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**3D-C/SHAPE MEMORY POLYMER COMPOSITE FOR
SPACE DEPLOYABLE APPLICATIONS**

RANJANA SHIVAKUMAR

School of Electrical & Electronic Engineering

A thesis submitted to the Nanyang Technological University
in partial fulfilment of the requirement for the degree of
Doctor of Philosophy

2020

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research, is free of plagiarised materials, and has not been submitted for a higher degree to any other University or Institution.

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Ranjana Shivakumar

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I have reviewed the content and presentation style of this thesis and declare it is free of plagiarism and of sufficient grammatical clarity to be examined. To the best of my knowledge, the research and writing are those of the candidate except as acknowledged in the Author Attribution Statement. I confirm that the investigations were conducted in accord with the ethics policies and integrity standards of Nanyang Technological University and that the research data are presented honestly and without prejudice.

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Assoc Prof Teo Hang Tong Edwin

Authorship Attribution Statement

This thesis contains material from two paper(s) which is submitted for publication in the following peer-reviewed journal(s).

Chapter 4 submitted for publication as **Shivakumar. R.**, Leong F., Tsang, S.H., and Teo. E. H. T. (2020) Effect of loading fraction of three-dimensional graphene foam (3D-C) on thermal, mechanical and shape memory properties of 3D-C/SMP composite. *Materials Research Bulletin*.

The contributions of the co-authors are as follows:

- Dr. Tsang Siu Hon provided the initial project direction.
- I wrote the drafts of the manuscript. The manuscript was revised together by Assoc Prof. Teo Hang Tong Edwin and Dr. Tsang Siu Hon.
- I performed all the composite material synthesis, conducted characterization experiments and data evaluation.
- Mrs. Fei Ni Leong performed the 3D-C Graphene foam synthesis.

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- Dr. Tsang Siu Hon provided the initial project direction and edited the manuscript drafts.
- I prepared the manuscript drafts. The manuscript was revised by Dr Asaf Bolker, , Dr Nurit Atar, Prof. Teo Hang Tong Edwin and Dr Tsang Siu Hon.
- Sample preparation and characterization was conducted by me at NTU.
- POSS-PI sample preparation and PI infusion was done by Ms. Mor Hala and Ms Nehora Moshe at Soreq NRC, Israel.
- Data analysis was done by me, with assistance from Dr Asaf bolker for measurements done at Soreq.
- Dr Ronen Verker and Dr Irina Gouzman were guiding the infiltration process.
- Atomic oxygen exposure test was conducted by Prof. Timothy. K. Minton and Ms. Alexandra Jones at Montana State University.

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Abstract

Large components such as solar panels, solar sails and antenna in the satellite are generally designed as deployable structures, that are stowed during launch and deployed in orbit using electromechanical deployment systems. The structural integrity, reliability, weight and stowage volume of the deployment system are always critical factors to be accounted for satellite design. The traditional deployment mechanism has certain drawbacks such as increased mass, stowage volume, high cost and failure modes. Smart deployable structures using shape memory materials are being researched extensively due to their lightweight, low cost, ability to be packed easily and controllable deployment. In this thesis, I have developed and tested a new smart material using three- dimensional graphene (3D-C) and shape memory polyimide (SMPI) which can be used to build a simple, reliable, and low-cost self-deployable component for space.

Any material developed for space should be resilient to harsh environmental conditions such as atomic oxygen (AO), ultraviolet and ionising radiation, extreme thermal cycles and vacuum. Polyimides (PIs) are a suitable candidate for space application due to their high thermal stability, excellent radiation shielding capacity, and high glass transition temperature. Recently, several shape memory polyimides (SMPIs) were developed by combining the shape memory effect with the excellent mechanical and thermal properties of PI to extend their application to deployable satellite structures. However, they have poor thermal conductivity leading to non-uniform temperature distribution and increased time to conduct heat throughout the SMPI. Since the majority of the SMP are heat activated, the poor thermal conductivity leads to a large thermal gradient across the material. The large temperature gradient results in non-uniform shape recovery leading to internal stress and eventually crack formation. Their poor thermal conductivity hinders

their application and reliability as large area actuator. Hence in this thesis, 3D-C with high electrical and thermal conductivity is combined with SMPI's good mechanical strength and environmental stability.

First, the effect of loading fraction of 3D-C interconnected filler on the properties of epoxy-based shape memory polymer (SMP) is studied. A series of 3D-C/SMP composite with different volume fractions of 3D-C (0.1 to 1.5 vol.%) are prepared, and their thermal, mechanical and shape memory properties are studied and compared. It is observed that, as the 3D-C content increases, the thermal conductivity of the composite increases and as well as the shape transformation performances. However, interestingly, in conflict with typical nanofillers, the mechanical strength decreases at higher loading fraction due to the obstruction of polymer chains by interconnected branches. Hence, to leverage on the extraordinary improvement of thermal conductivity by 3D-C, a careful design based on the amount of loading is essential to obtain a balance between thermal conductivity, mechanical strength and shape memory performance. Proofs of concept experiments are also conducted to demonstrate the applicability of 3D-C/SMP composites for large area actuator as well as tape spring hinge design.

3D-C/SMPI composite is synthesised by infusing 60 ppi 3D-C (foam with large pores) with a viscous PAA followed by thermal imidization. The developed 3D-C/SMPI composite exhibits greatly enhanced thermal conductivity (500%), high glass transition temperature ($\sim 175^{\circ}\text{C}$) and thermal decomposition temperature (5% weight loss at $\sim 500^{\circ}\text{C}$), showing excellent thermal stability required for space application. 3D-C/SMPI also demonstrates good shape memory behaviour with high shape fixity (97.6%) and shape recovery (90.27%) in the third thermomechanical cycle with stable electrical and shape memory behaviour after ground-

stimulated space environmental tests. 3D-C/SMPI composite exhibits good compatibility with the GEO environment as well.

To increase the lifetime of the composite at LEO altitudes, AO exposure study of 3D-C/PI (Polyimide similar to Kapton), is conducted. Polyhedral Oligomeric Silsesquioxane (POSS) is added to 3D-C or PI or both and the resulting composite's AO durability, electrical and mechanical properties are compared. It is revealed that adding POSS to PI, reduces the erosion yield to $4.67 \times 10^{-25} \text{ cm}^3/\text{O-atom}$ (one order of magnitude lower than that of Kapton), extending its durability beyond 10 years in Low earth orbit. Adding POSS to 3D-C alone does not seem to have any significant effect on the AO durability since the majority of the film mass is PI. Thus, the films with unprotected PI have an erosion yield similar to pure PI films.

Lastly, the utilisation of 3D-C/SMPI in deployment mechanism is also investigated by building two shapes of 3D-C/SMPI samples. A box-shaped 3D-C/SMPI is fabricated with an infused heater to demonstrate the high complexity sequential deployment of a multi-joint structure. The seamless shape recovery process of the box into a flat structure is seen, demonstrating the feasibility of large area actuator with 3D-C infused SMPI. The sample is scheduled to be launched and tested in space (in collaboration with SaRC, NTU). It is being subjected to a series of pre-flight qualification tests including launch vibration test and thermal vacuum cycling test. The model is intact after being subjected to launch vibrational loads (acceleration levels of 7g in longitudinal and 2.5g in the lateral axis). In addition, a tape spring shaped 3D-C/SMPI sample is fabricated, demonstrating the ability of the SMPI to be manufactured as a hinge structural material with the addition of 3D-C. The developed 3D-C/SMPI material can be used in small deployable mechanisms (hinges or release devices) as well as large structural members.

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List of Abbreviations

2D	two-dimensional
3D	three-dimensional
AlN	aluminium nitride
AO	atomic oxygen
BN	boron nitride
CNF	carbon nano fibre
CNT	carbon nanotube
CVCM	collected volatile condensable material
CVD	chemical vapour deposition
DMA	dynamic mechanical analysis
DMAc	dimethylacetamide
DSC	differential scanning calorimetry
EMC	elastic memory composite
EMI	electromagnetic interference
ESD	electrostatic discharge
FTIR	fourier transform infrared
GEO	geosynchronous equatorial orbit
GPS	global positioning system
HOPG	highly oriented pyrolytic graphite
IR	infrared
LEO	low earth orbit
LED	light emitting diode
Ni	nickel
PAA	poly(amic acid)

PCM	phase change material
PCL	polycarprolactone
PDMS	polydimethylsiloxane
PI	polyimide
PMMA	poly(methyl methacrylate)
POSS	polyhedral oligomeric silsesquioxane
ppi	pores per inch
PVDF	polyvinylidene fluoride
RML	recovered mass loss
SEM	scanning electron microscopy
SiC	silicon carbide
SMP	shape memory polymer
SMPI	shape memory polyimide
TVAC	thermal vacuum chamber
TCVD	thermal chemical vapour deposition
TGA	thermogravimetric analysis
THF	therahydrofuron
TIM	thermal interface material
TML	total mass loss
TrGO	thermally reduced graphite oxide
TSP	trisilanophenyl
UV	ultraviolet
VRH	variable range hopping
WVR	water vapour regained
XPS	X-ray photoelectron spectroscopy

1 Introduction

1.1 Background

Currently, satellites are being used in almost all applications such as ground mapping, weather forecasting, communications, global positioning (GPS), disaster management and for basic science such as studies on atmosphere, astronomy and space exploration. Satellites are always expensive to design, build and launch as well as impossible to repair. Any malfunctions or repair in one system leads to decommissioning of the whole satellite (along with other functional systems onboard), potentially wasting the money and materials. The reliability of all the components in the satellite is a critical factor. The performance requirement of the components in the aerospace sector is one of the major driving forces for the development of advanced materials. New advanced materials are being developed to obtain improved efficiency (performance) at low cost (easy fabrication) and lightweight. The key factors to be accounted for, while developing a space material, includes mechanical properties, weight, physical properties such as resistance to corrosion and the ability to withstand harsh environmental conditions in space. The materials used in space are constantly exposed to atomic oxygen (AO), ultraviolet (UV) and ionising radiation, plasma, extreme thermal cycles (-120 °C to +120 °C every orbital cycle), vacuum and impact of tiny meteoroids and space debris.¹⁻⁴

Due to the limited space available in the launch vehicle, most of the satellite structures are designed as appendages.⁵ Components such as antenna and solar panels are stowed and secured during transportation into space. Once the satellite is placed in its orbit, the secured structures will be translated or rotated from their stowed position to deployed configuration by a deployment device. The appendages are stowed in compact volume and deployed into large surface

area/volume in space. A typical example is the deployable solar panel, which is stowed during launch and deployed in orbit to provide for the power requirement of the satellite.⁶ The complete mission success is highly reliant on the deployment process and in turn, the deployment device should be built in a way to provide high deployment reliability. Thus, it is significant to design the deployable structures with higher reliability.⁷

Traditional approaches for deployment incorporates explosive techniques or electromechanical mechanisms to initiate the actuation.⁸ Associated with it are certain drawbacks such as complex process, increased mass, stowage volume, high cost, and massive impacts during deployment. Although the mechanism meets the MIL-DTL- 23659 standard/requirement of separation devices, use of explosives has issues associated with it, such as significant impacts during deployment. It requires extensive safety measurements leading to higher mission cost. The pyrotechnic devices generate great shock ($>1000G$, at high frequency), which might induce physical damage to the satellite or malfunctioning of the electrical components. This might eventually lead to mission failure.⁹ Rather than structural failure, equipment such as relays or glass oscillators are more affected by high-frequency shock. Besides, there will be more mechanical parts to deploy the structures fully and to maintain the deployed configuration. These deployment mechanisms and the associated support structures contribute to more than 90% of the total mass budget.¹⁰ Reducing the cost of the satellite and increasing reliability is the primary factor that demands the development of a new deployment system using smart materials. This ongoing challenge in the aerospace industry has driven National Aeronautics and Space Administration (NASA) to investigate and develop new approaches for deployment with lower mass and smaller launch volume.¹¹ Shape memory polymers and their composites, a new class of smart materials are drawing more and more attention towards smart deployable structures due to their lightweight,

ease of fabrication, low cost, ability to be packed easily and controllable deployment.¹²⁻¹⁴

There are many studies on developing smart deployable structures for space using fibre reinforced shape memory polymer composites.¹⁵ In recent years, prototypes of several space-deployable components such as hinges, booms and trusses are being developed using shape memory composites and tested for their ability to deploy solar panels, antenna and other structures.¹³ Several shape memory deployable hinges were built using shape memory polymer (SMP) matrix and filler material such as carbon fibre.¹⁶⁻¹⁹ All these hinges are stimulated using heat through electrical resistive heating. Polyimides are known for their excellent radiation shielding capability and high transition temperature, making them a more suitable candidate for space applications in comparison to shape memory polymers studied so far. Polyimides are widely used in aerospace structures due to their high thermal stability, elastic modulus and tensile strength.²⁰ Most recently there has been a great deal of research carried out on developing shape memory polyimides (SMPI) - combining the shape memory effect with the excellent mechanical and thermal properties of PI to extend its application to the satellite deployment sector.²¹⁻²⁸

The main limitations for the application of the SMP in deployment systems are their low recovery stress (due to lower modulus), slow response time, low cycle life, weak material stability, and poor thermal conductivity.¹⁵ The poor thermal conductivity [$\leq 0.3 \text{ Wm}^{-1}\text{K}^{-1}$] is a major drawback that causes non-uniform heat distribution and increased time to conduct heat throughout the SMP,²⁹ limiting its application to smaller structures. The non-uniform temperature distribution creates high-temperature gradient at certain places which in turn results in internal stress and cracks hindering their application and reliability as large area actuator. Furthermore, SMPs are electrically insulating, preventing their application in a vast sector. The hinges developed using shape memory polymer and fibre-reinforced shape memory polymers, have external heaters bonded on the surface

or embedded inside the surface of the hinges to heat the SMP to actuate the deployment. The surface-bonded heaters have some disadvantages such as micro buckling resulting in de-bonding and heat loss to the external environment through radiation. The embedded heater wires are also vulnerable to buckling in the direction perpendicular to the hinge folding axis.³⁰ Many have attempted to increase the thermal conductivity by adding conductive fillers^{31,32} such as CNTs,³³⁻³⁵ talc and glass fibre,³⁶ aluminium nitride and boron nitride,^{37, 38} carbon fibres,³⁹ carbon nanofibers,⁴⁰ nanopaper,⁴¹ and other metallic fillers. While these fillers improve the recovery stress and thermal conductivity, they also decrease the shape recovery or fixity by arranging themselves into networks (agglomeration and inhomogeneous distribution).^{29,38} Thus, a more significant part of research goes into finding a filler material which improves the thermal conductivity without altering the shape memory properties of the SMP.

While many are still focusing on fibre based composite materials for various applications, there has been an increasing interest on porous three-dimensional Graphene (3D-C)⁴² foam-like structure synthesised by chemical vapour deposition (CVD).⁴³ It has the properties of both 2D and 3D graphene structures⁴⁴ such as high specific surface area, good mechanical strength, flexibility, excellent electrical properties and thermal conductivity with low density and good stability.^{43, 45, 46} These properties have made 3D-C a promising candidate for application in various fields such as energy storage and conversion (batteries, solar cells, fuel cells, supercapacitors),⁴⁷⁻⁵⁰ thermal management,⁵¹ sensors (chemical and mechanical),⁵²⁻⁵⁴ biological/medical applications,⁵⁵ and as multifunctional materials in aerospace systems for electromagnetic interference (EMI) shielding.^{56, 57} 3D-C as a filler for polyimide (PI) helped to improve the overall thermal and electrical characteristics of the PI and in turn protect against electrostatic discharge for long term space applications.⁵⁸ The 3D-C/PI composite has good thermal and electrical conductivity suitable for

high power electronics and high-temperature applications. Also, 3D-C/PI demonstrated stable long-term space reliability. Furthermore, Arvind et al. studied the damping characteristics of 3D-C/PI composite exposed to its glass transition temperature. The composite showed excellent thermo-oxidative stability and also retained its damping characteristics making it a suitable material for developing “smart multifunctional” material in space.⁵⁹

1.2 Motivation

As seen in the previous section, many PI-based SMPs were synthesised and studied for space application.²¹⁻²⁸ However, these studies have focused only on the material and shape memory characteristics of these polyimides. Their potential to be utilised for deployable hinge system is yet to be studied in detail. Utilising SMPI for deployment systems in the satellite will be very interesting, as the SMPs could help to cater the need for critical design considerations^{60, 61} such as lightweight, less stowage volume, increased structural integrity and the reliability of the deployment mechanism of satellites. Besides, polyimides are a suitable candidate for space applications owing to their high thermal stability, high transition temperature and excellent radiation shielding capability.

On the other hand, polyimide's low thermal conductivity and electrically insulating characteristics are its main limitation for use in space structures. Since the transformation is actuated by heat, poor thermal conductivity causes non-uniform heat distribution resulting in non-uniform shape change. This, in turn, might cause internal stress build-up and crack formation during transformation. So far, 2D-filler based nanomaterials were used to improve thermal conductivity. But these fillers tend to agglomerate and affect the shape memory performance. Studies have shown that 3D-C can perform as a better filler material compared to other nanofillers

such that the thermal and electrical performance increases several folds without any reduction in the matrix properties.⁶² Furthermore, studies have demonstrated that infusing SMP into 3D-material helps to improve the overall thermal conductivity of the SMP and thus aid in faster shape memory transformation by rendering self-heating capability while preserving the shape memory properties of the polymer.

So far, 3D-C has been proven to be an effective filler material for polyimide thermal blankets (EMI shielding) and shape memory polymers (Self heating capability). As can be seen, there is still no study on combining 3D-C and shape memory polyimide. It is thus suggested to infuse SMPI into 3D-C, which potentially can yield a novel high-temperature smart material for space applications with high transformation temperature and better durability in low earth orbits. This material could be used to build deployment release devices such as hinges and large deployable structural members such as panels and booms.

1.3 Objective

The primary focus of this thesis is to provide the space industry with a new high-temperature smart material for spacecraft deployable structures, which can be implemented to design, build and develop a simple, reliable and self-deployable hinge structure. This will be achieved by combining the flexibility, excellent electrical properties and thermal conductivity of low-density 3D-C filler material with that of the shape memory polyimide's high thermal and environmental stability.

To facilitate preliminary assessment on the effect of 3D-C loading fraction on the SMP properties, 3D-C will be first infused into an epoxy-based shape memory polymer (SMP). Effect of the 3D-C filling fraction on the SMP will be studied to determine the optimum filler loading

required to obtain the desired results without any detrimental influence on the SMP's intrinsic properties. Mechanical assessment on the hinge design will be conducted by setting up a force measurement system to determine the force exerted by the SMP composite hinge. The hinge prototype for the test will be developed using 3D-C and epoxy-SMP.

In parallel, a shape memory polyimide (SMPI) with high glass transition temperature will be selected from literature, synthesised and infused with 3D-C. The 3D-C/SMPI composite material will be subjected to material characterisation and space qualification tests.

Finally, a few proofs of concept samples for demonstrating the complex deployment mechanism will be built using 3D-C/SMPI composite. These samples will prove the usefulness of 3D-C in utilising SMPI for deployment system that is functional in space.

The key objectives are summarised as follows,

- To study the effect of 3D-C filler content on the shape memory polymer properties. Select an optimum hinge design by measuring the force exerted by the 3D-C/SMP composite during recovery.
- Integration of 3D-C into SMPI matrix and to confirm the quality and performance of the 3D-C/SMPI composite.
- Space qualification of 3D-C/SMPI.
- Polyhedral Oligomeric Silsesquioxane (POSS) study to improve AO durability of the 3D-C infused PI in the LEO environment.
- To Develop a box-shaped 3D-C/SMPI and a tape spring shaped 3D-C/SMPI prototype as a proof of concept and confirm its performance in space.

1.4 Major contribution of this thesis

In this thesis, the first integration of 3D-C into SMPI is investigated, resulting in a novel shape memory composite material that has high thermal conductivity, ideal shape memory properties and high transition temperature suitable for space applications. The main challenge in PI synthesis for the deployment system is the limitation in the thickness of the film and the shapes that can be obtained by thermal imidization or coating methods. Here, a highly porous 3D-C foam and viscous polyamic acid (PAA) is used to fabricate polyimides with thickness in the range of 1-2mm. The electrical, thermal and shape memory properties of the 3D-C/SMPI composite material is studied followed by space qualification of the same. Finally, the usefulness of the 3D-C/SMPI composite material in forming a deployable structure for space is tested by developing a box-shaped complex sample and a tape spring shaped hinge sample. The major contributions of this research are explained below.

1.4.1 Effect of 3D-C loading fraction on SMP (Epoxy)

Understanding the effect of nanofillers on the properties of Shape memory polymer is vital to their application in deployable devices. 3D-C as a filler has been proven to improve the thermal conductivity efficiently and hence, the efficiency of shape transformation in epoxy-based SMP. However, the effect of loading fraction of such interconnected filler on the SMP properties is yet to be studied. Hence, a series of 3D-C/SMP composite with different volume fractions of 3D-C are first prepared, and the effect of the 3D-C filling fraction on the SMP properties are investigated to determine the optimum filler loading required to obtain the desired results without any detrimental influence on the SMP's intrinsic properties. As expected, the increase in the volume fraction of 3D-C increases the thermal conductivity of 3D-C/SMP composite with no loss in shape-

memory performance. Interestingly, in conflict with typical nanofillers, a reduction in mechanical strength is observed at higher loading fraction due to the obstruction of polymer chains by interconnected branches. Hence, to leverage on the extraordinary improvement of thermal conductivity by 3D-C, a careful design based on the amount of loading is essential to obtain a balance between thermal conductivity, mechanical strength and shape memory properties.

1.4.2 3D-C infused SMPI composite

Shape memory polyimides (SMPIs) are more suitable for high-temperature applications because of their excellent thermal, mechanical and shape memory properties. They have specific outstanding features such as high glass transition temperature, better durability to harsh environmental conditions, dimensional stability and good shape memory characteristics (shape fixity, shape recovery and rapid response). Despite the advantages, their application and reliability as large area actuator are affected by their poor thermal conductivity. Low thermal conductivity causes non-uniform heat distribution and increased time to conduct heat throughout the sample. The non-uniform temperature distribution leads to a high-temperature gradient at certain places which in turn results in polymer cracking. Here 3D-C is combined with SMPI, and the developed 3D-C/SMPI composite exhibits greatly enhanced thermal conductivity (by 500%), high glass transition temperature ($>170^{\circ}\text{C}$) and thermal decomposition temperature (5% weight loss at 500°C), showing excellent thermal stability required for space application. 3D-C/SMPI demonstrates good shape memory behaviour with high shape fixity and shape recovery.

1.4.3 Space qualification of 3D-C/SMPI

Any material developed for space should be resilient to harsh environmental conditions in space such as atomic oxygen (AO), ultraviolet and ionizing radiation, extreme thermal cycles and

vacuum. The reliability and long-term stability of the 3D-C infused SMPI composite in outer space is studied by ground-based space simulation tests. The composite material is subjected to thermal cycling, outgassing, and thermo-optical property measurements. The material is space qualified according to European Space standards. Standard 4-point electrical measurements are conducted before and after thermal cycling to quantify the effect of the space environment on the composite property.

1.4.4 POSS study for AO endurance

3D-C/SMPI composites are susceptible to atomic oxygen erosion in Low Earth Orbit (LEO). A ground-based AO exposure study is conducted on 3D-C/PI made from a polyimide similar to Kapton. Polyhedral Oligomeric Silsesquioxane (POSS) is used to enhance the AO durability of 3D-C/PI films. POSS is added to the composite films in three different ways, and all the samples are subjected to ground-based AO exposure. For all infusion approaches, their electrical conductivity behaviour is well preserved even after exposure, and the presence of POSS results in reduced AO erosion yield. Of all the methods used, it is seen that incorporating POSS directly into PI results in the lowest erosion yield of $4.67 \times 10^{-25} \text{ cm}^3/\text{O-atom}$ (One order of magnitude lower than that of Kapton). Adding POSS to PI, extends the durability of the composite film beyond ten years, making it an ideal material for long term mission in LEO. This study directs towards developing an SMPI matrix with POSS to improve the AO durability of 3D-C/SMPI composite.

1.4.5 Space deployable structures using 3D-C/SMPI

As proof of concept, a box-shaped 3D-C/SMPI sample of dimensions 4x3x3 cm is build using 3D-C/SMPI to demonstrate that 3D-C can be used to enhance the ability of shape memory polyimide to form a large surface area deployable structure. The model demonstrates the complex

sequential deployment of multi-joint structure built using 3D-C/SMPI. The sample will be tested for its functionality in space in collaboration with Satellite research centre (SaRC), NTU, Singapore. The box model is subjected to ground-based vibration test equivalent to vibrational loads experienced during launch (acceleration levels of 7g in longitudinal and 2.5g in lateral axis). The shape recoverability of the sample is tested under vacuum and room temperature inside a thermal vacuum chamber. Similarly, a tape spring shaped 3D-C/SMPI sample is fabricated, and its ability to be bent and recover its original shape without any crack formation is demonstrated.

1.5 Organization of this Thesis

Chapter 1 provides the background, motivation, objective and major contribution of this thesis. Chapter 2 introduces the concepts of shape memory deployment structures, as well as the applicability of shape memory polyimide and 3D-C foams for deployment. Chapter 3 summarizes the basic experimental set up for the synthesis and characterization of 3D-C infused shape memory polymer/polyimide. Chapters 4 to 7 present the stepwise implementation of the research objectives, which includes the study on the effect of the 3D-C filling fraction on SMP properties, synthesis and material characterization of 3D-C/SMPI and POSS study to improve the Atomic oxygen durability of 3D-C/PI. Chapter 8 describes the demonstration of the application of 3D-C/SMPI for deployable space system. Lastly, Chapter 9 gives a summary of the work accomplished in this thesis and future recommendations.

2 Literature review

2.1 Satellite deployable structures

Most of the structures in a satellite are folded and stowed during launch due to the limited space available in the launch vehicle as well as to avoid damage due to high vibrational loads experienced during launch.⁵ Several large structures are required for any space mission, for example, solar panels to provide for power requirements for the satellite. Solar panels and other space structures such as antenna, booms, optical mirrors, planetary detector and masts are also designed as deployable structures.^{6, 63}

A hinge is a deployable device used to drive the deployment process of structures such as solar panels.⁶⁴ Traditionally, explosive techniques (uncontrolled deployment) or electromechanical mechanisms (controlled deployment) are used to initiate the actuation.⁸ The complex system contributes to increased mass, stowage volume, high cost, and failure modes. The pyrotechnic devices generate great shock in the order of thousands of g's (>1000G) at high frequency (>GHz) inducing physical damage to the satellite components. The highest failure rate in a space system is experienced during deployment, but the system performs well after the successful deployment.⁶⁵ Two cases of mission failure caused by deployment system are Alexis (damaged solar array likely to be caused by breakage of attachment bracket after deployment) and Mars global surveyor (failure to launch solar array caused by structural failure of damper arm attach fitting).⁶⁶ Between 1964 to 2009, a total of 52 known failures were caused by deployment system anomaly.⁶⁷

Besides, there will be more mechanical parts to deploy the structures fully and to maintain the deployed configuration. These deployment mechanisms and the associated support structures

contribute to more than 90% of the total mass budget.¹⁰ Due to the complexity involved in the mechanical hinge and its actuation technique (illustrated in **Figure 2.1** and **Figure 2.2**), shape memory polymer, and its composites are attracting more attention towards developing smart deployable structures. These smart deployable structures can be used to achieve smooth, controlled deployment with a minimum amount of mechanical parts. This thesis deals with developing a smart material for deployable hinge only.

Figure 2-1. Sequential illustration of deployment of pulley actuated translational hinge system.⁶⁸

Figure 2-2. Pyrotechnic hinge deployment system. a) cable, and b) bolt cutters.⁶⁹

2.2 Shape memory polymer hinges

A hinge is a device that drives the deployment process of the satellite-deployable structures. The hinge should be capable of successful deployment, latching the structure after deployment, control latching shock by avoiding sudden deployment and prevent collision with other subsystems.⁶⁹ Conventional hinge types for deployable satellite structures are mechanical hinges (complex integrated system) and strain energy hinges (metal tape spring hinge). The mechanical hinge has intricate systems that are heavy and bulky with movable parts adding to the complexity. The tape-spring hinge produces significant shock effect during deployment making it undesirable for most space applications.^{64, 70, 71} This being the main challenge for the hinge deployment system in aerospace, paved the way for the development of smart material deployment system using shape memory polymers and their composites.

There have been multiple studies carried out on developing new types of hinge composed of smart materials to overcome the issues of conventional mechanical or metal tape spring hinge. The spring-steel hinges are simple and reliable compared to mechanical hinges but produces a large amount of shock upon deployment. The tape spring concept was first used in hinges as early as the 1960s. A self-actuating, self-locking tape spring hinge mechanism was developed in 1968.⁷² Later, the shock effect of this tape spring hinge model is reduced by adding a rubber material to the metal tape spring. This improved the stored strain energy and bending characteristics.⁷³ Besides, composite materials were also used to replace the metal tape springs.⁷⁴ Theoretical studies were also carried out to analyse the mechanical properties of the tape springs assembled in the equal and opposite sense under moments.⁷⁵⁻⁷⁷

The high shock effect of the tape spring hinge was addressed by the elastic memory composite (EMC) hinges providing controlled, low-shock deployment and increased structural efficiency. The EMC hinge was designed based on the conventional spring steel hinges which utilise the geometry/concept of the carpenter-tape. Here the tape spring was replaced by the EMC material reducing the moving parts and deployment shock. EMCs are fibre/fabric reinforced SMPs for self-deployable space structures. The composite is made of T-300 graphite fabric and tape pre-impregnated with EMC resin. The EMC hinge demonstrates good controlled deployment.^{30, 70, 78- 80} Besides, several different types of SMP composite hinges are being designed and studied time and again for space-deployable structures. Leng et al. developed a carbon fibre reinforced hinge with two circular curved thin shells in the opposite sense.¹⁶⁻¹⁹ The SMPC hinge prototype was tested for its shape recoverability by applying direct current for actuation, and the recovery stages were captured (**Figure 2-3**). The SMPC hinge is capable of successfully deploying a prototype of a solar array in 80 seconds. All these hinges are stimulated using heat through indirect actuation by the application of electrical current.

Figure 2-3. Shape recovery process of carbon fibre reinforced SMPC hinge developed by Leng et al.¹⁷

2.3 Shape memory polymers

Shape memory polymers (SMPs) are smart materials that are capable of changing their macroscopic properties such as shape and colour upon stimulation by external sources.^{15, 81-89} In other words, they can be fixed to a temporary shape and then recover their original shape when subjected to an external stimulus such as heat,⁹⁰ light,⁹⁰⁻⁹³ water/moisture,⁹⁴⁻⁹⁷ electricity,⁹⁸⁻¹⁰⁸ microwave,¹⁰⁹ and magnetic field.¹¹⁰⁻¹¹² Most typical SMPs are heat-induced and electrically induced. SMPs have unique advantages such as lightweight, low cost, low density, ease of fabrication, biodegradability and high shape deformability compared to shape memory alloys and ceramics.^{14, 113, 114} These properties make them a suitable material for deployable structures in the aerospace industry^{13, 17} along with a variety of applications in biomedicine,^{108, 115-120} and textiles.^{121, 122}

The different material properties, above and below the transition temperature (T_{trans}), defines the property of a shape memory polymer. Above the transition temperature, the polymer is in the rubber state (viscous material), and below the transition temperature, the polymer is in the glass state (elastic material). Around the transition temperature, viscoelastic behaviour is seen. The process of shape recovery follows a thermomechanical cycle, as shown in **Figure 2-4**. The steps involved are; (1) Fabricating the original (permanent) shape. (2) Heating above transition temperature and deforming to a temporary shape. (3) cooling below the transition temperature and fixing the temporary shape. (4) Reheating to increase the temperature and recover the original shape.

Figure 2-4. Schematic of thermomechanical cyclic process of a shape memory polymer.¹⁵

SMPs are made of two segments or phases, namely hard segments or fixed phase and soft segments or reversible phase. The hard segments are responsible for preventing polymer chains from moving around when stressed. The hard segments fix the original shape below T_{trans} . The soft segments facilitate the movement of the polymer chains when stressed above T_{trans} . The working mechanism can be explained as follows: When the SMP is heated above its transition temperature and deformed to a temporary shape, the polymer chains are displaced, and as a result, they overlap and form secondary crosslinks between them. This secondary crosslink holds the temporary shape after the SMP is cooled down (while the deforming force is held constant). Upon reheating to transition temperature without external stress, the secondary crosslinks break, and the SMP returns to its permanent shape determined by the hard segments.⁸¹ **Figure 2-5** illustrates the shape memory effect.

Figure 2-5. Schematic of the typical structure of a polymer network during the shape memory process.¹⁵

2.4 Types of shape memory polymers

SMPs are broadly classified into two types as thermoplastic and thermoset, based on their molecular structure. The hard segments responsible for the permanent shape can be either chemical cross-links (covalent bonding) or physical cross-links. Thermoset SMPs are a chemically cross-linked polymer, while thermoplastic SMPs are physically cross-linked. The switching temperature for thermoset SMP is the glass transition temperature (T_g), and for thermoplastic SMP it can be either glass transition temperature (T_g) or crystalline melting temperature (T_m). Thermoset SMPs are more suitable for aerospace applications because of their excellent thermal, mechanical and shape memory properties. They have certain outstanding properties such as high switching temperature (ideal for satellite applications), better durability to harsh environmental conditions in space, dimensional stability and good shape memory characteristics (shape fixity, shape recovery and rapid response).^{13, 17, 81} Several high-temperature shape memory polymers have been reported so far.^{15, 123-127} However, there is no report on the SMPs that can withstand extreme temperature cycling, ultraviolet radiation, ionizing radiation, vacuum and Atomic Oxygen erosion.

2.5 Aromatic polyimides

Aromatic polyimides (PIs), are a class of polymer that exhibit high thermal stability, excellent mechanical properties, high elastic modulus and chemical resistance.^{20, 128} First synthesized at Dupont in 1956, PIs are widely used as a high-performance material in electronics and aerospace applications.¹²⁹ Their excellent radiation shielding capability and high T_g makes them suitable for applications in space.¹³⁰

Space qualified polyimides such as Kapton are generally used in thermal blankets for satellites as external layers of multilayer insulation.¹³¹ Polyimides are typically fabricated as thin films using

a poly(amic acid) (PAA) precursor. PAA is cast on to a substrate and thermally dehydrated to produce the films. The low solubility of PIs in common solvents and their high transition temperature makes it extremely difficult for further processing. In the recent years, several studies were carried out to develop shape memory polyimides (SMPIs) - combining the shape memory effect with the excellent mechanical and thermal properties of PI to extend its application to the deployable satellite systems.²¹⁻²⁸ Like polymers, shape memory polyimides can also be classified as thermoplastic (physically crosslinked) and thermoset (chemically crosslinked) polyimides. Thermoset shape memory polyimides are expected to be a promising candidate for deployable space structures due to their higher T_g , storage modulus and shape fixity compared to thermoplastic SMPIs.^{127, 129} Some of the SMPIs were also tested for their reliability in space by conducting ground-based space environment tests.^{132, 133} **Table 2-1** presents the list of high-temperature shape memory polyimides that are reported so far. Two SMPIs with T_g ranging from 150 to 240 °C is selected for this study.

Table 2-1. List of high-temperature shape memory polyimides reported in the literature.

	Shape memory polyimides (SMPIs)	Glass transition temperature (°C)	Year
1	Graphene Polyimide nanocomposites; Thermal, Mechanical and High-Temperature Shape Memory Effects SMP based on graphene polyimide nanocomposites. ²¹	230	2012
2	Polymer design for high temperature shape memory: Low crosslink density polyimides High temperature SMP. ²⁶	223-270	2013
3	Shape memory polymers with high and low temperature resistant properties. ²⁷	229 to 243	2015
4	AO-resistant shape memory polyimide/silica composites with excellent thermal stability and mechanical properties. ¹³⁴	265	2015
5	Shape-Memory Polymers with Adjustable High Glass Transition Temperatures. ²⁸	299 to 322	2015
6	High performance shape memory polyimides based on π - π interactions. ²⁴	>240	2015

7	High Performance multiple-shape memory behaviors of poly(benzoxazole-co-imide)s.polymer. ²³	230 - 350	2016
8	Optically transparent high temperature shape memory polymers. ²⁵	171	2016
9	*High Cycle-life Shape Memory Polymer at High Temperature. ²²	229.6	2016
10	Tunable Triple-Shape Memory Binary Mixtures with High Transition Temperature and Robust Mechanical Properties. ¹³⁵	261-291	2016
11	Shape Memory Induced Structural Evolution of High Performance Copolyimides. ¹³⁶	280, 355	2016
12	*A novel low coloured and transparent shape memory copolyimide and its T durability in space thermal cycling environments. ¹³⁷	179-220	2018
13	Electroactive High-Temperature Shape Memory Polymers with High Recovery Stress Induced by Ground Carbon Fibers. ¹³⁸	302	2019
14	Transparent, High Glass-Transition Temperature, Shape Memory Hybrid Polyimides Based on Polyhedral Oligomeric Silsesquioxane. ¹³⁹	351 - 372	2019

*Shape memory polyimides selected for this study.

2.6 Characteristics of shape memory polymers

Numerous factors should be considered to define the shape memory properties of the polymer.²⁹ These factors play a vital role in selecting an SMP for any application.

- Shape memory cycle - The response of the SMP, when subjected to a thermomechanical cycle, in which it is deformed and fixed to a temporary shape and then allowed to recover the original shape.
- Switching Temperature - The temperature, at which the SMP recovers its permanent shape. It should be as high as possible to suit the high thermal cycles in orbit.
- Shape fixity – The ability of the SMP to fix the strain imparted during the deformation step after cooling and unloading.

- Shape recovery – The ability of the SMP to recover the accumulated strain upon reheating to the transition temperature.
- Recovery speed - The percentage of recovery per unit time. It depends on material properties and experimental conditions.
- Shape memory cycle life - The repeatability and durability of the shape memory properties over consecutive shape memory cycles. The number of consecutive shape memory cycles achievable before failure.
- Shape memory cycle time – The overall time required for programming the SMP to its temporary shape and the recovery to its permanent shape. It depends on the material parameters, geometry and experimental conditions.

All these variables must be taken into consideration while selecting a polymer for the satellite deployment mechanism. In addition to the variables mentioned above, factors such as mechanical strength, environmental stability, cost and ease of fabrication should also be considered for selecting a suitable polymer for space application.

2.7 Typical fillers for SMP

The poor thermal conductivity of the SMP limits their application in deployment system since the deployment is thermally triggered. Many have conducted studies on improving the thermal conductivity of the SMP by using various filler materials.^{29, 140, 141} Two types of fillers are used for enhancing the properties of the SMP, namely particle fillers (functional fillers) and fibres.¹⁵ Some of the fillers used for SMP so far include glass fibre,¹⁴² nickel-zinc ferrite particles,¹²⁰ nanoclay,¹⁴³ SiC,^{144, 145} carbon fibre,^{17, 146} carbon nanofiber,^{40, 108, 147-151} carbon nanotube,^{104-107, 152} carbon

black,^{93, 103, 153} nanopaper,^{34, 41} and graphene.^{21, 102, 149, 150, 154-156} Although, the addition of fillers has been proven to increase the recovery stress or thermal conductivity, the shape memory properties are dramatically affected by these fillers.^{157, 158}

While 2D materials enhance the thermal conductivity, it is known that a higher concentration of these fillers are required to achieve percolation limits for electrical and thermal conductivity, while a minimal filling fraction is beneficial for mechanical and shape memory properties.¹⁵⁹⁻¹⁶¹ Gunes et al. observed that there is no shape recovery behaviour in the SMP when 5 wt% carbon black is added to SMP.¹⁵⁷ Adding 40 wt% aluminium nitride to the SMP increased the thermal conductivity by more than 3 times, and at the same time reduced the shape recovery from 96 to 70%.³⁸ At higher concentration, these fillers tend to agglomerate, causing inhomogeneous distribution and shape memory loss.²⁹ The reduction in shape recovery ability is also due to the reinforcing effect induced on the polymer matrix by the fillers.^{29, 38} The microfiber, fabric and mat type fillers, can lower the shape memory effect, in the reinforcement direction. Similarly, short or continuous fibre reinforcements used to increase the mechanical properties of the SMP reduces the shape recovery amount with an increase in the volume fraction.

SMPs with particle fillers cannot be used for building structural material due to their lower strength and stiffness. On the other hand, fibre reinforcements increase the strength and stiffness but decrease the recovery rate due to the reinforcement effect.¹⁵ Thus, it can be seen that these fillers bring about a trade-off between property enhancement and shape memory performance. One solution is to mitigate the problem of agglomeration in particle fillers or re-stacking in nanosheet fillers caused by Van der Waals interaction. This can be achieved by using a three-dimensional networked structure that maintains the intrinsic properties of the 2D material and prevents

agglomeration or re-stacking. One such filler that has attracted much attention in recent years is three-dimensional graphene (3D-C).

2.8 Three-dimensional graphene (3D-C)

Three-dimensional graphene is a free-standing foam-like graphene structure formed by up-scaling 2D graphene into the 3D networked structure.⁴³ A metal foam substrate is used to grow graphene on the foam surface, and the 2D graphene adapts the porous interconnected structure of the substrate. Three-dimensional graphene (3D-C) grown by template-assisted direct chemical vapour deposition (CVD)⁴³ is an ideal filler material for polymers to enhance the electrical and thermal properties. A metal foam (copper or nickel) is used as a substrate to grow 3D materials instead of flat 2D sheets. The metal foam will then be etched, resulting in a foam-like interconnected structure of the graphene. Growing graphene as 3D structures caters the material with a combination of intrinsic properties from 2D graphene and 3D porous structure such as high specific surface area, lightweight (highly porous, density in the range of 1 – 5 mg/cm³), good flexibility and strong mechanical strength along with excellent thermal and electrical conductivity properties.^{162, 163} These properties enable their application in high-performance polymer composites, thermal management, supercapacitors, electrode materials, sensors, batteries, biomedical applications, and so on.¹⁶² The three-dimensional network structure of the foam prevents agglomeration and inhomogeneous distribution seen in typical nanofillers.

The property of 3D-C foam can be tuned by controlling the CVD growth parameters, mainly the growth time. Loeblein, M. et al. increased the density of 3D-C foam by increasing the growth time as well as by compressing foam and studied the quality of the foam obtained from both methods. The quality remained stable for both the methods and also for different growth time. The

thermal conductivity of the foam increased with the increase in density.⁵¹ Both the microstructure and macrostructure of 3D-C can be controlled by changing the Ni foam substrate used, growth time and precursor concentration. Cheng et al. controlled the average number of graphene layers, specific surface area and density by changing CH₄ concentration. As the CH₄ concentration was increased, the average number of graphene layers increased. The thickness and mass of the foam increased with an increase in the average number of layers, while there is a decrease in the density and specific surface area.⁴³ Similarly, it was seen that the electrical conductivity increases with the number of graphene layers which can be obtained by increasing the CH₄ concentration, but tends to level out after about few layers of graphene (4 to 5 layers). The conductivity value remained saturated with further increase in the graphene layers.^{43, 164}

2.8.1 3D-C in various matrix

The interest in 3D-C reinforced polymer composite materials has been significant over the past decade, mainly due to its capability to overcome the issues related to 2D fillers. Various fabrication techniques such as dip coating, casting, vacuum infiltration of polymer into the porous 3D-C structure, a polymer-foam based template method, electrostatic spray deposition, natural sedimentation and centrifugal assisted method were adapted by researchers to fabricate 3D-C based polymer composites. The property of 3D-C/polymer matrix composite depends on the type of fabrication employed. 3D-C has been infused with several polymer matrices such as polypyrrole, epoxy, polydimethylsiloxane (PDMS), polyoxometalate, polyimide, and polydopamine for electrical (Super-capacitors, strain sensors, electrochemical biosensors, EMI shielding material in space and flexible electronics), mechanical (dampers, cushions, packaging and strain sensors), thermal (thermal interface materials, high power electronics and flame resistant material), magnetic (EMI and microwave shielding) and biomedical applications. This has been

extensively reviewed by Arvind et al.⁶² Of all the polymers, PDMS and epoxy are the most widely used matrices along with 3D-C for various applications. Typical 3D-C based polymer matrix composites studied thus far are presented in this section grouped under electrical, thermal and mechanical properties.

2.8.1.1 Thermal properties

Zhao et al. demonstrated that 3D-C could be used as a filler for PDMS, resulting in a composite material with a high thermal conductivity that can be used as thermal interface materials (TIM). The thermal conductivity increased by about 300% with the addition of 0.7 wt% of 3D-C to PDMS.^{165, 166} They also increased the thermal conductivity further by nearly 440% by adding multilayer graphene flakes to 3D-C.¹⁶⁷ Liu et al. impregnated epoxy resin into 3D-C to obtain epoxy/3D-C composite with high thermal conductivity ($1.52 \text{ W m}^{-1} \text{ K}^{-1}$) and electrical conductivity ($3.8 \times 10^{-2} \text{ S cm}^{-1}$) with a 5 wt% loading. The composite material is proposed to be useful in high power LED and microelectronic devices.¹⁶⁸ 3D-C was also infused in ceramic to utilise it for heat transfer and thermal energy storage.¹⁶⁹ In addition, 3D-C is used as a filler for various phase change material (PCM) matrix to increase the thermal conductivity and in turn, increase the heat transfer within the material.^{49, 170-172} 3D-C infused PDMS is shown to exhibit superior de-icing efficiency (about 477%) with only 0.1 vol% of 3D-C, making it a good alternative for high power de-icing system currently used in aircraft.¹⁷³ Similarly, the thermal behaviour of the polyimide⁵⁸ and polyamide¹⁷⁴ matrices were also shown to improve with the addition of 3D-C.

2.8.1.2 Electrical properties

Due to its excellent electrical behaviour, 3D-C is extensively used for enhancement of electrical properties of the polymers, mainly epoxy and PDMS. The natural flow of electrolytes in the highly porous structure of 3D-C combined with higher surface area, and surface hydrophilicity has

facilitated higher energy storage capacity. There were also studies focusing on utilising 3D-C as an electrode material for supercapacitors.¹⁷⁵⁻¹⁷⁷ Jia et al.¹⁶⁴ and G. Chen et al.¹⁷⁸ showed that the electrical conductivity of epoxy could be improved by CVD synthesised 3D-C. Sun et al. compared the electrical properties of 3D-C/PDMS with that of 3D-C/CNT/PDMS for EMI shielding applications.¹⁷⁹ The study showed that graphene foam could effectively interact with other carbon fillers as well, enhancing the electrical properties by several folds and their applicability in various fields. A further study conducted on the comparison of electrical properties of graphene foam/PDMS made from small and large flake graphite by Y. Jun et al. demonstrate that adding graphene foam to the polymer enables us to tailor and improve the electrical behaviour of the polymer composites as required.¹⁸⁰ Besides, 3D-C was also infused with polypyrrole, polyvinylidene fluoride (PVDF), polycaprolactone (PCL), polyimide and polyaniline nanofiber sponge (PANI-NFS) for various applications such as EMI shielding, high-performance supercapacitors, absorbents, strain sensors, electrochemical biosensors, space vehicle protection, flexible electronics and biomedical applications.⁶²

2.8.1.3 Mechanical properties:

Due to its exceptional electrical conductivity property, 3D-C is used to create a composite film with very high sensitivity to mechanical changes, and henceforth, several studies were focused on pressure and strain sensing with 3D-C/polymer composite films.¹⁸¹⁻¹⁸⁴ Polymers such as epoxy, PDMS, polylactic acid-poly ϵ caprolactone, and polyimide were incorporated with 3D-C for improving their mechanical property. 3D-C's continuous interconnected macroporous structure along with tailorable porosity accounts for improvements in the mechanical property of the polymer. This makes 3D-C based polymer composite a promising material for strain sensors, packaging material, dampers and cushions. This has driven much research into 3D-C/polymer

nanocomposites, and there are several review papers on the mechanical property enhancement of polymers by 3D-C.^{62, 185} In particular, Arvind et al. studied the damping behaviour of 3D graphene foam-polyimide composite.⁵⁹ The composite displayed a good damping behaviour which improved further with the addition of graphene nanoplatelets as an interface between the foam and polyimide. The polyimide-foam nanocomposite retained its damping characteristics after being treated to its glass transition temperature, making it a suitable material for high-temperature applications. By tweaking the 3D graphene foam structure or the interface material, we can possibly program the nanocomposite properties suitable for smart materials application.

2.8.2 3D-C as an effective filler for SMP

The highly interconnected macroporous structure with superior electrical, mechanical, and thermal properties makes 3D-C a better filler for SMP compared to two-dimensional fillers where agglomeration is a major limiting factor for its effectiveness. 3D-C can be utilised as the best filler for shape memory polymers due to its excellent comprehensive properties. Lee et al. demonstrated that 3D networked graphene - ferromagnetic hybrid filler is a better nanofiller for magneto-responsive SMPs compared to other nanofillers present in the market. The young's modulus and thermal conductivity improved considerably after infusing the polyurethane with 3D networked G-F. The 3D networked G-F proved to be an ideal choice of filler to achieve homogenous filler distribution and to improve the properties of the SMP, such as thermal conductivity, response time and mechanical stiffness.¹⁸⁶ Quite recently, Manuela et al. demonstrated that CVD grown porous three-dimensional graphene (3D-C) could increase the thermal conductivity of epoxy SMP without any reduction to the shape memory properties and render self-resistive heating capability to the SMP.¹⁸⁷

2.9 Space environment effects on materials

Satellites for long term space missions are typically launched to low Earth orbit (LEO, at 200 - 800 km altitude) and geosynchronous equatorial orbit (GEO, at 35,786 km altitude) characterised by prevailing harsh environmental conditions such as atomic oxygen (AO), ultraviolet (UV) and ionising radiation, plasma, extreme thermal cycles (-120 °C to +120 °C every orbital cycle), vacuum and impact of tiny meteoroids and space debris.¹⁴ Almost, 25% of spacecraft failure modes are linked to interactions with the outer environment.¹⁸⁸ Atomic oxygen exposure and radiation effects have a dominating impact on the space materials (at LEO) leading to oxidation, surface erosion and mass loss (degradation of material properties). It is of more significant concern for high speed and long-term missions.¹⁸⁹ Prolonged exposure to these environment leads to degradation in physical, thermal, optical and chemical properties of the polymer. Besides having high thermal stability, excellent mechanical properties and chemical resistance,²⁰ polyimides are vulnerable to AO erosion at LEO and electrostatic discharge (ESD) in LEO and mostly on GEO. The effects of the space environment on satellite materials play a vital role in determining the reliability and lifetime of the components.¹⁹⁰ The effects are briefly described below.^{191, 192}

- Atomic oxygen: Interaction with AO leads to erosion of the polymer surface, changes in chemical composition, surface morphology and optical properties. AO reacts with any material that contains carbon, nitrogen, hydrogen and sulfur. Many polymers react with AO and erode contaminating the neighbouring surfaces.
- Ultraviolet radiation: Exposure to UV radiation darkens the satellite materials. UV radiation damages the polymer by either hardening (cross-linking) or weakening (chain scission reaction). This can lead to a reduction in the performance through reduced mechanical properties or overheating, resulting in mission failure.

- Ionising radiation: Ionising radiation consists of charged particles such as electrons, protons and heavy ions. These particles cause spacecraft internal charging and degradation of electronics. When a high energy particle impacts and ionises the electronic circuit, it causes single-event upsets.
- Thermal cycles: The satellite will be exposed to extreme temperature cycles (-120 °C to +120 °C) as it completes each orbital cycle (sun phase and eclipse). The temperature of the satellite components depends on its thermo-optical properties. Care should be taken that the temperature of each component lies within their operating temperature ranges.
- Vacuum: Ultra-high vacuum in space (5×10^{-10} Torr) will result in outgassing, i.e. release of trapped or absorbed molecules. These molecules might contaminate satellite surfaces changing the chemical composition, volume or density. These contaminants could significantly affect the performance of the surfaces such as mirrors or detectors.
- Meteoroids and space debris: Orbital debris is man-made objects in orbit. The size of the debris might vary from microns to several meters. They have collision velocities of up to 60 km/s. Upon impact with the satellite surface, they can cause physical surface damage.

In order to ensure the reliability of a material in space, it should be subjected to the following accelerated space environment reliability tests before their application in space-deployable structures.^{193, 194}

- Thermo-optical properties - Heat transfer in the vacuum is predominantly dependent on radiation. The solar absorptance α_s and the emittance ε of the material will be measured at room temperature by IR/solar reflectometer.
- Thermal cycling - Electrical conductivity measurements under thermal cycling. (Temperature range from -100 °C to 140 °C)

- Ionising radiation - The material will be exposed to several doses of γ radiation, and the effect on electrical resistivity will be measured.
- Atomic oxygen exposure - The material will be subjected to a range of AO fluences, and the mass loss will be measured after each exposure.
- Outgassing test - Outgassing is the release of molecules from the material surface in vacuum. Low outgassing is essential to avoid contaminating other structures in the spacecraft.

Fukher et al. studied the influence of radiation on the mechanical properties of the thermoset SMP. The SMP was subjected to nanoindentation after γ ray exposure.¹⁹⁵ Similarly, Leng et al. studied the effect of γ radiation on the structural properties of epoxy-based shape memory polymer.¹⁹⁶

2.10 Polyhedral oligomeric silsesquioxane to improve AO durability

Polyhedral oligomeric silsesquioxane(POSS), a novel organic-inorganic hybrid, has been reported to improve the atomic oxygen resistance of the polymers.¹⁹⁷ POSS has a cubic cage-like molecular structure, made of inorganic Si-O-Si framework (0.53 nm side length), surrounded by eight organic groups with the empirical formula $(\text{RSiO}_{1.5})_n$. POSS has already been used in a wide range of applications such as electronics, biological systems and aerospace.^{193, 198-201} It is being incorporated both in polymers and carbon nanostructures to improve their properties. Copolymerisation, or incorporating POSS in polymer functional groups helps to resist AO induced degradation.^{197, 202-205} When exposed to AO, the POSS organic groups etches away forming a surface SiO_2 passivation layer to protect the polymer from further O-atom attack.²⁰⁶ POSS was also incorporated into polymer matrices to improve their thermal stability, mechanical strength,

viscosity, impact and chemical resistance.^{207, 208} Nevertheless, they are electrically insulating, leading to electrostatic discharge when exposed to space plasma which in turn is hazardous for the on-board electronics. POSS nanoparticles were also chemically grafted (functionalisation) on to different carbon surfaces such as graphene, carbon nanotube,²⁰⁹ carbon dots,²¹⁰ graphene oxide film,²¹¹ carbon fibre,²¹² and fullerenes, to improve the properties of the composite structures, and for various other applications.²¹³⁻²¹⁷ POSS is said to be an ideal modifying agent as the organic groups provide high reactivity and compatibility with the polymers and the organic group can be changed depending on the polymer used and its end application.²¹⁸ The main advantage of POSS is the ability to resist atomic oxygen erosion. In a recent study, it was shown that adding POSS to CNT-PI film could improve the AO durability of the film.¹⁹³ In this thesis, both 3D-C and PI will be incorporated with POSS, and the AO erosion of 3D-C/PI films with POSS in 3D-C or PI or both will be compared with one another.

3 Experimental Methods

In this Thesis, 3D-C foam is used as a filler to improve the thermal conductivity of the shape memory polyimide films, to facilitate their application in deployable structures. 3D-C is first infused into shape memory epoxy polymer (SMP) for preliminary mechanical assessment. The effect of 3D-C filler fraction on the SMP is studied to determine the optimum filler loading required to obtain the desired results without any detrimental influence on the SMP's intrinsic properties.

A shape memory polyimide (SMPI) with high glass transition temperature ($>170\text{ }^{\circ}\text{C}$) is chosen from literature and infused with 3D-C. The 3D-C/SMPI composite material properties are studied, followed by space qualification. POSS study is conducted to improve the durability of 3D-C infused polyimide (3D-C/PI) in the LEO environment. POSS is incorporated into the composite to enhance the AO durability, and a ground-based AO exposure study is conducted. Finally, a tape spring shaped hinge model is fabricated using 3D-C/SMPI.

The experimental methods used to synthesize 3D-C foams, 3D-C/SMP composite, 3D-C/SMPI composite and 3D-C/POSS/PI composite materials along with their characterization and space qualification techniques are described in this chapter.

3.1 Materials

The raw materials used for this work are as below:

Nickel (Ni) foam substrate for 3D-C growth is purchased from Latech Scientific Supply Pte.Ltd. Bisphenol A diglycidyl ether (EPON 826), Neopentyl glycol diglycidyl ether (NGDE), poly (propylene glycol) bis (2-aminopropyl) ether (Jeffamine D-230) are purchased from Sigma-

Aldrich and used as received. POSS-NH₂ is bought from Alfa Chemistry (USA) as crystalline powder and used as received. Tetrahydrofuran, anhydrous (THF) is purchased from Sigma Aldrich (401757). Polyamic acid (PAA) solution of 15 wt% PMDA-ODA in N-methyl-2-pyrrolidone (NMP) is purchased from Sigma-Aldrich (575801) to form the pristine PI matrix. Blends containing 5 and 15 wt% TSP-POSS in PAA are bought from Hybrid Plastics (PM1215.5 and PM1215.15, respectively) to form the TSP-POSS-PI matrices.

For the SMPI synthesis, Dimethylacetamide (DMAc) and Dimethylformamide (DMF) are bought from Sigma-Aldrich and used as received. (1,3-bis(3-aminophenoxy)benzene (BAB), (4,4'-(1,1'-biphenyl-4,4'-diyldioxy)dianiline (BAPB) and dianhydride (Bisphenol A dianhydride (BPADA) are purchased from TeeHai and used as received.

3.2 Synthesis methods

3.2.1 Growth of 3D-C

The three-dimensional graphene (3D-C) foam is obtained by template-assisted direct thermal chemical vapour deposition (TCVD). Ni foam is used as a template and catalytic substrate. Ni foam is first annealed at 1000 °C in a quartz tube placed inside TCVD furnace under constant Ar and H₂ flow. Annealing is done to clean the Ni surface and to remove the oxide layer from the surface. After annealing for about 5 minutes, a small amount of methane (CH₄) is introduced into the tube. The methane decomposes and deposits as graphene film on the Ni surface. The whole synthesis process is carried out under ambient pressure. After the growth period, the samples are subjected to rapid cool down to room temperature under constant Ar and H₂ flow. The flow rate of CH₄ and the growth time depends on the concentration of total gas flow and the substrate dimensions. The Ni substrate is then etched to obtain free-standing 3D-C. 3D-C/Ni sample is first

dip-coated with PMMA to protect the 3D-C structure while etching the Ni substrate. Once the PMMA has hardened forming a protective film on the graphene surface, the samples are treated with hot dilute HCl for about 3 to 5 hours or until the Ni is completely etched off. Finally, PMMA is removed to obtain free-standing, ultralight and flexible 3D-C foam. This is done by annealing the samples at 700 °C for 1 hour under Ar and H₂ atmosphere.^{43, 45, 58} The porosity of the 3D-C foam depends on the Ni foam porosity.

3.2.2 Growth of 3D-C/POSS

POSS-NH₂ is incorporated into the as grown freestanding 3D-C foams as shown schematically in **Figure 3.1**.

Figure 3-1. Schematic of the POSS-NH₂ used and its incorporation into 3D-C. a) POSS-NH₂ molecular structure showing eight organic groups attached to the cubic Si-O-Si (inorganic) framework (Si atom - red, O atom - dark blue and organic group - light blue); b) Schematic illustration of POSS-NH₂ incorporation onto 3D-C.

THF is used as a solvent to disperse POSS-NH₂ agglomerates and to provide a medium for attaching the POSS-NH₂ particles to the 3D-C foam surface. A small quantity of POSS-NH₂ powder is added to THF and mixed by ultra-sonication in an ultrasonic bath for about 15 minutes to disperse or de-agglomerate the POSS particles in the solvent. The fabricated 3D-C foams are immersed in the solution and heated at 50 °C for about 4 hours. The foams are then removed, washed with DI water and dried by heating at 110 °C for 30 minutes. The result is a POSS coated 3D-C foam structure.

3.3 3D-C infusion of polymer

3.3.1 Epoxy SMP

Epoxy-based SMP is synthesised and infused with 3D-C foam using the previously reported approach.^{156, 187} Three chemicals are used for the SMP preparation: EPON 826, NGDE and Jeffamine. EPON 826 is the polymer resin that provides the shape memory properties to the polymer. EPON is first heated to about 75 °C to reduce the viscosity, in order to enable easier mixing. NGDE and Jeffamine D-230 are the curing agents that chemically cross-link EPON 826. The resin and the curing agents are mixed in the ratio of 1.3: 1: 0.7 (EPON: Jeffamine: NGDE) and the mixture is thoroughly stirred until a clear solution is obtained. The solution is then added in drops to 3D-C foams placed in an Al mould, and the setup is first degassed in a vacuum oven to remove any air bubbles. Afterwards, the samples are cured at 100 °C for one hour and post-cured at 130 °C for another hour. Once cured, the 3D-C/SMP composites are removed from the Al mould and cut into required shapes and sizes for various tests. The density of the 3D-C in the 3D-C/SMP composite depends on the Ni foam used.

3.3.2 PI

3D-C is infused with PI matrix and PI-POSS matrix to conduct an AO exposure study on the 3D-C/PI composite sample. Pyromellitic dianhydride-oxydianiline (PMDA-ODA) PAA solution of 15 wt.% PMDA-ODA in N-methyl-2-pyrrolidone (NMP) is used to form the pristine PI matrix. PMDA-ODA blends containing 5 and 15 wt.% Trisilanolphenyl (TSP)-POSS in PAA are used to create the TSP-POSS-PI matrices.

The infiltration of 3D-C with PI is done using the multistep imidization process as described in the previous report.⁵⁸ As the name indicates, the infiltration process is carried out in several steps. First, a small amount of diluted PAA solution is poured onto the 3D-C-foams and cured, resulting in a thin layer of PI film at the bottom of the foam. In the second step, some more PAA is poured onto the foam and cured, forming an additional layer of PI film on the top of the first layer. The process is repeated (2 to 3 times) until the PI covers the entire thickness of the foam. This multistep imidization process helps to prevent strain build-up at the interface between the foam and the PI during curing.

3.3.3 SMPI

For synthesis and infusion of SMPI with 3D-C foams, two different shape memory polyimides with high glass transition temperatures are chosen from the literature.¹³⁷ The SMPI is synthesised via a two-step polycondensation process, similar to the approach reported by Leng et al¹³⁷ and Kong et al.²²

Briefly, three chemicals, diamine [(1,3-bis(3-aminophenoxy)benzene (BAB), (4,4'- (1,1'-biphenyl-4,4'-diyldioxy)dianiline (BAPB)] and dianhydride (Bisphenol A dianhydride (BPADA)) are dissolved in the solvent Dimethylacetamide (DMAc). The ratio of diamine to dianhydride, i.e.

BAB/BAPB: BPADA is kept constant at 1:1, and the total solid content is maintained as 15 wt.%. 0.95:0.05 molar ratio of BAB: BAPB is added to DMAc and stirred until completely dissolved. 10 mmol of BPADA is added in batches of four within one hour. The solution is then stirred under room temperature for 24 hours resulting in a viscous PAA. The whole polycondensation process is carried out under a dry nitrogen atmosphere inside a glovebox. The infiltration process is done in 1-2 steps using a Viscous PAA. A small amount of PAA is drop-cast on to the 3D-C foams placed on a glass substrate, and the setup is allowed to rest until the PAA flows down to the bottom of the foam. The samples are then degassed in a vacuum oven for 15 minutes to remove any air bubbles trapped in the bottom layer. This is followed by stepwise thermal imidization at 80 °C, 110 °C, 180 °C, 200 °C and 250 °C for 2 hours each. Then, the second layer of PAA is poured on the sample, followed by degassing and curing. Freestanding 3D-C/SMPI composites are then obtained by detaching the samples from the glass substrate in DI water and heated at 100 °C to remove water. For the second SMPI, similar synthesis method is followed using BAPB and BPADA. Dimethylformamide (DMF) is used as the solvent.²²

3.4 Standard characterisation techniques

3.4.1 Morphological and chemical characterisation

Scanning electron microscopy, SEM (JEOL JSM-IT100) is used to investigate the surface morphology of the foam structure and composite samples.

Fourier transform infrared, FTIR spectra are measured in the range of 400 – 4000 cm⁻¹ in the absorbance mode using Shimadzu IRPrestige-21 to investigate the chemical composition of the foam.

Raman spectroscopy (UHT S300 & WITEC CRM200 Raman with an Nd:YAG 532 nm laser as excitation source) is performed at room temperature to determine the crystalline configuration of the films.

X-ray photoelectron spectroscopic, XPS measurements are performed to assess the surface chemical composition of the foams. Survey scan is performed to determine the detectable elements, and also high-resolution spectra are obtained for C 1s for both 3D-C and 3D-C-POSS foams.

3.4.2 Wettability

Video contact analyser (Dataphysis OCA) and SCA 20 software are used to measure the contact angle at the interface of polymer and 3D-C surface to determine the wettability of 3D-C. Sessile drop setup is used to place a single drop of the polymer on the 3D-C surface, and the contact angle between the polymer and foam surface is observed. The capability of the polymer to infiltrate 3D-C is determined by the contact angle measured. Contact angle greater than 90° indicates hydrophobic surface and smaller than 90° indicates hydrophilic surface (better absorptivity of the polymer) in terms of the polymer used.²¹⁹

3.4.3 Polymer integrity

Thermogravimetric analysis, TGA (TA Instruments Q500 and Shimadzu Scientific Instruments DTG-60H) is performed to study the decomposition profile of the 3D-C/Polymer composites. The thermal stability of the samples is studied at elevated temperatures by measuring the mass loss while heating them from room temperature to ~1000 °C at a heating rate of 10 °C/min.

Differential scanning calorimetry, DSC (TA Instruments Q100) is used to characterise the phase transitions of the 3D-C/polymer composites. The experiment is carried out under nitrogen atmosphere in temperature modulation mode. Sample weight of 5 – 10 mg is used, and thermal transitions within the composite, glass transition temperature can be detected from the heat flow curve.

3.5 Thermal measurement

Thermal conductivity of the samples in the thickness direction is measured using the Laser Flash technique (NETZSCH LFA 447 NanoFlash).²²⁰ The laser flash method is a contact-less temperature sensing method. Due to the isotropic thermal conductivity behaviour of 3D-C,⁵¹ cross-plane thermal conductivity is measured here using the laser flash method. In this method, a short light pulse is passed through one side of the sample, and the resulting temperature rise on the other side of the sample is recorded using an IR-detector. A high-performance Xenon flash lamp is used for the light source, and the radiation from the lamp is focused homogeneously onto the entire surface of the sample using a parabolic mirror. This contact-less technique helps to measure the thermal diffusivity of materials that are temperature-dependent.

The requirements and procedure for the test are specified in ASTM E1461-13²²¹ and ISO 22007-4.²²² For this method, the laser penetration depth must be smaller than the total thickness of the sample (i.e. Optical penetration depth > Sample thickness). Laser flash instruments can be used to measure samples of thickness 100 μm and above. The composite samples studied in this thesis (3D-C/SMP, 3D-C/SMPI, 3D-C/POSS/PI) are all greater than 100 μm (thick samples). In addition, the composite samples have higher surface roughness due to 3D-C infusion, and hence a contactless thermal conductivity measurement is preferred.

In-plane thermal diffusivity α ($\text{mm}^2 \text{S}^{-1}$) is first calculated using equation (3-1),

$$\alpha(T) = 0.1388 \frac{d^2}{t_{1/2}} \quad (3-1)$$

Where d is the thickness of the sample (cm), and $t_{1/2}$ is the time taken to reach half of the maximum temperature (s). The thermal conductivity, κ ($\text{W m}^{-1} \text{K}^{-1}$) can then be calculated using the thermal diffusivity in equation (3-2),²²³

$$\alpha(T) = \frac{\kappa(T)}{C_p(T) \cdot \rho} \quad (3-2)$$

C_p , is the specific heat capacity ($\text{J g}^{-1} \text{K}^{-1}$) measured using DSC (Netzsch DSC F3 Maia) and ρ (kg m^{-3}) is the density at room temperature. The thermal conductivity through the thickness direction of the sample is obtained.

3.6 Electrical measurement

Electrical resistivity of the composite is measured using the Van-der-Pauw four-point probe method.^{58, 193} Van-der-Pauw method is used to measure the temperature-dependent electrical conductivity of any sample with an irregular shape.²²⁴ This method eliminates the effect of contact resistance and sample geometry. In this method, all four points are located on four corners of the sample as opposed to the standard four-point probe method, where the four points are aligned in a straight line. This method helps to determine average resistivity of a composite sample of any arbitrary shape. Current is applied on one edge of the sample, and the resulting voltage is measured on the opposite side. This method provides the average sheet resistivity of the sample as opposed to linear four-point probe method, which provides the resistivity in sensing direction.²²⁵

A THMS600 Linkam stage is used to control the sample temperature in N₂ atmosphere. Current is applied and measured using a Keithley 220 programmable current source and Keithley 485 picoammeter respectively. Silver paint dots are spread on the four corners of the sample surface to apply electrical contacts on the four points. This non-destructive method prevents any substantial damage to the sample surface. A very high input impedance ($>200\text{T}\Omega$) Keithley 6514 electrometer is connected to each of the four contact points. A Keithley 2000 multimeter is used to measure the voltage difference between each of the two electrometers. The current source, electrometers, multimeter, and sample contacts are connected to a Keithley 7001 switch.

3.7 Thermo-mechanical characterisation

The thermo-mechanical properties such as storage modulus and loss factor versus the temperature are characterised by dynamic mechanical analysis (DMA), using TA instruments Q800, USA. DMA is conducted in single-cantilever mode with a heating rate of $3\text{ }^{\circ}\text{C min}^{-1}$ and a frequency of 1Hz. The peak of the loss factor curve gives the glass transition temperature for the rigid chain polymers.

3.8 Shape memory characterisation

Shape memory performances of the composites are evaluated using the single-cantilever and controlled force mode test on DMA (TA Instruments Q800). The process involves a cyclic test divided into following steps: a) heating the sample to about $T_g + 20^{\circ}\text{C}$ at $5\text{ }^{\circ}\text{C/min}$, b) applying a load to get an ε of about 10%, c) Cooling down the sample to $25\text{ }^{\circ}\text{C}$ at a rate of 5°C/min keeping the load constant, d) removal of the force at a uniform rate, and e) heating the sample to $T_g + 20^{\circ}\text{C}$ at $5\text{ }^{\circ}\text{C/min}$. Once the recovery of the sample has reached a constant value, the cycle is repeated

three times by applying the same force. The stress, strain and displacement values are monitored while samples undergo temperature changes and force application. Shape recovery (R_r) and shape fixity (R_f), the two essential factors in determining the shape memory effect are calculated by the strain measured under each step using the formulas in Equation (3-3) and (3-4),¹⁴

$$R_r = \frac{\varepsilon_m(N) - \varepsilon_{rec}(N)}{\varepsilon_m(N) - \varepsilon_{rec}(N-1)} \times 100\% \quad (3-3)$$

$$R_f = \frac{\varepsilon_u}{\varepsilon_m} \times 100\% \quad (3-4)$$

Where,

ε_{rec} = Strain after recovery

ε_u = Fixed strain after cooling and removing the load

ε_m = Maximum strain under load

N = Cycle number

The shape fixity and shape recovery rate determine the ability of the shape memory material to hold its temporary shape and recover its permanent shape, respectively.

3.9 Space qualification

The resilience of the composite material in the space environment is characterised by accelerated space environment reliability studies using ground-based space simulation systems involving AO exposure, outgassing, thermal cycling and thermo-optical property measurements.

Space environmental tests are performed as per European space standards. The effect of some of these environments on the composite material is quantified by electrical resistivity measurements, before and after exposure, along with SEM imaging in some cases.

3.9.1 Thermal cycling

Electrical conductivity measurements are recorded under repeated heating and cooling cycles to investigate the effect of extreme hot and cold temperature cycles in space. The temperature range is chosen according to the requirements for the vehicle in space. It depends on the operating temperature of the material in space, which in turn depends on the thermo-optical characteristics.

3.9.2 Thermo-optical properties

The solar absorptance and emissivity of the composite samples are measured at room temperature using PerKinElmer Lambda 950 UV/VIS/NIR spectrophotometer, with 150mm integrating sphere.^{226, 227} ASTM E903-12 Standard test method is followed for determining solar absorptance, reflectance, and transmittance of materials using integrating spheres. ASTM C1371- 15 standard test method is used for the determination of emittance near room temperature using portable emissometers.

3.9.3 Atomic-Oxygen exposure

Ground-based AO exposure of the composite sample is carried out using a laser detonation hyperthermal AO pulsed beam.²²⁸ RF plasma source (Litmas RPS 1.5-3kW, 1.7-3MHz) is used as the AO source. A mass flow controller is used to feed the RF plasma source with oxygen (99.99%). The RF plasma source creates oxygen plasma. The oxygen atoms in the AO beam are generated by breaking down O₂ gas in a conical nozzle using a CO₂ laser with 7 Joules/pulse. The AO source

is connected to a small vacuum chamber located at the end of the pumping stream. The chamber has a sample holder at an angle of 90° to the stream.

The samples are cut into required dimensions and attached to the Si substrate with aluminium tape. The samples are exposed to specific AO fluences, and the mass loss versus AO fluence is plotted. The erosion yield E ($\text{cm}^3 \text{O-atom}^{-1}$) of the composite is calculated using equation (3-5) as per ASTM E2089 standard testing method.²²⁹

$$E = \frac{\Delta m}{A \rho F} \quad (3-5)$$

Where,

Δm = Mass loss (g)

A = Exposed area (cm^2)

ρ = Density of the sample (g cm^{-3})

F = Atomic oxygen fluence (O-atoms cm^{-2}), determined from the reference sample erosion.

Here the reference sample is Kapton H.²²⁸

Δm is measured using a microbalance (Sartorius SE2 – readability of 0.1 μg), and from the measured Δm , the etch depth can be calculated using the equation (3-6),

$$\Delta d = \frac{\Delta V}{A} = \frac{\Delta m / \rho}{A} \quad (3-6)$$

Where, Δd is the etch depth (cm), and ΔV is the etched volume (cm^3), calculated from mass loss and density of the sample.

3.9.4 Outgassing

Standard test methods, ECSS-Q-ST-70-02C (15 November 2008)²³⁰ and ASTM-E595-15²³¹ are followed to perform the outgassing test. The samples are held at a temperature of 125 °C and a pressure of less than 5×10^{-5} Torr for 24 hours. The parameters measured are total mass loss (TML, wt%) and collected volatile condensable material (CVCM, wt%). The mass loss of the specimen without the water volatile is the recovered mass loss (RML, wt%). A collecting plate held at 25 °C is used to measure the amount of CVCM. The amount of water vapour regained (WVR, wt%) can also be obtained.

4 Effect of 3D-C loading fraction on SMP (Epoxy)

4.1 Introduction

Despite the advantages of SMPs, their application is limited to small deployable parts due to their poor thermal conductivity [$\leq 0.3 \text{ Wm}^{-1} \text{ K}^{-1}$]. The scalability of deployable structures using SMP is limited to smaller structures rather than a much larger area of deployment. If the scalability can be improved to cover larger areas, conventional deployable structures can be replaced with lightweight and low cost smart deployable structures that are easy to fabricate as well.

Quite recently, our group demonstrated that porous three-dimensional graphene (3D-C) could increase the thermal conductivity of epoxy SMP without any reduction in the shape memory performance.¹⁸⁷ As such, the 3D-C/SMP showcased faster and efficient transformation with lower input energy, and at the same time, 3D-C renders self-resistive heating capability to the SMP. As observed with thermal imaging, the addition of 3D foams improves the temperature uniformity across the sample, thereby reducing the mechanical failure caused by a thermal gradient. The findings show that 3D-C is critical in improving the performance of SMP and herein, the correlation between the 3D-C filling factor and the resulting SMP property is investigated further in-depth. This is done to determine the optimum filler loading required to obtain the desired results without any detrimental influence on the SMP's intrinsic properties.

In this chapter, 3D-C foams of different densities are synthesised and infused into SMP to investigate the effect of 3D-C filler content on the mechanical, thermal and shape memory properties of the SMP. Thermal stability and thermo-mechanical characteristics are studied to recognise the impact of 3D-C filler content on the intrinsic properties of the SMP. As expected,

the 3D-C/SMP composites are able to demonstrate a notable increase in the thermal conductivity (up to 800% for 1.5 vol.% of 3D-C) along with excellent shape recovery, shape fixity and fast response time. However, the mechanical strength test reveals that the presence of the interconnected structure of 3D-C would reduce the mechanical performance of the SMP (decrease in flexural modulus by about ~50% for 1.5 vol.% of 3D-C), when present at a higher concentration as the polymer is distributed as distinct pockets interrupted by the foam structure. As such, while the thermal conductivity of 3D-C/SMP tends to increase with the volume fraction of 3D-C, the mechanical properties decreases with the increasing volume of 3D-C. Hence, a careful design focusing on the foam density and infusion process is required to obtain 3D-C/SMP composite with high thermal conductivity along with good mechanical and shape memory properties.

4.2 Material preparation and characterisation

The preparation of 3D-C foams and infusion with the SMP is carried out as described in sections 3.2.1 and 3.3.1, respectively. The effect of 3D-C content on the 3D-C/SMP sample's intrinsic properties, such as thermal stability and thermo-mechanical characteristics, were studied along with thermal conductivity and mechanical strength properties. The shape memory performance of the composite was also evaluated using dynamic mechanical analysis.

4.3 Effect of 3D-C on SMP properties

4.3.1 3D-C/SMP composite – Morphological observation

The surface morphology of 3D-C structure observed by SEM is presented in **Figure 4-1**. A highly porous structure of three-dimensional graphene foam with continuously interconnected branches can be observed. It is seen that 3D-C incorporates the structure of the Ni foam template.

The highly porous structure results in a lightweight and low-density foam. Optical images of 3D-C, bare SMP and 3D-C/SMP samples are shown in **Figure 4-1e**.

Figure 4-1. a-d) Top view and close up SEM images of 3D-C showing three-dimensional interconnected foam-like structure and a smooth surface; e) Optical image of 3D-C, bare SMP and the 3D-C/SMP Composite.

It can be seen from the Raman spectra of 3D-C⁵⁸ (Figure 7.2b) that the intensity of the G-peak is about two times the intensity of the 2D peak indicating multi-layer graphene.^{232, 233} Hence for 3D-C synthesised by chemical vapour deposition method, the density of pyrolytic graphite (2.267 g/cm³)²³⁴ is used to calculate the volume fraction of 3D-C in 3D-C/SMP composite. The solid volume of the foam (excluding the pore volume) is calculated as $V_f = m/\rho_g$,²³⁵ Where m is the weight of the 3D-C foam and ρ_g is the density of graphite. From V_f , the loading fraction of 3D-C

is estimated to be approximately 0.1, 0.2, 0.6, 1 and 1.5 vol.%. The different loading volume percentage of 3D-C is obtained by using 3D-C foams of varying weight/density.

In order to determine the infiltration of SMP on 3D-C, contact angle measurement is carried out, and the result is shown in **Figure 4-2**. Immediate absorption of the SMP is seen, indicating that the SMP rapidly infiltrates the foam structure.

Figure 4-2. Contact angle measurement for SMP on 3D-C Surface.

Figure 4-3 shows the top view SEM images of bare SMP and 3D-C/SMP composites with different amount of 3D-C foams. The surface roughness of the composite samples can be seen to increase with the increasing amount of 3D-C. The interconnected structure of 3D-C is visible in the cross-sectional SEM view of the samples (**Figure 4-4**). The foam branches are visible as interconnected shadow structures embedded within the SMP matrix. The 0.1% 3D-C/SMP has lower foam volume with more space occupied by the matrix, while 1.5% 3D-C/SMP has a majority of its cross-sectional area occupied by foam branches. For all filling fractions from 0.1 vol.% to 1.5 vol.%, it can be seen that the foam could fill the whole volume of the sample homogeneously. With only a volume fraction of 0.1 vol.% the foam expands homogeneously and fills up the entire structure, in agreement with observations in the previous work.¹⁸⁷

Figure 4-3. Top surface SEM images (500 μm resolution) of bare SMP and 3D-C/SMP composites. a) Bare SMP; b) 0.1% 3D-C/SMP; c) 0.2% 3D-C/SMP; d) 0.6% 3D-C/SMP; e) 1.0% 3D-C/SMP; f) 1.5% 3D-C/SMP. The images display smooth surface for bare SMP as well as the SMP with 0.1 vol% 3D-C, whereas the surface roughness increases for the composites with 0.2 to 1.5 vol.% 3D-C.

Figure 4-4. Cross-sectional SEM images (500 μm resolution) of bare SMP and 3D-C/SMP composites. a) Bare SMP; b) 0.1% 3D-C/SMP; c) 0.2% 3D-C/SMP; d) 0.6% 3D-C/SMP; e) 1.0% 3D-C/SMP; f) 1.5% 3D-C/SMP. The images show a complete infusion of the polymer on the porous 3D-C structure with no air pockets.

4.3.2 Effect on thermal stability

The decomposition profile of the 3D-C/SMP composites at elevated temperature is studied using TGA as described in section 3.4.3. The weight loss curves of the bare SMP and 3D-C/SMP samples are shown in **Figure 4-5**. From the thermogravimetric analysis, it is seen that all the samples have similar decomposition profile. Two-step degradation is apparent for all the samples.

Figure 4-5. TGA curves of bare SMP and 3D-C/SMP composite materials from room temperature to 850 °C showing similar degradation curves. Insert shows the TGA curves enlarged near the decomposition temperature. The point of 5% mass loss corresponding to the decomposition temperature is marked with the red dashed line.

The major weight loss or decomposition (5% mass loss) temperature is in the range of $285 \pm 1^\circ\text{C}$ for bare SMP, 0.1% 3D-C/SMP and 0.2% 3D-C/SMP. With further increase in 3D-C volume fraction from 0.6 to 1.5%, the decomposition temperature (major weight loss) decreases only slightly below that of the bare SMP ranging from 275 °C to 270 °C. 3D-C/SMP samples with

higher 3D-C content have a slightly lower onset temperature for both first and second stage degradation. The difference is minimal, and the slight drop in thermal stability is due to the spatial obstruction of 3D-C on the molecular cross-link structure of the SMP matrix.²³⁶ The reduction in the network structure facilitates easy-break down of SMP, and hence there is a slight decrease in the thermal stability with increasing filler content. The temperature for 5%, 20% and 80% weight loss for all the samples are tabulated (**Table 4-1**). The temperature for 20% weight loss decreases slightly with an increase in the foam content. This shows that, with increasing filler ratio, the decomposition of the polymer takes place at a lower temperature due to spatial obstruction. Alternatively, the temperature to reach 80% weight loss increases with increasing filler content as the primary decomposition temperature of 3D-C is around 800 °C and it takes a slightly higher temperature to decompose up to 80% of the composite material. Thus, the decomposition temperature of the composite is stable with up to about 0.2 vol.% of 3D-C and then decreases only to a slight extent with further increase in the 3D-C content. It should be noted that the decrease in the primary decomposition temperature with a higher volume fraction of 3D-C is negligible enough to have any significant effect on the polymer application.

Table 4-1. Temperature list for Bare SMP and 3D-C/SMP composites corresponding to 5%, 20% and 80% mass loss during thermogravimetric analysis.

Sample	Temperature [°C]		
	5% Mass loss	20% Mass loss	80% Mass loss
Bare SMP	285.94	321.17	414.38
0.1% 3D-C/SMP	284.43	321.13	438.97
0.2% 3D-C/SMP	285.04	320.11	438.66
0.6% 3D-C/SMP	275.14	319.02	486.57
1.0% 3D-C/SMP	276.24	318.31	496.80
1.5% 3D-C/SMP	270.00	316.57	511.08

4.3.3 Effect on thermal conductivity

Figure 4-6 shows the measured thermal conductivity results for bare SMP and 3D-C/SMP composites at room temperature. Bare SMP has a thermal conductivity of $0.148 \text{ Wm}^{-1}\text{K}^{-1}$ at room temperature. Thermal conductivity of the composite samples increases from 0.240 to $1.334 \text{ Wm}^{-1}\text{K}^{-1}$, with an increase in the filler content from 0.1 to 1.5 vol.%.

Figure 4-6. Thermal conductivity through-thickness direction versus 3D-C vol.% in the composite samples showing an increase in thermal conductivity with increase in the foam content.

The thermal conductivity values of the samples along with the percentage increase from that of bare SMP are shown in **Table 4-2**. Due to the interconnected structure of 3D-C, adding a small amount (0.2 vol.%) of 3D-C can enhance the thermal conductivity of the SMP by about 3 times. The homogeneous distribution of 3D-C within the SMP facilitates the improvement in thermal conductivity with uniform heat spread. It can be noted that the thermal conductivity of 0.1% 3D-C/SMP measured in this work is closer to the conductivity measured for 0.3 vol.% of

3D-C/SMP from our previous work.¹⁸⁷ This difference is attributed to be mainly due to the difference in the growth parameters (CH₄ flow rate, growth time and etching time) and Ni substrate used for preparing 3D-C foams of much higher density.

Table 4-2. Thermal conductivity at room temperature and its percentage increase with respect to 3D-C vol.%.

Sample	Thermal conductivity [W m ⁻¹ K ⁻¹]	Percentage increase at room temperature [%]
Bare SMP	0.148	
0.1% 3D-C/SMP	0.240	62.16
0.2% 3D-C/SMP	0.473	219.59
0.6% 3D-C/SMP	0.639	331.76
1.0% 3D-C/SMP	0.875	491.22
1.5% 3D-C/SMP	1.334	801.35

Table 4-3 summarises the enhancement of thermal conductivity of the polymer matrix by various fillers compared with 3D-C. The average value of thermal conductivity improvement per filling fraction is calculated for various filler materials as [(Increase in thermal conductivity)/% filling factor]/10.⁵⁸ The thermal conductivity of the SMP improves by about 0.097 times per 0.1 vol.% of 3D-C infused. Other filler material such as CNT shows an improvement in thermal conductivity by only about 0.005 times per 0.1 vol.%. Apart from 3D-C, the next higher values of 0.05 and 0.018 are seen for 0.1 vol.% of Copper and carbon nanofibers with nickel strands, respectively. The high thermal conductivity of the 3D-C/SMP composite can be attributed to the interconnected three-dimensional structure of 3D-C. The networked structure facilitates smooth

conduction of heat across the entire thickness devoid of any thermal interface resistance between the polymer and the foam. This property of 3D-C makes it a better filler for polymers, in terms of thermal conductivity compared to other nanofillers that are embedded entirely within the polymer matrix and thus their ability to enhance the polymer conductivity being quite low. The increase in thermal conductivity achieved by these fillers is relatively lower than that of 3D-C. It is well-known that in the case of nanocomposite fillers, the filler content has to reach the percolation threshold after which a conductive network will be formed, leading to improved thermal conductivity. 3D-C being an interconnected three-dimensional structure, only a small volume fraction is capable of improving the thermal conductivity in all directions. Thus, 3D-C eliminates the problem of inhomogeneous distribution and aggregation associated with typical nanofillers.

Table 4-3. Comparison of thermal conductivity of filler-polymer composite materials.

Sample	Filling Factor		Thermal Conductivity [W m ⁻¹ K ⁻¹]		Normalized increase per 0.1% filling factor		Ref
	[wt.%]	[vol.%]	Bare Polymer	Filled Polymer	[wt.%]	[vol.%]	
*Short carbon fibres with carbon black	2		0.17	0.33	0.008		31
CNF ^{a)} with nickel strands	10		0.17	2	0.018		40
Carbon black		0.275	0.242	0.246		0.0014	33
SWCNTs ^{b)}		0.4	0.242	0.243		0.00025	33
DWCNTs ^{c)}		0.6	0.242	0.252		0.0017	33
MWCNTs ^{d)}		0.175	0.242	0.251		0.005	33
Copper		15	0.25	0.6		0.05	36
Glass fibre		15	0.35	0.5		0.0017	36
Talc		15	0.25	1.5		0.0082	36
AlN ^{e)}		50	0.35	1.08		0.0015	37
*AlN		19.7	0.20	0.40		0.0010	38
BN ^{f)}		50	0.35	3.66		0.0066	37
*TrGO ^{g)}	2		0.18	0.2	0.001		220
*CNT ^{h)}	0.75		0.159	0.19	0.003		35
*3D-C		0.3	0.09	0.361		0.090	187
*3D-C		0.1	0.148	0.240		0.097	This work

*Shape memory polymers; a) Carbon Nano fiber; b) Single-walled CNTs; c) Double walled CNTs; d) Multiwalled CNTs; e) Aluminium nitride; f) Boron nitride; g) Thermally reduced graphite oxide; h) Carbon Nanotube

4.3.4 Effect on mechanical properties

Mechanical performances of the samples are tested through the three-point bending test. The corresponding stress-strain curves, flexural modulus and flexural strength versus 3D-C volume fraction are shown in **Figure 4-7**.

Figure 4-7. Three-point bending test results. a) Stress-Strain curves at room temperature; b) Stress-Strain curves at 45 °C showing large deformation capacity near transition temperature; c) Flexural strength at room temperature; d) Flexural modulus at room temperature; e) Flexural modulus at 45 °C; f) Maximum strain at room temperature. It is observed that the mechanical properties decrease with the increasing foam volume as the foam interrupts the polymer chains.

Bare SMP and 0.1% 3D-C/SMP have a similar flexural strength of about 40 MPa and flexural modulus of ~ 2 to 2.4 GPa at room temperature. The flexural modulus (E) of the samples plotted against the filler content is shown in **Figure 4-7d** and **4-7e**. At 25 °C, 0.1% 3D-C/SMP has a higher flexural modulus (2.4 GPa), higher maximum stress (σ_m), and flexural strength closer to that of bare SMP (40 MPa). In agreement with the tensile test results observed in the previous work,

reduced elongation can be seen for 3D-C/SMP samples at room temperature. With increasing 3D-C content, a decrease in the modulus, maximum stress and flexural strength are observed. This decrease in the mechanical property is attributed to the spatial obstruction (interruption of the polymer chains)²³⁷ of the polymer material by 3D-C foam structure unlike carbon fibres, that helps to improve the polymer mechanical properties in the direction of its reinforcement.

Only a slight yielding is observed in the composite samples at room temperature (**Figure 4-7a**) as opposed to prolonged yielding near transition temperature (**Figure 4-7b**). At high temperature, 3D-C/SMP demonstrates a ductile behaviour with a lower modulus (One order of magnitude lower), low strength and high strain. No breakage is observed at 45 °C due to increased ductility. Both bare SMP as well as 3D-C/SMP samples bent and started to touch the fixture, and the experiment had to be stopped. It is to be noted that bare SMP can reach high strain even at room temperature. This shows that adding 3D-C foams makes the polymer sample brittle at room temperature and renders large deformation capacity near the transition temperature. 3D-C foams having excellent thermal conductivity helps to improve the ductility of the composite at elevated temperature.

The results also indicate that adding a higher volume of 3D-C reduces the mechanical strength of the SMP at room temperature as the matrix is distributed as distinct pockets between the branches of porous 3D-C structure. 3D-C spatially obstructs the polymer chains. There is no continuous layer of the matrix as in the case of CNT or other unidirectional/single-layered fillers. A schematic of the cross-section of 3D-C/polymer compared with CNT/polymer composite is shown in **Figure 4-8**. Furthermore, at high temperature, all the samples display the ability to be plastically deformed without fracture irrespective of 3D-C vol.%. Adding 3D-C makes the SMP soft/malleable near the transition temperature.

Figure 4-8. Schematic of a) 3D-C/SMP showing the polymer chains interrupted by 3D-C branches. At high filler content, the percolation of the polymer through the foam material will be very low, resulting in pockets of matrix interrupted by foam branches; b) CNT/Polymer nanocomposite showing continuous matrix (polymer chains) with carbon nanotube fillers.

4.3.5 Effect on thermo-mechanical properties

The thermomechanical properties such as storage modulus (E') and loss factor (δ) against the temperature for bare SMP, 0.1% 3D-C/SMP, 0.6% 3D-C/SMP and 1.5% 3D-C/SMP are shown in **Figure 4-9**. It is seen that E' decreases slowly with increasing temperature in the glassy state (**Figure 4-9a**). The storage modulus curve for 0.1% 3D-C/SMP indicates a shift in the onset of storage modulus to a slightly lower temperature. However, with the increase in the filler content, the onset of storage modulus seems to increase linearly. The storage modulus for all the samples at room temperature is around 1.3 – 1.6 GPa. Since the storage modulus corresponds to the degree of crosslinking, it can be seen that the storage modulus of the composite sample is lower than that of pure SMP. This is attributed to the weakening of polymer crosslink density by 3D-C. Whereas, in the rubbery region, the storage modulus of the composite sample is higher than that of the pure

matrix. Above T_g , the storage modulus increases from 7.9 MPa to 16 MPa with an increase in the filler content. The addition of 0.6 vol.% of 3D-C results in an increase in the storage modulus by 71% at temperatures above T_g .

Figure 4-9. DMA curves showing the change in a) storage modulus and; b) Tan delta (δ) of bare SMP and 3D-C/SMP composite materials with filler content 0.1, 0.6 and 1.5 vol.% during the temperature ramp from 25 to 80 $^{\circ}\text{C}$. Above T_g , an increase in the storage modulus with increasing filler content is seen. The glass transition temperature is determined from the peak of the tan delta curve.

The tan delta curves for the four samples are shown in **Figure 4-9b**. The T_g of the rigid-chain polymer is often taken from the peak of the tan delta (δ) curve, and the T_g of the polymer material is usually used as the transition temperature. T_g of the bare SMP is found to be 60 $^{\circ}\text{C}$, and for the composite samples, the T_g ranges within ± 3 $^{\circ}\text{C}$ from the bare SMP. The glass transition temperature obtained using differential scanning calorimetry (DSC) from previous work is 56.7 ± 3 $^{\circ}\text{C}$ for 0.3 vol.% 3D-C/SMP.¹⁸⁷ Taking into consideration the different experimental procedure for DMA and DSC, it can be stated that the addition of 3D-C even up to about 1.5 vol.% does not affect the T_g of the SMP. The sequence of preparation of 3D-C (etching of Ni template before infusion with SMP), renders the foam a non-invasive characteristic preventing any direct

bond between the SMP and 3D-C.⁴⁵ The aromatic bond that holds the carbon atoms in the case of graphene makes it chemically stable and inert, accounting for the non-invasiveness of 3D-C.⁶² The non-invasiveness of 3D-C prevents any structural changes within the polymer infused, thus, in turn, maintaining the shape memory performance of the SMP.

4.3.6 Effect on shape memory properties

To investigate the deformation-recovery properties of 3D-C/SMP composite controlled force mode test in single-cantilever mode is carried out with repeated temperature and load cycles on 1.5% 3D-C/SMP (the composite with the highest 3D-C loading fraction) as per section 3.8. The temperature range is chosen to be from 25 to 80 °C since the T_g for the composite material is 60 ± 3 °C, and a force of 1.5 N is applied. The ability of the sample to fix the temporary shape (shape fixity) and to recover its permanent shape (shape recovery) is calculated by measuring the strain under each step.

Figure 4-10a shows the deformation recovery cycle of 1.5% 3D-C/SMP composite. High shape fixity and shape recovery percentage can be observed for all the cycles. Shape memory cycle data for the 1st cycle is presented in **Figure 4-10b**. Excellent shape recovery ability can be seen for the composite. Creeping behaviour is noticed during the cooling process, and hence final deformation is recorded as the maximum strain achieved before unloading. The calculated values of shape fixity and shape recovery are shown in **Table 4-4**. The shape recovery and shape fixity are above 98% and 97% respectively. This indicates that addition of 1.5 vol.% 3D-C foams, does not drastically reduce the shape memory properties of the polymer indicating that the shape memory properties will not be deteriorated by the 3D-C content of 0.1 to 1.0 vol.% as well. The values are in parallel with previous work on 3D-C/SMP,¹⁸⁷ where the shape recovery and fixity

were 97.1% and 98.6% respectively. Thus, the negative strain values in the present work can be attributed to an experimental error pertaining to the DMA instrument.

Figure 4-10. Controlled force mode single cantilever shape memory cyclic DMA test of 1.5% 3D-C/SMP. a) Deformation recovery cycle for four consecutive cycles showing excellent repeatability and shape memory properties; b) Shape memory cycle data for the first cycle. Creeping behaviour of the composite SMP can be seen clearly.

Table 4-4. Shape recovery (R_r) and Shape fixity (R_f) of 1.5% 3D-C/SMP for four cycles.

Cycle	1	2	3	4
Shape recovery R_r [%]	98.08	98.69	98.89	99.13
Shape fixity R_f [%]	96.95	97.66	97.63	97.66

The influence of 3D-C on the shape memory performance of the SMP is studied using rectangular samples of dimensions 35 x 15 x 2 mm³. All the samples were heated, deformed into a similar shape, fixed the temporary shape by cooling and then placed on a hot plate. The recovery of the bare SMP and 3D-C/SMP composites were recorded through video images to measure the

time taken for each sample. Snapshots of the recovery process are shown in **Figure 4-11**, and the recovery time for all the samples are shown in **Table 4-5**. The shape recovery of the composites with 0.1 to 0.6 vol.% of 3D-C is found to be much faster than that of bare SMP due to their high thermal conductivity. **Figure 4-11a** shows the initial state where all the samples were deformed into temporary shape. It can be seen that at about 58 seconds 0.1 to 0.6% 3D-C/SMP composites have completely recovered (**Figure 4-11c**) and the bare SMP reached its full deployment only after almost 1 minute and 24 seconds. The recovery rate increases considerably with the addition of 0.1 vol.% of 3D-C. This is clear from the fact that thermal conductivity increases with the addition of 3D-C. Within the composite samples, it is observed that the recovery rate slightly slows down with an increase in the filler content from 0.1 to 0.6 vol.%. This is in parallel with the results from mechanical characterization that the polymer is distributed as distinct pockets rather than a continuous matrix due to the interconnected branch structure of 3D-C and these interconnected branches hinder the movement of the polymer chains resulting in a long time for shape recovery. However, the shape recovery time for 3D-C/SMP composite with an appropriate volume of 3D-C (0.1 to 0.6%) is always much faster than bare SMP. Those samples with higher filler content (1.0 and 1.5 vol.%) showed only ~98% recovery due to the hindering of the polymer chain movement by 3D-C. 3D-C, when present at higher volume tends to interfere with the polymer chain movement (segmental mobility) during recovery, and as a result, leads to a slight decrease in the shape recovery. The percentage of decrease is insignificant (~2%) compared to the reduction in shape recovery suffered by polymers with fillers such as CNT and carbon fibre.^{31, 35}

Figure 4-11. Photographs showing the shape recovery process of the bare SMP and 3D-C/SMP composites. 0.1, 0.2 and 0.6% 3D-C/SMP samples are observed to recover faster than bare SMP.

Table 4-5. Time taken for recovery of the bare SMP and 3D-C/SMP composites.

Sample	Recovery time [s]
Bare SMP	84
0.1% 3D-C/SMP	52
0.2% 3D-C/SMP	54
0.6% 3D-C/SMP	58
1.0% 3D-C/SMP	92 (~98% recovery)
1.5% 3D-C/SMP	92 (~98% recovery)

Table 4-6 gives a comparison of a few shape memory composite materials studied so far with 3D-C/SMP in terms of thermal conductivity and shape memory properties. It is observed that these fillers have a lower thermal conductivity improvement per filling fraction and at the same time hinders/obstructs the shape recovery of the polymer to a great extent. CNT is reported to be decreasing the recovery ratio with increasing filling fraction.³⁵ In our present work, we are able to demonstrate good shape fixity and shape recovery while also increasing the thermal conductivity by more than 800%. 3D-C being an interconnected three-dimensional structure eliminates the problem of inhomogeneous distribution and aggregation associated with typical nanofillers.

Table 4-6. Comparison of thermal conductivity increase and shape memory properties of filler-SMP composite materials.

Fillers	Filling Factor		Normalized increase in thermal conductivity per 0.1% filling factor		Shape memory property		Ref
	[wt.%]	[vol.%]	[wt.%]	[vol.%]	R _r [%]	R _f [%]	
Short carbon fibres with carbon black	2		0.008		75		31
AlN		19.7		0.0010	75	45	38
TrGO	2		0.001		100	99.4	220
CNT	0.75		0.003		83.7	97.6	35
3D-C	0.35	0.3	0.077	0.090	98	98.5	187
3D-C	0.3	0.1	0.031	0.092	99.13	97.66	This work

4.4 Deployment investigation

Currently, due to their limited thermal conductivity and non-uniform heat distribution, shape memory polymers can only perform well in small samples. The non-uniform heat distribution induces an increase in the internal strains leading to mechanical failure. It is one of the most significant hindrances for the real-time application of the SMP. They can be used only as a part of the deployable structure such as joints, hinges and booms, where the deployment takes place. High thermal conductivity, uniform temperature distribution and high shape memory properties demonstrated for 3D-C/SMP have proven the composite to be suitable for large area and complex deployment mechanism. In order to illustrate the applicability of the 3D-C/SMP composite for a complex deployable structure, two different samples were fabricated using 3D-C/SMP. For this, a box-shaped structure and a tape spring shaped structure were built and tested as presented in this section.

4.4.1 Large area deployable structure (Sequential deployment)

In a previous study, Manuela et al. demonstrated the performance of SMP and 3D-C/SMP for large area applications.¹⁸⁷ Samples of size 7 cm $\times$ 1.5 cm were synthesised and integrated with resistive heating wire. Upon heating (by applying current) the 3D-C/SMP sample recovered its original shape. However, the poor thermal conductivity of bare SMP sample resulted in crack development due to internal stress. It was seen that the large size attainable for the bare SMP without 3D-C foam is about 3 cm in length. Here, to demonstrate that 3D-C as a filler enhances the performance of the SMP for large-area complex deployment application by uniform temperature distribution, we built a box-shaped 3D-C/SMP sample of dimensions 3 $\times$ 3 $\times$ 3 cm³ using the 3D-C foam of size 9 cm $\times$ 12 cm. The model, when heated, can open from box-shape to

a flat material. With the help of 3D-C, heat is distributed uniformly to the entire structure, and the shape recovery process takes place seamlessly. Total time taken for the recovery is 160 seconds. The 3D-C/SMP sample recovered its original shape without any damage, and this shows the significant improvement of thermal conductivity along with uniform heat distribution achieved by adding 3D-C to the SMP. **Figure 4-12** shows the photograph of 3D-C/SMP box model at regular interval during recovery. The continuous and sequential opening of the box can be seen. Initially, the bottom section opens up, followed by the side sections attached to the centre part. Once the side sections have entirely opened, the last two sides of the cube open up one by one. Thus, with the help of 3D-C, the thermal conductivity of the shape memory polymer can be increased along with uniform temperature distribution. In turn, SMPs can be made suitable for application in large area deployable structures. The largest size of 3D-C grown in the lab is 20 cm $\times$ 20 cm using a quartz tube of $\sim$ 20 cm diameter. Foams of an even larger area can also be synthesised by carefully rolling larger Ni foam substrate to fit into the quartz tube.

Figure 4-12. Video images showing the shape recovery of $3 \times 3 \times 3 \text{ cm}^3$ 3D-C/SMP box structure placed on a hot surface. Inset shows the schematic of each step from the side view.

4.4.2 Tape spring shaped 3D-C/SMP (Hybrid structure)

Due to the advantages of tape spring hinge system (simple mechanism, lightweight and low cost)²³⁸ over the rigid type mechanical hinges, many of the shape memory composite hinges developed so far have adapted similar design concept. A tape spring, also known as carpenter tape is a straight strip section of a cylindrical shell.⁷⁶ Replacing the metal tape spring with SMP composite structure helps to overcome the issues of low controllability of deployment and large shock effect associated with metal tape spring hinges.¹³ In order to demonstrate the applicability of 3D-C infused SMP material to deployable hinge structures, tape spring hinge design is selected. Here we have developed a tape spring hinge sample with 3D-C/SMP (epoxy-based SMP) as well as a hybrid sample with a steel tape spring embedded within the composite.

An Al mould is designed and fabricated, specifically for the synthesis of tape spring shaped 3D-C/SMP (**Figure 4-13**). The bottom part of the mould has a concave surface with a radius of curvature 13 mm. The top part of the mould has a convex surface with the same radius of curvature. When the mould is closed, there is a gap of 2 mm between the top and bottom surface. The sample is cured within this gap. For the preparation of 3D-C/SMP composite, the same procedure as described in section 3.3.1 is followed. Briefly, 3D-C is placed on the bottom mould, and the SMP is added carefully in drops using a syringe. The amount of SMP added is equal to the volume of the gap between the curved surface area of the bottom and top mould. The top mould is then placed carefully on the bottom mould and pressed gently to close the setup. The setup is degassed in a vacuum oven for 15 minutes and then cured at 100 °C/1hr and 130 °C/1hr. The final product has a radius of curvature 13 mm and a thickness of 2 mm.

Figure 4-13. Aluminium mould design for fabricating tape spring shaped 3D-C/SMP sample. a) Bottom part and b) Top part.

Figure 4-14 shows the tape spring shaped 3D-C/SMP sample. The sample is heated to its transition temperature and bent to a temporary shape as shown. It can be observed that the centre portion of the sample is made flat to enable bending (since the stiffness of the tape spring structure is higher than a flat structure). Upon cooling, the sample can hold its temporary shape. The portion of the sample near to the region of bending is flat, and the remaining part still retains its curvature. Upon heating to its transition temperature, the sample recovers to its permanent straight configuration as well as regains its curvature without any loss in shape recovery.

Figure 4-15 shows the video image of the sample recovery when placed on a hot plate. A controlled shape recovery process is seen. In order to utilise the self-resistive heating capability of 3D-C, the foam is connected to copper wires on both ends with the help of cable lug and silver paint before infusion. Silver paint helps to achieve a good contact area between the wire and the foam. Copper wire is connected to the cable lug and is placed inside the Al mould. Silver paint is applied on the cable lug, and the foam is placed on the top of the setup. Few drops of silver paint are then added to the foam directly above the cable lug. This way, a good contact area between the foam and the cable can be established. Once the silver paint dries, SMP is infused and cured to

obtain the 3D-C/SMP/ tape spring sample with self-resistive heating capability. **Figure 4-16** shows the recovery of the sample when triggered by applying a direct current of 2V and 1.5A.

Figure 4-14. Tape spring shaped 3D-C/SMP sample in its original and bent configuration.

Figure 4-15. Video images showing the shape recovery of 3D-C/SMP tape spring sample upon direct heating on a hot plate. Total recovery takes place in 100 seconds.

Figure 4-16. Video images showing the shape recovery of 3D-C/SMP tape spring sample upon resistive heating with a power input of 2V and 1.5A.

Hybrid 3D-C/SMP with a metal tape spring embedded within is also fabricated using the same technique described above. A strip of carpenter's tape is cut and placed on the mould first. 3D-C is placed on the top, followed by SMP infusion and curing. **Figure 4-17** shows the hybrid 3D-C/SMP/metal tape spring in its original configuration and bent configuration. **Figure 4-17d** shows the hybrid 3D-C/SMP/metal tape spring sample (with copper wire) in a bent configuration. The sample is triggered by applying a current (2V and 1.5A) through the sample using a programmable DC power supply.

Figure 4-17. Hybrid 3D-C/SMP/metal tape spring sample. a) Original shape; b) Bottom surface showing the tape spring metal (from carpenter's tape); c) Bent configuration and e) 3D-C/SMP/metal tape spring samples in its bent configuration, with a copper wire connected on both sides to enable resistive heating.

Figure 4-18 shows the video images of the shape recovery of 3D-C/SMP/metal tape spring sample triggered by direct heating and electrical resistive heating. The presence of metal tape spring provides additional stiffness to the sample compared to 3D-C/SMP. SMP controls the metal tape spring from snapping back to its original configuration due to its high stiffness and thus, in turn, prevents massive shock associated with metal tape springs. Hence, with the help of 3D-C/SMP, a controlled deployment with no shock effect can be achieved in a tape spring shaped hinge design. Besides, 3D-C as filler helps in internal heating, making the composite applicable for cases where external heating is not feasible.

Figure 4-18. Video images of the shape recovery of 3D-C/SMP/metal tape spring sample. a-d) Recovery through direct heating; e-h) Recovery through resistive heating with a power input of 2V and 1.5A.

4.4.2.1 Mechanical assessment of hinge design with 3D-C/SMP sample

An in-house made force measurement system is used to measure the force exerted by 3D-C/SMP and 3D-C/SMP/metal tape spring samples during recovery. Three samples: Flat 3D-C/SMP, 3D-D/SMP tape spring and 3D-C/SMP/metal tape spring are tested. For this test, a force measurement system is built, as shown in **Figure 4-19**. Nextech DFS-X500 (500N) digital force gauge with external S-beam load cell is used for this measurement. The setup includes two manual operating slide columns. One column has a platform on which the force sensor is fixed, with the probe pointing upwards. The platform can be moved up and down. A sample fixture is attached to the other column, and the fixture can be moved up or down. The height of the sample fixture is fixed such that the sample and the tip of the force sensor probe are on the same horizontal plane. The sample fixture position is not changed throughout the experiment. The samples are heated using a hot gun placed at a fixed distance from the sample. A longer probe is used to eliminate the drift effect in the force sensor due to heating. The angles of measurement are set

before the experiment by heating a sample and bending it by moving up the sensor. The sample is cooled down, removed from the fixture, and the stored angle is noted down. Likewise, three samples are bent to three different stored angles. The angle and the corresponding position of the sensor platform are noted down.

Figure 4-19. Apparatus used for 3D-C/SMP recovery force test.

The procedure followed for the test is as follows,

- The force sensor is zeroed before the measurement.
- The hot gun is turned on for one minute to heat the sample, and the sample is bent to a curved shape as in Figure 4-14. The temporary shape is fixed by cooling.
- The force sensor is moved upward to a position corresponding to an angle measured before the experiment.

- The hot gun is turned back on, and the sample is allowed to recover. The maximum reading on the force sensor is recorded as the recovery force at that particular angle.
- The force sensor is moved down, and the SMP is allowed to recover freely.

The above procedure is repeated for all the samples, and the recovery force is measured at three different angles for each sample. The results are summarised in **Table 4-7**.

Table 4-7. Recovery angle and the corresponding recovery force measured for 3D-C/SMPI samples

Recovery Angle (°)	Recovery force (gram-force, gf)	
	3D-C/SMP tape spring hinge	3D-C/SMP/metal tape spring hinge
175	60	130
170	55	110
165	50	100

Recovery force is measured at three different angles, namely 175°, 170°, and 165°. As can be seen from the table, the recovery force is proportional to the recovery angle. The recovery force increases with the recovery angle, i.e. the force of recovery is smaller during the initial stages of shape recovery and increases linearly towards the end. As expected, the hybrid 3D-C/SMP/metal tape spring sample has greater recovery force, exerting almost twice the amount of force generated by 3D-C/SMP tape spring hinge sample. The trend remains the same for all three angles. Besides the tape spring hinge sample, a flat sample is also tested for its recovery force at these angles. The force produced by the sample is too small to be reflected in the force sensor. The results show that tape spring 3D-C/SMP samples have higher recovery force compared to flat 3D-C/SMP, and

among the tape spring samples, 3D-C/SMPI with an embedded metal tape spring performs better with higher recovery force.

4.5 Summary

In this chapter, the influence of 3D-C content on the mechanical, thermal and shape memory property was evaluated. It was shown that 3D-C significantly improves the thermal conductivity of the SMP matrix, higher than any other nanofiller for the same vol.%. The thermal conductivity increases linearly with increase in the foam volume fraction. The mechanical strength test revealed that at a higher filling fraction, 3D-C causes a reduction in the mechanical properties due to the interruption of polymer chains by the 3D-C branches, lowering the polymer chain connectivity and causing easy breakage. In addition, the Shape memory cyclic test in DMA has shown that infusion of 3D-C does not alter the shape memory performance of the SMP. The study shows that a careful design based on the amount of 3D-C as well as infusion process is needed to obtain a balance between thermal conductivity, mechanical strength and shape memory properties for better results. The mechanical properties of the 3D-C/SMP composites could be further improved by controlling the density of the foam used or by enhancing the infusion technique to prevent the compartmentalisation of polymer into distinct pockets. The uniform heat spread facilitated by the interconnected structure of 3D-C enables an increase in the SMP actuation area. The proof-of-concept experiments demonstrate the applicability of 3D-C/SMP composites for large area actuator as well as tape spring hinge design. 3D-C/SMP renders self-heating capability and controlled deployment, while the metal tape spring provides additional stiffness to the sample.

5 3D-C infused shape memory polyimide composite

5.1 Introduction

The extreme temperature cycles in space (-120 °C to +120 °C every orbital cycle), demands an SMP with high transition temperature. Polyimides have high thermal stability along with good resistance to AO attack, and UV radiation prevalent in the space environment.^{20, 128} Combining the shape memory effect with the excellent mechanical and thermal properties of PI extends its application to satellite deployment systems.²¹⁻²⁸ Currently, PI-based shape memory polymers (SMPIs) are of great interest.¹²⁹ Their excellent radiation shielding capability and high glass transition temperature makes them suitable for applications in space such as large-area flexible electronics.¹³⁰ Several SMPIs were synthesised and tested for their reliability in space through accelerated space environment tests (**Table 2-1**). Despite their advantages, their synthesis process and reduced thermal conductivity limit their application and reliability as large area actuator for satellites. Thermal conductivity can be increased by adding conductive fillers. The non-invasiveness of 3D-C preventing any structural changes within the SMP matrix, as shown in the previous chapter can be utilised to obtain 3D-C infused SMPI for space application. 3D-C being a networked structure, eliminates the need for a higher concentration of the filler to form a conductive network. The problem of agglomeration and inhomogeneous distribution associated with nanofiller can be eliminated by employing 3D-C as filler for the SMPI. This way, the thermal conductivity of the SMPI can be increased and at the same time render self-heating capability to the SMPI, making it a suitable material for deployable satellite structures.

In this chapter, the first-time infusion of 3D-C with high-temperature shape memory polyimide is carried out. A suitable high-temperature SMPI¹³⁷ is chosen from literature for the infusion. 3D-C

with high electrical and thermal conductivity is combined with SMPI's good mechanical strength and environmental stability. The developed 3D-C/SMPI composite is shown to be suitable for smart deployable systems. It is seen that 3D-C enhances the thermal conductivity of the SMPI by about 500% with a filling factor of 0.4 vol.%. In addition, 3D-C/SMPI composite exhibits high glass transition temperature ($\sim 175^{\circ}\text{C}$) and thermal decomposition temperature (5% weight loss at 500°C), showing excellent thermal stability required for space application. 3D-C/SMPI also demonstrates good shape memory behaviour with high shape fixity and shape recovery.

5.2 Material preparation and characterisation

For the preparation of 3D-C/SMPI samples, 3D-C foams are grown and infused with SMPI as described in section 3.3.3. Apart from standard thermal and electrical measurements (sections 3.5 and 3.6), shape memory characterisation of the composite sample is also carried out using dynamic mechanical analysis (section 3.8). The stress, strain and displacement for a given force, temperature and time are measured.

5.3 Novel 3D-C/SMPI composite

Figure 5-1d shows the bare SMPI and 3D-C/SMPI composite. One of the main drawbacks concerning the application of aromatic PIs as a structural material is its synthesis process. Polyimides are generally fabricated by thermal imidization of poly(amic acid) (evaporation of solvent and curing) resulting in a thin film with thickness ranging in micrometres.²⁰ Techniques such as spin coating, spray coating, dip coating and roller coating are commonly used for PI film synthesis. Thick films can be produced by curing subsequent layers on the top of the cured PI layer. However, the thickness that can be achieved by multi-step curing is further limited by

cracking and delamination of the layers when the thickness reaches 1000s of μm . Moreover, since aromatic PIs have a high melting temperature, the cured PI film cannot be moulded into a structural material, limiting them to thin-film structures.

Figure 5-1. 3D-C/SMPI composite. a) optical image of 110 ppi and 60 ppi 3D-C foam; b) Top view SEM image of 60 ppi 3D-C foam showing holes of diameter around 1.14 mm; c) Top view SEM image of 110 ppi 3D-C foam showing holes of diameter around 450 μm ; d) Optical image of bare 3D-C, bare SMPI, and 3D-C/SMPI; e) Cross-sectional SEM image of 110 ppi 3D-C/SMPI showing incomplete infusion; f) Cross-sectional SEM image of 60 ppi 3D-C/SMPI synthesised using viscous PAA showing good infusion of the foam without any air bubbles.

Thermoforming is a technique developed for transforming PI films into 3D structures. The PI film will be subjected to high pressure and high temperature in a mould to obtain the desired shape.²³⁹ Recently, two dimensional 3D-C/PI composite film was transformed into 3D contours using the thermoforming technique.²⁴⁰ In this study, 2mm thick 3D-C foam and a viscous PAA is used to produce 3D-C/SMPI composites. For this, 3D-C foams grown on 110 pores per inch (ppi) and 60 ppi, Ni foam substrates are studied. Unlike the previous technique,⁵⁸ where the PAA is

diluted with solvent and then infused in 3D-C in multiple steps, a viscous PAA is used here for infusion. Since the amount of solvent used is less in this technique, the procedure yields a 3D-C/SMPI composite of thickness 2 mm in two or three infusions. The first layer of PAA is poured on to the foam placed on a glass substrate. The setup is allowed to rest for some time until the PAA infiltrates and settles at the bottom. The setup is then degassed in a vacuum chamber for 15 minutes to aid further infiltration and remove any air bubbles. Finally, thermal curing is carried out, and the above steps are repeated for subsequent layers until the SMPI covers the top of the 3D-C. It is found that adding viscous PAA to the 110 ppi 3D-C results in a highly porous composite (**Figure 5-1e**). The PI coats only the top layer of the foam. The percolation of the PI matrix within the foam structure is very low, resulting in matrix pockets with air gaps, as described in section 4.3.4.

However, in the case of 60 ppi 3D-C (foam with large pores), the PAA can easily flow through the pores, and a better infusion of 3D-C foam is achieved in two steps as shown in the cross-sectional SEM View of the 3D-C/SMPI composite (**Figure 5-1f**). Since the PAA is not diluted with the solvent before infusion, the effect of residual stress caused by evaporation of the solvent is minimised, and relatively thick samples can be produced. This process enables the production of 3D-C/SMPI based structural materials for various applications.

Contact angle measurement is carried out to determine the ability of SMPI to infiltrate 3D-C, and the result is shown in **Figure 5-2**. The initial contact angle between the SMPI drop and foam surface is 78.8°. The contact angle decreases to 29.9° in 8 minutes after which the PI solidifies due to exposure to air and moisture. This indicates that the PAA can eventually infiltrate the 3D-C foam structure in the inert gas atmosphere when sufficient time for the infiltration is given before curing. Though the viscosity of the PAA matrix is higher, the dimensions of the foam structure used (larger pore size) enable good infiltration.²⁴¹

Figure 5-2. 3D-C/SMPI interfacial contact observed optically in a sessile single drop experiment.

Raman spectroscopy is performed to determine the crystalline configuration of the 3D-C/SMPI composite. **Figure 5-3** shows the Raman spectra of 3D-C, SMPI and 3D-C/SMPI. G-peak (1580 cm^{-1}) and 2D-peak (2700 cm^{-1}) can be seen for the pure 3D-C sample. The intensity of the G-peak is about two times the intensity of the 2D peak indicating high-quality multi-layer graphene.^{232, 233} The peak corresponding to aromatic imide ring configuration (di-anhydride) can be seen at $\sim 1610\text{ cm}^{-1}$ for the SMPI, and it merges with the G-Peak of 3D-C in 3D-C/SMPI. Three distinct peaks corresponding to C-H, C=O and C-N stretching vibrations are seen for the SMPI sample at $\sim 3074\text{ cm}^{-1}$, $\sim 1778\text{ cm}^{-1}$, and $\sim 1368\text{ cm}^{-1}$, respectively.²⁴² The peak related to aromatic ring vibration is also seen at 1000 cm^{-1} . The Raman spectra of 3D-C/SMPI shows the G and 2D

peaks of 3D-C as well as the characteristic bands of SMPI spectrum confirming the infiltration of SMPI into 3D-C.

Figure 5-3. Raman spectra of 3D-C (Blue), SMPI (Black) and 3D-C/SMPI (Red).

TGA and DSC measurements are carried out to evaluate the effect of infusion on the intrinsic properties of the SMPI (section 3.4.3). The decomposition profile from TGA and heat flow curve from DSC is shown in **Figure 5-4** and **5-5**, respectively. For TGA, the samples are heated from room temperature to 850 °C under nitrogen atmosphere. From the decomposition profile, it can be seen that the effective decomposition temperature, T_d corresponding to 5% mass loss is ~503 °C for both SMPI and 3D-C/SMPI indicating no change in the matrix properties even after infusion. It is observed that carbonaceous char of about 50 wt.% remains at the end of the experiment. TGA results indicate that the composite material is suitable for high-temperature applications.

Figure 5-4. Thermogravimetric analysis. TGA curves of a) Bare SMPI and; b) 3D-C/SMPI from room temperature to 850 °C showing similar degradation curves for both samples. The decomposition temperature is marked with the red dashed lines at the point of 5% mass loss.

Figure 5-5. DSC results to determine glass transition temperature (T_g) of SMPI and 3D-C/SMPI studied. The glass transition temperature is determined by the mid-point of the slope and is marked with red dashed lines.

The DSC measurement of the SMPI and 3D-C/SMPI is done under nitrogen atmosphere in temperature modulation mode. A temperature sweep from room temperature to 300 °C (heating rate of 2 °C/min) is performed, and the heat flow curve versus temperature of the samples are shown in **Figure 5-5**. The glass transition temperature of the SMPI and 3D-C/SMPI is ~164 °C and ~165 °C respectively indicating no effect of infusion on the T_g of the SMPI. The value corresponds to previous results from DSC reported for the bare SMPI.¹³⁷

5.3.1 Thermal conductivity improvement

The thermal conductivity of the bare SMPI and composite samples are measured at room temperature to 200 °C using the laser flash technique. **Figure 5-6** shows the thermal conductivity of 3D-C/SMPI and bare SMPI over a temperature range of 25 °C to 200 °C. The thermal conductivity of the bare SMPI is found to be 0.06 Wm⁻¹K⁻¹ at 25 °C. Upon adding 3D-C, the thermal conductivity increases to 0.36 Wm⁻¹K⁻¹ (with error deviation of 0.0016 Wm⁻¹K⁻¹). For both bare SMPI and 3D-C/SMPI, the thermal conductivity is found to be more or less stable throughout the temperature range. The thermal conductivity enhancement in SMPI by 3D-C is in good agreement with the previous trend. However, the conductivity values for both bare SMPI and 3D-C/SMPI composite is quite low (more than one order of magnitude) compared to other PI and 3D-C/PI samples measured previously.

Figure 5-6. Thermal conductivity of bare SMPI and 0.4 vol% 3D-C/SMPI at a temperature range of 25 °C – 200 °C measured by laser flash technique.

Table 5-1 shows the comparison of thermal conductivity improvement of SMPI by 3D-C, with other reported filler materials (table reproduced from previous report).⁵⁸ The most significant increase in thermal conductivity per filling fraction is obtained for 3D-C filled PI (PI similar to Kapton) followed by SMPI (This work). It can be seen that thermal conductivity improvement achieved for 3D-C/SMPI (0.075 per 0.1 vol.%) is lower than that obtained for 3D-C/PI (0.5167 per 0.1 vol.%). This might be attributed to the fact that a highly porous 3D-C (low-density foam) is infused into SMPI and that majority of the composite volume is filled with SMPI matrix. Whereas, in the case of 3D-C/PI, 110 ppi foams of thickness 0.5 mm were infused. The primary factor leading to the difference in thermal conductivity improvement for PI and SMPI might be the difference in foam porosity (110 ppi foam for PI and 60 ppi foam for SMPI). However, the increase in SMPI's thermal conductivity by 3D-C is still more significant than other filler materials such as silver particles, nanowires, CNTs and AlN nanoparticles. Further improvement can be achieved by fine-tuning the 3D-C foam and infusion process.

Table 5-1. Comparison of improvement in thermal conductivity of polyimide by various fillers.

Sample	Filling Factor		Thermal Conductivity [W m ⁻¹ K ⁻¹]		Normalised increase per 0.1% filling factor		Ref
	[wt.%]	[vol.%]	Bare PI	Filled PI	[wt.%]	[vol.%]	
SiC nanowires on graphene	7		0.25	0.577	0.0047		243
	11		0.25	2.63	0.022		244
MWCNTs	3		0.18	0.25	0.0023		245
BN-c-MWCNTs	3		0.18	0.38	0.0067		245
Silver particles		45	0.2	15		0.033	246
BN	30		0.18	1.2	0.0034		247
Aluminium nitride		30	0.22	0.6		0.0013	248
Nanoparticles		10	0.26	0.32		0.0006	249
3D-C	0.35	0.3	0.15	1.7	0.443	0.5167	58
3D-C		0.4	0.06	0.36		0.075	This work

5.3.2 Electrical conductivity

Temperature-dependent resistivity measurements are performed to investigate the effects of infusion of SMPI on the 3D-C conductivity. The measurement is made using the four-point van der Pauw method, as described in section 3.6 at temperatures ranging from -100 °C to 200 °C. The sheet resistance is plotted against temperature, as shown in **Figure 5-7**. $\ln(R_s T^{-1/2})$ is plotted against $T^{-1/4}$ as Arrhenius curves in the inset and fit with linear trend lines. The conduction behaviour of the sample follows the three-dimensional variable range hopping (VRH) behaviour. This

behaviour was predicted by Godet²⁵⁰ as due to the carriers hopping between energy levels within band-tails. The linear fitting lines of the VHR model by Godet²⁵¹ is shown in **Figure 5-7** inset.

Equation 5-1 describes this conduction mechanism.

$$R_s(T) = R_{00} T^{\frac{1}{2}} \exp\left(\left(\frac{T_0}{T}\right)^{\frac{1}{1+d}}\right) \quad (5-1)$$

Where R_{00} is the band tail's resistivity pre-factor, T_0 is the temperature coefficient containing the hopping parameters, and d is the dimensionality of the hopping space.

Figure 5-7. Electrical conductivity characterisation. The sheet resistivity of 3D-C/SMPI composite at a temperature range of -100 to 200 °C (inset: fitting of the sheet resistance measurement to the VRH conductivity model).

The hopping parameters are the density of the states and the localisation length of the wave function. Here, it is seen that the results fit the VRH model with the temperature dependence of $T^{-1/4}$. The VRH model shows a temperature dependence of $\exp((T_0/T)^{1/(1+d)})$. The data fits the expression $\exp((T_0/T)^{1/4})$ indicating that $d = 3$ and hence three-dimensional electrical conduction in 3D-C based composites.²⁵² Similar electrical conductivity behaviour was reported earlier for both 3D-C infused polyimide⁵⁸ and other carbon-based materials.^{58, 193} The temperature-dependent resistivity of 3D-C/SMPI follows the same trend as that of 3D-C⁵⁸ with similar slopes signifying identical electrical conductivity properties. This is due to the fact that the electrical conductivity behaviour is mainly dependent on the intrinsic characteristic of the 3D-C foams. The composite sample shows a maximum electrical resistance of $1.26 \text{ } \Omega/\square$ at $-100 \text{ } ^\circ\text{C}$ and decreases proportionally with increasing temperature to a minimum of $0.88 \text{ } \Omega/\square$ at $200 \text{ } ^\circ\text{C}$. This indicates that the addition of SMPI to 3D-C did not change or affect the electrical conductivity behaviour of 3D-C. The VRH conductivity mechanism is well preserved even after SMPI infiltration.

Equation 5-2 gives the conductivity by the VRH model, according to Godet.²⁵³

$$\sigma(T) = \sigma_{00} T^{-\frac{1}{2}} \exp\left(-\left(\frac{T_0}{T}\right)^{\frac{1}{1+d}}\right) \quad (5-2)$$

By transferring to resistivity $(1/\sigma) = \rho$, we get

$$\rho(T) = \rho_{00} T^{\frac{1}{2}} \exp\left(\left(\frac{T}{T_0}\right)^{-\frac{1}{1+d}}\right) \quad (5-3)$$

In the linear representation,

$$\ln\left(\rho T^{-\frac{1}{2}}\right) = \ln(\rho_{00}) + \left(\frac{1}{T_0}\right)^{-\frac{1}{1+d}} T^{-\frac{1}{1+d}} \quad (5-4)$$

Where ρ is the resistivity, T is the temperature, d is the dimensionality of the conductivity, T_0 is a factor related to localisation parameter, and ρ_{00} is the exponential pre-factor. ρ_{00} is dependent on both lattice disorder and localisation parameter. The correlation between localisation parameter ($N(E_F) \gamma^{-3}$) and the T_0 factor, according to Goddet's VRH model is:

$$310 = T_0 N(E_F) \gamma^{-3} \quad (5-5)$$

where $N(E_F)$ is the density of states in the Fermi level, and γ^{-1} is the localisation radius which equals the decay length of the electron wave function. Linear fitting is used to extract various parameters for the sample. As reported earlier, the dimensionality d is found to be 3, indicating the multi-layered structure of the 3D-C. The localisation parameter ($N(E_F) \gamma^{-3}$) and the pre-factor (ρ_{00}) are calculated to be 0.008 1/K (93 eV⁻¹) and 0.0002 (K^{-1/2}) respectively from the **equations 5-3** and **5-5**.

It can be seen, that the localisation parameter falls within the weak localisation range, $1 \times 10^{-5} \ll N(E_F) \gamma^{-3} \ll 1$ as expected for a composite material with graphene layers.²⁵³ The localisation parameter is proportional to the density of states in the graphene grain boundaries, where the hopping conductivity process takes place.

5.3.3 Thermo-mechanical properties

Dynamic mechanical analysis of the 3D-C/SMPI composite is performed as per section 3.7 to study the thermomechanical properties such as storage modulus (E') and loss factor (δ) against the temperature. The storage modulus and loss factor curves from the temperature sweep experiment are shown in **Figure 5-8**. It is seen that E' for the composite sample is 390 MPa at room temperature and decreases slowly with increasing temperature in the glassy state, followed by a sharp decrease near the glass transition temperature. At 195 °C (20 °C above T_g), the storage

modulus of the composite is 1.573 MPa. The T_g of the sample taken from the peak of the $\tan \delta$ is found to be $\sim 175^\circ\text{C}$. The Value of T_g measured for 3D-C/SMPI composite is in close agreement with the T_g of the SMPI film reported previously,¹³⁷ conforming that 3D-C does not change the intrinsic properties of the SMPI. However, the storage modulus of the 3D-C/SMPI composite studied in this work is lower than that of the pure SMPI. This is due to the weakening of the polymer crosslinking by 3D-C, as reported in section 4.3.5.

Figure 5-8. Dynamic mechanical analysis. Storage modulus and loss modulus of 3D-C/SMPI composite.

5.3.4 Shape memory performance

The shape memory properties of the 3D-C/SMPI composite is assessed through controlled force mode cyclic test in DMA (section 3.8). The stress, strain and displacement of the sample due to the applied force is monitored as the temperature changes. Shape memory performance of the

3D-C/SMPI composite is tested using a similar procedure used for 3D-C/SMP composite (section 4.3.6). A force of 0.3N and a switching temperature of 200 °C (~20 °C above glass transition temperature) is used for testing 3D-C/SMPI composite. The force required for shape transformation is obtained through a force ramp test conducted prior to the cyclic test.

Figure 5-9 shows the deformation recovery cycle of 3D-C/SMPI composite. It is observed that the shape fixity (R_f) for the first, second, third and fourth cycle is 97.78%, 97.75%, 97.60% and 97.85% respectively. The shape fixity is excellent and consistent from one cycle to another, indicating no creeping behaviour of the composite. However, the shape recovery (R_r) for the first cycle is 52% and then increases to 85.55%, 90.27% and 92.14% for the second, third and fourth cycle respectively. This phenomenon is attributed to the aromatic groups in the SMPI, forming more net points (cross-links responsible for shape recovery) during the shape training process. When the 3D-C/SMPI sample is deformed, more aromatic groups come together, forming net points, and this increases with increase in the shape training cycle. After the first thermo-mechanical cycle, the net points formed by the aromatic groups preserve the orientation of the polymer chain and hence the shape recovery rate increases with each cycle.^{23,24} The shape memory parameters are calculated based on the strain values in the third cycle ($N = 3$). The recovery rate R_r and shape fixity R_f for the third cycle is 90.27% and 97.60% respectively. The composite shows deformation of 13.54% in the first cycle and remains stable in the remaining cycles. It can be seen that all the values approach the ideal value of 100% in the subsequent cycles. There is no decrease in the degree of shape recovery or shape fixity. Hence the shape memory performance of the 3D-C/SMPI composite is considered ideal for applications in smart actuator system. Different SMPs from the literature (Table 2.1) can now be infused with 3D-C to obtain 3D-C/SMPI with better shape recovery.

Figure 5-9. Controlled force mode single cantilever shape memory cyclic DMA test of 3D-C/SMPI. a) Deformation recovery cycle for three consecutive cycles; b) Shape memory cycle data for the first three cycles. No creeping behaviour can be seen indicating good shape fixity.

5.4 Summary

In this chapter, 3D-C was successfully infused into SMPI matrix for the first time. A highly porous 3D-C foam (foam with 60 ppi porosity) and viscous PAA were used in the synthesis process, and the SMPI composite, with thickness in the range of 2 to 3mm was fabricated through stepwise thermal imidization process. The high decomposition temperature of the composite ($\sim 503^\circ\text{C}$) makes it ideal for use in satellite deployment systems. The thermal conductivity of the SMPI improved by about six-folds with the infusion of 0.4 vol.% of 3D-C. The interconnected structure of the 3D-C foam helps to improve the thermal conductivity of the SMPI without altering its intrinsic properties (decomposition temperature and glass transition temperature). Through shape memory cyclic test in DMA, it was shown that the shape fixity and recovery rate approaches the ideal value of 100% for each consecutive cycle. Thus, using 3D-C as a filler for polyimide-based SMP opens up the application of SMPI material for space structures.

The networked structure of 3D-C prevents any inhomogeneous distribution, that is prevalent in particulate fillers. It effectively improves the thermal and electrical conductivity of the SMPI at a lower filling fraction (0.4 vol.%). Besides, with 3D-C, SMPI can be fabricated into any structural material instead of a 2D planar film, for deployment applications. 3D-C also renders uniform temperature distribution to the SMPI, preventing any thermal gradient across the sample that causes internal stress build-up and cracking during recovery. This has extended the application of SMPI to deployment actuator and large area deployable structures. It has been demonstrated by fabricating a tape spring shaped (structural material) and a box-shaped (large area deployable structure) 3D-C/SMPI sample in Chapter 8.

6 Space qualification of 3D-C/SMPI

6.1 Introduction

In order to design a deployable structure that is reliable, it is vital to recognise the performance of the composite material in space environments. Satellites for long term space missions are typically launched to LEO and GEO where atomic oxygen (AO) (at LEO only), Ultraviolet (UV) and ionising radiation, plasma, extreme thermal cycles (-120 °C to 120 °C every orbital cycle), vacuum, micrometeoroids, and space debris are prevalent.¹⁻⁴ 3D-C/SMPI composite should be tested for its stability and resistance to degradation in these environmental conditions. The results of space qualification will help in designing and promoting the reliability of the material in both LEO and GEO. Besides having high thermal stability, excellent mechanical properties and chemical resistance,²⁰ polyimides are vulnerable to AO erosion at LEO and electrostatic discharge in GEO environment.

The ESD and AO erosion of the PI's, are usually mitigated by applying protective coatings on the outer layer. Conductive coating made of indium tin oxide (ITO) is used for ESD protection and AO durability. Protective coatings such as Al₂O₃, SiO₂, SnO₂, or ITO,²⁵⁴⁻²⁵⁷ are used to reduce AO erosion. However, these coatings are very brittle and are prone to crack upon folding or bending, even to a small extent, resulting in increased sheet electrical resistance.²⁵⁸ In addition, they are also vulnerable to damage by micrometeoroids and space debris. Once the crack is formed, the underlying substrate is subjected to AO attack, leading to erosion.^{254, 258} Another method for AO protection, is by adding fillers (nanomaterials) as additives²⁵⁹⁻²⁶² or by tweaking polymer backbone.²⁶³⁻²⁶⁵ These nanofillers tend to cause inhomogeneous distribution, affecting the structural integrity of the polymer matrix.^{266, 267} 3D-C has already been infused as filler in PI to

mitigate the electrostatic discharge.⁵⁶⁻⁵⁸ Adding 3D-C to PI demonstrated good compatibility with GEO environment.⁵⁸

In this chapter, the space reliability of the 3D-C/SMPI composite is tested through a series of simulated space environment exposure tests.

6.2 Material preparation and characterisation

The samples for space qualification are prepared using 3D-C foams and SMPI, as described in Section 5.3. The composite material is characterised according to European Space Standards. The accelerated space reliability tests include gamma-ray exposure, AO exposure, outgassing, thermal cycling and thermo-optical property measurements. Electrical resistivity measurements are carried out as described in section 3.6, to quantify the effect of these environments on the composite material.

6.3 Space qualification results

6.3.1 Thermo-optical properties

Since the composite deployable structure will be directly exposed to the space environment, over-heating of the 3D-C/SMPI structure is undesirable. The temperature of the composite must be well below its transition temperature to avoid premature deployment. The equilibrium temperature $T(K)$ of the 3D-C/SMPI composite in space must be calculated in order to evaluate the material. This can be done by measuring the thermo-optical properties. The majority of heat transfer in space is through radiation.²⁶⁸ The thermo-optical properties measured are solar absorptance, α_s (heat absorbed from the sun) and emittance, ε (heat radiated to the surroundings).

The thermo-optical characteristics of the composite, α_s and ϵ , are measured at room temperature using UV/VIS/NIR spectrophotometer, with 150 mm integrating sphere. The values of absorptivity and emissivity measured for 3D-C/SMPI composite are,

Solar absorptance, α_s : 0.924

Emittance, ϵ : 0.92

The equilibrium temperature, $T(K)$ of an object in space is dependent on the heat absorbed from the sun (solar absorptance α_s), and the heat radiated to the surroundings (emissivity ϵ). Since the majority of heat transfer in space is due to radiation. The equilibrium temperature of the composite material is calculated using the equation (6-1),¹⁸⁸

$$T = \left(\frac{\alpha_s}{\epsilon} \right)^{1/4} \left(\frac{SA_n}{\sigma A} \right)^{1/4} \quad (6-1)$$

Where,

S = Solar flux per unit area (W/m^2)

A_n = Sample's surface area normal to the solar flux (m^2)

A = 3D-C/SMPI's total surface area (m^2)

σ = Stefan-Boltzmann constant ($5.67 \times 10^{-8} W/m^2K^4$)

Here, the equilibrium temperature is calculated using a solar flux of $1366.1 w/m^2$ (average flux value at 1AU from the sun)²⁶⁹ and a normal area factor of $A_n/A = 0.25$ ²⁷⁰ (related to sample with spherical geometry).²⁷⁰ The equilibrium temperature is calculated to be $5.73^\circ C$ and thus the maximum temperature that the 3D-C/SMPI composite is expected to experience in space is far below its transition temperature of $\sim 175^\circ C$.

6.3.2 ESD protection

Since PIs are insulating material or poor conductor of electric current, application of SMPI based material in the satellite might cause electrostatic discharge (ESD). ESD is caused by space plasma mostly in GEO environment and can lead to degradation of the surfaces exposed to the space environment.¹⁸⁸ The spacecraft is surrounded by space plasma (ions and electrons). This creates a potential difference between the spacecraft and space plasma (spacecraft charging). A difference in the voltage between spacecraft conducting surface and insulator leads to discharge. ESD can lead to degradation of the external surface, contamination of the material surfaces as well as cause damages to onboard electronics.²⁷¹ 3D-C being a conductive material, makes the whole composite conductive and in turn, helps to mitigate ESD of the SMPI material. From the electrical conductivity measurement of 3D-C/SMPI composite in section 5.3.2, it can be seen that the sheet resistance of the 3D-C/SMPI sample is around $0.9\text{--}1.3\ \Omega/\square$ which is well below the surface resistivity range $10^4 - 10^{10}\ \Omega/\square$ required for ESD build-up.²⁷²

6.3.3 Gamma-ray exposure

3D-C/SMPI composite is exposed to gamma radiation from ^{60}Co source with two main emission peaks in the spectrum at 1173.3 KeV and 1332.5 KeV. The exposure is conducted at room temperature. Two samples are exposed to a dose of 0.5 mega rad and 1 mega rad. respectively. The temperature-dependent sheet resistance is measured after exposure, and the results are compared to the unexposed sample, as shown in **Figure 6-1**. It can be seen that the exposed samples have nearly the same sheet resistance as that of the unexposed sample (including the measurement error). In addition, no change in the conductivity mechanism is observed. The

fitting of VRH conductivity model in **Figure 6-1b** shows that the conductivity mechanism is unchanged after exposure.

Figure 6-1. Electrical properties after gamma-ray exposure for 3D-C/SMPI. a) Electrical conductivity measurement at a temperature range of -100°C to 200°C ; b) Fit of VRH model for all three samples.

6.3.4 AO exposure

For AO exposure study, 3D-C/SMPI sample and a reference PI (Kapton) film are exposed to AO fluences of up to 2.967×10^{20} O-atoms/ cm^2 , equivalent to about 5 months at an LEO altitude of 500 Km.²⁷³ **Figure 6-2** shows the mass loss values versus AO fluence for 3D-C/SMPI and Kapton. It can be seen from the slope of the curves that the etch rate of 3D-C/SMPI is nearly twice that of the reference PI film. The erosion yield is obtained from the slope of the mass loss curves, using equation (3-5). The average density of the SMPI from the literature is used for the calculation.¹³⁷ The erosion yield of 3D-C/SMPI is found to be $7.68 \times 10^{-24} \pm 1.06 \times 10^{-24} \text{ cm}^3/\text{O-atom}$. The obtained value is higher than the accepted erosion yield of Kapton H ($3.0 \times 10^{-24} \text{ cm}^3/\text{O-atom}$).²²⁸ Thus, it is necessary that the 3D-C/SMPI composite is made

suitable for application in LEO altitudes by incorporating additional protection to decrease the AO erosion and increase the durability in low earth orbits.

Figure 6-2. a) Mass loss versus AO fluences of 3D-C/SMPI and reference PI film (Kapton); b) Mass loss for AO fluences up to 1×10^{19} O-atoms/cm².

6.3.5 Outgassing

Outgassing is the release of absorbed or trapped molecules from the material exposed to the vacuum environment. The released molecules might contaminate the neighbouring surfaces in the satellite. The performance of satellite mirrors or detectors will be significantly affected by these contaminants. In some cases, the contamination might even change the chemical composition, volume or density of the surfaces.⁵⁸ Hence, it is essential to use low outgassing materials for space application. The outgassing properties measured for 3D-C/SMPI composite as per section 3.9.4 is shown in **Table 6-1** compared to low outgassing criterion requirements as per ASTM E595-15²³¹ and ECCS-Q-ST-70-02C.²³⁰ The outgassing parameters obtained for 3D-C/SMPI composite are

well below the range described for low outgassing criterion. Thus, the composite is suitable for use in space structures.

Table 6-1. The outgassing parameters obtained for 3D-C/SMPI composite compared with standard requirements.

Measured outgassing parameters	wt. %	Low outgassing requirements
Residual Mass Loss (RML)	0.144	< 1%
Collected volatile condensable materials (CVCM)	0.003	< 0.1%
water vapour regained (WVR)	0.256	
Total mass loss (TML)	0.400	

6.3.6 Thermal cycling

Electrical conductivity measurements are performed under repeated heating and cooling cycles to investigate the stability of 3D-C/SMPI composite in extreme thermal cycles in space. The temperature range is chosen to be -100 °C to 100 °C. Measurements are made using Van der Pauw four-point probe method with the same procedure described in section 3.6. **Figure 6-3** shows the change in sheet resistance (%) for 30 repetitions at -100 °C (top graph) and 100 °C (bottom graph). It can be seen that the change in sheet resistivity after 30 thermal cycles is very minimal to have any effect on the electrical conductivity of the 3D-C/SMPI composite. This is in agreement with the results obtained for 3D-C/PI film.⁵⁸ 3D-C/SMPI is capable of functioning in the space environment.

Figure 6-3. Thermal cycling test. Measurement of change in sheet resistance (%) after repeated heating and cooling for 30 cycles.

6.4 Summary

In this chapter, the suitability of 3D-C/SMPI for space application is investigated by conducting space environment reliability tests. It was demonstrated that 3D-C/SMPI has excellent thermo-optical properties with operational temperature far below the SMPI trigger temperature. The electrical sheet resistance of the composite is also well below the resistivity range required for electrostatic discharge in GEO. It was also shown that 3D-C/SMPI is stable under extreme temperature cycles in space. Also, the outgassing properties, RML and CVCM are far below the criterion set for low outgassing materials in ECCS-Q-ST-70-02C. The composite performance is

found to be stable with gamma-ray exposure since the electrical conductivity property remained unchanged after exposure. 3D-C/SMPI composite is expected to perform well in GEO environment since electrical conductivity property of the similar sample (3D-C/PI film) remained unchanged after exposure to a higher dose of gamma radiation equivalent to 15 years in GEO.⁵⁸ However, the composite is expected to erode under long term AO exposure at LEO altitudes.²⁷⁴ 3D-C/SMPI has an erosion yield higher than that of the accepted erosion yield of Kapton. The AO durability of the 3D-C/SMPI could be improved by incorporating Polyhedral oligomeric silsesquioxane (POSS) to the composite.¹⁹³

7 POSS study for AO endurance

7.1 Introduction

Through the space qualification tests conducted in chapter 6, it is understood that 3D-C/SMPI composite is suitable for GEO environment. Adding 3D-C to PI demonstrates good compatibility with the GEO environment. 3D-C has already been infused as filler in PI to mitigate the electrostatic discharge.⁵⁶⁻⁵⁸ Similarly, the electrical conductivity measurements of 3D-C/SMPI (Section 6.3.2) shows that it is ESD durable. However, the composite is expected to erode under long term AO exposure at LEO altitudes, where AO exposure is known to have a dominating effect on the space materials leading to oxidation, surface erosion and mass loss. It is of greater concern for long-term missions.¹⁸⁹ Carbon-based materials, e.g. 3D-C and PI, are susceptible to erosion due to collision with AO at a high relative velocity (5 eV), both in LEO and in laboratory testing.²⁷⁴ For example, PIs such as Kapton® have a high erosion yield of 3×10^{-24} cm³/O-atom when exposed to AO and are commonly used for assessing the AO flux in LEO ground simulation facilities.²⁷⁵ 3D-C/SMPI composite can be made suitable for application in LEO altitudes with the incorporation of additional protection to increase AO exposure. Currently, protective coatings²⁵⁴⁻²⁵⁷ or nanofiller additives²⁵⁹⁻²⁶² are used for AO protection. These methods have their own disadvantages such as crack formation^{254, 258} or inhomogeneous distribution in the case of nanofillers.^{266, 267}

In this chapter, a ground-based AO exposure study is conducted to improve the AO durability of 3D-C/SMPI composites. For this study, a PI similar to Kapton and Polyhedral oligomeric silsesquioxane (POSS) is used. The POSS nanoparticles regarded as one of the smallest silica particles are of approximately 1 to 3 nm in diameter.²¹¹ Two ways of adding POSS to the composite

film will be explored, to find the optimised method of AO protection using POSS. Three different hybrid films: 3D-C-POSS/PI (POSS in 3D-C alone), 3D-C/PI-POSS (POSS incorporated in PI alone) and 3D-C-POSS/PI-POSS (POSS incorporated in both 3D-C and PI) will be studied and compared. The effect of POSS on the electrical and mechanical properties of the samples will also be investigated. It is essential to observe the impact that the addition of POSS in various ways has on the composite mechanical properties. It is demonstrated that adding POSS to the PI results in a composite film with good AO resistance along with higher mechanical properties proving to be suitable for long term space applications.

7.2 Material preparation and characterization

For this study, 3D-C foams and 3D-C-POSS are prepared as described in section 3.2. Infusion of 3D-C and 3D-C-POSS with PI and PI-POSS matrices are carried out using a multistep imidization process as described in section 3.3.2. 3D-C/PI, 3D-C-POSS/PI, 3D-C/PI-POSS and 3D-C-POSS/PI-POSS are exposed to AO fluence of 7.18×10^{19} and 2.72×10^{20} O-atom/cm² with the setup described in 3.9.3. AO fluence of 2.72×10^{20} O-atoms/cm² is equivalent to about 5 months at an altitude of 500 Km.²⁷³ The effect of AO exposure is quantified by electrical measurements before and after the exposure (section 3.6).

7.2.1 PI-POSS

PMDA-ODA polyamic acid blends with different concentration of TSP-POSS were cured to produce PI-POSS films using the previously published procedure (a process developed by DuPont, Inc.).²⁷⁶ Briefly, a premixed solution of PAA and TSP-POSS in NMP is cast onto a glass substrate and heated at a rate of 4°C /min to 200 °C in air. The temperature is held for about 30 minutes.

Following this, the sample is heated at a rate of 2 °C /min to 350 °C under nitrogen atmosphere. This temperature is held for about 60 minutes. The sample is then cooled down to room temperature at a rate of 2 °C/min and then peeled off the glass substrate. Verker, R., et al. has extensively characterised PI-POSS films.^{277, 278} Hence in this chapter, 3D-C-POSS characterisation is being focused more followed by ground simulated AO exposure test for all four samples.

7.2.2 3D-C-POSS

We have incorporated 3D-C with aminopropyl isobutyl POSS (NH₂-POSS) for the first time resulting in the entire surface of all the branches of 3D-C to be uniformly covered with NH₂-POSS nanoparticles. The POSS nanoparticles are physically absorbed on the 3D-C surface, forming a 3D-C-POSS composite foam structure. The growth technique is described in section 3.2.2.

7.2.3 Morphological and chemical characterisation

The morphological and chemical characterisation of the POSS incorporated 3D-C foam is performed as described in 3.4.1. The surface morphology of 3D-C-POSS structure is observed using SEM. The top view SEM images presented in **Figure 7-1**, shows the free-standing 3D-C foams, and it can be seen in the low magnification view images that the POSS-NH₂ is incorporated on the surface of the 3D-C foams. POSS agglomerates of various sizes are clearly visible, coating almost the entire surface of the 3D-C. The structure of the foam is preserved even after adding POSS.

Figure 7-1. a-c) SEM images of 3D-C showing 3D interconnected foam-like structure and a smooth surface; d-f) SEM images of 3D-C after treating with POSS-NH₂ in THF solution showing the coating of POSS-NH₂ on the foam surface. It can be seen that the POSS-NH₂ agglomerates cover almost the entire surface of the foam branches.

Surface functional group analysis is performed by FTIR spectroscopy. **Figure 7-2a** shows the FTIR spectra for 3D-C, POSS-NH₂ and 3D-C-POSS hybrid structure. Bonds of absorbed carbon dioxide from air can be seen in all the samples. The small peak at 2800 cm⁻¹ in the 3D-C foam can be attributed to C-H, indicating that the graphene foam is H- terminated as Ar and H₂ were used as the carrier gas for synthesis in the TCVD system. The FTIR spectra of POSS-NH₂ shows a strong peak at 1110 cm⁻¹, corresponding to the Si-O-Si bond in the POSS cage structure. Strong double peaks due to C-H stretching of the CH₂ groups in the organic groups (R) were also observed in the range of 2873-2960 cm⁻¹. The C-N bond stretching causes the band at 1223 cm⁻¹ conforming the amine group in POSS. The peak for Si-C bond at 1230 cm⁻¹ can also be seen. Similarly, the FTIR spectra for 3D-C-POSS shows the strong peak at 1110 cm⁻¹ and correspondingly weak bands over 2750-3000 cm⁻¹ (due to the isobutyl groups in POSS), signifying the absorption of POSS onto 3D-C surface. There is also a broad band in the range of 3200 to 3600 cm⁻¹ corresponding to O-H

and N-H stretching vibrations.²⁷⁹ The FTIR results indicate that POSS-NH₂ is embedded on the 3D-C surface through Van der Waals bonding. Raman spectra of 3D-C, POSS-NH₂ and 3D-C-POSS is presented in **Figure 7-2b**. G-peak and 2D peak can be seen for the pure 3D-C sample. The intensity of the G-peak is about two times the intensity of the 2D peak indicating multi-layer graphene.^{232, 233} It can be seen from the Raman spectra of 3D-C-POSS that the characteristic band of C-H functional group belonging to POSS spectra is also present in 3D-C-POSS spectrum conforming that the POSS has been physically absorbed on the 3D-C surface.

Figure 7-2. a) FTIR spectra of 3D-C (black, top) before the incorporation of POSS nanoparticles, 3D-C-POSS (red, middle) and POSS-NH₂ powder (green, bottom). FTIR spectra for 3D-C-POSS displays a strong peak at 1110 cm⁻¹ (characteristic of Si-O-Si stretching band) and comparatively weak bands over 2750-3000 cm⁻¹ (characteristic of isobutyl groups in POSS-NH₂) due to POSS nanoparticles;²⁷⁹ b) Raman spectroscopy of 3D-C, POSS-NH₂, and 3D-C-POSS. The Raman band in the range of 2800 to 3000 cm⁻¹ indicates the presence of C-H functional group in 3D-C-POSS.

XPS measurements are performed to validate the incorporation of POSS onto 3D-C further. The elements and functional groups on the foam surface were examined. **Figure 7-3a** shows the XPS survey spectrum for the samples. 3D-C shows only C 1s (284 eV) peak along with a very small trace of oxygen (O 1s peak). As expected, XP spectrum of POSS-NH₂ shows C 1s (284.7 eV), O 1s (532 eV), N 1s (358.9 eV), Si 2p (101 eV) and Si 2s (151.7 eV) peaks. The

appearance of Si 2p, Si 2s, and N 1s peaks along with increased O 1s peak in 3D-C-POSS with respect to 3D-C indicates that the POSS molecules are successfully incorporated on the 3D-C surface. The surface composition for 3D-C and 3D-C-POSS are summarized in **Table 7-1**. 3D-C foam is mainly composed of carbon with trace amounts of oxygen. After adding POSS, the carbon content decreased from 98.2 to 66.3% and elements such as nitrogen and silicon were seen accounting to 1.6% and 12.4%, respectively. The oxygen content also increased considerably, from 1.8 to 19.7%. This increase in oxygen content is due to the Si-O-Si structure in the POSS cages. This is also reflected in the surface atomic ratio of O/C indicative of the successful incorporation of POSS. **Figure 7-3b** and **7-3c** shows the high-resolution C 1s spectra for 3D-C-POSS and 3D-C, respectively. The C-C content of 3D-C was 87.22%, which decreased to 78.98% after adding POSS coating on its surface. Similarly, C-O % in the 3D-C and 3D-C-POSS is 8.46 and 16.25, respectively. Thus, it is evident that the C-C content of the 3D-C foam decreased, and the C-O content increased considerably after adding POSS-NH₂.

Table 7-1. Surface element analysis of 3D-C and 3D-C-POSS foams

	Element Content (%)				
	C	O	N	Si	O/C
3D-C	98.2	1.8	---	---	0.018
3D-C-POSS	66.3	19.7	1.6	12.4	0.297

Figure 7-3. a) XPS survey spectra of the 3D-C, 3D-C-POSS, and POSS-NH₂ showing only C1s peak for pure 3D-C whereas the peaks of N1s (398.98 eV), Si 2p (101 eV), and Si 2s (152 eV) can be seen in both POSS and 3D-C-POSS indicating the successful incorporation of POSS onto 3D-C; b-c) High resolution C 1s spectra for 3D-C-POSS and 3D-C with their respective bonding modes obtained via deconvolution of the main signal.

7.2.4 Thermal stability

Thermogravimetric analysis (TGA) is used to measure the thermal stability of 3D-C, POSS-NH₂ and 3D-C-POSS. **Figure 7-4a** shows the sample weight as a function temperature for the three samples from room temperature to about 1100 °C under dry air atmosphere. POSS follows two-step thermal degradation in air, in which evaporation and oxidation compete with each other. This complex phenomenon results in a thermally stable residue. In other words, oxidation takes place in the organic chains and produces ceramic, silica-like phase as a result of cage crosslinking.²⁸⁰

Figure 7-4. a) TGA curves of 3D-C (black), 3D-C-POSS (red) and POSS-NH₂ (green) under dry air atmosphere, showing residual weight for both POSS-NH₂ and 3D-C-POSS due to highly dense Si-O structure of POSS formed by partial cross-linking; b) FTIR spectra of 3D-C-POSS after TGA (red) treatment showing a broad band from Si-O stretching. The centre of the absorption band shifted to lower wavenumbers (1090 cm⁻¹) compared to FTIR absorbance peak of 3D-C-POSS before TGA (black) (1110 cm⁻¹) conforming the formation of Si-O structure during thermal degradation.²⁸⁰

The initial weight loss for POSS-NH₂ occurs at 250 °C and fully subsides by 375 °C. This is due to the incomplete decomposition (evaporation) of organic segments in the POSS molecule. This is followed by oxidation in the organic chains leaving a residue of ~ 38% at 1000 °C. From the TGA curve of 3D-C, it can be seen that there is a minor weight loss region (3 to 4% below 300 °C) followed by major weight loss. This is due to the evaporation of absorbed water and oxygen decomposition of surfactant residue. The primary decomposition (complete oxidation of carbon) of 3D-C takes place at 803 °C. The complete weight loss for 3D-C is attributed to its purity.²⁸¹ The thermogravimetric profile of 3D-C-POSS is characterized by an initial 3% weight loss up to 200 °C due to thermal desorption of absorbed water molecules on the foam surface followed by ~20% weight loss at ~ 300 °C due to POSS cage oxygen decomposition. The higher weight loss associated with oxygen decomposition in 3D-C-POSS compared to 3D-C can be

attributed to the oxygen group in POSS molecules. 3D-C-POSS shows a residual weight of around 25% at 1000 °C, which can be recognized to be due to the formation of dense Si-O structure resulting from partial cross-linking of the POSS cages. This residue after TGA was subjected to FTIR analysis. The absorbance spectrum is shown in **Figure 7-4b** in comparison to the spectra of 3D-C-POSS before TGA. It can be seen that Si-O-Si peak at 1110 cm⁻¹ has shifted to 1090 cm⁻¹ indicating the formation of Si-O structure as a result of partial cross-linking of POSS cages.^{280, 282} From the TGA analysis, it is clear that the addition of POSS particles has not altered the thermal stability of 3D-C.

7.3 Comparison of 3D-C/PI, 3D-C-POSS/PI, 3D-C/PI-POSS and 3D-C-POSS/PI-POSS

7.3.1 Morphological and chemical characteristics

TGA curves similar to Figure 7.4a is obtained for the composite samples (3D-C/PI, 3D-C-POSS/PI, 3D-C/PI-POSS and 3D-C-POSS/PI-POSS). Thermogravimetric Analysis of 3D-C/PI/POSS composite samples under dry air atmosphere from room temperature to 1000 °C is shown in **Figure 7-5a**. It can be seen that the Si-O structure of POSS has been formed due to partial cross-linking of POSS cages resulting in residual weight for the composite films that contained POSS. In addition, the composite samples with POSS in PI (3D-C/PI-POSS and 3D-C-POSS/PI-POSS) has more Si-O residue indicating the higher amount of POSS in these films compared to 3D-C-POSS/PI. The Si-O stretching band at 1090 cm⁻¹ in the FTIR absorbance spectrum confirms the formation of Si-O residue (**Figure 7-5b**).

Figure 7-5. TGA curves of 3D-C/PI/POSS composite samples; b) FTIR spectra of the residue from TGA of 3D-C-POSS/PI, 3D-C/PI-POSS and 3D-C-POSS/PI-POSS.

7.3.2 AO durability

Figure 7-6a-c shows the surface of the composite films before AO exposure. Good infusion of the PI in 3D-C can be seen for all the samples. Exposing 3D-C/PI and 3D-C-POSS/PI samples to 7.18×10^{19} O-atoms/cm² resulted in the erosion of the top PI matrix leaving the 3D-C network exposed, as seen in **Figure 7-6d-e**. Before exposure, only the top layer of 3D-C structure can be seen, and after exposure, the underlying branches of 3D-C is visible as the PI is etched away. This shows the lower AO erosion yield of 3D-C compared to that of PI as a result of strong carbon atoms bonding present in 3D-C. Similar results of relatively low erosion yield were previously reported for carbon structures, such as amorphous carbon or highly oriented pyrolytic graphite (HOPG).^{188, 193, 283, 284} Under the same AO fluence it can be seen that the PI layer of 3D-C-POSS/PI has been etched away creating small holes and increasing the roughness, whereas for 3D-C-POSS/PI-POSS and 3D-C/PI-POSS the PI top layer remained largely intact, as seen in **Figure 7-6f**. The samples exposed to a higher fluence of 2.72×10^{20} O-atoms/cm² showed a similar

trend as visible in **Figure 7-6g-i**, where both sample containing POSS in the PI matrix experience the least damage to the PI phase compared to the samples with no POSS content in the PI. **Figure 7-6j** shows the damaged surface of the 3D-C/PI sample after the AO exposure at a higher magnification. The typical morphology of a PI surface damaged by hyperthermal AO is clearly seen.²⁷⁵ While most of the damaged surface of the 3D-C-POSS/PI sample is similar to that of the 3D-C/PI surface, the extensive PI etching exposed the POSS covered 3D-C branches, as seen in **Figure 7-6k**. This POSS cover layer on the 3D-C prevents its surface from being completely exposed to AO. Unlike samples with no POSS content in the PI, both the 3D-C-POSS/PI-POSS and 3D-C/PI-POSS samples show relatively uniformly spread micron-sized particles on the damaged PI surface, as seen in **Figure 7-6l**. These particles are most likely silica (SiO_2) produced from the oxidation process of the POSS. This has been verified previously for the same TSP-POSS/PI film exposed to AO fluence of 2.6×10^{20} O-atoms/cm².²⁸⁵ XPS survey spectra was obtained before and after the AO exposure. It was found that the carbon content decreased significantly, and the oxygen content increases, indicating the formation of SiO_2 . Furthermore, high-resolution spectra of the Si 2p peak indicated the oxidation of the POSS silicon oxide ($\text{Si/O}=1/1.5$) and the formation of SiO_2 ($\text{Si/O}=1/2$) passivation layer. Thus, under further exposure of 3D-C/PI-POSS and 3D-C-POSS/PI-POSS to higher AO fluences, the SiO_2 particles will eventually form a protective passivation layer on the PI, preventing further etching from taking place.

Figure 7-6 a-l. HRSEM images of three composite films (3D-D/PI, 3D-C-POSS/PI, 3D-C-POSS/PI-POSS) exposed to different AO fluences (0 , 7.18×10^{19} , and 2.79×10^{20} O-atoms cm^{-2}) showing the effect of AO exposure in each composite films. SEM images of the 3D-C/PI-POSS before and after AO exposures show similar surface morphology to that of the 3D-C-POSS/PI-POSS sample (not shown).

The composite films with POSS in the PI matrix have enhanced resistance to AO as the silsesquioxane moiety ($\text{RSiO}_{1.5}$) reacts with the oxygen and forms a SiO_2 protective layer. The silicon in the PI surface gets oxidized to SiO_2 , after exposure to O-atoms. Hence with increasing AO fluence, the organic content of the PI-POSS surface gets eroded and replaced by silica. The surface of the composite film becomes almost entirely SiO_2 . The SiO_2 passivation layer ultimately

limits the AO erosion rate.²⁰⁶ Mass loss of the composite films are measured after they were exposed to the AO fluence. **Figure 7-7a** shows the normalized mass loss measurements vs AO fluences and their linear fit. The erosion yield is obtained from the slope of the mass loss curves using equation (3-5) and are shown in **Figure 7-7a**. The results (**Figure 7-7b**) are compared to the accepted erosion yield of Kapton H, which is $3.0 \times 10^{-24} \text{ cm}^3/\text{O-atom}$.²²⁸ It can be seen that the erosion yields of the two samples with no POSS content in the PI are similar, and their measured values are close to that measured for Kapton H. In contrast, the measured erosion yield of two samples with POSS content in the PI (15 wt%) are about 70-80% lower than that of Kapton H.

Figure 7-7. AO exposure test. a) Mass loss vs AO fluences for 3D-C/PI, 3D-C/PI-POSS, 3D-C-POSS/PI, and 3D-C-POSS/PI-POSS at three fluences (0, 7.18×10^{19} and 2.72×10^{20} $\text{O-atoms}/\text{cm}^2$); b) Erosion yield of the samples obtained from mass loss and corresponding AO fluence.

The erosion yield of 3D-C/PI and 3D-C-POSS/PI are found to be $2.16 \times 10^{-24} \text{ cm}^3/\text{O-atom}$ and $2.4 \times 10^{-24} \text{ cm}^3/\text{O-atom}$, respectively. Thus adding 3D-C to PI reduced the erosion yield (about 23% lower than Kapton H), mainly due to the lower erosion yield of the 3D-C compared to PI.⁵⁸ This is attributed to the strong bonding of carbon atoms in the foam compared to that of pure PI. Majority of mass loss in the composite samples are that of the PI which has an AO erosion yield

about one order of magnitude higher than that of sp_2 carbon materials.^{188, 193, 283, 284} Moreover, the measured erosion yield of 3D-C/PI-POSS and 3D-C-POSS/PI-POSS are found to be $4.67 \times 10^{-25} \text{ cm}^3/\text{O-atom}$ and $6.88 \times 10^{-25} \text{ cm}^3/\text{O-atom}$, respectively. These values are about 60-70% lower than that measured for the 3D-C/PI and 3D-C-POSS/PI samples that do not contain POSS in the PI. In addition, these values are 85 and 77% lower than the erosion yield of Kapton H, respectively. The lower erosion yield of 3D-C/PI-POSS and 3D-C-POSS/PI-POSS samples compared to that of 3D-C/PI and 3D-C-POSS/PI is due to the formation of SiO_2 protective layer in the former samples by POSS particles present in the PI matrix.

LEO erosion time can be estimated assuming a layer thickness of $51 \mu\text{m}$, equivalent to that of the outer layer of MLI blankets,¹³¹ and an AO flux of $2 \times 10^{13} \text{ O-atoms/sec} \times \text{cm}^2$ (AO flux at 500 km altitude).²⁷³ Hence based on the erosion yield measured, the film is estimated to be functional for about 15 years. The results show that protecting the PI by adding POSS reduces the composite film AO erosion yield. This is due to the fact that the majority of the composite film mass is POSS-PI with reduced erosion yield compared to pristine PI. In addition, it is understood that adding POSS only as a coating on the 3D-C does not effectively protect the composite film, as it protects only the foam and does not prevent the PI from etching away.

7.3.3 Electrical Conductivity

Temperature-dependent resistivity measurement is performed to investigate the effects of the addition of POSS to the composite films and the exposure to AO have on the embedded 3D-C conductivity. The measurements are made using the four-point van der Pauw method, as described in section 3.6 at temperatures ranging from -100°C to 200°C . Measurements are made before and after AO exposure, and the sheet resistance plotted against temperature is shown in **Figure 7-8a-b**.

$\ln(R_s T^{-1/2})$ is plotted against $T^{-1/4}$ as Arrhenius curves and fit with linear trend lines. The conduction behaviour of all the sample follows three-dimensional variable range hopping (VRH) behaviour as seen for 3D-C/SMPI. The linear fitting lines of the VHR model by Godet²⁵¹ is shown in **Figure 7-8c-d**.

The temperature-dependent resistivity of all the samples (3D-C/PI, 3D-C-POSS/PI, 3D-C/PI-POSS and 3D-C-POSS/PI-POSS) follows the same trend with similar slopes signifying identical electrical conductivity properties. This is due to the fact that the electrical conductivity behaviour is mainly dependent on the intrinsic characteristic of the 3D-C foams. As seen in **Figure 7-8a-b**, the resistivity curves for all the reference samples (red markings) are showing the same behaviour indicating that the addition of POSS to 3D-C or PI or both did not change the electrical conductivity behaviour of the composite. In addition, the VRH conductivity mechanism is well preserved even after PI infiltration as well as adding POSS to the foam or PI.

The sheet resistance of the composite films exposed to a LEO equivalent AO fluences of 7.2×10^{19} O-atoms/cm² (**Figure 7-8a**) and 2.7×10^{20} O-atoms/cm² (**Figure 7-8b**) are compared to the reference sample (before exposure) in order to examine their durability to AO fluences comparable to typical LEO spacecraft mission time. It can be seen that the sheet resistance of 3D-C/PI and 3D-C-POSS/PI have increased after each exposure while there is only a negligible change in the case of 3D-C/PI-POSS and 3D-C-POSS/PI-POSS. Moreover, it can be seen that the increase in sheet resistance measured for the 3D-C POSS/PI sample after exposure is lower than that measured for the 3D-C/PI sample. This is due to the added protection of the POSS covering the 3D-C and reducing the AO erosion.

Figure 7-8. Electrical conductivity characterization before and after AO exposure. The sheet resistance as a function of temperature of the various samples after exposure to , a) a fluence of 7.18×10^{19} O-atoms/cm² (black); b) a fluence of 2.72×10^{20} O-atoms/cm² (blue) compared to the reference measurements performed on the samples before the exposure (red); c-d) Fitting of the sheet resistance measurements to the VRH conductivity model. Results are shown according to the VRH model: $\ln(R_s T^{-1/2})$ as a function of $T^{-1/4}$ and compared to the model (dashed lines).

The VRH model is examined (based on equations 5-1 to 5-5) to gain further insight into the damage caused by AO to the 3D-C foams embedded in the PI. Linear fitting is used to extract various parameters for each sample and each exposure. As reported earlier for 3D-C/SMPI, the dimensionality d is found to be 3 for all the samples, indicating the multi-layered structure of the

3D-C. Both the localization parameter and σ_{00} of the different samples for AO exposures are extracted and compared, as seen in **Figure 7-9**.

Figure 7-9. a) The localization parameter ($N(E_F)\gamma^{-3}$) values, extracted from the linear fit to the Godet VRH model, as a function of the atomic oxygen exposure fluence; b) The exponential prefactor σ_{00} values, extracted from the linear fit to the Godet VRH model, as a function of the atomic oxygen exposure fluence.

It can be seen from **Figure 7-9a**, that all localization parameters fall within the weak localization range, $1 \times 10^{-5} \ll N(E_F)\gamma^{-3} \ll 1$. The extracted localization parameters are unaffected by AO exposure. The localization parameter is proportional to the density of states in the graphene grain boundaries, where the hopping conductivity process takes place. This is attributed to the fact that the majority of the AO induced defects are not located at the grain boundaries but on the surface of the top layer 3D-C grains themselves. Thus, no change in the hopping density of states and therefore, the localization parameter is expected. Indeed, the results depicted in **Figure 7-9a** shows that all the samples retain roughly the same localization parameter value, regardless of POSS content or AO exposure fluence. However, the conductivity of the samples with no POSS

content in PI are affected, most notably due to mobile charge scattering on the increased number of defects in the 3D-C grains. This is evident in the decrease in the σ_{oo} parameter, which is dependent on the lattice disorder. As seen in **Figure 7-9b**, the samples that did not contain any POSS in the PI matrix have a reduction in their σ_{oo} values indicating an increase in the 3D-C grains lattice disorder due to the AO damage. In summary, the composite samples without POSS in the PI shows an increase in the sheet resistance as a result of AO induced defects. These defects cause a reduction in the conductivity and are probably limited to the outer layers of the multi-layered 3D-C foam. The sheet resistance after exposure to 2.72×10^{20} O-atoms/cm² has increased by 200% to a value of $6 \Omega/\square$. However, the location and density of the AO induced defects are still not enough to drastically change the conductivity mechanism. The samples with the POSS containing PI show no change in the measured sheet resistance, indicating that no AO penetrated the POSS protected PI. These results show that PI with POSS content (15 wt%) serves as an effective protection layer to the 3D-C embedded in the composite, preventing AO damage.

7.3.4 Mechanical strength

The stress-strain curves obtained from the tension test is shown in **Figure 7-10a**, and the results are summarized in **Table 7-2**. The results show that the adding of POSS to the PI matrix increases the Young's modulus of the composite by a measurable amount, as seen in **Table 7-2** and **Figure 7-10b**. The small size of POSS nano-cages, which restricts the mobility of polymer chains under loading, is predicted to improve the modulus and possibly the yield strength of PI-POSS compared to that of pure PI. This effect was documented in previous work conducted on PI and various POSS types, showing that an increase of POSS concentration would lead to an increase in the rigidity of the composite system.²⁸⁶ In addition, previous work indicates that a POSS loading

of 15 wt.% will lead to a reduction in the PI mechanical properties compared to that of PI with a POSS loading of 5 wt.%.²⁷⁸ This trend is visible in the decreased Modulus values measured for the 15 wt.% POSS loaded PI films as compared to the 5 wt.% POSS loaded films. This is due to the formation of POSS aggregates at the 15 wt.% loading. These aggregates size and density affect the nanocomposite film mechanical properties.²⁷⁶

Figure 7-10. a) Stress-strain curves obtained from tension measurements on 4 types of samples. 3D-C/PI, 3D-C/PI-POSS (5 and 15 wt.%), 3D-C-POSS/PI, and 3D-C-POSS/PI-POSS (5 and 15 wt.%); b) The measured Young's modulus; (c) tensile strength and; (d) strain at break of the 6 sample types. Each result is an average of at least five measured samples.

Table 7-2. Stress-strain measurement results for 3D-C/POSS/PI composite samples.

Sample	Stress at break (MPa)	Strain at break (%)	Young's modulus (MPa)
3D-C/PI	4.61±0.62	6.45±1.54	164.12±8.36
3D-C/PI-POSS(5wt%)	6.52±1.64	4.44±2.24	287.1±27.76
3D-C/PI-POSS (15 wt%)	5.42±0.58	5.79±1.45	188.62±20.53
3D-C-POSS/PI	5.18±0.63	7.62±1.64	116.16±14.65
3D-C-POSS/PI-POSS (5 wt%)	4.41±1.43	3.58±2.1	215±31.45
3D-C-POSS/PI-POSS (15 wt%)	5.19±0.39	6.64±1.14	178.46±9.9
Pure PI	88.3±15	52.3±11	1979±42
PI-POSS (5 wt%)	73.41±20	44.6±8	2127±37

In contrast, adding POSS as a coating to the 3D-C structure has the opposite effect, reducing the Young's modulus slightly compared to that of the untreated composite material. This result is expected as the POSS coating was found to have no chemical bonding to the 3D-C structure. It, therefore, decreases the adhesion of the PI to the 3D-C surface, reducing the stiffness of the composite. The measured tensile strength and strain at break are found to be similar in all the sample types without any correlation to the POSS content, as seen in **Table 7-2** and **Figure 7-10**. This is contrary to previous works that show an increase in the tensile strength of PI with a POSS content of 5 wt.% compared to bare PI.^{278, 286} This may be due a lower than expected PI volume filling in the composite films.

The measured proprieties for the 3D-C/PI composite films are considerably lower than those of a pure PI film. The Young's modulus of pure PI films prepared in the same way as the PI infused into the 3D-C was measured and found to be roughly 2 GPa, one order of magnitude higher than

that of the various 3D-C/PI films. This significant variation in mechanical properties between the composite films and their equivalent PI films indicates the existence of voids in the composite film structure (regardless of the POSS content in the material used). This non-uniformity in PI infiltration into the 3D-C scaffolding can be seen clearly in SEM images of the 3D-C/PI films cross-section. Typical SEM images, such as the one depicted in **Figure 7-11a**, clearly show the lack of PI matrix material in the middle of the film. In addition, the images clearly show that the PI did not infiltrate inside the hollow 3D-C structure (**Figure 7-11b**). Furthermore, delamination between the 3D-C structure and the PI matrix can be seen in the interface area between the two materials. Thus, indicating the lack of proper adhesion which is the result of the weak physicals bonds and the lack of any chemical bonding between the 3D-C and PI matrix.

Figure 7-11. SEM images of a cleaved 3D-C/PI composite film. a) Delamination between the 3D-C scaffolding and the PI matrix is visible in the area marked by a dotted red line; b) Cross-section of the 3D-C scaffolding structure. While a PI cover is seen on the outer surface of the 3D-C structure, the inside remains hollow. This indicates that the PI failed to infiltrate inside the hollow 3D-C structure.

These results show that these composite samples are still suited for use as the outer layer in thermal blankets in satellites as they undergo mostly bending and are supported by the

multi-layered structure of the blanket. For other applications further optimization of the PI matrix should be explored, alternative PI-based matrix materials should be considered to further increase the adhesion of the 3D-C scaffolding to the PI matrix, thereby improving the composite film mechanical properties.

7.4 Summary

This chapter reports the improvement of AO durability of 3D-C/PI composite films by adding POSS. Different 3D-C/PI based composite films were prepared by adding POSS to 3D-C or PI or both, and a comparison of the impact of POSS on the electrical and mechanical properties along with their AO durability for LEO applications are reported. The electrical conductivity behaviour of all the composite films is mainly dependent on the intrinsic characteristic of the 3D-foams, and it is well preserved even after PI infiltration as well as adding POSS to the foam or PI. This is evident from the similar slopes followed by temperature-dependent resistivity of all the samples. The composite films demonstrated sheet resistivity as low as $1.8 \Omega/\square$ at room temperature. The samples were also subjected to the LEO equivalent hyperthermal (5 eV) AO fluences of 7.18×10^{19} O-atoms/cm² and 2.72×10^{20} O-atoms/cm². The 3D-C/PI composite samples without POSS content in the PI matrix exhibited an erosion yield close to that of Kapton H (23% lower). On the other hand, the erosion yield values of the samples with POSS content (5 & 15 wt.%) in the PI matrix were measured to be 77 to 85% lower than that of pure PI Kapton H. The electrical conductivity of the films with POSS in PI was found to be well-maintained even after AO exposure. For 3D-C/PI and 3D-C-POSS/PI an increase in the sheet resistance was measured as a result of AO exposure. However, the total conductivity is still very high, indicating that the defect induced conductivity reduction is limited to the outer layers of the multilayer 3D-C foam. Adding

POSS to the 3D-C foam reduced the Young's modulus of the material and adding 5 wt.% POSS to the PI increased it. However, adding 15 wt.% to the PI increased the AO protection but have reduced benefit to mechanical properties compared to 5 wt.% loading.

In conclusion, adding POSS as a coating to 3D-C alone does not seem to have any significant effect on the composite erosion yield. This is expected since the majority of the film mass is PI, and so films with unprotected PI will show an erosion yield similar to pure PI films. In terms of stiffness, 3D-C/PI-POSS has the highest Young's modulus, followed by 3D-C-POSS/PI-POSS, 3D-C/PI and 3D-C-POSS/PI. The results indicate that POSS in PI prevents AO erosion in the films with no detrimental effect on the electrical conductivity characteristics of the 3D-C material. The study shows that adding 5 to 15 wt.% POSS content to the PI matrix drastically improves the durability of the 3D-C/PI composite to AO. Thus, 3D-C/PI-POSS composite films made with appropriate amount of POSS in the polymer matrix results in a promising material for LEO space applications.

8 Space deployable structures using 3D-C/SMPI

In this chapter, the performance of the 3D-C/SMPI for hinge structure and large area actuator is assessed. Material characterisation and space reliability tests have proven 3D-C/SMPI composite material to be suitable for space applications. Owing to the ability of 3D-C to enhance thermal conductivity and achieve uniform heat spread in the composite, it is believed that 3D-C/SMPI can function well in large-area applications as well as enable complex structures. In order to test this, a box-shaped and a tape spring shaped samples are prepared. The box-shaped 3D-C/SMPI sample is scheduled to be launched into space, and its deployment in the space environment will be tested. The box-shaped sample demonstrates the ability of 3D-C/SMPI to achieve complex sequential deployment of a multi-joint structure. Similarly, the tape spring shaped 3D-C/SMPI composite reflects the ability of the composite to be fabricated as a structural material for deployment release device. The proofs of concept experiments are summarised herein.

8.1 Tape spring shaped 3D-C/SMPI sample

In order to demonstrate that 3D-C/SMPI composite can be fabricated as any required structural material using the infusion technique described in section 5.3, a tape spring shaped 3D-C/SMPI sample is fabricated and tested. A Si mould, similar to the Al mould in section 4.4.2, is fabricated (**Figure 8-1**). For the SMPI infusion, narrow slits are made on the top part of the mould, to facilitate infusion after placing the foam inside and closing the mould. Since viscous PAA is used for infusion, adding it before closing the mould will damage the foam. Similar to the procedure described in section 5.3, a small amount of PAA is added, followed by degassing and curing.

Again, some more PAA is added, degassed and cured. The procedure is repeated until the foam is fully covered.

Figure 8-1. a) Si mould fabricated for the synthesis of 3D-C/SMPI tape spring sample. b) Top view of the Si mould. Black markings indicate the slits on the top mould.

Figure 8-2 shows the tape spring 3D-C/SMPI sample. The curved structure of the sample can be seen in **figure 8-2c**. The shape memory property of the tape spring sample is tested by heating the sample to 200 °C and bent, as shown in **figure 8-2d-e**. It can be observed that the sample is made flat throughout its length and then bent at the centre portion. Upon heating, the sample recovers its original shape with the curvature (**Figure 8-2f**). A slight loss in the curvature is observed after recovery. **Figure 8-3** shows the video image of the recovery of the sample. The recovery rate is less than 95%, consistent with the DMA shape recovery test (Section. 5.3.4). With the help of 3D-C, the SMPI could be fabricated as a structural material for actuators rather than planar 2D films.

Figure 8-2. Tape spring shaped 3D-C/SMPI sample. a-c) The 3D-C/SMPI sample in its original fabricated shape showing its curved structure; d-e) The bent (temporary) configuration of the 3D-C/SMPI sample; f) 3D-C/SMPI sample after shape recovery. The curvature of the sample is observed to have reduced slightly.

Figure 8-3. Video images showing shape recovery of 3D-C/SMPI tape spring sample.

8.2 Box-shaped 3D-C/SMPI

The sample consists of a flat structure in the shape of a cross (Similar to Section 4.4.1), as shown in **Figure 8-4a**. It has a heater embedded within the composite structure. Since the SMPI used for tape spring sample has a shape recovery rate lower than 95%, the second SMPI²² synthesised using BAPB, BPADA and DMF is used here. The sample is fabricated as a cross structure which can be folded into a cube. The sample could transform from box shape to a flat material upon heating (similar to 3D-C/SMP sample in section 4.4.1). 3D-C/SMPI box sample is scheduled to be launched and deployed in space in collaboration with Satellite Research Centre (SaRC), NTU, Singapore. **Figure 8-4c-d** shows the folded (temporary shape) configuration of the sample.

Figure 8-4. Box-shaped 3D-C/SMPI sample. a-b) Deployed (original) configuration of the 3D-C/SMPI sample; c-d) Stowed (temporary) configuration, bent after heating it to its transformation temperature.

Due to the complexity in the sample shape, internal heating with wires connected to the ends of the sample is not practical, as the cables will be exposed to the space environment. There is also a risk of the wires entangling and hindering the shape recovery. One of the requirements for launching the material in space is that the wire connections/thermocouple be embedded within the polyimide. Embedding the wires inside the composite across the foam area is not desirable, as it might lead to burning of the sample at contact points or pose problems in shape training. Hence an embedded heater is used to trigger the deployment in space. The sample consists of a PI heater embedded within the composite (**Figure 8-5**). During the experiment in orbit, the heater will be switched ON to trigger deployment. A thermocouple is embedded within the payload to log its temperature during the experiment. An on-board camera will capture the deployment of the SMP payload. In the deployed configuration, the SMP payload has dimensions of 130 mm $\times$ 100 mm $\times$ 3 mm. **Figure 8-5** shows the sample in the deployed configuration and the position of the heater (Minco HAP6948) and thermocouple embedded inside the composite.

The power supply allotted for the SMPI payload: 45 W max @ 15 ± 0.5 V DC – Cut-off current: 4A. The thermocouple used is a K-Type with a measurement range from -50 °C to 350°C.

Figure 8-5. Schematic of 3D-C/SMPI payload in deployed configuration showing the location of the heater (All Polyimide thermofoil heater HAP6948, Resistance 7.89 Ω) and thermocouple (L-Type, P/N:Z3-K-F/G-1/0.315.1.0-T).

In the launch configuration, the SMPI is folded into a 30 mm × 40 mm × 40 mm cube. The sample will be housed inside an Al housing (as shown in **figure 8-6**), placed on the X-face of the satellite. 3D-C/SMPI composite will be clamped between two glass-fibre insulators (MISUMI HIPLKH glass fibre insulator, 2mm thickness, with thermal conductivity of 0.24 W/m. K), thermally isolating it from the housing.

Figure 8-6. Schematic of 3D-C/SMPI box sample inside the Al housing. a) stowed configuration; b) deployed configuration and; c) Cross-sectional image showing the sample sandwiched between glass fibre insulator on the top and bottom.

8.2.1 Space flight pre-qualification testing

We are working jointly with SaRC, NTU to pre-qualify the 3D-C/SMPI sample for flight by conducting a series of tests. The test includes, 1) Launch vibration response test, 2) Thermal-vacuum cycling testing of deployment reliability in TVAC and, 3) Deployment functional test under ambient temperature and vacuum. The sample is subjected to preliminary environmental tests such as launch vibration (random and sine vibration test in folded configuration) followed by deployment functional test inside a thermal vacuum chamber (to test

the deployment functionality of the material in space environment). The remaining test (shock and sine burst, TVAC) will be done in the near future.

8.2.1.1 Launch vibration response test

In order to demonstrate that the material can withstand the launch environment, i.e. hold its shape and structural integrity after launch, the sample is subjected to random and sine vibration test with respect to the launch environment data provided by SaRC. Vibration test is performed using an electrodynamic vibration test system (TV 55240/LS). The shaker can reproduce the vibration environment under laboratory conditions. The details of the vibration/shock tests for the 3D-C/SMPI is given in **tables 8-1, 8-2 and 8-3**.

Table 8-1. Maximum acceleration levels for launch vehicle in the longitudinal and lateral directions.

	Loads	Stiffness
Longitudinal	7g Compression 3.5g Tension	>90 Hz
Lateral	±2g	>45Hz

Table 8-2. Sinusoidal vibrations levels

	Frequency Range [Hz]	Qualification	Acceptance
Longitudinal Axis	5-8 8-100	34.5 mm (DA) 4.5 g	23 mm (DA) 3 g
Lateral Axis	5-8 8-100	24 mm (DA) 3 g	16 mm (DA) 2 g
Sweep rate		2 Oct/min	4 Oct/min

Table 8-3. Random vibration levels, qualification and acceptance levels.

Frequency [Hz]	Qualification	Acceptance
	PSD [g^2/Hz]	PSD [g^2/Hz]
20	0.002	0.001
110	0.002	0.001
250	0.034	0.015
1000	0.034	0.015
2000	0.009	0.004
g RMS	6.7	4.47
Duration	2 min/axis	1 min/axis

The sample is placed inside the Al housing clamped between glass fibre insulators and subjected to random and sine vibration along with the housing. **Figure 8-7** shows the setup of the sample on the shaker system. The sample is tested on all three-axis orientation. A base plate is used to fix the housing to the shaker system.

Figure 8-7. 3D-C/SMPI box sample with the Al housing mounted on the shaker system for vibration test in X, Y and Z-axis.

Figure 8-8 shows the optical image of the 3D-C/SMPI sample after sinusoidal and random vibration test. It is seen that the composite sample is intact after the vibration test and can hold its temporary shape throughout the experiment (good shape fixity). There is no crack formation or damage due to vibrational load, especially at the region of interface between the housing and 3D-C/SMPI.

Figure 8-8. 3D-C/SMPI sample after sine and random vibration test.

This preliminary vibration test shows that the sample could withstand random and sine vibration loads experienced during launch. The shape fixity of the SMPI is also maintained throughout the test period.

8.2.1.2 Functional test

For the functional test in ambient temperature, the sample is placed inside the thermal vacuum chamber, and the deployment is initiated by electrical resistive heating of the embedded polyimide heater. The functional test is carried out at room temperature and a pressure of 1×10^{-5} pa. Power

input of 20V and 1.95 A is supplied through EA-PSI 8065-10 T power source. **Figure 8-9** shows the video image of the deployment of the sample inside the thermal vacuum chamber. The total deployment takes place for about 120 minutes. It can be seen that the heat is spread to all the edges of the cubic structure with the help of 3D-C, and the shape recovery process takes place seamlessly. It is to be noted that only two out of five edges are in direct contact with the heater and the complete shape recovery indicates that heat is conducted throughout the structure enabling all the sides of the cube to recover.

Figure 8-9. Video images showing shape recovery of 3D-C/SMPI box structure inside the vacuum chamber.

Carbon fibre reinforced SMPC hinge developed by Leng. et al.¹⁷ was actuated by a total power of about 32W. The hinge consists of two circular laminates of length 100 mm, thickness 3 mm and a radius of 12.5 mm. The SMPC had a T_g of about 64 °C. The higher actuation power and recovery time for the 3D-C/SMPI box sample is attributed to its higher T_g (230 °C) and larger surface area,

respectively. The actuation power and recovery time could be decreased by utilising the direct resistive heating property of the foam instead of embedding an external heater.

Before launch, the sample will be subjected to shock test and thermal-vacuum cycling test for deployment reliability. The sample will be placed inside a thermal vacuum chamber along with the housing and exposed to 8 thermal cycles. Four cycles of $-9\text{ }^{\circ}\text{C}$ to $-61\text{ }^{\circ}\text{C}$ and four cycles of $-77\text{ }^{\circ}\text{C}$ to $107\text{ }^{\circ}\text{C}$. The sample will be in stowed condition for the first four cycles and then deployed at the end of the 4th cycle at $-9\text{ }^{\circ}\text{C}$ (the worst cold condition in sunlit). For the remaining four cycles, the sample will be in the deployed configuration. The temperature of the thermal cycling test is evaluated using the thermal simulation of the payload for 15 orbital cycles.

8.3 Summary

In this chapter, a tape spring shaped 3D-C/SMPI sample is fabricated and tested for its shape recovery highlighting the ability of 3D-C to enable the fabrication of SMPI as a structural material for actuators rather than planar 2D films. The study shows that the infusion process has to be streamlined further to obtain a full shape recovery for curved samples. Various other SMPIs from the literature can also be infused and tested to obtain better shape recovery. The design parameters can be tailored to obtain a simple and lightweight 3D-C/SMPI hinge actuator that has lower stowage volume, good mechanical strength and full functionality in space.

A deployable spaceflight structure has also been developed using 3D-C/SMPI composite material, and the spaceflight readiness of the structure is evaluated using a series of preliminary testing. The launch vibration test and functionality test in vacuum environment conducted so far confirm the robustness and shape memory performance. The prototype will be subjected to further qualification tests (shock & sine burst vibration test, thermal cycling) in collaboration with SaRC,

NTU, after which the sample will be launched for deployment in orbit. Tape spring 3D-C/SMPI shows the potential of 3D-C/SMPI for use as deployable structures in space and the box-shaped 3D-C/SMPI demonstrates its use for large area actuator.

9 Conclusions and recommendations for future work

9.1 Conclusions

This work has extended the fabrication of polyimide-based material from 2d planar to 3D contours, enabling the synthesis of SMPI-based structural materials. For the first time, integration of 3D-C into SMPI was shown, extending the fabrication of polyimide-based composites to 3D contours. This work has provided the space industry with a new high-temperature smart material. This material can be used to build a simple, reliable, and low-cost self-deployable hinge structure. The new material combines the advantages of the SMPI such as high-thermal and environmental stability with that of 3D-C's electrical and thermal properties, enabling improved thermal conductivity and shape memory properties of the polyimide.

The effect of filling fraction of 3D-C on the SMP's intrinsic properties was first studied using epoxy-based SMP. It was shown that 3D-C could significantly improve the thermal conductivity of the SMP without any loss in the shape memory performance. However, the mechanical property of the SMP was found to be decreasing with increasing 3D-C content due to the interruption of polymer chains by 3D-C branches. 0.1 vol.% of 3D-C increases the thermal conductivity of the SMP by 62%. 3D-C could also drastically increase the SMP actuation area. This was demonstrated with proof of concept box-shaped sample that could open sequentially due to the improved heat dissipation achieved with the help of 3D-C. The applicability of the tape spring hinge concept using 3D-C/SMP was illustrated by fabricating a 3D-C/SMP composite sample as a tape spring model. 3D-C renders self-heating capability along with uniform temperature distribution. Significant improvement in the recovery force was demonstrated by adding a metal tape spring to

the composite. 3D-C/SMP helps in achieving a controlled deployment with no shock effect from the metal tape spring and the metal tape spring, in turn, imparts additional force during recovery.

Until now, shape memory polyimides were fabricated only as thin films, due to the limitation in the thickness achievable using the existing fabrication techniques. Hence, they cannot be actively implemented in deployable devices. It was shown in this thesis, that SMPI could be fabricated as a thick structural material with the infusion of 3D-C foams. This was achieved by fine-tuning the infusion steps and porosity of the 3D-C. The incorporation of 3D-C into SMPI exhibited an improvement in thermal conductivity of the SMPI (by 500% for 0.4 vol.% of 3D-C), without altering the intrinsic properties. Using a highly porous 3D-C and viscous PAA, fabrication of SMPI based composite material of thickness greater than 1mm is done for the first time. With the help of this technique, SMPI based structural materials of required shapes and sizes could be obtained. Shape memory cyclic test in DMA showed that the composite has ideal shape recovery and shape fixity to be used in deployment applications.

Furthermore, adding 3D-C could increase the resilience of the SMPI in space environment where ultra-high vacuum, gamma-ray irradiation, extreme thermal cycling, ESD and atomic oxygen attack is prevalent. It was shown that 3D-C renders electrical conductivity to the SMPI, which in turn helped to prevent the electrostatic discharge build up in space. The composite's thermo-optical and outgassing properties were also found to be within the acceptable range for space application.

An AO exposure study was conducted to increase the AO durability of 3D-C/SMPI and in turn the composite's lifetime in LEO altitudes. Through ground-based AO exposure study of a 3D-C/PI composite, it was shown that adding POSS in the PI matrix could improve the AO durability of the composite with no detrimental effect on the electrical conductivity characteristics of the 3D-C

material. This study has demonstrated that POSS could be used to improve the AO durability of the 3D-C/SMPI composite material for its application in LEO.

Finally, the potential of 3D-C/SMPI composite for use as complex deployable structures in space was demonstrated by fabricating a box-shaped and tape spring shaped 3D-C/SMPI sample. The box-shaped 3D-C/SMPI sample is being subjected to space flight pre-qualification tests (vibration, thermal vacuum cyclic test & functional test) and is scheduled to be launched and tested for its deployment in space.

The results show that 3D-C/SMPI could be used to build a deployment release device such as hinges and large deployable structural members such as panels or booms. Thus, the conventional deployable parts such as solar panels, and antennas could be replaced with lightweight 3D-C/SMPI that has a specific actuation temperature and better durability in the space environment. This way, the components could be deployed seamlessly without any mechanical or pyrotechnic release devices. In turn, the operational reliability of the satellite will be improved significantly. The tape spring hinge concept can be used to build deployment release devices (hinges) which can be triggered by electrical resistive heating. 3D-C/SMPI hinges can be used along with metal tape spring. The metal tape spring could provide the hinge with required deployment force, and the 3D-C/SMPI composite, in turn, could control the shock effect from the metal tape spring rendering a controlled deployment mechanism. This concept was demonstrated with the proof of concept hybrid 3D-C/SMP/metal tape spring sample.

Overall, this thesis has extended the application of SMPI to large area deployable space structure as well as complex structural material such as tape spring hinge design for smart deployment in satellites.

9.2 Recommendations for future work

To further enhance the performance of 3D-C/SMPI composite and to fabricate smart deployable systems using 3D-C/SMPI, the following next steps are suggested for future work.

9.2.1 Further improvement of thermal conductivity and mechanical strength

Since the thermal conductivity of the SMPI increased with increase in foam density, it is recommended to decrease the foam porosity (smaller pore size). This way, the volume fraction of the foam can be increased, and in turn, thermal conductivity can be increased further. However, it should be noted that smaller pores hinder the percolation of SMPI matrix into the foams, resulting in air gaps trapped within the composite. High foam density also affects the mechanical strength of the polymer. The fabrication technique must be improved, focusing on the foam density and SMPI matrix to obtain a balance between thermal conductivity, mechanical strength and shape memory properties. Besides, optimisation of the SMPI matrix should also be explored. Alternative SMPI based matrix materials should be considered to further increase the composite mechanical properties as well as thermal conductivity. Solvent-free SMPI synthesis should be investigated to improve the composite properties. This could help to improve the adhesion of the 3D-C scaffolding to the SMPI matrix, thereby enhancing overall characteristics of the composite. PMDA-ODA films made by solvent-free CVD process is suggested as a reference.^{287, 288}

9.2.2 Further improvement in space reliability

Also, for space application, it is recommended to add POSS to the SMPI matrix to improve its AO durability. Since it was demonstrated that adding POSS to the PI matrix reduces the AO erosion yield by 60-70%, this method could improve the reliability of the 3D-C/SMPI based

structure in LEO orbits. This should be done through a study of POSS wt.% versus AO durability, mechanical, thermal, and shape memory properties of 3D-C/SMPI. Increase in POSS content will decrease the AO erosion yield, but at the same time, it might decrease the mechanical strength and shape recovery. Optimum wt.% of POSS should be found such that AO erosion is reduced and at the same time, the properties of the SMPI are well maintained.

9.2.3 Hybrid hinge structure

The 3D-C/SMPI composite developed in this study could be used to build a hinge for solar panel deployment. The weight of the panel, power budget for deployment, trigger temperature, deployment time and operational temperature should be considered while designing the hinge. The hinge made using the 3D-C/SMPI composite should be highly reliable compared to the current state-of-art systems.

An issue to be taken care while designing a hinge for real-time application is the material strength near its transition temperature. The modulus of the 3D-C/SMPI is lower near its transition temperature, and hence the hinge should be designed in a way to support the solar panel during deployment as well. It is shown in this study that a tape spring hinge design along with a metal tape spring embedded in the composite could improve the strength and stiffness of the material. A hybrid hinge structure using metal or fibre reinforcement could be explored. Deployable tape spring hinge structure fabricated with carbon-fibre reinforced shape memory polymer is suggested as reference.³⁰ FEA software may be used to determine the optimum design for the hinge structure such as dimensions, number of tape spring parts needed and the hinge fixture design. Another major challenge is to reduce the power required to deploy the hinge. Experiments should be

conducted to find the optimum foam fraction to allow the shape memory material to change from temporary to permanent shape with as low power as possible.

9.2.4 Hinge deployment testing

A comprehensive test program should be followed to avoid failures and to correct issues before launch. Some of the expected failures are poor lock-in, no deployment, premature deployment stoppage, incorrect final position, high impact (latch-up) shock due to high rate of deployment and improper wiring. Thus, hinge performance test is significant to measure the functional ability, alignment, stiffness, strength and deployed dynamics of the hinge. Four-point bending test, deployment torque test and latch-up shock test should be conducted to investigate the deployment functionality of the hinge.²⁸⁹ Testing of deployable appendages for spacecraft requires special tailor-made complex facilities to simulate the flight environment as closely as possible.

9.2.5 3D-C/SMPI antennas

Since 3D-C is radio-reflective²⁹⁰ and 3D-C/SMPI can be fabricated into any required shapes, the reflector antennas in the satellite could be developed using 3D-C/SMPI. An antenna is an essential tool for communication between the satellite and the earth. Need for lightweight and small packaging volume of the antenna demands for a smart deployable antenna. Antenna developed using 3D-C/SMPI could be stowed in a small volume and deployed using resistive heating. Since 3D-C helps in uniform temperature distribution over a large area, the antenna could conform to the satellite body and unfold upon deployment. This way, the structural weight and cost could be reduced effectively. Many researchers have developed smart deployable reflector antennas using shape memory polymer composites.¹³ Some key factors to be taken care of is the fabrication technique for large antennas, method of actuation and reflector precision.

9.2.6 Triple-shape memory 3D-C/SMPI

Multi-shape memory polymers are gaining more attention due to their ability to transform into one or more shapes between temporary and permanent shape.²⁹¹ These polymers can fix two or more temporary configurations and recover sequentially from one temporary shape to another and eventually to their initial shape. They are of great interest to deployable actuators. Infusing 3D-C with a triple-shape memory polyimide¹³⁵ will be very interesting since it will allow us to design a deployment release system that could deploy (open) upon stimulation and can be stowed back (closed) later. This could have potential application in satellite components such as camera, where the lens cover could be opened and closed as and when required. Similarly, solar panels and antennas could also be deployed and stowed back, or its orientation could be changed in the orbit as and when needed.

List of Publications

Journals

1. **Ranjana Shivakumar**, Asaf Bolker, Siu Hon Tsang, Nurit Atar, Ronen Verker, Irina Gouzman, Mor Hala, Nehora Moshe, Alexandra Jones, Eitan Grossman, Timothy K. Minton, and Edwin Hang Tong Teo (2020). POSS Enhanced 3D Graphene - Polyimide Film for Atomic Oxygen Endurance in Low Earth Orbit Space Environment. *Polymer*, 191, 122270.
2. **Ranjana Shivakumar**, Fei Ni Leong, Siu Hon Tsang, and Edwin Hang Tong Teo. (2020) Effect of loading fraction of three-dimensional graphene foam (3D-C) on thermal, mechanical and shape memory properties of 3D-C/SMP composite. *Materials Research Bulletin*. (Under Review)
3. 3D-C/Shape memory polyimide for space applications. (Manuscript in preparation, Chapter 5,6 and 8 of this thesis)

References

- [1] J. Chen, N. Ding, Z. Li, W. Wang, Organic polymer materials in the space environment, *Progress in Aerospace Sciences*, 83 (**2016**), 37-56.
- [2] L.W. Townsend, R.J.M. Fry, Radiation protection guidance for activities in low-Earth orbit, *Space Life Sciences: Biological Research and Space Radiation*, (**2002**), 957-963.
- [3] R.K. Tripathi, J.W. Wilson, R.C. Youngquist, Electrostatic space radiation shielding, *Advances in Space Research*, 42(6) (**2008**), 1043-1049.
- [4] P. Spillantini, Active shielding for long duration interplanetary manned missions, *Advances in Space Research*, 45(7) (**2010**), 900-916.
- [5] Military Specification: Assemblies, Moving, Mechanical For Space And Launch Vehicles, General specification for MIL-A-83577B (USAF), **1988**.
- [6] T.R. Cawsey, A deployment mechanism for the double roll-out flexible solar array on the space telescope, *The 16th Aerospace Mechanisms Symposium (NASA. Kennedy Space Cente)*, **1982**.
- [7] H. Herbert, H. Myron, *Reliability Prediction for Spacecraft*, **1985**.
- [8] C.D. Brown, *Elements of spacecraft design*, Reston, VA : American Institute of Aeronautics and Astronautics, Inc., **2002**.
- [9] C. Moening, Pyrotechnic shock flight failures, IES Pyrotechnic Shock Tutorial Program. 31st Annual Technical Meeting, Institute of Environmental Sciences, Citeseer, **1985**.
- [10] J. Carey, D. Cadogan, L. Pacini, E. Goldstein, M. Lou, Inflatable Sunshield in Space (ISIS) versus Next Generation Space Telescope (NGST) sunshield - A mass properties comparison, *Collection of the 41st Aiaa/Asme/Asce/Ahs/Asc Structures, Structural Dynamics, and Materials Conference and Exhibit*, 4 (**2000**), 3-9.
- [11] W.M. Sokolowski, S.C. Tan, Advanced Self-Deployable Structures for Space Applications, *Journal of Spacecraft and Rockets*, 44(4) (**2007**), 750-754.
- [12] C. Liu, H. Qin, P.T. Mather, Review of progress in shape-memory polymers, *Journal of Materials Chemistry*, 17(16) (**2007**), 1543-1558.
- [13] Y.J. Liu, H.Y. Du, L.W. Liu, J.S. Leng, Shape memory polymers and their composites in aerospace applications: a review, *Smart Materials and Structures*, 23(2) (**2014**), 023001.
- [14] Z.G. Wei, R. Sandstrom, S. Miyazaki, Shape-memory materials and hybrid composites for smart systems - Part I Shape-memory materials, *Journal of Materials Science*, 33(15) (**1998**), 3743-3762.
- [15] J.S. Leng, X. Lan, Y.J. Liu, S.Y. Du, Shape-memory polymers and their composites: Stimulus methods and applications, *Progress in Materials Science*, 56(7) (**2011**), 1077-1135.
- [16] J. Leng, S. Du, *Shape-Memory Polymers and Multifunctional Composites*. [electronic resource], Hoboken : CRC Press, **2010**.

- [17] J. Leng, Y. Liu, X. Lan, H. Lv, X. Wang, J. Leng, S. Du, Y. Liu, Fiber reinforced shape-memory polymer composite and its application in a deployable hinge, *Smart Materials & Structures*, 18(2) (2009), 024002.
- [18] X. Lan, X. Wang, H. Lu, Y. Liu, J. Leng, Shape recovery performances of a deployable hinge fabricated by fiber-reinforced shape-memory polymer, *Proc. SPIE, Behavior and Mechanics of Multifunctional Materials and Composites*, (2009), 728910
- [19] J. Leng, H. Lv, Y. Liu, S. Du, Electroactivate shape-memory polymer filled with nanocarbon particles and short carbon fibers, *Applied Physics Letters*, 91(14) (2007).
- [20] M.K. Ghosh, K.L. Mittal, *Polyimides : fundamentals and applications*, New York : M. Dekker, 1996.
- [21] M. Yoonessi, D.M. Tigelaar, D.A. Scheiman, M. Lebron-Colon, M.A. Meador, Y. Shi, R.A. Weiss, Graphene Polyimide Nanocomposites; Thermal, Mechanical, and High-Temperature Shape Memory Effects, *ACS NANO*, 6(9) (2012), 7644-7655.
- [22] D. Kong, X. Xiao, High Cycle-life Shape Memory Polymer at High Temperature, *Scientific Reports*, 6 (2016), 33610.
- [23] Z. Yang, Y. Chen, Q. Wang, T. Wang, High performance multiple-shape memory behaviors of Poly(benzoxazole-co-imide)s, *Polymer*, 88 (2016), 19-28.
- [24] Q. Wang, Y. Bai, Y. Chen, J. Ju, F. Zheng, T. Wang, High performance shape memory polyimides based on π - π Interactions, *Journal of Materials Chemistry A*, 3(1) (2015), 352-359.
- [25] X. Xiao, X. Qiu, D. Kong, W. Zhang, J. Leng, Y. Liu, Optically transparent high temperature shape memory polymers, *Soft Matter*, 12(11) (2016), 2894-2900.
- [26] H. Koerner, R.J. Strong, M.L. Smith, D.H. Wang, L.-S. Tan, K.M. Lee, T.J. White, R.A. Vaia, Polymer design for high temperature shape memory: Low crosslink density polyimides, *Polymer*, 54 (2013), 391-402.
- [27] J. Leng, X. Xiao, D. Kong, X. Qiu, W. Zhang, S. Zhang, Y. Hu, F. Zhang, J. Leng, Y. Liu, Shape memory polymers with high and low temperature resistant properties, *Scientific Reports*, 5 (2015), 14137.
- [28] J. Leng, X. Xiao, F. Zhang, J. Leng, D. Kong, X. Qiu, W. Zhang, S. Zhang, Y. Hu, L. Liu, Y. Liu, Shape-Memory Polymers with Adjustable High Glass Transition Temperatures, *Macromolecules*, 48(11) (2015), 3582-3589.
- [29] I.A. Rousseau, Challenges of Shape Memory Polymers: A Review of the Progress Toward Overcoming SMP's Limitations, *Polymer Engineering and Science*, 48(11) (2008), 2075-2089.
- [30] W. Francis, M. Lake, K. Mallick, G. Freebury, A. Maji, Development and Testing of a Hinge/Actuator Using Elastic Memory Composites, 44th AIAA/ASME/ASCE/AHS/ASC Structures, Structural Dynamics, and Materials Conference, American Institute of Aeronautics and Astronautics, (2003), 1496.
- [31] J. Leng, Y. Liu, K. Yu, H. Lu, H. Lu, K. Yu, J. Leng, S. Sun, Y. Liu, Mechanical and shape-memory behavior of shape-memory polymer composites with hybrid fillers, *Polymer International*, 59(6) (2010), 766-771.

- [32] W. Sun Lee, J. Yu, Comparative study of thermally conductive fillers in underfill for the electronic components, *Diamond & Related Materials*, 14(10) (2005), 1647-1653.
- [33] F.H. Gojny, M.H.G. Wichmann, B. Fiedler, I.A. Kinloch, W. Bauhofer, A.H. Windle, K. Schulte, Evaluation and identification of electrical and thermal conduction mechanisms in carbon nanotube/epoxy composites, *Polymer*, 47(6) (2006), 2036-2045.
- [34] H. Lu, J. Leng, S. Du, J. Gou, Magnetically aligned carbon nanotube in nanopaper enabled shape-memory nanocomposite for high speed electrical actuation, *Applied Physics Letters*, 98(17) (2011), 174105.
- [35] J. Zhao, Y. Liu, J. Zhao, L. Zhao, W. Li, H. Zhang, Z. Zhang, X. Yu, High Performance Shape Memory Epoxy/Carbon Nanotube Nanocomposites, *ACS Applied Materials & Interfaces*, 8(1) (2016), 311-320.
- [36] B. Weidenfeller, M. Höfer, F.R. Schilling, Thermal conductivity, thermal diffusivity, and specific heat capacity of particle filled polypropylene, *Composites Part A: Applied Science and Manufacturing*, 35(4) (2004), 423-429.
- [37] G.-W. Lee, M. Park, J. Kim, J.I. Lee, H.G. Yoon, Enhanced thermal conductivity of polymer composites filled with hybrid filler, *Composites Part A: Applied Science and Manufacturing* 37(5) (2006), 727-734.
- [38] M.Y. Razzaq, L. Frommann, Thermomechanical studies of aluminum nitride filled shape memory polymer composites, *Polymer Composites*, 28(3) (2007), 287-293.
- [39] Y.M. Chen, J.M. Ting, Ultra high thermal conductivity polymer composites, *Carbon*, 40(3) (2002), 359-362.
- [40] L. Haibao, G. Jihua, L. Jinsong, D. Shanyi, Synergistic effect of carbon nanofiber and sub-micro filamentary nickel nanostrand on the shape memory polymer nanocomposite, *Smart Materials and Structures*, 20(3) (2011), 035017.
- [41] F. Liang, H. Lu, H. Lu, F. Liang, J. Gou, Nanopaper enabled shape-memory nanocomposite with vertically aligned nickel nanostrand: controlled synthesis and electrical actuation, *Soft Matter*, 7(16) (2011), 7416-7423.
- [42] C. Li, G. Shi, Three-dimensional graphene architectures, *Nanoscale*, 4(18) (2012), 5549-5563.
- [43] Z.P. Chen, W.C. Ren, L.B. Gao, B.L. Liu, S.F. Pei, H.M. Cheng, Three-dimensional flexible and conductive interconnected graphene networks grown by chemical vapour deposition, *Nature Materials*, 10(6) (2011), 424-428.
- [44] A.K. Geim, Graphene: Status and Prospects, *Science*, 324(5934) (2009), 1530-1534.
- [45] M. Loeblein, R.Y. Tay, S.H. Tsang, W.B. Ng, E.H.T. Teo, Configurable Three-Dimensional Boron Nitride-Carbon Architecture and Its Tunable Electronic Behavior with Stable Thermal Performances, *Small*, 10(15) (2014), 2992-2999.
- [46] M.T. Pettes, H.X. Ji, R.S. Ruoff, L. Shi, Thermal Transport in Three-Dimensional Foam Architectures of Few-Layer Graphene and Ultrathin Graphite, *Nano Letters*, 12(6) (2012), 2959-2964.

- [47] S. Nardecchia, D. Carriazo, M.L. Ferrer, M.C. Gutierrez, F. del Monte, Three dimensional macroporous architectures and aerogels built of carbon nanotubes and/or graphene: synthesis and applications, *Chemical Society Reviews*, 42(2) (2013), 794-830.
- [48] V. Chabot, D. Higgins, A. Yu, X. Xiao, Z. Chen, J. Zhang, A review of graphene and graphene oxide sponge: material synthesis and applications to energy and the environment, *Energy & Environmental Science*, 7(5) (2014), 1564-1596.
- [49] L.B. Zhang, R.Y. Li, B. Tang, P. Wang, Solar-thermal conversion and thermal energy storage of graphene foam-based composites, *Nanoscale*, 8(30) (2016), 14600-14607.
- [50] Y. Li, X. Wang, Q. Yang, M.S. Javed, Q. Liu, W. Xu, C. Hu, D. Wei, Ultra-fine CuO Nanoparticles Embedded in Three-dimensional Graphene Network Nano-structure for High-performance Flexible Supercapacitors, *Electrochimica Acta*, 234 (2017), 63-70.
- [51] M. Loeblein, S.H. Tsang, M. Pawlik, E.J.R. Phua, H. Yong, X.W. Zhang, C.L. Gan, E.H.T. Teo, High-Density 3D-Boron Nitride and 3D-Graphene for High-Performance Nano-Thermal Interface Material, *Acs Nano*, 11(2) (2017), 2033-2044.
- [52] J. Kuang, L. Liu, Y. Gao, D. Zhou, Z. Chen, B. Han, Z. Zhang, A hierarchically structured graphene foam and its potential as a large-scale strain-gauge sensor, *Nanoscale*, 5(24) (2013) 12171-12177.
- [53] X.C. Dong, X.W. Wang, L.H. Wang, H. Song, H. Zhang, W. Huang, P. Chen, 3D Graphene Foam as a Monolithic and Macroporous Carbon Electrode for Electrochemical Sensing, *ACS Applied Materials & Interfaces*, 4(6) (2012), 3129-3133.
- [54] M.A. Ali, K. Mondal, Y.F. Wang, H.W. Jiang, N.K. Mahal, M.J. Castellano, A. Sharma, L. Dong, In situ integration of graphene foam-titanium nitride based bio-scaffolds and microfluidic structures for soil nutrient sensors, *Lab on a Chip*, 17(2) (2017), 274-285.
- [55] Q. Song, Z. Jiang, N. Li, P. Liu, L. Liu, M. Tang, G. Cheng, Anti-inflammatory effects of three-dimensional graphene foams cultured with microglial cells, *Biomaterials*, 35(25) (2014), 6930-6940.
- [56] L. Zhang, M. Liu, S. Bi, L. Yang, S. Roy, X.-Z. Tang, C. Mu, X. Hu, Polydopamine decoration on 3D graphene foam and its electromagnetic interference shielding properties, *Journal of Colloid and Interface Science*, 493 (2017), 327-333.
- [57] Y. Wu, Z. Wang, X. Liu, X. Shen, Q. Zheng, Q. Xue, J.-K. Kim, Ultralight Graphene Foam/Conductive Polymer Composites for Exceptional Electromagnetic Interference Shielding, *ACS Applied Materials & Interfaces*, 9(10) (2017), 9059-9069.
- [58] M. Loeblein, A. Bolker, S.H. Tsang, N. Atar, C. Uzan-Saguy, R. Verker, I. Gouzman, E. Grossman, E.H.T. Teo, 3D Graphene-Infused Polyimide with Enhanced Electrothermal Performance for Long-Term Flexible Space Applications, *Small*, 11(48) (2015), 6425-6434.
- [59] P. Nautiyal, B. Boesl, A. Agarwal, Harnessing Three Dimensional Anatomy of Graphene Foam to Induce Superior Damping in Hierarchical Polyimide Nanostructures, *Small*, 13(10) (2017), 1603473.
- [60] J. Coopersmith, Affordable Access to Space, *Issues in Science and Technology*, 29(1) (2012), 57-62.

- [61] MISSE: Testing materials in space., National Aeronautics and Space Administration.
- [62] A. Idowu, B. Boesl, A. Agarwal, 3D graphene foam-reinforced polymer composites – A review, *Carbon*, 135 (2018), 52-71.
- [63] J. Unda, J. Weisz, J. Rivacoba, I.R. Urien, R.S. Capitanio, Family of deployable/retractable structures for space application, *Acta Astronautica*, 32(12) (1994), 767-784.
- [64] P. Conley, D. Packard, W. Purdy, *Space vehicle mechanisms : elements of successful design*, New York : Wiley, 1998.
- [65] M. Salama, M. Lou, H. Fang, Deployment of inflatable space structures - A review of recent developments, 41st Structures, Structural Dynamics, and Materials Conference and Exhibit, American Institute of Aeronautics and Astronautics, 2000.
- [66] L. Sarsfield, *The cosmos on a shoestring : small spacecraft for space and earth science*, RAND, Critical Technologies Institute, Santa Monica, CA, 1998.
- [67] J.W. Evans, L. Gallo, M. Kaminsky, A bayesian framework for reliability analysis of spacecraft deployments, *IEEE Aerospace Conference*, MT, United States, 2012.
- [68] M. Thomson, S. Davis, Pulley actuated translational hinge system, 2003.
- [69] G. Sebestyen, S. Fujikawa, N. Galassi, A. Chuchra (Eds.), *Low Earth Orbit Satellite Design*, Springer International Publishing, Cham, 2018, 161-171.
- [70] S.C. Arzberger, M.L. Tupper, M.S. Lake, R. Barrett, K. Mallick, C. Hazelton, W. Francis, P.N. Keller, D. Campbell, S. Feucht, D. Codell, J. Wintergerst, L. Adams, J. Mallioux, R. Denis, K. White, M. Long, N.A. Munshi, K. Gall, Elastic Memory Composites (EMC) for deployable industrial and commercial applications, *Proc. SPIE*, 5762, 2005, 35-47.
- [71] Shape Memory Composite Hybrid Hinge, NASA's Jet Propulsion Laboratory, Pasadena, California, 2012.
- [72] W.W. Vyvyan, Self-actuating, self-locking hinge, US Patent Specification, 3386128, 1968.
- [73] S.S. Schwartz, C.P. Rubin, Self actuating self locking flexible hinge, US Patents Specifications 3670358, 1972.
- [74] F.R. Chiappetta, C.L. Frame, K.L. Johnson, Hinge element and deployable structures including hinge element, US Patent Specification, 5239793, 1993.
- [75] K. A. Seffen, S. Pellegrino, Deployment Dynamics of Tape Springs, *Proceedings: Mathematical, Physical and Engineering Sciences*, 455(1983) (1999), 1003-1048.
- [76] O. Soykasap, Analysis of tape spring hinges, *International Journal of Mechanical Sciences*, 49(7) (2007), 853-860.
- [77] K.A. Seffen, S. Pellegrino, G.T. Parks, Deployment of a panel by tape-spring hinges, *Iutam-Iass Symposium on Deployable Structures: Theory and Applications*, 2000, 355-364.
- [78] F. Beavers, N. Munshi, M. Lake, A. Maji, K. Qassim, B. Carpenter, S. Rawal, Design and Testing of an Elastic Memory Composite Deployment Hinge for Spacecraft, 43rd AIAA/ASME/ASCE/AHS/ASC Structures, Structural Dynamics, and Materials Conference, American Institute of Aeronautics and Astronautics, 2002, 1452.

- [79] M. Tupper, N. Munshi, F. Beavers, K. Gall, M. Mikulas, T. Meink, Developments in elastic memory composite materials for spacecraft deployable structures, IEEE Aerospace Conference Proceedings, 1-7 (**2001**), 2541-2547.
- [80] R. Barrett, W. Francis, E. Abrahamson, M. Lake, M. Scherbarth, Qualification of Elastic Memory Composite Hinges for Spaceflight Applications, 47th AIAA/ASME/ASCE/AHS/ASC Structures, Structural Dynamics, and Materials Conference, American Institute of Aeronautics and Astronautics, **2006**, 2039.
- [81] M. Behl, A. Lendlein, Shape-memory polymers, *Materials Today*, 10(4) (**2007**), 20-28.
- [82] M. Behl, M.Y. Razzaq, A. Lendlein, Multifunctional Shape-Memory Polymers, *Advanced Materials*, 22(31) (**2010**), 3388-3410.
- [83] D. Ratna, J. Karger-Kocsis, Recent advances in shape memory polymers and composites: a review, *Journal of Materials Science*, 43(1) (**2008**), 254-269.
- [84] P.T. Mather, X.F. Luo, I.A. Rousseau, Shape Memory Polymer Research, *Annual Review of Materials Research*, 39(1) (**2009**), 445-471.
- [85] W.M. Huang, Z. Ding, C.C. Wang, J. Wei, Y. Zhao, H. Purnawali, Shape memory materials, *Materials Today*, 13(7-8) (**2010**), 54-61.
- [86] J.S. Leng, H.B. Lu, Y.J. Liu, W.M. Huang, S.Y. Du, Shape-Memory Polymers-A Class of Novel Smart Materials, *MRS Bulletin*, 34(11) (**2009**), 848-855.
- [87] H. Meng, G. Li, A review of stimuli-responsive shape memory polymer composites, *Polymer*, 54(9) (**2013**), 2199-2221.
- [88] G.J. Berg, M.K. McBride, C. Wang, C.N. Bowman, New directions in the chemistry of shape memory polymers, *Polymer*, 55(23) (**2014**), 5849-5872.
- [89] Q. Zhao, H.J. Qi, T. Xie, Recent progress in shape memory polymer: New behavior, enabling materials, and mechanistic understanding, *Progress in Polymer Science*, 49-50 (**2015**), 79-120.
- [90] Y. Wu, J. Hu, C. Zhang, J. Han, Y. Wang, B. Kumar, A facile approach to fabricate a UV/heat dual-responsive triple shape memory polymer, *Journal of Materials Chemistry A*, 3(1) (**2015**), 97-100.
- [91] Y. Zheng, J. Li, E. Lee, S. Yang, Light-induced shape recovery of deformed shape memory polymer micropillar arrays with gold nanorods, *RSC Advances*, 5(39) (**2015**), 30495-30499.
- [92] A. Lendlein, H. Jiang, O. Jünger, R. Langer, Light-induced shape-memory polymers, *Nature*, 434 (**2005**), 879-882.
- [93] J. Leng, Y. Liu, X. Wu, J. Leng, X. Wu, Y. Liu, Infrared Light-Active Shape Memory Polymer Filled with Nanocarbon Particles, *Journal of Applied Polymer Science*, 114(4) (**2009**), 2455-2460.
- [94] H. Lv, J. Leng, S. Du, Y. Liu, Shape-memory polymer in response to solution, *Advanced Engineering Materials*, 10(6) (**2008**), 592-595.
- [95] Y. Liu, Y. Li, H. Chen, G. Yang, X. Zheng, S. Zhou, Water-induced shape-memory poly(d,l-lactide)/microcrystalline cellulose composites, *Carbohydrate Polymers*, 104 (**2014**), 101-108.
- [96] B. Yang, W.M. Huang, C. Li, L. Li, Effects of moisture on the thermomechanical properties of a polyurethane shape memory polymer, *Polymer*, 47(4) (**2006**), 1348-1356.

- [97] Y. Chae Jung, H. Hwa So, J. Whan Cho, Water-Responsive Shape Memory Polyurethane Block Copolymer Modified with Polyhedral Oligomeric Silsesquioxane, *Journal of Macromolecular Science, Part B*, 45(4) (**2006**), 453-461.
- [98] F.-P. Du, E.-Z. Ye, W. Yang, T.-H. Shen, C.-Y. Tang, X.-L. Xie, X.-P. Zhou, W.-C. Law, Electroactive shape memory polymer based on optimized multi-walled carbon nanotubes/polyvinyl alcohol nanocomposites, *Composites Part B: Engineering*, 68 (**2015**), 170-175.
- [99] H. Luo, Z. Li, G. Yi, X. Zu, H. Wang, Y. Wang, H. Huang, J. Hu, Z. Liang, B. Zhong, Electro-responsive silver nanowire-shape memory polymer composites, *Materials Letters*, 134 (**2014**), 172-175.
- [100] W. Wang, D. Liu, Y. Liu, J. Leng, D. Bhattacharyya, Electrical actuation properties of reduced graphene oxide paper/epoxy-based shape memory composites, *Composites Science and Technology*, 106 (**2015**), 20-24.
- [101] H. Lu, Y. Liu, J. Gou, J. Leng, S. Du, Electroactive shape-memory polymer nanocomposites incorporating carbon nanofiber paper, *International Journal of Smart and Nano Materials*, 1(1) (**2010**), 2-12.
- [102] H. Lu, J. Gou, Study on 3-D High Conductive Graphene Buckypaper for Electrical Actuation of Shape Memory Polymer, *Nanoscience and Nanotechnology Letters*, 4(12) (**2012**), 1155-1159.
- [103] H.H. Le, O. Osazuwa, I. Kolesov, S. Ilisch, H.J. Radusch, Influence of carbon black properties on the Joule heating stimulated shape-memory behavior of filled ethylene-1-octene copolymer, *Polymer Engineering and Science*, 51(3) (**2011**), 500-508.
- [104] H.-F. Lee, H.H. Yu, Study of electroactive shape memory polyurethane-carbon nanotube hybrids, *Soft Matter*, 7(8) (**2011**), 3801-3807.
- [105] K. Yu, Z. Zhang, J. Leng, Y. Liu, Carbon nanotube chains in a shape memory polymer/carbon black composite: To significantly reduce the electrical resistivity, *Applied Physics Letters*, 98(7) (**2011**), 074102.
- [106] H. Lu, J. Gou, Fabrication and electroactive responsive behavior of shape-memory nanocomposite incorporated with self-assembled multiwalled carbon nanotube nanopaper, *Polymers for Advanced Technologies*, 23(12) (**2012**), 1529-1535.
- [107] Y.C. Jung, N.S. Goo, Electroactive shape-memory polyurethane composites incorporating carbon nanotubes, *Macromolecular Rapid Communications*, 26(5) (**2005**), 412-416.
- [108] Z. Tang, D. Sun, D. Yang, B. Guo, L. Zhang, D. Jia, Vapor grown carbon nanofiber reinforced bio-based polyester for electroactive shape memory performance, *Composites Science and Technology*, 75 (**2013**), 15-21.
- [109] K. Yu, Y. Liu, J. Leng, Shape memory polymer/CNT composites and their microwave induced shape memory behaviors, *RSC Advances*, 4(6) (**2014**), 2961-2968.
- [110] R. Mohr, K. Kratz, T. Weigel, M. Lucka-Gabor, M. Moneke, A. Lendlein, Initiation of shape-memory effect by inductive heating of magnetic nanoparticles in thermoplastic polymers, *Proceedings of the National Academy of Sciences of the United States of America*, 103(10) (**2006**), 3540.

- [111] A.M. Schmidt, Electromagnetic activation of shape memory polymer networks containing magnetic nanoparticles, *Macromolecular Rapid Communications*, 27(14) (2006), 1168-1172.
- [112] C.M. Yakacki, K. Gall, R. Likos, N.S. Satarkar, J.Z. Hilt, Shape-Memory Polymer Networks with Fe₃O₄ Nanoparticles for Remote Activation, *Journal of Applied Polymer Science*, 112(5) (2009), 3166-3176.
- [113] E. Hornbogen, Comparison of shape memory metals and polymers, *Advanced Engineering Materials*, 8(1-2) (2006), 101-106.
- [114] W. Voit, T. Ware, R.R. Dasari, P. Smith, L. Danz, D. Simon, S. Barlow, S.R. Marder, K. Gall, High-Strain Shape-Memory Polymers, *Advanced Functional Materials*, 20(1) (2010), 162-171.
- [115] A. Lendlein, R. Langer, Biodegradable, Elastic Shape-Memory Polymers for Potential Biomedical Applications, *Science*, 296(5573) (2002), 1673-1676.
- [116] A. Metcalfe, A.-C. Desfaits, I. Salazkin, L.H. Yahia, W.M. Sokolowski, J. Raymond, Cold hibernated elastic memory foams for endovascular interventions, *Biomaterials*, 24(3) (2003), 491-497.
- [117] H.M. Wache, D.J. Tartakowska, A. Hentrich, M.H. Wagner, Development of a polymer stent with shape memory effect as a drug delivery system, *Journal of Materials Science: Materials in Medicine*, 14(2) (2003), 109-112.
- [118] Y. Wong, J. Kong, L.K. Widjaja, S.S. Venkatraman, Biomedical applications of shape-memory polymers: how practically useful are they?, *Science China Chemistry*, 57(4) (2014), 476-489.
- [119] M. Bao, X. Lou, Q. Zhou, W. Dong, H. Yuan, Y. Zhang, Electrospun Biomimetic Fibrous Scaffold from Shape Memory Polymer of PDLA-co-TMC for Bone Tissue Engineering, *ACS Applied Materials & Interfaces*, 6(4) (2014), 2611-2621.
- [120] P.R. Buckley, G.H. McKinley, T.S. Wilson, W. Small, W.J. Bennett, J.P. Bearinger, M.W. McElfresh, D.J. Maitland, Inductively heated shape memory polymer for the magnetic actuation of medical devices, *Ieee Transactions on Biomedical Engineering*, 53(10) (2006), 2075-2083.
- [121] H. Jinlian, L. Jing, Shape memory polymers in textiles, *Advances in Science & Technology*, 80 (2013), 30-38.
- [122] J. FengLong, Z. Yong, H. JinLian, L. Yan, Y. Lap-Yan, Y. GuangDou, Smart polymer fibers with shape memory effect, *Smart Materials and Structures*, 15(6) (2006), 1547-1554.
- [123] J.A. Shumaker, A.J.W. McClung, J.W. Baur, Synthesis of high temperature polyaspartimide-urea based shape memory polymers, *Polymer*, 53(21) (2012), 4637-4642.
- [124] F. Xie, Y. Liu, L. Huang, J. Leng, Synthesis and characterization of high temperature cyanate-based shape memory polymers with functional polybutadiene/acrylonitrile, *Polymer*, 55(23) (2014), 5873-5879.
- [125] Y. Shi, M. Yoonessi, R.A. Weiss, High Temperature Shape Memory Polymers, *Macromolecules*, 46(10) (2013), 4160-4167.
- [126] Y. Shi, R.A. Weiss, Sulfonated Poly(ether ether ketone) Ionomers and Their High Temperature Shape Memory Behavior, *Macromolecules*, 47(5) (2014), 1732-1740.

- [127] F. Xie, L. Huang, J. Leng, Y. Liu, Thermoset shape memory polymers and their composites, *Journal of Intelligent Material Systems and Structures*, 27(18) (2016), 2433-2455.
- [128] T.L.S. Clair, Structure-property relationships in linear aromatic polyimides, in: D. Wilson, H.D. Stenzenberger, P.M. Hergenrother (Eds.), *Polyimides*, Springer Netherlands, Dordrecht, 1990, 58-78.
- [129] I. Gouzman, E. Grossman, R. Verker, N. Atar, A. Bolker, N. Eliaz, *Advances in Polyimide-Based Materials for Space Applications*, *Advanced Materials*, 31(18) (2019), 1807738.
- [130] R. Yokota, Recent Trends and Space Applications of Polyimides, *Journal of Photopolymer Science and Technology*, 12(2) (1999), 209-216.
- [131] M.D. Finckenor, D, *Multilayer Insulation Material Guidelines*, NASA/TP-1999-209263, National Aeronautics and Space Administration, Washington, D.C., 1999.
- [132] H. Gao, X. Lan, L. Liu, X. Xiao, Y. Liu, J. Leng, Study on performances of colorless and transparent shape memory polyimide film in space thermal cycling, atomic oxygen and ultraviolet irradiation environments, *Smart Materials and Structures*, 26(9) (2017), 095001.
- [133] H. Gao, L. Huang, X. Lan, L. Liu, Y. Liu, J. Leng, The research of vacuum thermal cycling resistant transparent shape memory polyimide and its application in space flexible electronics, *Proc. SPIE*, 10165 (2017).
- [134] Z. Yang, Q. Wang, Y. Bai, T. Wang, AO-resistant shape memory polyimide/silica composites with excellent thermal stability and mechanical properties, *RSC Advances*, 5(89) (2015), 72971-72980.
- [135] Z.H. Yang, Q.H. Wang, T.M. Wang, Tunable Triple-Shape Memory Binary Mixtures with High Transition Temperature and Robust Mechanical Properties, *Macromolecular Chemistry and Physics*, 217(11) (2016), 1305-1313.
- [136] Z. Yang, F. Song, Q. Wang, T. Wang, Shape memory induced structural evolution of high performance copolyimides, *Journal of Polymer Science Part A: Polymer Chemistry*, 54(24) (2016), 3858-3867.
- [137] H. Gao, J. Li, F. Xie, Y. Liu, J. Leng, A novel low colored and transparent shape memory copolyimide and its durability in space thermal cycling environments, *Polymer*, 156 (2018), 121-127.
- [138] X. Li, L. Wang, Z. Zhang, D. Kong, X. Ao, X. Xiao, Electroactive High-Temperature Shape Memory Polymers with High Recovery Stress Induced by Ground Carbon Fibers, *Macromolecular Chemistry and Physics*, 220(17) (2019), 1900164.
- [139] Z. Lan, X. Chen, X. Zhang, C. Zhu, Y. Yu, J. Wei, Transparent, High Glass-Transition Temperature, Shape Memory Hybrid Polyimides Based on Polyhedral Oligomeric Silsesquioxane, *Polymers*, 11(6) (2019), 1058.
- [140] C. Liu, P. Mather, High thermal conductivity shape memory polymers, *Annual Technical Conference - ANTEC*, Conference Proceedings 3 (2004).
- [141] Q. Meng, J. Hu, A review of shape memory polymer composites and blends, *Composites Part A: Applied Science and Manufacturing*, 40(11) (2009), 1661-1672.

- [142] T. Ohki, Q.-Q. Ni, N. Ohsako, M. Iwamoto, Mechanical and shape memory behavior of composites with shape memory polymer, *Composites Part A*, 35 (2004), 1065-1073.
- [143] F. Cao, S.C. Jana, Nanoclay-tethered shape memory polyurethane nanocomposites, *Polymer*, 48 (2007), 3790-3800.
- [144] Y. Liu, K. Gall, M.L. Dunn, P. McCluskey, Thermomechanics of shape memory polymer nanocomposites, *Mechanics of Materials*, 36(10) (2004), 929-940.
- [145] K. Gall, M.L. Dunn, Y. Liu, G. Stefanic, D. Balzar, Internal stress storage in shape memory polymer nanocomposites, *Applied Physics Letters*, 85(2) (2004), 290-292.
- [146] C.-S. Zhang, Q.-Q. Ni, Bending behavior of shape memory polymer based laminates, *Composite Structures*, 78 (2007), 153-161.
- [147] G.A. Jimenez, S.C. Jana, Polyurethane-carbon nanofiber composites for shape memory effects, ANTEC, conference proceedings. Society of plastics engineers annual technical conference: plastics encounter at ANTEC, Cincinnati, OH, United States, 2007, 18-22.
- [148] I.S. Gunes, G.A. Jimenez, S.C. Jana, Carbonaceous fillers for shape memory actuation of polyurethane composites by resistive heating, *Carbon*, 47(4) (2009), 981-997.
- [149] J. Dong, J. Ding, J. Weng, L. Dai, Graphene Enhances the Shape Memory of Poly (acrylamide-co-acrylic acid) Grafted on Graphene, *Macromolecular Rapid Communications*, 34(8) (2013), 659-664.
- [150] Y. Dong, J. Ding, J. Wang, X. Fu, H. Hu, S. Li, H. Yang, C. Xu, M. Du, Y. Fu, Synthesis and properties of the vapour-grown carbon nanofiber/epoxy shape memory and conductive foams prepared via latex technology, *Composites Science and Technology*, 76(Supplement C) (2013), 8-13.
- [151] L. Haibao, L. Yanju, G. Jihua, L. Jinsong, D. Shanyi, Electrical properties and shape-memory behavior of self-assembled carbon nanofiber nanopaper incorporated with shape-memory polymer, *Smart Materials and Structures*, 19(7) (2010), 075021.
- [152] S. Mondal, J.L. Hu, Shape memory studies of functionalized MWNT-reinforced polyurethane copolymers, *Iranian Polymer Journal*, 15(2) (2006), 135-142.
- [153] F. Li, L. Qi, J. Yang, M. Xu, X. Luo, D. Ma, Polyurethane/conducting carbon black composites: Structure, electric conductivity, strain recovery behavior, and their relationships, *Journal of Applied Polymer Science*, 75(1) (2000), 68-77.
- [154] N. Karak, S. Thakur, S. Thakur, N. Karak, Bio-based tough hyperbranched polyurethane-graphene oxide nanocomposites as advanced shape memory materials, *Rsc Advances*, 3(24) (2013), 9476-9482.
- [155] C. Jin Taek, D. Trung Dung, O. Kyung Min, L. Hyung-il, J. Han Mo, K. Byung Kyu, Shape memory polyurethane nanocomposites with functionalized graphene, *Smart Materials and Structures*, 21(7) (2012), 075017.
- [156] X. Xiao, T. Xie, Y.-T. Cheng, Self-healable graphene polymer composites, *Journal of Materials Chemistry*, 20(17) (2010), 3508-3514.
- [157] I. Gunes, F. Cao, S. Jana, Evaluation of Nanoparticulate Fillers for Shape Memory Polyurethane Nanocomposites, *Polymer*, 49(9) (2008), 2223-2234.

- [158] I.H. Paik, N.S. Goo, Y.C. Jung, J.W. Cho, Development and application of conducting shape memory polyurethane actuators, *Smart Materials and Structures*, 15(5) (**2006**), 1476-1482.
- [159] A. Kausar, Z. Anwar, B. Muhammad, Recent Developments in Epoxy/Graphite, Epoxy/Graphene, and Epoxy/Graphene Nanoplatelet Composites: A Comparative Review, *Polymer-Plastics Technology and Engineering*, 55(11) (**2016**), 1192-1210.
- [160] V. Goyal, A.A. Balandin, Thermal properties of the hybrid graphene-metal nano-micro-composites: Applications in thermal interface materials, *Applied Physics Letters*, 100(7) (**2012**), 073113.
- [161] K.M.F. Shahil, A.A. Balandin, Graphene–Multilayer Graphene Nanocomposites as Highly Efficient Thermal Interface Materials, *Nano Letters*, 12(2) (**2012**), 861-867.
- [162] Y. Ma, Y. Chen, Three-dimensional graphene networks: synthesis, properties and applications, *National Science Review*, 2(1) (**2014**), 40-53.
- [163] Q. Fang, Y. Shen, B. Chen, Synthesis, decoration and properties of three-dimensional graphene-based macrostructures: A review, *Chemical Engineering Journal*, 264 (**2015**), 753-771.
- [164] Jia, J, Sun, X, Lin, X, Shen, X, Mai, Y.W, and Kim, J.K, Exceptional Electrical Conductivity and Fracture Resistance of 3D Interconnected Graphene Foam/Epoxy Composites, *ACS Nano*, 8(6) (**2014**), 5774-5783.
- [165] Y.-H. Zhao, Z.-K. Wu, S.-L. Bai, Study on thermal properties of graphene foam/graphene sheets filled polymer composites, *Composites Part A: Applied Science and Manufacturing*, 72 (**2015**), 200-206.
- [166] Y.-H. Zhao, Z.-K. Wu, S.-L. Bai, Thermal resistance measurement of 3D graphene foam/polymer composite by laser flash analysis, *International Journal of Heat and Mass Transfer*, 101 (**2016**), 470-475.
- [167] Y.-H. Zhao, Y.-F. Zhang, S.-L. Bai, High thermal conductivity of flexible polymer composites due to synergistic effect of multilayer graphene flakes and graphene foam, *Composites Part A: Applied Science and Manufacturing*, 85 (**2016**), 148-155.
- [168] Z. Liu, D. Shen, J. Yu, W. Dai, C. Li, S. Du, N. Jiang, H. Li, C.-T. Lin, Exceptionally high thermal and electrical conductivity of three-dimensional graphene-foam-based polymer composites, *RSC Advances*, 6(27) (**2016**), 22364-22369.
- [169] M. Zhou, T. Lin, F. Huang, Y. Zhong, Z. Wang, Y. Tang, H. Bi, D. Wan, J. Lin, Highly Conductive Porous Graphene/Ceramic Composites for Heat Transfer and Thermal Energy Storage, *Advanced Functional Materials*, 23(18) (**2013**), 2263-2269.
- [170] A. Fedden, M. Franke, Graphitized Carbon Foam with Phase Change Material for Thermal Energy Storage, 9th AIAA/ASME Joint Thermophysics and Heat Transfer Conference, American Institute of Aeronautics and Astronautics, **2006**, 3133.
- [171] J. Yang, G.-Q. Qi, Y. Liu, R.-Y. Bao, Z.-Y. Liu, W. Yang, B.-H. Xie, M.-B. Yang, Hybrid graphene aerogels/phase change material composites: Thermal conductivity, shape-stabilization and light-to-thermal energy storage, *Carbon*, 100 (**2016**), 693-702.

- [172] J. Yang, E. Zhang, X. Li, Y. Zhang, J. Qu, Z.-Z. Yu, Cellulose/graphene aerogel supported phase change composites with high thermal conductivity and good shape stability for thermal energy storage, *Carbon*, 98 (2016), 50-57.
- [173] J. Bustillos, C. Zhang, B. Boesl, A. Agarwal, Three-Dimensional Graphene Foam–Polymer Composite with Superior Deicing Efficiency and Strength, *ACS Applied Materials & Interfaces*, 10(5) (2018), 5022-5029.
- [174] X. Li, L. Shao, N. Song, L. Shi, P. Ding, Enhanced thermal-conductive and anti-dripping properties of polyamide composites by 3D graphene structures at low filler content, *Composites Part A: Applied Science and Manufacturing*, 88 (2016), 305-314.
- [175] X. Cao, Y. Shi, W. Shi, G. Lu, X. Huang, Q. Yan, Q. Zhang, H. Zhang, Preparation of Novel 3D Graphene Networks for Supercapacitor Applications, *Small*, 7(22) (2011), 3163-3168.
- [176] B.G. Choi, M. Yang, W.H. Hong, J.W. Choi, Y.S. Huh, 3D Macroporous Graphene Frameworks for Supercapacitors with High Energy and Power Densities, *ACS Nano*, 6(5) (2012) 4020-4028.
- [177] Z. Yang, S. Chabi, Y. Xia, Y. Zhu, Preparation of 3D graphene-based architectures and their applications in supercapacitors, *Progress in Natural Science: Materials International*, 25(6) (2015), 554-562..
- [178] G. Chen, Y. Liu, F. Liu, X. Zhang, Fabrication of three-dimensional graphene foam with high electrical conductivity and large adsorption capability, *Applied Surface Science*, 311 (2014), 808-815.
- [179] X. Sun, X. Liu, X. Shen, Y. Wu, Z. Wang, J.-K. Kim, Graphene foam/carbon nanotube/poly(dimethyl siloxane) composites for exceptional microwave shielding, *Composites Part A: Applied Science and Manufacturing*, 85 (2016), 199-206.
- [180] Y.-S. Jun, S. Sy, W. Ahn, H. Zarrin, L. Rasen, R. Tjandra, B.M. Amoli, B. Zhao, G. Chiu, A. Yu, Highly conductive interconnected graphene foam based polymer composite, *Carbon*, 95 (2015), 653-658.
- [181] R. Xu, Y. Lu, C. Jiang, J. Chen, P. Mao, G. Gao, L. Zhang, S. Wu, Facile Fabrication of Three-Dimensional Graphene Foam/Poly(dimethylsiloxane) Composites and Their Potential Application as Strain Sensor, *ACS Applied Materials & Interfaces*, 6(16) (2014), 13455-13460.
- [182] Y.R. Jeong, H. Park, S.W. Jin, S.Y. Hong, S.-S. Lee, J.S. Ha, Highly Stretchable and Sensitive Strain Sensors Using Fragmentized Graphene Foam, *Advanced Functional Materials*, 25(27) (2015), 4228-4236.
- [183] M. Chen, L. Zhang, S. Duan, S. Jing, H. Jiang, C. Li, Highly Stretchable Conductors Integrated with a Conductive Carbon Nanotube/Graphene Network and 3D Porous Poly(dimethylsiloxane), *Advanced Functional Materials*, 24(47) (2014), 7548-7556.
- [184] Y.A. Samad, Y. Li, S.M. Alhassan, K. Liao, Novel Graphene Foam Composite with Adjustable Sensitivity for Sensor Applications, *ACS Applied Materials & Interfaces*, 7(17) (2015), 9195-9202.
- [185] L.-Z. Guan, L. Zhao, Y.-J. Wan, L.-C. Tang, Three-dimensional graphene-based polymer nanocomposites: preparation, properties and applications, *Nanoscale*, 10(31) (2018), 14788-14811.

- [186] I. Oh, S.-H. Lee, J.-H. Jung, I.-K. Oh, 3D Networked Graphene-Ferromagnetic Hybrids for Fast Shape Memory Polymers with Enhanced Mechanical Stiffness and Thermal Conductivity, *Small*, 10(19) (2014), 3880-3886.
- [187] M. Loeblein, A. Bolker, Z.L. Ngoh, L. Li, E. Wallach, S.H. Tsang, M. Pawlik, R. Verker, N. Atar, I. Gouzman, E.H.T. Teo, Novel timed and self-resistive heating shape memory polymer hybrid for large area and energy efficient application, *Carbon*, 139 (2018), 626-634.
- [188] A.C. Tribble, *The space environment : implications for spacecraft design*, Princeton, N.J. ; Woodstock : Princeton University Press, 2003. Rev. and expanded ed.2003.
- [189] M.R. Reddy, Effect of Low-Earth-Orbit Atomic Oxygen on Spacecraft Materials, *Journal of Materials Science*, 30(2) (1995), 281-307.
- [190] E. Silverman, *Space environmental effects on spacecraft: LEO materials selection guide*, NASA Contractor report 4661, part 1, tech. rep, 1995.
- [191] E. Grossman, I. Gouzman, *Space environment effects on polymers in low earth orbit*, *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*, 208 (2003), 48-57.
- [192] M. Ann Garrison Darrin, *The Impact of the Space Environment on Material Remains*, in: B.L. O'Leary, P.J. Capelotti (Eds.), *Archaeology and Heritage of the Human Movement into Space*, Springer International Publishing, Cham, (2015), 13-28.
- [193] N. Atar, E. Grossman, I. Gouzman, A. Bolker, V.J. Murray, B.C. Marshall, M. Qian, T.K. Minton, Y. Hanein, Atomic-Oxygen-Durable and Electrically-Conductive CNT-POSS-Polyimide Flexible Films for Space Applications, *ACS Applied Materials & Interfaces*, 7(22) (2015), 12047-12056.
- [194] R. Kamenetzky, M. Finckenor, J. Vaughn, D. Edwards, A. Nolen, H. Burns, *Space Environmental Effects Testing in Support of the International Space Station*, 38th Aerospace Sciences Meeting and Exhibit, (2000), 0242.
- [195] J.T. Fulcher, Y.C. Lu, G.P. Tandon, D.C. Foster, Thermomechanical characterization of environmentally conditioned shape memory polymer using nanoindentation, *Proc. SPIE, Behavior and Mechanics of Multifunctional Materials and Composites*, (2010), 7644.
- [196] J. Leng, X. Wu, F. Xie, Y. Liu, Effect of the γ -radiation on the properties of epoxy-based shape memory polymers, *Journal of Intelligent Material Systems and Structures*, 25(10) (2014), 1256-1263.
- [197] M. Qian, V.J. Murray, W. Wei, B.C. Marshall, T.K. Minton, Resistance of POSS Polyimide Blends to Hyperthermal Atomic Oxygen Attack, *ACS Applied Materials & Interfaces*, 8(49) (2016), 33982-33992.
- [198] J.D. Froehlich, R. Young, T. Nakamura, Y. Ohmori, S. Li, A. Mochizuki, M. Lauters, G.E. Jabbour, Synthesis of multi-functional POSS emitters for OLED applications, *Chemistry of Materials*, 19(20) (2007), 4991-4997.
- [199] Y.-L. Liu, M.-H. Fangchiang, Polyhedral oligomeric silsesquioxane nanocomposites exhibiting ultra-low dielectric constants through POSS orientation into lamellar structures, *Journal of Materials Chemistry*, 19(22) (2009), 3643-3647.

- [200] R.Y. Kannan, H.J. Salacinski, J. De Groot, I. Clatworthy, L. Bozec, M. Horton, P.E. Butler, A.M. Seifalian, The antithrombogenic potential of a polyhedral oligomeric silsesquioxane (POSS) nanocomposite, *Biomacromolecules*, 7(1) (**2006**), 215-223.
- [201] Y.L. Chu, C.C. Cheng, Y.P. Chen, Y.C. Yen, F.C. Chang, A new supramolecular POSS electroluminescent material, *Journal of Materials Chemistry*, 22(18) (**2012**), 9285-9292.
- [202] B. Viers, R.I. Gonzalez, S.H. Phillips, POSS Polymers for Space: Entrepreneurial Research, Air Force Research Lab Edwards AFB CA Propulsion Directorate, **2003**.
- [203] Y.Z. Liu, Y. Sun, F.L. Zeng, Q.H. Zhang, L. Geng, Characterization and analysis on atomic oxygen resistance of POSS/PVDF composites, *Applied Surface Science*, 320 (**2014**), 908-913.
- [204] T.K. Minton, M.E. Wright, S.J. Tomczak, S.A. Marquez, L.H. Shen, A.L. Brunsvold, R. Cooper, J.M. Zhang, V. Vij, A.J. Guenther, B.J. Petteys, Atomic Oxygen Effects on POSS Polyimides in Low Earth Orbit, *ACS Applied Materials & Interfaces*, 4(2) (**2012**), 492-502.
- [205] S.H. Phillips, T.S. Haddad, S.J. Tomczak, Developments in nanoscience: polyhedral silsesquioxane (POSS)-polymers oligomeric, *Current Opinion in Solid State & Materials Science*, 8(1) (**2004**), 21-29.
- [206] A.L. Brunsvold, T.K. Minton, I. Gouzman, E. Grossman, R. Gonzalez, An Investigation of the Resistance of Polyhedral Oligomeric Silsesquioxane Polyimide to Atomic-Oxygen Attack, *High Performance Polymers*, 16(2) (**2004**), 303-318.
- [207] Y.Q. Zhao, D.A. Schiraldi, Thermal and mechanical properties of polyhedral oligomeric silsesquioxane (POSS)/polycarbonate composites, *Polymer*, 46(25) (**2005**), 11640-11647.
- [208] G.Z. Li, L.C. Wang, H.L. Ni, C.U. Pittman, Polyhedral oligomeric silsesquioxane (POSS) polymers and copolymers: A review, *Journal of Inorganic and Organometallic Polymers*, 11(3) (**2001**), 123-154.
- [209] F. Zhao, Y.D. Huang, Preparation and properties of polyhedral oligomeric silsesquioxane and carbon nanotube grafted carbon fiber hierarchical reinforcing structure, *Journal of Materials Chemistry*, 21(9) (**2011**), 2867-2870.
- [210] D. Wang, J. Liu, J.-F. Chen, L. Dai, Surface Functionalization of Carbon Dots with Polyhedral Oligomeric Silsesquioxane (POSS) for Multifunctional Applications, *Advanced Materials Interfaces*, 3(1) (**2016**).
- [211] L. Valentini, S.B. Bon, M. Cardinali, O. Monticelli, J.M. Kenny, POSS vapor grafting on graphene oxide film, *Chemical Physics Letters*, 537 (**2012**), 84-87.
- [212] H. Mahfuz, F. Powell, R. Granata, M. Hosur, M. Khan, Coating of Carbon Fiber with Polyhedral Oligomeric Silsesquioxane (POSS) to Enhance Mechanical Properties and Durability of Carbon/Vinyl Ester Composites, *Materials*, 4(9) (**2011**), 1619-1631.
- [213] A. Gomathi, K. Gopalakrishnan, C.N.R. Rao, Covalent functionalization of metal oxide and carbon nanostructures with polyoctasilsesquioxane (POSS) and their incorporation in polymer composites, *Materials Research Bulletin*, 45(12) (**2010**), 1894-1898.
- [214] D.J. Clarke, J.G. Matison, G.R. Simon, M. Samoc, A. Samoc, Polyhedral oligomeric silsesquioxane bound fulleropyrrolidines, *Applied Organometallic Chemistry*, 22(8) (**2008**), 460-465.

- [215] A. Tan, S.Y. Madani, J. Rajadas, G. Pastorin, A.M. Seifalian, Synergistic photothermal ablative effects of functionalizing carbon nanotubes with a POSS-PCU nanocomposite polymer, *Journal of Nanobiotechnology* 10(34) (**2012**), 1477-3155.
- [216] G. Potsi, A. Rossos, A. Kouloumpis, M.K. Antoniou, K. Spyrou, M.A. Karakassides, D. Gournis, P. Rudolf, Carbon Nanostructures Containing Polyhedral Oligomeric Silsesquioxanes (POSS), *Current Organic Chemistry*, 20(6) (**2016**), 662-673.
- [217] D. Gnanasekaran, K. Madhavan, B.S.R. Reddy, Developments of polyhedral oligomeric silsesquioxanes (POSS), POSS nanocomposites and their applications: A review, *Journal of Scientific & Industrial Research*, 68(6) (**2009**), 437-464.
- [218] F. Zhao, Y. Huang, Grafting of polyhedral oligomeric silsesquioxanes on a carbon fiber surface: novel coupling agents for fiber/polymer matrix composites, *Journal of Materials Chemistry*, 21(11) (**2011**), 3695-3703.
- [219] R. Förch, H. Schönherr, and A. T. A. Jenkins, Surface design: applications in bioscience and nanotechnology. John Wiley & Sons, **2009**.
- [220] L. Chen, W. Li, Y. Liu, J. Leng, Nanocomposites of epoxy-based shape memory polymer and thermally reduced graphite oxide: Mechanical, thermal and shape memory characterizations, *Composites Part B: Engineering*, 91 (**2016**), 75-82.
- [221] ASTM E-13, Standard test method for thermal diffusivity by the flash method, ASTM International West Conshohocken, PA, **2013**.
- [222] BS EN ISO 22007-4:2017 - Plastics. Determination of thermal conductivity and thermal diffusivity. Laser flash method, **2017**.
- [223] S. Min, J. Blumm, A. Lindemann, A new laser flash system for measurement of the thermophysical properties, *Thermochimica Acta*, 455(1) (**2007**), 46-49.
- [224] L.J. van der Pauw, A method of measuring specific resistivity and Hall effect of discs of arbitrary shape, *Philips Research Reports*, 13(1) (**1958**), 1-9.
- [225] D. W. Koon and C. J. Knickerbocker, What do you measure when you measure resistivity?, *Review of Scientific Instruments*, 63 (1)(**1991**), 207-210.
- [226] K. F. Carr, Integrating sphere theory and applications Part I: Integrating sphere theory and design, *Surface Coatings International*, 80(8) (**1997**), 380-385
- [227] K.F. Carr, Integrating sphere theory and applications Part II: Integrating sphere applications. *Surface Coatings International*, 80(10) (**1997**), 485-490.
- [228] D.M. Buczala, A.L. Brunsvold, T.K. Minton, Erosion of Kapton® H by hyperthermal atomic oxygen, *Journal of Spacecraft and Rockets*, 43(2) (**2006**), 421-425.
- [229] Standard Practices for Ground Laboratory Atomic Oxygen Interaction Evaluation of Materials for Space Applications, ASTM International, West Conshohocken, PA, **2015**.
- [230] ECSS-Q-ST-70-02C –Thermal vacuum outgassing test for the screening of space materials, **2008**.
- [231] A. International, Standard Test Method for Total Mass Loss and Collected Volatile Condensable Materials from Outgassing in a Vacuum Environment, ASTM International, West Conshohocken, PA, **2015**.

- [232] A. C. Ferrari, J. C. Meyer, V. Scardaci, C. Casiraghi, M. Lazzeri, F. Mauri, S. Piscanec, D. Jiang, K. S. Novoselov, S. Roth, and A. K. Geim, Raman spectrum of graphene and graphene layers, *Physical Review Letters*, 97(18) (**2006**).
- [233] D. Yoon, H. Moon, H. Cheong, J. S. Choi, J. A. Choi, and B. H. Park, Variations in the Raman Spectrum as a Function of the Number of Graphene Layers. *Journal of the Korean Physical Society*, 55(3) (**2009**), 1299-1303.
- [234] J. Pappis, and S.L. Blum, Properties of Pyrolytic Graphite. *Journal of the American Ceramic Society*, 44(12) (**1961**), 592-597.
- [235] S. Chen, G. He, H. Hu, S. Jin, Y. Zhou, Y. He, S. He, F. Zhao, and H. Hou, Elastic carbon foam via direct carbonization of polymer foam for flexible electrodes and organic chemical absorption. *Energy & Environmental Science*, 6(8) (**2013**), 2435-2439.
- [236] X. Zhang, O. Alloul, J.H. Zhu, Q.L. He, Z.P. Luo, H.A. Colorado, N. Haldolaarachchige, D.P. Young, T.D. Shen, S.Y. Wei, Z.H. Guo, Iron-core carbon-shell nanoparticles reinforced electrically conductive magnetic epoxy resin nanocomposites with reduced flammability, *Rsc Advances*, 3(24) (**2013**), 9453-9464.
- [237] T. Kuilla, S. Bhadra, D. Yao, N.H. Kim, S. Bose, J.H. Lee, Recent advances in graphene based polymer composites, *Progress in Polymer Science*, 35(11) (**2010**), 1350-1375.
- [238] J. Jeong, Y. Yoo, J. Lee, J.h. Lim, K. Kim, Development of a Tape Spring Hinge with a SMA Latch for a Satellite Solar Array Deployment Using the Independence Axiom, *IERI Procedia*, 1 (**2012**), 225–231.
- [239] M. Hecke, W.K. Schomburg, Review on micro molding of thermoplastic polymers, *Journal of Micromechanics and Microengineering*, 14(3) (**2003**), R1-R14.
- [240] R. Verker, M. Ozeri, A. Bolker, M. Loeblein, E.H.T. Teo, I. Gouzman, Enhancement of polyimide and 3D graphene-polyimide through thermoforming and its effect on mechanical properties and associated creep phenomenon, *Polymer Degradation and Stability*, 134 (**2016**), 237-244.
- [241] L. Embrey, P. Nautiyal, A. Loganathan, A. Idowu, B. Boesl, and A. Agarwal, Three-Dimensional Graphene Foam Induces Multifunctionality in Epoxy Nanocomposites by Simultaneous Improvement in Mechanical, Thermal, and Electrical Properties, *ACS Applied Materials & Interfaces*, 9(45) (**2017**), 39717-39727.
- [242] S. Devasahayam, D.J.T. Hill, J.W. Connell, FT-Raman studies of a range of polyimides subjected to high-energy radiations at room and elevated temperatures, *Journal of Applied Polymer Science*, 101(3) (**2006**), 1575-1582.
- [243] W. Dai, J. Yu, Z. Liu, Y. Wang, Y. Song, J. Lyu, H. Bai, K. Nishimura, N. Jiang, Enhanced thermal conductivity and retained electrical insulation for polyimide composites with SiC nanowires grown on graphene hybrid fillers, *Composites Part A*, 76 (**2015**), 73-81.
- [244] W. Dai, J. Yu, Y. Wang, Y. Song, F.E. Alam, K. Nishimura, C.-T. Lin, N. Jiang, Enhanced thermal conductivity for polyimide composites with a three-dimensional silicon carbide nanowire@graphene sheets filler, *Journal of Materials Chemistry A*, 3(9) (**2015**), 4884-4891.

- [245] W. Yan, Y. Zhang, H. Sun, S. Liu, Z. Chi, X. Chen, J. Xu, Polyimide nanocomposites with boron nitride-coated multi-walled carbon nanotubes for enhanced thermal conductivity and electrical insulation, *Journal of Materials Chemistry A*, 2(48) (**2014**), 20958-20965.
- [246] T. Murakami, K. Ebisawa, K. Miyao, S. Ando, Enhanced Thermal Conductivity in Polyimide/Silver Particle Composite Films Based on Spontaneous Formation of Thermal Conductive Paths, *Journal of Photopolymer Science and Technology*, 27(2) (**2014**), 187-191.
- [247] T.-L. Li, S.L.-C. Hsu, Enhanced Thermal Conductivity of Polyimide Films via a Hybrid of Micro- and Nano-Sized Boron Nitride, *The Journal of Physical Chemistry B*, 114(20) (**2010**), 6825-6829.
- [248] S.-H. Xie, B.-K. Zhu, J.-B. Li, X.-Z. Wei, Z.-K. Xu, Preparation and properties of polyimide/aluminum nitride composites, *Polymer Testing*, 23(7) (**2004**), 797-801.
- [249] P.C. Irwin, Y. Cao, A. Bansal, L.S. Schadler, Thermal and mechanical properties of polyimide nanocomposites, 2003 Annual Report Conference on Electrical Insulation and Dielectric Phenomena, (**2003**), 120-123.
- [250] C. Godet, Physics of bandtail hopping in disordered carbons, *Diamond and Related Materials*, 12(2) (**2003**), 159-165.
- [251] C. Godet, Hopping model for charge transport in amorphous carbon, *Philosophical Magazine B*, 81(2) (**2001**), 205-222.
- [252] L. Gan, A. Bolker, C. Saguy, R. Kalish, D.L. Tan, B.K. Tay, D. Gruen, P. Bruno, The effect of grain boundaries and adsorbates on the electrical properties of hydrogenated ultra nano crystalline diamond, *Diamond and Related Materials*, 18(9) (**2009**), 1118-1122.
- [253] C. Godet, Variable range hopping revisited: the case of an exponential distribution of localized states, *Journal of Non-Crystalline Solids*, 299-302 (**2002**), 333-338.
- [254] M.R. Reddy, N. Srinivasamurthy, B.L. Agrawal, Atomic Oxygen Protective Coatings for Kapton Film - A Review, *Surface & Coatings Technology*, 58(1) (**1993**), 1-17.
- [255] B.A. Banks, A. Snyder, S.K. Miller, K.K. de Groh, R. Demko, Atomic-oxygen undercutting of protected polymers in low earth orbit, *Journal of Spacecraft and Rockets*, 41(3) (**2004**), 335-339.
- [256] D. Angirasa, P.S. Ayyaswamy, Review of Evaluation Methodologies for Satellite Exterior Materials in Low Earth Orbit, *Journal of Spacecraft and Rockets*, 51(3) (**2014**), 750-761.
- [257] K. Gotlib-Vainstein, I. Gouzman, O. Girshevitz, A. Bolker, N. Atar, E. Grossman, C.N. Sukenik, Liquid Phase Deposition of a Space-Durable, Antistatic SnO₂ Coating on Kapton, *ACS Applied Materials & Interfaces*, 7(6) (**2015**), 3539-3546.
- [258] D.R. Cairns, R.P. Witte, D.K. Sparacin, S.M. Sachsman, D.C. Paine, G.P. Crawford, R.R. Newton, Strain-dependent electrical resistance of tin-doped indium oxide on polymer substrates, *Applied Physics Letters*, 76(11) (**2000**), 1425-1427.
- [259] P. George, Space Environmental Effects on LDEF Low Earth Orbit Exposed Graphite Reinforced Polymer Matrix Composites, NASA Conference Publication, 3162 (**1992**), 543-570.

- [260] H. Fong, R.A. Vaia, J.H. Sanders, D. Lincoln, A.J. Vreugdenhil, W. Liu, J. Bultman, C. Chen, Self-Passivation of Polymer-Layered Silicate Nanocomposites, *Chemistry of Materials*, 13(11) (**2001**), 4123-4129.
- [261] S. Yagnamurthy, Q. Chen, C. Chen, I. Chasiotis, Erosion yield of epoxy-silica nanocomposites at the lower earth orbit environment of the International Space Station, *Journal of Composite Materials*, 47(1) (**2012**), 107-117.
- [262] R.L. Kiefer, R.A. Orwoll, E.C. Aquino, A.C. Pierce, M.B. Glasgow, S.A. Thibeault, The effects of atomic oxygen on polymer films containing bis(triphenyltin) oxide, *Polymer Degradation and Stability*, 57(2) (**1997**), 219-226.
- [263] K.A. Watson, F.L. Palmieri, J.W. Connell, Space Environmentally Stable Polyimides and Copolyimides Derived from [2,4-Bis(3-aminophenoxy)phenyl]diphenylphosphine Oxide, *Macromolecules*, 35(13) (**2002**), 4968-4974.
- [264] E. Miyazaki, M. Tagawa, K. Yokota, R. Yokota, Y. Kimoto, J. Ishizawa, Investigation into tolerance of polysiloxane-block-polyimide film against atomic oxygen, *Acta Astronautica*, 66(5) (**2010**), 922-928.
- [265] H.R. Fischer, K. Tempelaars, A. Kerpershoek, T. Dingemans, M. Iqbal, H. van Lonkhuyzen, B. Iwanowsky, C. Semprimoschnig, Development of Flexible LEO-Resistant PI Films for Space Applications Using a Self-Healing Mechanism by Surface-Directed Phase Separation of Block Copolymers, *ACS Applied Materials & Interfaces*, 2(8) (**2010**), 2218-2225.
- [266] L.-C. Tang, Y.-J. Wan, D. Yan, Y.-B. Pei, L. Zhao, Y.-B. Li, L.-B. Wu, J.-X. Jiang, G.-Q. Lai, The effect of graphene dispersion on the mechanical properties of graphene/epoxy composites, *Carbon*, 60(Supplement C) (**2013**), 16-27.
- [267] R. Prasher, Thermal interface materials: Historical perspective, status, and future directions, *Proceedings of the IEEE*, 94(8) (**2006**), 1571-1586.
- [268] Y.A. Çengel, Heat transfer : A practical approach, 2nd ed. ed., McGraw-Hill, Boston, **2003**.
- [269] Standard Solar Constant and Zero Air Mass Solar Spectral Irradiance Tables, ASTM International, ASTM International., **2014**.
- [270] P. Poinas, In The ESA initiative training courses, Small and Medium Sized Enterprises SME04: Satellite Thermal Control Engineering, **2004**.
- [271] Design guidelines for assessing and controlling spacecraft charging effects, National Aeronautics and Space Administration, Scientific and Technical Information Branch, **1984**.
- [272] E. Association, Packaging Materials for ESD Sensitive Items, ESD Association, USA, **2008**.
- [273] D. R. Peplinski, G. S. Arnold, and E. N. Borson, Introduction to Simulation of Upper Atmosphere Oxygen Satellite Exposed to Atomic Oxygen in Low Earth Orbit, 13th Space Simulation Conference, **1984**, 133-145.
- [274] Z.A. Iskanderova, J.I. Kleiman, Y. Gudimenko, R.C. Tennyson, Generalization of the predictive model of erosion of carbon-based materials by atomic oxygen, *Protection of Space Materials from the Space Environment*, **2001**, 33-50.

- [275] E. Grossman, I. Gouzman, G. Lempert, Y. Noter, Y. Lifshitz, Assessment of Atomic-Oxygen Flux in Low-Earth-Orbit Ground Simulation Facilities, *Journal of Spacecraft and Rockets*, 41(3) (2004), 356-359.
- [276] R. Verker, E. Grossman, and N. Eliaz, Effect of the POSS–Polyimide nanostructure on its mechanical and electrical properties, *Composites Science and Technology*, 72(12) (2012), 1408-1415.
- [277] R. Verker, E. Grossman, I. Gouzman, and N. Eliaz, TriSilanolPhenyl POSS–polyimide nanocomposites: Structure–properties relationship, *Composites Science and Technology*, 69(13) (2009), 2178-2184.
- [278] R. Verker, E. Grossman, and N. Eliaz, Erosion of POSS-polyimide films under hypervelocity impact and atomic oxygen: The role of mechanical properties at elevated temperatures, *Acta Materialia*, 57(4) (2009), 1112-1119.
- [279] Y.H. Xue, Y. Liu, F. Lu, J. Qu, H. Chen, L.M. Dai, Functionalization of Graphene Oxide with Polyhedral Oligomeric Silsesquioxane (POSS) for Multifunctional Applications, *Journal of Physical Chemistry Letters*, 3(12) (2012), 1607-1612.
- [280] A. Fina, D. Tabuani, F. Carniato, A. Frache, E. Boccaleri, G. Camino, Polyhedral oligomeric silsesquioxanes (POSS) thermal degradation, *Thermochimica Acta*, 440(1) (2006), 36-42.
- [281] S. Chabi, Electrochemical study of 3D graphene composites and the creation of ultralight 3D SiC, (2015).
- [282] M. Le Bras, Fire retardancy of polymers. [electronic resource] : new applications of mineral fillers, Cambridge, UK : Royal Society of Chemistry, 2005.
- [283] R.E. Camacho, A.R. Morgan, M.C. Flores, T.A. McLeod, V.S. Kumsomboone, B.J. Mordecai, R. Bhattacharjea, W. Tong, B.K. Wagner, J.D. Flicker, S.P. Turano, W.J. Ready, Carbon nanotube arrays for photovoltaic applications, *JOM*, 59(3) (2007), 39-42.
- [284] K.T. Nicholson, T.K. Minton, S.J. Sibener, Temperature-dependent morphological evolution of HOPG graphite upon exposure to hyperthermal O(3P) atoms, *Progress in Organic Coatings*, 47(3) (2003), 443-447.
- [285] R. Verker, E. Grossman, I. Gouzman, N. Eliaz, POSS-Polyimide Nanocomposite Films: Simulated Hypervelocity Space Debris and Atomic Oxygen Effects, *High Performance Polymers*, 20(4-5) (2008), 475-491.
- [286] J.-c. Huang, C.-b. He, Y. Xiao, K.Y. Mya, J. Dai, Y.P. Siow, Polyimide/POSS nanocomposites: interfacial interaction, thermal properties and mechanical properties, *Polymer*, 44(16) (2003), 4491-4499.
- [287] R.F. Saraf, C. Dimitrakopoulos, M.F. Toney, S.P. Kowalczyk, Near Surface Structure of Solvent-free Processed Polyimide Thin Film, *Langmuir*, 12(11) (1996), 2802-2806.
- [288] S.P. Kowalczyk, C.D. Dimitrakopoulos, S.E. Molis, Growth Of Polyimide Films By Chemical Vapor Deposition And Their Characterization, *MRS Proceedings*, 227 (1991), 55.
- [289] Spacecraft Deployed Appendage Test Guidelines, Preferred Reliability Practices, NASA, 1995

- [290] Z. Chen, C. Xu, C. Ma, W. Ren, H.-M. Cheng, Lightweight and Flexible Graphene Foam Composites for High-Performance Electromagnetic Interference Shielding, *Advanced Materials*, 25(9) (**2013**), 1296-1300.
- [291] J. Hu, Y. Zhu, H. Huang, J. Lu, Recent advances in shape-memory polymers: Structure, mechanism, functionality, modeling and applications, *Progress in Polymer Science*, 37(12) (**2012**), 1720-1763.