extrinsic and intrinsic multi-SMP properties, which allows the use of SMP for larger area applications with a more practical and efficient heating mechanism. Moreover, as the infusion with 3D-foam does not affect the shape memory performance at all and is completely independent from the polymer, this concept can be adapted to any kind of shape memory polymer.

### 4. CONCLUSION

The advantages of implementing 3D-Foams into composite materials have been demonstrated for two potential space applications.

In the first example a composite film composed of PI and 3D-C demonstrated greatly enhanced thermal conductivity (enhanced by 1033%) as well as electrical conductivity (enhanced by 10 orders of magnitude). These enhancements were achieved using a low filling fraction (0.3 vol%, 0.35 wt%) and did not affect the films intrinsic flexibility and mechanical strength. In addition, simulated space environment test results show that gamma radiation has no effect on the composite’s electrical conductivity, and its outgassing properties are compliant with the European Cooperation for Space Standard (ECSS). Furthermore, exposure to AO fluence revealed that implementing POSS into the composite film reduces the reaction yield by a factor of 5, from ~5 ×10^{-25} cm^2/AO to ~2.4×10^{-24} cm^2/AO.

In the second example 3D-Foams (3D-C, 3D-BN, and 3D-BNC) were infused into a SMP matrix. Thus, thermal conductivity was improved from 1.5 to 4-fold over bare SMP without affecting the intrinsic properties of the SMP, such as thermal decomposition profile, Tg and shape memory performance. The enhanced homogeneous thermal conductivity leads to a larger area, where uniform heat spreads, reducing by 20% the total energy input required to trigger the SMP. In addition, tuneable self-heating characteristics were demonstrated through the use of 3D-BNC infused SMPs.

Currently, 3D-foams are considered for a variety of applications that take advantage of their superior thermal and electrical properties. Composites containing 3D-foams are tested for a vast array of potentially space related applications, showing promising results. These applications range from traditional thermal interface materials to electrodes for fuel-cells and photovoltaic devices. Thus, the use of 3D-Foams such as 3D-C, 3D-BN, and 3D-BNC is expected to improve existing material solutions and enable new applications.

### REFERENCES

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