Resistance of CFRP structures to environmental degradation in low Earth orbit.

by

Agnieszka Suliga

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Department of Mechanical Engineering Sciences
Faculty of Engineering and Physical Sciences
University of Surrey

Supervisor: Dr Andrew Viquerat

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Abstract

Within this study, a development of a protection strategy for ultra-thin CFRP structures from degrading effects of low Earth orbit (LEO) is presented. The proposed strategy involves an application of a modified epoxy resin system on outer layers of the structure, which is cycloaliphatic in its chemical character and reinforced with POSS nanoparticles. The core of the CFRP structure is manufactured using a highly aromatic epoxy resin system which provides excellent mechanical properties, however, its long-term ageing performance in space is not satisfactory, and hence a surface treatment is required to improve its longevity.

The developed resin system presented in this thesis is a hybrid material, designed in such a way that its individual constituents each contribute to combating the detrimental effects of radiation, atomic oxygen (AO), temperature extremes and vacuum induced outgassing of exposed material surfaces while operating in LEO. The cycloaliphatic nature of the outer epoxy increases UV resistance and the embedded silicon nanoparticles improve AO and thermal stability. During the study, a material characterization of the developed cycloaliphatic epoxy resins was performed including the effects of nanoparticles on morphology, curing behaviour, thermal-mechanical properties and surface chemistry. Following on that, the efficacy of the modified resin system on space-like resistance was studied. It was found that when the ultra-thin CFRP structures are covered with the developed resin system, their AO resistance is approximately doubled, UV susceptibility decreased by 80% and thermal stability improved by 20%.

Following on the successful launch of the InflateSail mission earlier this year, which demonstrated a sail deployment and a controlled de-orbiting, the findings of this study are of importance for the future generation of similar, but significantly longer missions. Ensuring resistance of CFRP structures in a highly corrosive LEO environment is a critical requirement to make their use in space applications truly feasible.
Statement of Originality

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- **Agnieszka Suliga**, *Deployable ultra-thin CFRP structures with improved resistance to low Earth orbit* presented at SAMPE UK & Ireland annual seminar on 23rd February 2017 at Cranfield University (UK).

Raw data is downloadable from: https://figshare.com/s/26fd2e11f7e9a9ca1382
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I dedicate this thesis to my family.
Nomenclature

$\alpha$ Solar absorptance
AO Atomic oxygen
ATR-FTIR Fourier-transform infrared spectroscopy in the Attenuated total reflection mode
BRC Bistable reeled composite
CFRP Carbon fibre reinforced plastic
CTE Coefficient of thermal expansion
DSC Differential scanning calorimetry
E Erosion yield
EDX Energy dispersive x-ray spectroscopy
$\epsilon$ Solar emittance
ESA European Space Agency
FRC Fibre reinforced composites
H Enthalpy of reaction
HDT Heat distortion temperature
ISS International Space Station
LEO Low Earth orbit
LSM Laser scanning microscope
MISSE Materials International Space Station Experiment
NASA National Aeronautics and Space Administration
PDMS Polydimethylsiloxane
POSS  Polyhedral Oligomeric Silsequioxane

PTFE  Polytetrafluoroethylene

$S_a$  Average surface roughness

$T_d$  Temperature of decomposition

$T_g$  Glass transition temperature

TML  Total mass loss

$T_{onset}$  The temperature at which weight loss begins

$T_{peak}$  The peak temperature of the first derivative of TGA curve

sccm  standard cubic centimetre per minute

UV  Ultraviolet radiation

wt%  Weight content in percentages
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Chapter 1

Introduction

Space exploration has developed significantly in recent years. Satellites that used to be expensive to build and launch, are becoming more universal and affordable through small satellite technologies such as CubeSats, and new lightweight materials like composites and plastics.

The destination for most small satellites is usually not that far from the Earth, in the region referred to as low Earth orbit (LEO). The conditions in LEO are somewhere between those observed on Earth and deep space. The proximity to our planet makes this environment abundant in residual gases originating in the Earth’s atmosphere. In LEO the vacuum is not complete but rather filled with effects that have a degrading influence on the exposed surfaces of materials.

The residual atmosphere is very hazardous, especially one component known as atomic oxygen, which is a very reactive radical created by photodissociation of molecular oxygen by ultraviolet radiation. Atomic oxygen (AO) is the most abundant species in LEO between 200 and 700 km and consequently the most significant hazard for materials operating at these altitudes. The reactive species travel with high orbital velocities and impinge on spacecraft surfaces, causing surface recession and erosion. The degrading effects of atomic oxygen can be overlooked in the case of many metal based materials, although some metals such as silver are strongly affected. The real concern arises with replacing traditionally used metals and ceramics with a new generation of lightweight materials that are organic in nature. This group erodes quite rapidly, because all carbon based materials get oxidized and form volatile species which leads to slow material evaporation. Additionally, atomic oxygen hitting the surfaces with orbital velocities is capable of physically removing matter. As one can clearly see, the degrading effects of atomic oxygen are quite significant even without other damaging factors which include ultraviolet and ionizing radiation, temperature extremes, debris impact, high vacuum and abnormalities in space weather.

To decrease costs of space exploration, spacecraft designers have turned to a family of lightweight materials in order to reduce payload mass and consequently the
1.1 Project background

Ultra-thin, bistable CFRP masts were proposed for the Cubesail mission by Lappas et al. (2011) with a primary aim of supporting the deployment of a solar sail and demonstrating solar sailing in LEO. After the successful ground-based testing, they are planned to be used in other demonstration missions such as InflateSail (Viquerat et al., 2016) or RemoveDebris (Forshaw et al., 2016). The main aim for ESA’s Gossamer Deorbiter missions was to use deployable structures as deorbiting devices, to assist in removal of accumulated space debris in LEO that poses a real threat to other operational spacecraft (Fernandez et al., 2014; Forshaw et al., 2017).

So far the objectives of aforementioned missions have been focused on verifying the functionality of the deployable structures on board, however, little work has been
1.2. Motivation

The aim of this project is to address the issue of CFRP resistance in LEO and to develop a low-cost protection strategy that can be implemented in ultra-thin bistable CFRP space masts. These masts are a very promising strategy for deploying solar or deorbiting sails, however, the long nature of such missions requires higher material longevity than purely organic and unmodified CFRP structures offer.

Since degradation due to AO is most severe for materials with an organic, volatile phase, the incorporation of inorganic and nonvolatile components to the organic matrix, creating a hybrid, can be viewed as a promising strategy to extend the useful life of organic materials. The inorganic portion of the composite will not become volatile upon reaction with AO, but will rather form an ash residue on the surface. The remains of inorganic particles protect the underlying organic portion and effectively slow down further degradation. In the case of modification with silicon, which exhibits strong chemical affinity towards oxygen, the silicon atoms from the filling may react with the incoming oxygen radicals in the formation of a silica protective layer. Such smart behaviour of the structure is desirable for space materials, therefore using silicon as a modifier is one of the most promising low-cost mitigation strategies. Inorganic particles embedded in organic matrices also contribute to better UV stability since they act as UV filters by absorbing or scattering the incoming radiation.
Polymer nanocomposites are those materials in which the fillers have at least one dimension in nanometers. The nanoscale of the additive enables homogeneous distribution and interactions at atomic levels which often result in superior thermal, mechanical, chemical and environmental properties among others. Many types of polymer nanocomposites are still in laboratory development, despite the enormous activity in this field. The main problem with the space materials industry is that the market is often too small for materials manufacturers to invest in development and consequently space compatible polymers are not readily available off-the-shelf. Therefore, it is within the scope of this project to develop a material that can be used for manufacturing of ultra-thin bistable CFRP masts or other similar structures that will enhance their space resistance, without significantly affecting their structural properties.

This project specifically concerns the protection of ultra-thin bistable, deployable CFRP masts but can be extended to other applications and geometries. However, the solution presented here takes into consideration the particular behaviour of these structures and hence the material selection process was tailored for this specific application. The main aim of this work is to demonstrate that the LEO protection of CFRP structures can be achieved by using low cost, commercially available resin systems and nanoadditives, which might be of interest for small companies (or academia) which build low-cost spacecraft for long duration missions and are concerned about the material survivability.

1.3 Scope and novel contribution

Within the scope of this thesis an attempt was made to answer some of the questions about how the nanoadditive and curing agent influence some properties of epoxy resin systems which are important for space applications. The prime concern is the distribution of nanophase within the polymeric medium and any influence on the curing behaviour. To the best of the author’s knowledge, the selected components (cycloaliphatic epoxy and POSS nanoparticles) have never been blended together, therefore an evaluation of properties of the novel mixture is presented.

Another objective of this thesis is to evaluate thermal and thermo-mechanical properties of the novel cycloaliphatic epoxy resin system reinforced with silicon nanoparticles. Of particular concern is the influence on the glass transition and onset of degradation in order to make sure that the proposed structures can be used in the temperature extremes of LEO.

Previously encountered problems with high surface roughness of ultra-thin CFRP structures have also been addressed. Studies of surface topography and morphology had been performed before and after applying the protection strategy. The evalu-
tion of nanoparticle distribution was performed on protected surfaces, together with a chemical analysis in order to evaluate the elemental content and silicon presence on the surface.

After the initial study of material properties, the proposed material was exposed to some of the space-like degrading effects, including high vacuum, oxygen plasma, UV radiation and temperature extremes. An attempt to calculate the acceleration factor which allows to relate the rate of degradation in the simulated facility with the one in LEO was made. Another attempt was made to establish the correlation between the chemistry of the resin system and response to the certain degrading factors. Post-exposure changes in thermo-mechanical and surface properties are also discussed.

Summary of objectives:

- Development of a low-cost protection strategy, using commercially available materials.

- Selection of the types of silicon nanoparticles that blend well with a hosting cycloaliphatic epoxy and result in enhanced atomic oxygen, ultraviolet radiation and thermal resistance.

- Experimental verification by exposure in a space-simulation facility.

The novelty of this thesis lies in the development of a low-cost resin system that is cycloaliphatic in its chemical character and reinforced with silicon nanoparticles, in particular with octa-POSS nanoadditive that proved to be the most compatible with the host resin. It has been demonstrated that this resin system, used on the outer surfaces of ultra-thin CFRP laminates, provides better environmental stability than unmodified aromatic epoxy resin.

This thesis also contributes to the state of art by characterizing the properties of the novel resin system, therefore other research entities can decide whether it is suitable for other applications, not only within the space industry, but in any demanding thermo-oxidative environment and/or exposure to sunlight. The novel contribution is also based on prediction of the behaviour of ultra-thin CFRP structures in LEO after modification with silicon nanoparticles. So far, the aspects of longevity of epoxy resins in space-like environments have been relatively unexplored, especially regarding the ultra-thin structures that to the best of the author’s knowledge are launched into space without any protection strategies. The original work presented in this thesis, extends the field of space materials by discussing how the use of epoxy resins can be translated to more demanding environments with the low-cost modification and manufacturing strategy.
Chapter 2

Background

2.1 Space exploration driven by satellite miniaturisation

Space exploration which began sixty years ago with the launch of Sputnik, has seen an outstanding development in recent years. Nowadays, not only big space agencies such as NASA or ESA are involved in launching new spacecraft, but also private entities such as SpaceX, universities or spin-off companies originating from academia.

With the pioneering concept of reusable rockets presented by SpaceX, launching a spacecraft has become more accessible and affordable. The development in space systems has also resulted in satellite miniaturization, making it possible to launch a number of spacecraft in one go. The current record belongs to Indian Space Research Organization (ISRO) which launched 103 satellites at once, from which most belonged to the private company Planet Labs with the primary aim of Earth observation.

2.1.1 CubeSat - mission concept

Miniaturization of spacecraft is a direct way to reduce the mass and consequently the launch cost, which is one of the main components of space missions and a primary concern for space companies. Mass minimization can be achieved by choosing lightweight materials and structures with high packaging efficiency. A CubeSat is a satellite which is built of 1 unit components (1U), each of maximum 1 kg mass and dimensions of 10 x 10 x 10 cm³ (Heidt et al., 2000). Various sizes of CubeSats get launched, in the range of 0.25U to 16U, with 1U and 3U being the most frequently selected.

The number of potential applications for small satellites increased with the development of CubeSat technology. A popular approach is to launch satellites in constellations in order to build a network between devices which can take measurements at
different positions in orbit (Ley and Merkle, 2009). Constant observation of Earth, astronomical objects or space weather, combined with simultaneous scientific measurements attracts much interest. The unavoidable consequence of this scenario is an increased number of man-made objects in orbit, increasing the probability of collisions which threatens not only the safety of operational satellites but also the crew working inside the International Space Station (ISS).

Deorbiting devices

To tackle the problem of an increasing amount of space debris, various ideas have been presented, including passive or active debris removal. The RemoveDebris project of Surrey Space Centre is an example of such mission, which is going to demonstrate both active space removal strategies and passive deorbiting using a drag-sail.

Drag-deorbiting sails can operate in two modes, above and below 1000 km. Above 1000 km, where drag forces are low, the sail is used to propel the satellite by using solar radiation pressure as the means of propulsion. Below 1000 km, drag sails operate in a drag sail mode, where the surface of a sail increases the interaction area with atmospheric particles and consequently reduces the deorbiting time.

Polymers are particularly susceptible to degradation in LEO. Thin membranes are often metallized in order to obtain certain properties, such as conductivity or reflectivity. The pressure of photons acting on a sail, can be doubled if the surface is ideally reflecting, which can be achieved by applying thin layers of silver or aluminium. Such metal coatings can also protect the membranes from the hazardous
space environment to some extent. However, drag-sails might not be metallized because reflective sails have an adverse effect on the passive altitude stability under drag-conditions (Visagie et al., 2015). Transparent sails settle into a position where a force acts perpendicularly which contributes to an altitude decay and to the controlled spacecraft deorbiting, but purely organic sails of thickness in the micrometer range are likely not to survive long duration missions. If the sail or the supporting boom erodes, resulting in either tearing of a sail or exposure of fibres, a mission can end prematurely and unsuccessfully. Because of this, the materials selection process for composite booms and sail membranes must ensure the structural integrity in LEO for the required period of time.

Selection of structural materials for small satellites - Metal alloys versus Fibre reinforced composites (FRC)

Metallic alloys hold a leading position among structural materials for space structures and include aluminium, titanium and beryllium alloys. However, metallic alloys are heavier than composite materials. For example using a CFRP structure saves approximately 26% on 1 kg of weight in comparison to an aluminium structure (ECSS/ESA, 2011).

The successful use of FRCs in terrestrial and aerospace applications paved the way for space applications. Glass fibre reinforced composites are used for insulation purposes or when conductivity is not desired and carbon fibre reinforced plastic are used as structural materials (Ley and Merkle, 2009). In comparison to the metallic alloys, CFRP materials reinforced with epoxy (the most commonly used matrix for space applications) exhibit higher strength and stiffness, lower density and coefficient of thermal expansion (CTE) (Ley and Merkle, 2009). The main disadvantages of CFRP materials for space applications are their organic character and high susceptibility to space induced degradation. Additional concerns raised by ECSS/ESA (2011) relate to the availability of a consistent source of material from the same manufacturer. Since the market of structural materials for space is often too small to be of interest for manufacturers, there is a lack of design data. Most composite parts are developed with highly directional properties and an understanding of composite failure and fracture characteristics is often difficult.

CFRP materials can be coated in metals to create a hybrid with mechanical properties of fibres and higher thermal resistance of metals (Ley and Merkle, 2009) known as aluminium coated sandwich panels. The Korean Multi-Purpose Satellite (KOMP-SAT) launched in 1999 included a solar array that was an aluminium honeycomb sandwich structure, however, issues with thermally induced distortions initiated research into substituting the aluminium facesheets with composite ones. The studies
of Shin et al. (2001) showed that replacing aluminium with a composite, which has a significantly lower CTE, enabled the reduction of thermal distortions in the solar array, together with weight savings and a more even temperature distribution. The same research team also looked into the degradation of composite materials using their dedicated space simulation facility and concluded that material properties were significantly altered due to exposure. Although, metallic coatings are often used to improve resistance to the hazardous space environment, the problem of CTE mismatch between the substrate and the coating remains.

2.1.2 Deployable structures

In order to increase the functionality of small satellites, there has been extensive activity in the field of deployable structures, with the primary aim of developing novel methods for packaging and deployment into volumes many times smaller than the structures themselves (Belvin et al., 2016). Both metallic alloys and CFRP materials are prime candidates for deployable structures, each with their own set of advantages and disadvantages. For example, the NEA (Near-Earth Asteroid) Scout mission of NASA is a 6U CubeSat (expected to be launched in mid-2018) which is going to demonstrate the fly-by of an asteroid using a deployable solar sail supported by four metallic booms (Mcnutt et al., 2014). On the other hand, Figure 2.2 presents a range of recently developed and commercially available CFRP deployable structures for space applications including solar arrays, antennas and sails underpins.

There are several requirements that booms need to meet in order to work properly in the space environment. Critical design parameters include mass per unit length, bending and torsional stiffness, and out-of-plane buckling moment (Soykasap, 2009). Additional parameters concern the deployment repeatability and the ability to retract the structure if desired. Material properties such as creep of the matrix, minimal outgassing and resistance to the LEO environment are also critical and should not be neglected, especially in case of ultra-thin structures that are intended to operate in space for many years.

In recent years deployable composite booms have gained significant attention in the space industry (Block et al., 2011; Chu and Lei, 2014; Datashvili, 2010; Hillebrandt et al., 2014; Soykasap, 2009). It is mostly due to the fact that using composite material instead of metal contributes to mass savings and reduces the overall mission cost. The drawbacks of metal booms is that, whilst they provide extremely compact extendible struts, they require considerable restraint and relatively heavy and complex mechanisms are needed for their deployment (Daton-Lovett and Compton-Bishop, 2000). Also, metallic booms lack thermal stability (Stohlman and Loper, 2016).

CFRP booms can be stowed in a compact shape before launch and deployed in
space after a desired position and altitude have been reached, into a much larger structures. Using composite booms provides a structure with enough rigidity to support a sail membrane and the longer the booms are, the bigger the surface of a sail, which is particularly important in terms of increasing the area of a spacecraft that interacts with atmospheric particles. This interaction is a foundation of both deorbiting and solar sailing mechanisms, since the large area of a sail is responsible for converting pressure of photons to a driving force (Block et al., 2011). In the case of the Surrey Space Centre InflateSail mission (Figure 2.2f), a gossamer sail spread over four booms deploys to a 10 m² sail, however, much bigger sails can be used as demonstrated by LightSail-1 that successfully deployed a 32 m² sail in June 2015.


Bistable reeled composite (BRC) booms

Many types of booms are being used in the space industry, however, booms exhibiting a phenomenon of bistability are especially interesting for space deployable structures. Those tubular structures can be rolled up by flattening one end, like a standard tape measure. Such booms, developed and patented by the British company RolaTube Technology Ltd. (Daton-Lovett, 2001) enable simple and compact deployment mechanisms, which is expected to increase the chances of proper deployment while in space (Fernandez and Viquerat, 2014). This type of tube can be rolled into a volume many times smaller than the original one, with no need for a constraint mechanism to keep them in a coiled shape. This fact further benefits the mass savings of a payload, which is critical in space applications. Moreover, this is very important for solar sails, since with smaller mass, spacecraft acceleration increases, and in order to actually convert a driving force caused by reflected photons into an acceleration, the mass of the spacecraft must be minimized. BRC booms were used in the construction of CubeSail (Fernandez et al., 2011; Lappas et al., 2011), InflateSail (Viquerat et al., 2016) and RemoveDebris (Forshaw et al., 2016, 2017).

The phenomenon of bistability lies in a certain layup that makes a boom flip into the alternative coiled configuration when deformed from its original shape (Iqbal and Pellegrino, 2000) (Figure 2.3). Bistability arises as a result of the manipulation of Poisson’s ratio and anisotropy in the various layers of the material, the stacking sequence of these structures is asymmetrical in respect to the midplane, which results in a curved structure that exhibits anisotropic bending properties (Daton-Lovett and Compton-Bishop, 2000). Asymmetric layups are not common in the composite industry, as unbalanced laminates twist and warp. In the case of BRC booms, a curvature is a desired property which enables it to coil along the shorter edge and as a result both the extended and coiled configurations are stable because the structure favours same-sense bending. Bistability is also a result of the resultant opposing stresses which arise from thermal contraction of a matrix material due to thermo-forming (Daynes et al., 2009). It has been found experimentally that bistability can also be obtained using a symmetrical layup provided that a braid fabric is used for manufacturing (Fernandez and Viquerat, 2014) or the plies are pre-stressed prior to manufacturing (Daynes et al., 2009).

Neutrally stable behaviour of CFRP booms

Bistable CFRP booms exhibit the potentially disadvantageous property of spontaneously springing out from the partially rolled configuration to the fully extended one, because the system endeavours to reach the energy minimum. To overcome this, Murphey and Pellegrino (2004) suggested a concept of neutrally stable masts, by se-
lecting an appropriate stacking sequence of plies in a composite and pre-stressing the material. The result is a structure with non-zero strain energy in both extended and coiled configurations, with very little energy input required. However, it was noted by Schultz et al. (2008) that their manufacturing technique proved to be difficult to control and repeat, therefore in their work they suggested obtaining naturally stable behaviour by controlling the fibre angles, manufacturing tool, and stiffness of the resin material. They showed that by using a relatively low stiffness resin, the structure favours naturally stable behaviour rather than a more robust, snap-like deployment observed in more rigid booms.

Each type of behaviour can be advantageous for different mission types and the selection depends on the spacecraft designers and the mission objectives. However, it should be noted that low-stiffness, neutrally stable masts may not possess sufficient stiffness to support very long 3-5 metre structures, usually required for deployment of large sails, hence are not practical for sail underpins. As one can clearly see, the material selection process for bistable booms is critical because the structural behaviour depends on it. From the point of view of this project it is important to note that with any alteration of material, the structural properties may change. Also, some space resistant materials such as fluoropolymers may not be appropriate for bistable mast manufacturing due to very high processing temperatures.
2.2 Space environmental effects and their influence on the decay of organic structures

Materials exposed in space for any period of time will experience environmental conditions that are very different from those on Earth. The space environment is considered much harsher and material damage is caused by a number of factors and mechanisms acting simultaneously. In order to properly design any structure for operation in this specific environment, firstly the space environment and its components must be well understood. This chapter will list the main environmental effects present in low Earth orbit, which is a region approximately 200-1000 km from Earth and will focus on the effects that are the most detrimental for organic materials.

2.2.1 Low Earth orbit environment

Low altitude spacecraft usually occupy regions up to 800 km, which is called the neutral thermosphere (Barth, 2004). This region is in close proximity to Earth and its atmosphere is primarily composed of residual gases, atomic oxygen in lower parts, and helium and hydrogen in the higher parts of the thermosphere (Figure 2.4). In terms of material degradation in space, LEO is particularly hazardous for polymeric materials and some metals because of the very reactive residual gases that induce material corrosion. These act simultaneously with other environmental components resulting in a significant material deterioration over time.

Space environmental effects can be classified into two main categories: short term effects such as charging or outgassing, and long term ones such as ageing due to neutral, thermal and radiation environments. Interactions can be divided into physical (for instance when a structure is damaged by an impact of micrometeor or debris) and chemical when the acting effect induces chemical reactions within the material (Sample, 2009).

Neutral atmosphere

The neutral atmosphere is composed of approximately 80% atomic oxygen and 20% nitrogen. AO is created by photodissociation of diatomic oxygen by ultraviolet rays into single-oxygen (neutral, free radical) atoms in the upper atmosphere. Wavelengths below 243 nm carry sufficient energy to break the bond of molecular oxygen (5.12 eV) and a relatively long mean free path of neutrals in the order of $10^4$ m at 400 km prevents from re-association of particles and formation of ozone (De Groh et al., 2006).

The AO exposure is characterized by two parameters: AO fluence in atoms/cm$^2$ which indicates how many oxygen atoms have impinged on a material during a par-
2.2. Space environmental effects and their influence on the decay of organic structures

Figure 2.4: Density of species in LEO as a function of altitude (Reprinted with permission from: Dever et al. (2012)).

ticular mission, and AO flux in atoms/cm$^2$s which measures the number of impinging atoms per second. The nominal AO flux for LEO altitudes is in the range of $10^{14}$-$10^{15}$ atoms/cm$^2$s (Grossman and Gouzman, 2003). The number density varies with altitude and solar activity and on average is in the order of $10^8$ atoms/cm$^3$ (Bitetti et al., 2007). At the altitude of International Space Station, AO flux is calculated to be approximately $5.23 \times 10^{13}$ atoms/cm$^2$s (NASA, 2014). Nevertheless, it must be taken into account that ram surfaces (perpendicular to the travelling vector) will experience AO flux higher by orders of magnitude than other surfaces, and often the AO flux prediction is erroneous due to unpredictable solar activity (Dever et al., 2012).

**AO interactions with materials**

AO is the most abundant species in LEO and the most significant factor in terms of material degradation, especially in the case of organic materials which contain a volatile phase or are easily oxidized, for example metals such as silver, copper and osmium. In the case of polymers containing elements such as carbon, nitrogen, sulphur and hydrogen, erosion progresses by recombination with reactive oxygen (Finckenor and de Groh, 2015). After continued AO exposure, interactions with polymers eventually lead to the creation of volatile oxidation products and gradual erosion of these materials (Dever et al., 2012).

The orbital velocity of an object depends on the mass of Earth (M), radius between the centre of Earth and the object (R) and the gravitational constant (G). Substituting these values into the velocity equation (Equation 2.1), it can be calculated that at LEO altitudes objects travel with a speed of approximately 8 km/s.
2.2. Space environmental effects and their influence on the decay of organic structures

\[ v = \sqrt{\frac{GM}{R}} \]  

AO gains sufficient energy to break bonds of composite materials and polymers by colliding with a spacecraft that orbits at such a speed. These collisions result in high energy AO particles of approximately 5 eV impinging on the surface of a material. This provides sufficient energy to break most of the bonds present in organic materials. For instance, the dissociation energy is 3.1 eV, 3.6 eV, 3.7 eV, 4.3 eV and 4.8 eV for C-N, C-C, C-O, C-H and O-H bonds respectively, which is well below the energy of orbital AO particles (Luo, 2007).

A number of processes can take place when a surface is bombarded by atomic oxygen; for example chemical reactions with molecules on the surface, elastic or inelastic scattering of oxygen or recombination with other atoms (Figure 2.5). As a result, the oxygen content of a surface increases and depending on the acting mechanism, further reactions may occur. All of them eventually lead to the creation of volatile products such as CO$_2$, H$_2$O$_2$, HCO$_2$, CH$_3$. Portions of matter can also be physically removed from the surface by AO impinging at orbital velocities.

The erosion rate caused by AO progresses linearly and the probability of reaction increases with the rate at which atoms are delivered to the surface. Eventually, the morphology of organic materials exposed to AO gradually changes and a characteristic cone-like surface is developed, which is a distinctive sign of AO induced erosion.

![Diagram of possible interactions](image)

Figure 2.5: Some of the possible interactions between the organic surfaces and atomic oxygen/UV radiation present in LEO.
2.2. Space environmental effects and their influence on the decay of organic structures

**AO erosion yield**

To determine the AO reactivity for a particular material, it needs to be exposed for a period of time sufficient to observe any measurable changes. The erosion yield of a material is defined as the volume loss per incident atomic oxygen atom, in units of cm$^3$/atom (NASA, 2014). This term describes materials that can produce volatile oxygen products and is dependent on the material’s density, its mass loss due to AO erosion and the number of incident oxygen atoms that attack a surface.

A thoroughly characterized material that is also one of the most commonly used in space applications is Kapton Polyimide film (Du Pont). This material serves as a witness sample to compute the acting AO fluence, provided that its mass loss is known (Equation 2.2). The calculated value of AO fluence can be then used to estimate an erosion yield of any other sample using Equation 2.3 (Dever et al., 2012), where subscript $s$ denotes a sample of any material.

\[ F = \frac{\Delta M_k}{A_k \rho_k E_k} \]  

(2.2)

where:

- $\Delta M_k$ is the mass loss of Kapton sample in grams
- $A_k$ is the surface area of Kapton sample exposed to AO in cm$^2$
- $\rho_k$ the density of Kapton (1.42 g/cm$^3$)
- $E_k$ the erosion yield of Kapton ($3 \cdot 10^{-24}$ cm$^3$/atom).

\[ E_s = \frac{\Delta M_s}{A_s \rho_s F} \]  

(2.3)

where:

- $\Delta M_s$ is the mass loss of a sample in grams
- $A_s$ the surface area exposed in cm$^2$
- $\rho_s$ density of a sample in g/cm$^3$
- $F$ is the fluence of atomic oxygen in atoms/cm$^2$

**Solar environment and ultraviolet radiation**

Earth’s atmosphere shields the surface from ultraviolet radiation shorter than 290 nm and protects humans and materials on Earth from its most hazardous components, however, in space material surfaces are unprotected and exposed to the whole UV
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spectrum. In LEO, UV radiation is of particular interest for spacecraft material designers since at one astronomical unit from the Sun (referred to as the air mass zero solar spectrum, AM0) the UV radiation ≤400 nm makes up 8% of the whole solar spectrum.

The energy contained in a photon rises with decreasing wavelength, based on Equation 2.4 where \( h \) is Plank’s constant, \( c \) is the speed of light and \( \lambda \) is the photon’s wavelength.

\[
E = \frac{hc}{\lambda}
\]  

For materials analysis, it is convenient to only examine those wavelengths that carry energies of UV photons comparable with the dissociation energies of polymeric covalent bonds which lie in the range of 290-460 kJ/mol (3-4.8 eV) (Roylance and Roylance, 2013) which correspond to the photon wavelengths of ≈250-400 nm. Integrated solar irradiance in various wavelengths ranges is shown in the Table 2.1.

Table 2.1: The solar spectrum at AM0 (Dever et al., 2012).

<table>
<thead>
<tr>
<th>Wavelength range</th>
<th>Irradiance [W/m²]</th>
<th>Percent of solar constant [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \lambda &lt;1000 \text{ nm} )</td>
<td>1366</td>
<td>100</td>
</tr>
<tr>
<td>( \lambda &lt;400 \text{ nm} )</td>
<td>107</td>
<td>8</td>
</tr>
<tr>
<td>( \lambda &lt;200 \text{ nm} )</td>
<td>0.1</td>
<td>0.007</td>
</tr>
<tr>
<td>( \lambda &lt;120 \text{ nm} )</td>
<td>negligible</td>
<td>negligible</td>
</tr>
</tbody>
</table>

Structures containing organic phases operating at LEO altitudes are exposed to the full solar spectrum and require protection from the high energy so-called UVB (280-315 nm) and UVC radiation (100-280 nm). Wavelengths in this region are the most harmful for organic materials, because photons in this range carry energy greater than 3.9 eV which is sufficient to break polymer chains and produce destructive free radicals.

**UV interactions with materials**

Light transmission through polymers is limited by electronic transitions in the ultraviolet to visible region and is specific to each polymer (Degroot, 2007). Organic materials are susceptible to UV degradation because many chemical bonds that make up their backbones are strong UV absorbents (also known as chromophores) which results in initiation of photochemical reactions in the radiation environment. For example the carbonyl group (-C=O) has broad UV absorption at approximately 300 nm and an aromatic ring around 255 nm depending on the substituents (Wypych, 2015). Once a portion of radiation in absorbed, a polymer (RH) forms free radicals (denoted with a bullet) as in Equation 2.5. The added thermal energy might break the chem-
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ical bond through a thermal degradation mechanism or by excitation of electrons in the covalent bonds of polymers, because the excited bond becomes weaker (Gintert et al., 2013). Some of the possible subsequent photochemical reactions are: dissociation (Equation 2.6), recombination with other species (Equation 2.7), isomerization (Equation 2.8) or ionization (Equation 2.9) (Wypych, 2015). Free radical polymerization may involve multiple steps once initiated. The presence of reactive gases such as atomic oxygen can intensify the process.

\[
RH \xrightarrow{h\nu} R\cdot + H\cdot \quad (2.5)
\]

\[
AB^* \rightarrow A^* + B^* \quad (2.6)
\]

\[
AB^* + C \rightarrow AC + B \quad (2.7)
\]

\[
AB^* \rightarrow BA \quad (2.8)
\]

\[
AB^* \rightarrow AB^+ + e^- \quad (2.9)
\]

Under high fluxes of UV radiation, generated heat causes material discolouration. A well recognized sign of UV induced degradation is yellowing or darkening of organic materials, observed also on Earth, which indicates an increase in solar absorptance. Discolouration may not only cause material degradation but also alterations in optical properties of thermal control materials. Ensuring low solar absorptance and high thermal emittance is one of the most important parameters for thermal control systems of spacecraft materials.

Two main mechanisms of material degradation due to UV radiation can be distinguished: cross-linking which leads to material hardening, and embrittlement or chain-scission which causes mass loss and general weakening of the material. The former is a result of defects introduced into the material by photochemical reactions (such as free radical polymerization) and a subsequent formation of new chemical bonds in the material, while the latter arises from absorbing sufficient energy to break polymeric bonds. The results of both mechanisms (which might act simultaneously), lead to the loss of mechanical properties due to chemical changes in the material. Surfaces of organic materials are the most susceptible to UV radiation, since most polymers absorb approximately 95% of incident radiation below 250 nm within 0.3 μm from the surface (Dever et al., 2012).
2.2. Space environmental effects and their influence on the decay of organic structures

Thermal environment

Structural stability of CFRP materials in the space environment may be disturbed by undergoing thermal cycles which arise from changing the spacecraft position from sun to shadow. The number of cycles depends on the particular orbit, and in LEO spacecraft orbit every 90 min. The temperature a particular material is experiencing depends on its thermal-optical properties (solar absorptance and thermal emittance), and on various flight parameters, such as its position with respect to the Sun and duration of time spent in sunlight and in shadow. Due to unexpected solar events that can elevate or reduce temperature, as a general rule the materials for LEO applications should be prepared for cycling variation from \(-120^\circ C\) to \(+120^\circ C\) (Finckenor and de Groh, 2015).

Thermal cycling effect on materials

In the case of fibre reinforced polymers, the mismatch in CTE between matrix and fibres can introduce microscopic strains that enlarge during thermal cycling. In the case of coated materials and CFRPs, where two phases with different CTE are present, a common result of this CTE mismatch is cracking of the coating/matrix or coating spalling.

As a general rule, structural polymers are not used above their glass transition temperature. This is because of the transition from a glassy to rubbery material once the \(T_g\) is surpassed and the increased chain mobility which might make the polymer vulnerable to other forms of degradation (Gintert et al., 2013). However, in the case of thermosetting polymers such as epoxy resins which do not melt, the usage above the \(T_g\) is not as detrimental. In some cases the added compliance from working above the \(T_g\) for a short period of time might add additional stiffness to the bonds. Another parameter that determines the usage of certain polymers at elevated temperatures is the HDT (heat distortion temperature) which denotes the temperature regime at which a specimen distorts to a certain extent. Usually HDT indicates the maximum service temperature and is set below the \(T_g\). HDT is experimentally determined for a particular material due to its strong dependence on molecular structure and crosslinking density.

Temperature changes may result not only in microcracking, but also in composite delamination. Elevated temperatures accelerate physical ageing because materials are subjected to working in non-equilibrium conditions and molecular relaxations cause physical ageing (no chemical reactions occur) leading to degradation by thermal fatigue. Additionally, the strain put on chemical bonds makes them more vulnerable to other degrading factors and in the presence of oxygen, which acts as a chemical agent, reactions that would not happen at ambient temperature may occur as well.
2.2. Space environmental effects and their influence on the decay of organic structures

(White, 2006).

**High vacuum**

Composites and polymers operating in space are subjected to high vacuum conditions. The LEO vacuum is typically in the range of $10^{-9}$-to-$10^{-11}$ Torr (Grossman and Gouzman, 2003) and organic materials, which are composed of a volatile phase, tend to release portions of it under vacuum. Organics are also prone to moisture absorption. Moisture absorbed during the pre-launch period will remain in the polymer until the structure is deployed in space and the dramatic reduction in atmospheric pressure may cause a violent removal of molecular water, leading to delamination or small vibrations in rigid structures.

Outgassing results in a loss of dimensional stability, deterioration of material properties and a contamination of surfaces by volatile components released from the outgassing materials of other surfaces. In order to mitigate this undesired phenomenon, materials for space applications must show low outgassing properties. The NASA developed *Standard Test Method for Contamination Outgassing Characteristics of Spacecraft Materials, ASTME1559* (Garrett et al., 1995) instructs a material’s developer to thermal vacuum bake the specimen for a minimum of 24 hours at 125 °C. This standard testing takes into consideration only effects of temperature and vacuum and does not consider other degrading factors present in space.

Creation of vacuum-like LEO conditions in ground-simulation facilities is relatively straightforward and the findings of such tests translate well to actual space conditions.

**Ionizing radiation and plasma environment**

Ionizing radiation consists of charged particles, such as galactic cosmic rays, solar protons and trapped radiation belts. At the altitudes of LEO, the effects of ionizing radiation are negligible and overshadowed by the strong synergistic effect on AO and UV. Ionizing radiation interacts with atomic nuclei and their surrounding electron clouds without specificity to particular chemical bonds, unlike ultraviolet radiation that is absorbed by particular chemical bonds (Dever et al., 2012). The degrading effects of ionizing radiation on polymer materials are also similar to those caused by UV radiation (mainly crosslinking and chain scission) (Finckenor and de Groh, 2015) which lead to degradation in physical and mechanical properties. For this reason, in terms of degradation in LEO, a material’s response to ionizing radiation may be simulated in ground-based facilities by exposure to UV radiation only.

Plasma is an ionized gas, composed of approximately equal number of positively charged particles (ions) and negatively charged (electrons). The ionosphere is the region between 75-1000 km above the earth in which the diluted gases are ionized.
2.2. Space environmental effects and their influence on the decay of organic structures

into plasma by the high energies of solar and cosmic radiation. Plasma fluxes and direct ionizing radiation interact similarly with materials.

Space debris

Spacecraft materials are endangered by micrometeoroids and space debris originating from previous missions and travelling with an average velocity of 8-10 km/s. Collisions with large debris can be avoided since each piece above 10 cm is monitored, however, the number of smaller objects is unknown and increases dangerously with each mission. Impact damage is especially threatening to coatings and outer layers of material since a damaged coating can result in erosion of underlaying layers due to other space effects such as AO and UV. Concentrations of erosion in one location can result in a catastrophic material failure. It has been observed by Verker et al. (2004) that polymeric materials experience ductile to brittle fracture transition with increasing impact velocity, which causes coating spalling and removal of large portions of matter from the surface.

Composite laminates subjected to hyper-velocity impact testing showed severe surface pitting, cracking and delamination. The extent of degradation was found to be a function of impact angle (Tennyson, 2010). It has been shown by Laurenzi et al. (2013) that incorporation of shock absorbents such as carbon nanotubes into polymer matrices increases their ballistic behaviour and can decrease damage by small debris.

Degradation due to synergistic effects

Degradation due synergistic effects happens because the environmental factors combine and produce changes in materials that are different from the individual effects acting alone (Tighe, 2010).

The ability of AO to react with spacecraft materials can be enhanced by solar UV radiation and thermal cycling. Ground-based simulation experiments show a higher level of deterioration due to synergistic effects than due to AO alone. The extent of degradation strongly depends on the type of polymer, which will be discussed in detail later in this chapter. It is important to test the response of polymeric materials to a combination of effects rather than only to individual ones. The studies of Grossman and Gouzman (2003) showed that oxidation alone does not cause significant changes in fluorocarbons, but in the presence of UV radiation the erosion is intensified. Zhao et al. (2005) showed that sample temperature has a similar effect. The process is explained in more details in Section 2.2.4. Studies of Kapton performed by Tagawa and Yokota (2008) indicate that the polymer is resistant to UV, but in the presence of AO the erosion rate increased by 400%. A similar trend was observed by studies of epoxy based CFRPs by Han and Kim (2006) who recorded doubled mass loss
2.2.2 In-space material testing

The primary objective of performing material test missions in the actual space environment is to collect reliable data which can be used for predictive model development and for ground-facility calibration (De Groh, 2010). The first mission focusing on long duration material testing in space started in mid-1980s, it was operated by ESA and NASA and is known as the Long Duration Exposure facility (LDEF). It was a free-flying satellite, carrying more than 10 000 material specimens, with the same samples exposed in ram and wake directions in order to compare the difference in atomic oxygen fluence received, and some stored internally or shielded (De Groh, 2010; Levine, 1991). Before the LDEF, a number of short testing missions which exposed materials for a few hours were also performed. However, a deep understanding of the interactions between materials and the space environment was not fully obtained until after the retrieval of LDEF which had spent 69 months in space (Figure 2.6a). The findings of the LDEF mission were summarized by De Groh (2010). The most important are:

- Organic materials showed severe recession and mechanical degradation while inorganic materials mostly resisted the degradation and maintained their thermal control functions.

- Degrading materials are a source of contamination for the nearby surfaces, especially optics.

- Polymers susceptible to UV radiation experience crosslinking and more severe degradation due to the combined effects of AO and UV.

- Erosion depth increases with mission duration hence the short testing missions provided very limited data.

Because of the Challenger accident the LDEF samples spent considerably more time in space than the mission was designed for, and many samples eroded completely. NASA decided to continue the material studies with a series of experiments known as MISSE (Materials International Space Station Experiment, Figure 2.6b). In the meantime other space agencies tested materials in space, with the main purpose of evaluation the adequacy of materials for future missions and to compare the results to ground simulation testing, some examples include the ESA’s EURECA mission, JAXA’s Space Flyer Unit and Russian experiments on Mir.

Perhaps the widest and most comprehensive database of degradation of polymeric materials has been provided by NASA through the analysis of the MISSE 2 PEACE
2.2. Space environmental effects and their influence on the decay of organic structures

(a) LDEF mission  
(b) MISSIE 2 PEACE mission

Figure 2.6: Examples of in-space material testing (source: NASA).

Figure 2.7: The MISSE 2 PEACE experiment results, a) before flight, b) after four years of space exposure in LEO (source: NASA, (De Groh et al., 2008a)).

(Polymers Erosion And Contamination Experiment) results (De Groh et al., 2008a; McCarthy et al., 2010). The objective of this mission was to expose a wide range of polymeric materials with diverse chemical structures in order to characterize and describe the correlation between chemistry and the rate of degradation. Figure 2.7 presents the pre-launch (a) and the retrieved tray (b) with 41 different polymers exposed during the MISSE 2 PEACE mission for almost four years.

So far, eight MISSE missions have been successfully retrieved and each provided a specific set of data (De Groh et al., 2008b). The program has evolved from passive experiments involving pre- and post-launch analysis to an in-situ evaluation platform with data downloadable via telemetry. MISSE 1-4 missions provided data about performance of materials such as ceramics, metals, paints, gossamer films, adhesives and labels among others and also included finished parts such as sensors, switches, panels, solar cells, semiconductors and many more. The most important of these from this project’s point of view is the aforementioned MISSE 2 PEACE tray with the polymeric samples. The objective of the MISSE 5 mission was to test candidate
materials for solar cells (DeGroh et al., 2007). MISSE 6 included a wide range of materials including polymers and nanocomposites and for the first time carried active devices such as AO fluence monitors or particles detectors to evaluate materials in situ (Prasad and Kinard, 2008; Waters et al., 2013). The most recent MISSE 7 and 8 are connected to ISS, meaning the experiment can be actively monitored by the crew. The objective of those missions is to provide specific information about the behaviour of space hardware, materials used in construction of the ISS and other spacecraft, spacesuit fabrics and many others. The data obtained during the recent missions has not yet been thoroughly analysed, therefore only portions of it are widely available.

2.2.3 Ground-based simulated space environments

The aim of simulated space environment facilities is to replicate one or more specific degrading components of the space environment, to establish the correlation between the laboratory simulation and the actual space exposure, and to interpret the results with confidence (Tighe, 2010). The actual flight experiments are not practical in terms of accelerated tests and although such simulations are never perfect, they are an invaluable resource in evaluating the performance of materials in long duration missions.

A few organisations have established ground-based simulated facilities, of which perhaps the first and oldest was developed at the University of Toronto Institute for Aerospace Studies in Canada. This institution has been active in the testing of space materials, including organics for almost 30 years now and has the most experience and achievements in this field including the patented Photosil™ (Gudimenko et al., 2004) and Implantox™ (Iskanderova et al., 2004) technologies for protection of space materials.

Another active simulation centre was established in the Korean Advanced Institute of Science and Technology (KAIST), Daejeon, Korea. This facility can expose materials to all main degrading effects, including high vacuum \((10^{-6} \text{ torr})\), UV radiation (less than 200 nm wavelength), thermal cycling (-70 to 100°C), and AO (equivalent flow rate with 5 eV AO flux: \(9.08 \times 10^{14} \text{ atoms/cm}^2\text{s}\)) simultaneously (Awaja et al., 2010).

AO ground-simulation facilities

AO ground simulation facilities can be divided into two main groups: thermal and hyperthermal sources. Examples of different facilities and a comparison between them is presented in Table 2.2. Thermal sources are usually plasma generators which are able to produce high AO fluxes for accelerated testing, but the energies of neutrals are limited to tenths of an electron volt, which corresponds to velocities below 1
2.2. Space environmental effects and their influence on the decay of organic structures

km/s. Such speed does not accurately represent collisions occurring between AO and spacecraft in LEO, however, using common laboratory plasma generators is simple and affordable and has proven to be a valuable test in order to perform general material screening and accelerated tests (Tighe, 2010). The environment produced by plasma generators is not pure AO, but rather a quite complex mixture comprised of ions, excited species, UV radiation and heat. Also, the AO neutrals being not energetic enough in comparison with the AO in orbit (5 eV) are unable to break some bonds of polymer materials, therefore such sources can only predict the relative behaviour of materials.

The hyperthermal sources are capable of producing directed atom beams at velocities more comparable to those that occur at LEO. Firstly, molecular oxygen needs to be dissociated, which often produces ions that require neutralization prior to acceleration of the beam (Tighe, 2010). AO beam facilities can produce energies comparable to those in LEO by laser detonation or microwave sources. The results obtained from this testing can be translated more accurately to the actual ones, but this process is more complex and requires more resources in construction and set-up, therefore it is not widely available and usually very costly to perform.

Both thermal and hyperthermal AO sources have a lot in common, but the main difference between them is that thermal AO is strictly a chemical etching process involving bond breaking and chemistry alteration, while hypethermal AO also possesses the kinetic energy which can cause physical sputtering and removal of the surface matter (Cool, 1996).

Because of the fact that AO ground-simulation facilities differ from one another, a standard to calculate the AO fluence has been developed in order to be able to compare samples tested at various locations. The most common approach to validating the lab findings is to normalize the data to Kapton H or Kapton HN polyimide, which is a well defined, thoroughly studied material with a known and universally used erosion yield parameter that can be used to calculate the AO fluence in a particular lab facility. Other methods involve the evaluation of created species by emission spectroscopy, or plasma diagnostics with Langmuir probes. It is of advantage to implement more than one diagnostic technique in order to accurately describe the simulation facility.

Simulation of ultraviolet radiation

In terms of material degradation, photons with wavelength below 400 nm carry sufficient energy to break most chemical bonds in organic materials. In laboratory conditions, UV radiation is simulated by lamps that are capable of emitting this portion of solar spectrum and since the degradation is mainly due to high energetic photons
Table 2.2: Some of the active AO ground based simulation facilities worldwide.

<table>
<thead>
<tr>
<th>Institution</th>
<th>AO source type</th>
<th>AO flux*</th>
</tr>
</thead>
<tbody>
<tr>
<td>NASA Lewis Research Centre</td>
<td>Thermal: 0.01-0.1 eV</td>
<td>$4.4 \times 10^{16}$</td>
</tr>
<tr>
<td>BUAA (Beijing University of Aeronautics &amp; Astronautics)</td>
<td>Thermal: 0.04 eV</td>
<td>$10^{15}$-$10^{16}$</td>
</tr>
<tr>
<td>UTIAS (University of Toronto Institute of Aerospace Studies)</td>
<td>HyperThermal: 2.2 eV</td>
<td>$10^{16}$</td>
</tr>
<tr>
<td>KAIST (Korean Advanced Institute of Science and Technology)</td>
<td>HyperThermal: 5 eV</td>
<td>$9.08 \times 10^{14}$</td>
</tr>
<tr>
<td>ESTEC (European Space Research and Technology Centre)</td>
<td>HyperThermal: 5.5 eV</td>
<td>$2.8 \times 10^{-20}$</td>
</tr>
<tr>
<td>University of Princeton</td>
<td>HyperThermal: 4-20 eV</td>
<td>$5 \times 10^{16}$</td>
</tr>
</tbody>
</table>

* [atoms/cm$^2$s]

with short wavelengths the simulation of the whole solar spectrum is generally not needed.

Deuterium light sources are often used to simulate the shortwave portion of UV radiation because their continuous spectrum is approximately 115-400 nm. Additional popular sources of UV include xenon lamps which closely mimic natural sunlight and have strong emission spectra in the short and middle wavelength range (250-600 nm). Mercury lamps also have emissions in UV-C region (around 250 nm). Weathering chambers can be used to assess material UV stability, but they are usually not equipped to mimic radiation below 300 nm.

For the purpose of calculating the acceleration factor of UV degradation tests, UV meters or phototubes sensitive to short wavelengths can be used. In order to do that, firstly the parameter called number of suns (NOS) is calculated by dividing the UV lamp irradiance ($E_{\text{lamp}}$) by the sun’s irradiance in the same wavelength range (Equation 2.10).

$$NOS = \frac{E_{\text{lamp}}}{E_{\text{sun}}}$$ \hspace{1cm} (2.10)

where:

- $E_{\text{lamp}}$ - lamp irradiance in a certain range [W/m$^2$]
- $E_{\text{sun}}$ - sun irradiance in a certain range [W/m$^2$]

Researchers often relate their testing parameters to the actual space exposure by the value known as equivalent sun hours which is calculated for a specific wavelength range ($\lambda$) and is obtained using Equation 2.11.

$$ESH_{\text{at}\lambda} = NOS \times t$$ \hspace{1cm} (2.11)
where:

- \( NOS \) - number of suns (obtained from Equation 2.10)
- \( t \) - exposure duration in hours

**Simulation of temperature cycles and high vacuum**

Thermal vacuum testing is one of the necessary qualification tests for any spacecraft. This test is designed to verify performance in temperature extremes and high vacuum. Thermal cycling which occurs in LEO is a result of the spacecraft changing its position from sun to Earth’s shadow.

In space simulation facilities which include other degrading effects such as AO and UV radiation, thermal cycling can be simulated by heating with halogen lamps and cooling with liquid nitrogen as shown by Moon et al. (2011) and Han and Kim (2006), this method can accurately simulate temperature cycles from approximately -100°C to +150°C.

**2.2.4 Polymers and their performance in LEO**

Spacecraft materials interact with the LEO environment in a number of ways. A material exposed for any period of time in LEO undergoes changes, however, the longer the time spent, the greater the damage that is expected since the erosion increases linearly with increasing AO fluence (Samwel, 2014). The susceptibility of these materials depends on the operating environment (orbit, ram direction, solar cycles and events etc.) and on the material properties themselves, such as atomic number, chemical composition, density, conductivity and surface roughness. Stress levels that particular materials are experiencing also greatly affect the space durability. Polymers suffer more than metals when exposed to space environmental effects, however, some metals such as silver are also heavily affected by AO. The outstanding properties of polymers make them popular in space applications regardless of their environmental susceptibility, however, different varieties of polymers show different levels of LEO resistance. For example, among polymers tested during the MISSE 2 PEACE mission, Teflon shows the highest and polyethylene the lowest resistance to AO (Samwel, 2014).

All of the described space environmental effects coexist in LEO, and their intensities can be enhanced by unexpected events during which materials are especially susceptible to failure. The main concern of a mission designer is material failure to function, collect the data needed, and achieve the desired mission purpose (Sample, 2009). In order to ensure reliable operation of spacecraft materials in the extreme conditions of LEO, two main approaches have been undertaken by researchers. The
first involves exposing candidate materials in a simulated space-like environment and assessing the properties before and after the exposure. This kind of testing is challenging, due to the difficulty in producing an accurate simulation of the combined environmental effects and, in predicting the material performance. On the other hand, ground-based testing allows test acceleration, which is necessary in order to test new materials and predict their LEO behaviour in a timely manner. Another way to determine the effects of LEO on material performance is to actually fly the candidates and evaluate them through testing in space. This approach is costly and time-consuming, but the data obtained is the most reliable and can be used for modelling and developing of predictive tools. Based on the erosion yield of polymers exposed during the MISSE 2 PEACE mission, the team of Banks et al. (2009) developed a predictive tool, that allows estimation of the atomic oxygen erosion on the basis of a polymer’s chemical structure and physical properties. From inspection of flown samples, it was concluded that an abundance of pendent fluorine and/or chlorine atoms results in a lower AO erosion yield with reference to Kapton polyimide film, whereas polymers with significant oxygen content in their backbone experience higher erosion yields. The products of reactions of AO with polymers could be both volatile (such as CO, CO$_2$, H$_2$O) and non-volatile oxides such as SiO$_2$ and TiO$_2$ among others (Skurat, 2010).

Kapton

Kapton is a polymer with substantial space heritage, used mainly for spacecraft thermal insulation blankets, solar arrays and inflatable structures. Because of this it has been the most thoroughly studied space polymer, and comparison to Kapton is the basis for determination of AO fluence as mentioned in Section 2.2.1.

Kapton provides a good example for understanding the polymer degradation in space. Each polymeric material containing a volatile phase has a certain probability of reaction in LEO and an attributed erosion yield expressed in cm$^3$/atom which indicates the material volume loss per incident AO atom. A probability of reaction of 1 means that every atom of Kapton will react with incoming oxygen and it is assumed that only simple oxides or water will be formed as follows: (Cool, 1996)

$$C_{22}H_{10}O_5N_2 + AO \rightarrow 22CO +5H_2O +2NO$$

By using Equation 2.12, the theoretical erosion yield of Kapton can be calculated and by dividing the actual value of erosion yield in space by this calculated theoretical value, the probability of reaction can be obtained (Equation 2.13).
2.2. Space environmental effects and their influence on the decay of organic structures

\[
R_{\text{e, theoretical}} = \frac{M}{N\rho} = \frac{6.34 \times 10^{-22}}{24 \times 1.42} = 1.86 \times 10^{-23} \text{cm}^3/\text{atom}
\]  

\[
p_r = \frac{R_{\text{e, LEO}}}{R_{\text{e, theoretical}}} = 3 \times 10^{-24}/1.86 \times 10^{-23} = 0.16
\]  

where:

- \( M \) is the atomic weight of the monomer in grams, calculated as follows:
  \[
  (22 \times 12 + 10 + 5 \times 16 + 2 \times 14)/6.022 \times 10^{23} \text{ g/mol} = 6.34 \times 10^{-22} \text{ g}
  \]

- \( N \) is the number of AO required to oxidize the monomer, in this case:
  \[
  29 - (5 \text{ intermolecular}) = 24
  \]

- \( \rho \) is Kapton’s density = 1.42 g/cm³

It can be observed that the presence of intermolecular oxygen plays an important role in the erosion yield and with an increasing number of oxygen atoms, the erosion yield also increases. This statement is in agreement with the flight test data from the MISSE 2 PEACE mission.

The probability of reaction obtained from Equation 2.13 is lower than the one provided by Roussel and Bourdon (2000) who measured the volatile mass products of Kapton in a flight test using a mass spectrometer flown on NASA’s STS-46. Even though the probability of reaction data is not available for other polymers, the theoretical equations can be used in material screening studies to calculate theoretical values and compare that to the database of already tested polymers.

**Hydrocarbons and oxygen containing polymers**

The mechanism of reaction between atomic oxygen and hydrocarbons progresses either by H-atom abstraction, H-atom replacement or O-atom addition (Dever et al., 2012). All reactions lead to the formation of reactive radicals and can be stabilised either by further fragmentation or collisions with other atoms. In the case of unsaturated hydrocarbons, oxygen is likely to be added to the double bond which leads to epoxide formation followed by a chain rearrangement or chain fragmentation (Minton and Garton, 2001).

Hydrocarbons belong to the group of materials most affected by the LEO environment and the most basic types of hydrocarbons, such as polyethylene (PE) and polystyrene (PS) both show very poor AO+UV resistance. During the MISSE 2 PEACE mission, PE eroded almost completely, leaving very little material for post-flight examination (McCarthy et al., 2010). Synergistic effects acting in space degrade hydrocarbons so significantly that they can not be used in space without modification. For example, PE and other simple hydrocarbons require UV stabilizers when
exposed to sunlight because these materials, when subjected to UV light, show signs of discoloration (yellowing), embrittlement and microcracking.

A useful parameter to evaluate a polymer susceptibility to AO is the so-called beta parameter (Equation 2.14) which describes the effect of relative carbon content on polymer erosion yield. It has been shown by Cool (1996) that generally, a higher carbon content means a lower reaction yield.

$$\beta = \frac{N_T}{N_C} \quad (2.14)$$

Another simple approach to approximate erosion yields of polymers proposed by Iskanderova et al. (1995) is based on the so-called gamma parameter which is calculated from the number of atoms in a polymer’s repeating unit (Equation 2.15). The comparison of erosion yields, beta and gamma parameters for selected polymers is presented in Table 2.3 (Cool, 1996). It can be noticed that the theoretical and the MISSE 2 PEACE values differ significantly. However, for the particular simulation facility used in this study, a clear correlation between $\beta/\gamma$ parameters and erosion yields exist.

$$P^\text{LEO}_e = \frac{M}{\rho} \cdot \gamma = \frac{M}{\rho} \cdot \frac{N_T}{N_C - N_O} \quad (2.15)$$

where:

- $M$ is the average atomic weight of the atoms in the unit in grams
- $\rho$ is the polymer density in g/cm$^3$
- $N_T$ is the total number of atoms in the polymer repeat unit
- $N_C$ is the number of carbon atoms in the polymer repeat unit
- $N_O$ is the number of oxygen atoms in the polymer repeat unit

**Thermoplastic matrices**

The most commonly used thermoplastic matrices for high-performance composite applications are Polyether ether ketone (PEEK), Polyphenylene sulfide (PES), Polysulfone (PSU), Polyimides (PI), Polyetherimide (PEI) and Polyamines (PA). Thermoplastic resins are less frequently used in space applications than thermosetting resins, which is mainly due to their higher processing temperatures and pressure, matrix creep while subjected to rapidly changing temperatures, and lower heat resistance. On the other hand, thermoplastics exhibit great chemical and impact resistance which is of advantage in demanding environments such as LEO and in comparison
2.2. Space environmental effects and their influence on the decay of organic structures

Table 2.3: Comparison of theoretical erosion yields, beta and gamma parameters for selected polymers tested by Cool (1996). MISSE 2 PEACE erosion yield results provided for reference.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$R_\text{e}$ (MISSE ref.)</th>
<th>$\beta$</th>
<th>$\gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphite (C)</td>
<td>1.2 (0.42)</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>PEEK ($C_{19}H_{12}O_3$)</td>
<td>2.2 (2.99)</td>
<td>1.8</td>
<td>2.1</td>
</tr>
<tr>
<td>Kapton ($C_{22}H_{10}O_5N_2$)</td>
<td>3 (3)</td>
<td>1.8</td>
<td>2.3</td>
</tr>
<tr>
<td>PE ($CH_2-CH_2$)</td>
<td>3.2 (&gt;3.7)</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>PET (Mylar) ($C_{10}H_8O_4$)</td>
<td>3.9 (3.1)</td>
<td>2.2</td>
<td>3.7</td>
</tr>
<tr>
<td>PA66 ($C_{12}H_{22}O_2N_2$)</td>
<td>4.4 (1.8)</td>
<td>3.2</td>
<td>3.8</td>
</tr>
<tr>
<td>PEO ($C_2H_4O$)</td>
<td>5.7 (1.93)</td>
<td>3.5</td>
<td>7</td>
</tr>
</tbody>
</table>

*[$\text{cm}^3/$atom$\times 10^{-24}$]

with aerospace thermosetting resins such as epoxies, engineering thermoplastics such as PEEK show superior fracture toughness ($\approx$50-100 times higher), lower moisture absorption ($\approx$10 times lower) and a continuous operating temperature of 250°C. Thermoplastics are also of advantage in terms of outgassing.

MISSE 2 PEACE mission results show almost identical values of erosion yield for polyimide (PI, CP1) and polyamide 66 (PA66), 1.91 and 1.80 [$\times 10^{-24}$ cm$^3$/atom], respectively. Polyamide 6 (PA6), which is built from shorter monomers, erodes almost twice as fast as PA66. The PEEK sample showed higher erosion than PI or PA6 ($2.99 \times 10^{-24}$ cm$^3$/atom) and was almost identical to the Kapton H witness sample (McCarthy et al., 2010). Based on this data, it can be observed that longer polymeric chains contribute to better erosion resistance, and polymers containing aromatic rings are in general more affected.

Additionally, the presence of aromatic rings in a polymeric backbone makes a polymer less UV resistant, therefore synergistic effects of atomic oxygen and UV radiation cause more significant damage to these materials. Phenyl rings are strong UV absorbents, therefore the usage of highly aromatic polymers in space applications requires UV stabilization. On the other hand, aromatic rings contribute to thermal and creep resistance of a polymer, providing a relatively high glass transition temperature. Also, rigid aromatic rings add additional stiffness to the backbone which is particularly important for long, deployable structures.

**Thermosetting matrices**

Epoxies resins are still the most popular matrix materials in engineering CFRP structures with a place of privilege, however, their susceptibility in LEO is well recognised based on flight test data. The epoxy resin system that was chosen to fly as a part of the MISSE 2 PEACE mission was Hysol EA 956, epoxy paste adhesive, that is used for general repair applications including laminating and coating. This mate-
2.2. Space environmental effects and their influence on the decay of organic structures

Material had shown a significant erosion in the LEO conditions of $4.21 \times 10^{-24} \text{ cm}^3/\text{atom}$ (McCarthy et al., 2010).

Also, epoxy resins and CFRP structures made thereof showed significant deterioration of properties in ground-based simulation testing, which raises a concern about the overall long-term durability of these materials. Epoxy resin based CFRPs that were examined in the ground-based simulation experiments by Han and Kim (2006) showed 1.51% mass loss and a significant surface erosion for the ageing period of only 5h and 45 min. Moreover, the simulated space environment caused a decrease in both tensile and surface properties, causing significant damage to the tested CFRP samples.

Studies of Shin et al. (2001) show that graphite/epoxy composites subjected to 80 thermal cycles experienced a loss in stiffness of up to 12%, and up to 20% in strength. Mass loss induced by thermal cycling caused matrix degradation by formation of volatiles and consequently an increase in the fibre content, which caused a drop in the CTE value.

Graphite/epoxy composites exposed in the Long Duration Exposure facility showed discolouration, embrittlement and signs of initiated microcracks, which are all effects related to UV degradation (Dever et al., 2012). Moreover, aromatic epoxies are more susceptible to UV radiation than aliphatic ones. Absorption of UV wavelengths by the aromatic rings does not make them suitable for long duration outdoor exposures, and it is apparent that UV-induced degradation will be significantly accelerated in space.

**Hybrid organic-inorganic polymers**

Fluoropolymers exposed to the LEO environment indicated the highest resistance to atomic oxygen and hence the lowest values of erosion yield (De Groh et al., 2008a). It was also noticed by Grossman and Gouzman (2003) that while fluoropolymers show high resistance to atomic oxygen, they are more affected by vacuum UV radiation that degrades fluoropolymers mainly by the chain scissioning mechanism. Breakage of a polymeric backbone occurs in random places, which consequently leads to formation of active radicals and a sudden decrease of molecular weight. As a result, $C_nF_m$ volatile fragments are created and released. It has also been observed that the degradation level increases with the fluorine content.

Chloropolymers also showed a very high LEO resistance compared to the purely organic or oxygen containing polymers which indicates that the presence of an inorganic phase slows down the erosion rate. Further evidence of this is provided by the erosion yield of silicones which is $\approx 10$ times lower than for organics. Silicon containing polymers are believed to be atomic oxygen resistant, therefore they have been
used in the past in protective coatings for oxidizable organic materials. Reactions of silicon incorporated in a polymeric backbone with high energy oxygen that bombards a polymer’s surface, result in the creation of a non-volatile, inorganic, glass-like SiO$_2$ layer. This barrier prevents the surface from further erosion by shielding the volatile organic portion of a polymer, and consequently retarding the degradation. Such a mechanism was observed by many research teams, both in ground based simulation and in LEO testing (Duo et al., 2008; Miyazaki et al., 2010; Tomczak et al., 2009).

2.2.5 Performance prediction of ultra-thin CFRP structures in LEO

Earlier in this chapter it was discussed how polymeric matrices are prone to degradation by various space environmental effects. Accurate prediction of a material’s performance in space is difficult due to the constant variations in space weather. However, the performance of a structure can be approximated. The spacecraft designer may use the studies of materials in LEO (especially the results of the MISSE series of missions) combined with ground-based simulation facilities and predictive modelling.

Thickness loss of a simple polymer (non-reinforced) can be calculated from Equation 2.16 (NASA, 2014) under the assumption that the erosion yield value has been obtained either experimentally or by means of predictive modelling.

\[
\Delta t = E \cdot F
\]  

(2.16)

where:

- $\Delta t$ - thickness loss in cm
- $E$ - erosion yield of a particular material in cm$^3$/atom
- $F$ - atomic oxygen fluence, calculated for the whole mission duration in atom/cm$^2$

Erosion yield in laboratory conditions can be calculated based on the mass loss of the tested sample provided that a reference Kapton sample is exposed as well. This method has been discussed earlier in this chapter (Section 2.2.1) and is based on the erosion yield calculation using Equation 2.3 and AO fluence using Equation 2.2.

In the case of mixed materials, the erosion yield calculation is slightly more complex. The thickness loss for a fibre reinforced material takes into consideration not only the erosion of the polymeric matrix, but the degradation of fibres as well (Equation 2.17) (NASA, 2014). In the case of ultra-thin structures, the degradation of the matrix alone is likely to affect the structural properties.
\[ E_{\text{CFRP}} = \frac{1}{V_f E_{\text{yf}} + V_m E_{\text{ym}}} \]  \hspace{1cm} (2.17)

where:

- \( E_{\text{CFRP}} \) - erosion yield of carbon fibre reinforced material in cm\(^3\)/atom
- \( V_f \) - volume fraction of fibres
- \( V_m \) - volume fraction of matrix
- \( E_{\text{yf}} \) - erosion yield of fibres in cm\(^3\)/atom
- \( E_{\text{ym}} \) - erosion yield of matrix in cm\(^3\)/atom

The performance of polymers in LEO can also be predicted by calculating their corresponding \( \beta \) and \( \gamma \) parameters (discussed in Section 2.2.4). In general, low value of these parameters indicates higher LEO resistance.

**Atomic oxygen erosion yield predictive tool**

The observation of retrieved polymeric samples flown with the MISSE PEACE 2 mission revealed the fact that not all materials that form volatile phases have the same erosion yield. Therefore, it is reasonable to assume that a correlation between chemical structure of a polymer and the probability of reactions with atomic oxygen must exist.

The predictive tool suggested by Banks et al. (2009) is based on the ash content of the polymeric material. Ash is the residue that results after AO exposure, and although all polymers contain some fraction of inorganic phase, the observation of retrieved samples and subsequent tests of epoxy with increasing fillings of silica, led to the conclusion that higher ash content resulted in lower AO erosion yield (Equation 2.18).

\[ E_{ya} = E_{yo} e^{\frac{-K A}{1 - A}} \]  \hspace{1cm} (2.18)

where:

- \( E_{ya} \) - erosion yield of polymer with a given ash content in cm\(^3\)/atom
- \( E_{yo} \) - erosion yield of neat polymer in cm\(^3\)/atom
- \( K \) - erosion yield attenuation constant
- \( A \) - mass fraction of ash in the polymer
Another assumption made by Banks et al. (2009) was that erosion yield is dependent on the packaging density of atoms, because in the case of materials with higher density, it takes more atomic oxygen atoms per square centimetre to oxidise than in the case of more loosely packed structures.

The atomic oxygen prediction tool takes into consideration physical features of a material including packaging density and ash content and the chemical characteristics of the polymer unit, such as the number of single and double bonds and the chemical composition. The full model takes into account eighteen constants based on the polymers chemistry and is described in detail by NASA (2014). The proposed model has a high correlation coefficient ($R^2 = 0.895$) and can be a very useful tool in assessing material performance prior to its exposure in space. The model requires a knowledge of the ash content, which was measured by the model creators by ashing samples in a RF plasma asher for several hundred hours. During this time contamination issues were reported which are probably why the predictive model produces erroneous results in some cases. Nevertheless, the prediction tool showed reasonable values for most of the MISSE 2 PEACE polymers and can be successfully used to approximate the LEO erosion yield for new polymers and composites without expensive and time consuming in-space exposures.

### 2.2.6 Modification of Space Materials

**Approaches to mitigate material degradation in space**

A significant advancement in material design and prediction of environmental degradation in space has been accomplished since the deterioration in properties was observed for the first time with return of the Space Shuttle. Nowadays, it is possible to approximate an average AO fluence for a particular mission and select candidate materials from an extensive database of materials already tested in space and in lab facilities, with known values of erosion yield. In the case of untested materials, prediction tools can be used to approximate their erosion yields.

Developments in ground-based simulation facilities are important in order to perform up to date testing of new candidate materials. Because of the complexity of the space environment, finding a material that is resistant to synergistic effects acting in space is a challenging task. In general, fluoropolymers and silicones show higher resistance to atomic oxygen erosion, but fluoropolymers are more affected by UV radiation and silicones generate outgassing products that can interact chemically with the substrate material (Gouzman et al., 2001). Epoxy resins are excellent rigid materials, showing desirable outgassing properties, but are strongly affected by UV radiation and AO. With all that in mind, it is apparent that no one material exists that is resilient to the general space environment and the implementation of protection strategies is
required.

This section will discuss several mitigation approaches that may be implemented in order to extend the life span of polymers and composites in LEO. The most commonly used are protective coatings, chemical modification of a particular material in order to obtain enhanced surface properties, and hybridization by adding an inorganic nano-phase.

**Protective coatings**

If it is advantageous to use a material susceptible to the space environment, a variety of coatings are available to enhance its longevity including elements such as Al, Si, Ge, Ni, Cr and F (Kleiman, 2010). The main requirements for protective coatings is to provide higher resistance to AO, UV and thermal cycling. The barrier must be flexible, lightweight, resistant to abrasion and show good adhesion to the substrate without forming defects. Protective coatings should not alter the thermal-optical properties of the surfaces (Kleiman et al., 1995b). In the case of deployable structures, which travel into space stowed and are deployed after months in such a configuration, any stresses in the coating layer must be avoided as they are likely to cause cracks during deployment.

Coatings are the most common mitigation technique to protect materials against the LEO environment, and they are usually thin layers of inorganic oxides, such as Al$_2$O$_3$ (Cooper et al., 2008), TiO$_2$ (Minton et al., 2010) or metals (in particular aluminium or gold (Banks et al., 2004)). Hybrid organic-inorganic coatings have also been proposed, for example an organic-inorganic approach was presented by Dworak and Soucek (2003), known as ceramer, fabricated using polysiloxane binder and nanophase silicon/metal oxo-clusters derived from sol-gel precursors.

Polymer materials have to be coated at significantly low temperatures because their chains can be damaged by high temperature vaporizing processes. Minton et al. (2010) showed that atomic layer deposition of Al$_2$O$_3$ coatings on Kapton and Teflon are best performed at temperatures of $\approx$90°C. In the case of curved structures such as BRCs, flattening the samples for coating might result in shape-distortions. The two main techniques to coat polymers are: physical (PVD) and chemical (CVD) vapour deposition. Coatings effectively protect materials, however, imperfections in the coating layer may become sources of degradation. Defects in coatings act as centres of degradation, because when the oxygen radical enters this constrained space, its probability of reaction greatly increases and the trapped oxygen atom has multiple opportunities to react and recombine before it escapes through the defect in the coating (Banks et al., 2004). Material degradation occurring under the coating had been detected in graphite/epoxy structures covered in mica paint by Rutledge et al.
(1987) where unattached mica flakes laying on the surface were observed while ma-
terial degraded underneath, and on aluminized Kapton in which severe undercutting
erosion was observed around defects (NASA, 2014).

Because of the limitations in coating technology, it appears that perhaps materials
may be better protected by using a multi-phase material, in which phases responsible
for each hazard are evenly distributed.

**Surface modification processes**

The main goal of surface modification processes is to apply a treatment which provides
new functionality and properties. Surface modification can protect materials from
degradation by LEO, or be used to increase surface adhesion prior to applying paints
or coatings.

A protective coating strategy might not be fully effective in environments where
structures undergo thermal cycling due to the CTE difference between the substrate
and coating, causing spalling or cracking of the coated surfaces. Surface modification
processes are not coatings and the aforementioned problems do not apply to them.
During the treatment, only the material surface is modified, therefore problems of
adhesion, thermal mismatch and dimensional changes are no longer relevant. Two
types of surface modification processes can be distinguished: chemical and physical.

The Photosil™ surface modification technology was developed by the University of
Toronto Institute for Aerospace Studies (UTIAS) for protection of organic materials
against AO in LEO (Cool, 1996). This chemical surface modification process is based
on incorporation of silicon-containing groups in the surface layer, up to 1µm in depth
and comprises three main stages: (i) surface photo-activation, (ii) liquid-phase sily-
lation and (iii) surface stabilization (Kleiman, 2010). The Photosil is a very powerful
technique which allows reduction of AO erosion yield by two orders of magnitude. It
also reduced the structure thickness to 0.2-0.5µm from 1-2 µm in case of thin film
coatings, without significant alterations of surface morphology and thermal optical
parameters (Kleiman, 2010). Currently, the Photosil™ treatment is successfully used
to protect painted external components of NASA’s Canadarm2 (Gudimenko et al.,
2004).

An example of a physical modification process is a method known as Implan-
tox™ developed and patented by the UTIAS research team (Iskanderova et al., 1997).
Implantox™ is based on high-dose ion implantation with either single ions or a combi-
nation of them, for instance Si, Al, Si + Al among others. Ion implantation combined
with surface treatment results in an oxide-rich surface, which is highly resistant to
erosion and oxidation (Kleiman, 2010).
2.2. Space environmental effects and their influence on the decay of organic structures

Hybrid organic-inorganic polymers and composites

When a material comprises two or more significantly different phases it can be referred to as a hybrid (Ashby, 2011; Ashby and Bréchet, 2003). The additives can be either in an organic or inorganic form and if at least one dimension is of a nano-scale they are referred to as nanocomposites. In contrast to surface modification or coatings, hybrid composites influence properties in the entire bulk.

Based on the space exposures of polyimides during the MISSE missions, it was observed that the addition of aluminium acetylacetonate to polyimide films greatly enhanced the resistance to erosion by AO, from eight months in the case of an unmodified film to four years in the case of the aluminium containing one (Kiefer et al., 2011). Following on from those results, NASA developed an AO resistant polyimide patented under the trade name of LaRC Tor. It contains 4.5% by weight phosphorus, which does not change the optical properties but offers a significantly enhanced AO stability (Pater and Curto, 2007).

Previous research shows that for protection of structures in space applications, carbon nanotubes (CNT) are an effective strategy for increasing AO and UV resistance (Atar et al., 2015; Moon et al., 2011). CNTs incorporated into organic polymer matrices such as epoxy resins act as alternative reinforcing agents, enhance mechanical properties and prevent crack propagation by acting as bridges. Graphene nanoplatelets, also proved to be an effective strategy to combat UV induced degradation of polymeric films (Clausi et al., 2017). Similarly, the addition of inorganic nano-phase oxides such as SiO₂, ZnO and TiO₂ to epoxy resins enhanced their LEO resistance (Liu et al., 2008).

Silicon is probably one of the most common elements used to enhance material resistance to AO. The high reactivity of silicon with oxygen, and formation of stable oxides can be viewed as a very effective protection strategy. Various approaches involving AO protection of Kapton polyimide include incorporation of silicone derivatives such as nano-silicon dioxide (Duo et al., 2006; Wang et al., 2006) or Polyhedral Oligomeric Silsesquioxane (POSS) (Lei et al., 2015; Minton et al., 2012; Song et al., 2015; Tomczak et al., 2009; Verker et al., 2009). Incorporation of POSS into different types of polymers such as polyurethanes showed a remarkable resistance of POSS containing polymers to AO (Phillips et al., 2000).

Various independent sources show that in a simulated space environment containing atomic oxygen, silicon present within the sample reacts with the bombarding AO in the formation of a silica-like protective layer on the surface (Fischer et al., 2010; Phillips et al., 2004). This experimental result was confirmed by the Japanese Space Agency, by directly exposing silicon-containing films outside of the ISS. During this experiment, the same phenomenon of silica formation was observed by Miyazaki et al.
(2013). The developed layer protects the underlaying portions of organic material that is vulnerable to degradation by AO, and consequently decreases the erosion yield of silicones or silicon-containing materials by 1-2 orders of magnitude.

2.3 Modification of epoxy resins with silicon derivatives

Epoxy resins are one of the most popular commercially and due to the extensive experience in studies of epoxy properties and behaviour, they hold a place of privilege in the thermosetting family. The most desired properties of epoxy resins for space applications are their excellent strength to weight ratio, and processing versatility. Because of their good adhesion, epoxy resins can be used in both composite matrices and coatings. Interest in using epoxy resins in more demanding environments has significantly grown, however, it has been known for a long time now that epoxy resins used without any modification are not resistant to the environment of LEO (Lukez, 1987).

Over the past few decades researchers have became aware of polymer limitations and therefore focused a lot of their efforts on nano-structured additives to epoxy resins, and the effects of the nano-size phase on polymer properties (Kumar et al., 2017). Multi-functional materials are often organic-inorganic hybrids, since they can offer enhanced performance by combining inorganic material properties such as hardness, strength and reduced flammability with organic material characteristics such as elasticity, process-ability and toughness (Kickelbick, 2003). A popular approach to improving the properties of epoxy resins that has attracted a lot of attention is to modify the thermoset with silicon nanoparticles such as the cage structure known as POSS or nanosilica.

This chapter will discuss examples of POSS/epoxy and nanosilica/epoxy nanocomposites, and how the properties of epoxy change with such modification. The influence on material characteristics which are important for space applications will be emphasised.

2.3.1 Epoxy resin matrices and matrix dominated properties

Epoxy resins can be classified into two main families: aromatic and aliphatic. The former (e.g. diglycidyl ether of bisphenol A, DGEBA) contain especially stable phenyl rings that result in superior thermal stability and mechanical properties in comparison with aliphatic epoxies. The presence of aromatic rings makes a polymer more rigid in contrary to softer aliphatic epoxies which can be advantageous for applications requiring flexibility. Speciality epoxy resins such as TGDDM or Novolac have
been developed mainly for aircraft grade composites which have better mechanical strength, chemical resistance and higher operating temperatures than DGEBA-like epoxy, which was achieved by introducing more benzene rings into the monomer. With an increasing aromatic content all those properties improve, however, those phenyl rings contribute to lower weather-stability, which is caused by the fact that phenyl rings exhibit strong UV absorption.

Aromatic polydiamines and carboxylic acid anhydrides are both commonly used as curing agents for high performance epoxy resins, however, the former has received more attention from industry due to the fact that lower curing temperatures are required for amine cured resin systems. For space applications, anhydride cured systems are more appropriate because they exhibit reduced moisture absorption since hydroxyl groups are not generated during the ring opening reactions (as in the case of amine-cured epoxies). Moisture absorbed during the pre-launch period will remain in the matrix until the structure is deployed in the space environment and the dramatic reduction in atmospheric pressure may cause a violent removal of the trapped water molecules - leading to delamination of composites or even small vibrations that can interfere with scientific measurements.

The presence of aromatic groups in the polymer has such a profound impact that it dominates the whole spectrum of properties. Since an important role of a matrix is to protect the reinforcement from the environment, in the following subsections, the main matrix-dominated properties will be discussed and the relationship between the resin chemical structure and its performance in space will be emphasised.

**Thermal properties**

The chemical structure of epoxy resin is responsible for its thermal stability. Thermosetting polymers, in contrast to thermoplastics, do not melt at elevated temperature. The crosslinking reaction is irreversible and instead of melting, above a certain temperature decomposition and char formation take place. The presence of aromatic content increases thermal stability, because more energy is required to break the benzene ring which consequently increases the HDT value of a polymer (heat distortion temperature). The general rule is that HDT increases in the following order: aliphatic (straight chain epoxy) 110-150°C, aliphatic (cyclial) 125-132°C, aromatic (straight chain) 130-145°C and aromatic (cyclial) 145-175°C (cyclial) (Strong, 2008). Thermal stability is a complex phenomenon which is affected by more than one factor. Apart from the aforementioned basic nature of the polymeric chain, the extent of crosslinking also contributes to increasing the allowable operating temperature, which is closely related to the type of curing agent used.
Resistance to Ultraviolet (UV) light

As mentioned at the beginning of this section, high aromatic content (common for high-performance epoxies) is not desired for applications requiring UV resistance. This is because the bond between the phenyl group and its substituent is about the same as the energy of UV light, which leads to an excitation and bond cleavage in this part of the polymeric chain (Strong, 2008). A comparison of different resin systems performed by Bellenger and Verdu (1983) showed that photodegradation of the aromatic epoxy/amine resin system starts from the phenoxy part of the polymeric chain. Additionally, the sites prone to UV degradation are the aromatic ethers and the CH$_3$ bonds, which leads to chain scissioning and fragmentation (Mailhot et al., 2005). The rate of chemical degradation does not correspond to the thickness loss. Rather than an uniform reduction in thickness, the UV radiation induces an inhomogeneous erosion process with formation of localised pits and nano-sized defects that with time result in cracking and loss of mechanical properties (Wypych, 2015).

In contrast, cycloaliphatic epoxy resin systems are better suited for applications involving exposure to UV radiation. This is due to the fact that they are composed of chemical moieties that absorb significantly less radiation, which in turn results in reduced yellowing, embrittlement and cracking.

Resistance to gases and Atomic Oxygen

The properties of epoxy resins also determine their reactivity with gases. Firstly, the extent of degradation depends on the crosslinking density. If atoms are tightly packed it is more difficult for gases to enter and initiate reactions. Generally the chemical affinity is greater between materials with similar chemical structures (Strong, 2008). For this reason, in LEO where there is an abundance of residual oxygen, the tested polymers with high intermolecular oxygen content experienced more severe degradation (De Groh et al., 2006). Materials exposed to ram surfaces are bombarded by atomic oxygen at orbital velocities. This can result either in chemical reactions or physical removal of the matter, however, in the case of ultra-thin structures it is believed that atomic oxygen can easily permeate and initiate reactions in each direction.

2.3.2 Silicones and their desired properties for space applications

Polymeric materials containing (-Si-O-) bonds in their backbone are referred to as silicone polymers or polysiloxanes. The siloxane bond forms the inorganic part of a polymer and the organic part is formed by substituents of the silicon atom. The dual
nature of silicones is the reason for their interesting properties, especially in regards to the modification of the original backbone (Yilgör and Yilgör, 2014). The reactivity of silicone polymers enables the creation of hybrids with organic materials, for example with epoxy resins, which results in materials with enhanced properties derived from both phases. The high dissociation energy of the Si-O bond provides both thermal and oxidative stability which are both very significant properties for space applications. The Si-O chemical bond is stronger than any single bond formed by carbon with the epoxy resin matrices (Table 2.4) (Yilgör and Yilgör, 2014). Additionally, silicones are highly transparent to radiation in the visible range all the way down to ultraviolet (Degroot, 2007) which makes them suitable materials for applications in the entire radiation spectrum, including in space.

Table 2.4: Energy associated with bonds present in epoxy resins and polysiloxanes (Yilgör and Yilgör, 2014).

<table>
<thead>
<tr>
<th>Bond</th>
<th>Energy [kJ/mol] (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-C</td>
<td>370 (3.8)</td>
</tr>
<tr>
<td>C-H</td>
<td>435 (4.5)</td>
</tr>
<tr>
<td>C-O</td>
<td>360 (3.7)</td>
</tr>
<tr>
<td>C-N</td>
<td>305 (3.2)</td>
</tr>
<tr>
<td>Si-O</td>
<td>460 (4.8)</td>
</tr>
<tr>
<td>Si-C</td>
<td>318 (3.3)</td>
</tr>
<tr>
<td>Si-Si</td>
<td>340 (3.5)</td>
</tr>
</tbody>
</table>

Nanosilica hybrids with epoxy resins

In numerous studies nanosilica powder was blended with epoxy resins as a filler in order to improve their various properties. A comprehensive review concerning epoxy/silica hybrids was published by Sprenger (2013) which states that nanosilica mainly improves mechanical characteristics of epoxy resins, such as elastic modulus, toughness and fatigue performance, demonstrating uniform dispersion and a very small influence on curing cycle and the network structure.

Allahverdi et al. (2012) investigated blends of DGEBA/nanosilica cured with cycloaliphatic amine and reported excellent levels of dispersion, confirmed with TEM and light transmittance. With addition of 5 wt% of nanosilica, thermal-mechanical properties also improved. The most significant enhancement noted was the material’s stiffness (storage modulus change from 1.36 GPa to 3.46 GPa at 100°C) and a slight increase in $T_g$ of approximately 5°C. Temperature stability also increases with addition of nanosilica. The temperature at with 5% mass loss occurs increased by 20°C. The studies of Rosso et al. (2006) show that low loadings of nanosilica (up to 5 wt%) result in outstanding improvements of fracture toughness by (70%) but a reduction
in $T_g$ by approximately 5°C was also observed.

Based on the above mentioned studies it can be concluded that the amount of nanoadditive should be low, because even if the level of dispersion with higher than 10 wt% silica loadings is satisfactory, deterioration of thermal-mechanical properties caused by decreased level of crosslinking is likely to occur (Chen et al., 2008).

**Polyhedral oligomeric silsesquioxanes (POSS)**

Polyhedral oligomeric silsesquioxanes (POSS) are organic-inorganic compounds described by a general formula $(RSiO_{1.5})_n$, where R can be any organic group or hydrogen and $n$ is an even integer $\geq 4$. Various conformations of POSS have been discovered, however, the cage structure that has received the most attention among the research community is the $T_8$ type of POSS that is comprised of eight silicon atoms, each bonded to three oxygen atoms and an organic group with the general formula $R_8Si_8O_{12}$ (Figure 2.8).

![Polyhedral oligomeric silsesquioxane (POSS) nano-cage. R stands for an organic group or hydrogen.](image)

What makes POSS a particularly interesting material is its hybrid character. The core of the cage is inorganic while the silicon substituents are organic, which offers up to eight reactive sites, one at each vertex. The inorganic support can be viewed as an inert part of the material, while the organic groups with their rich spectra of functionality are the reactive parts, giving the material its key features. The most basic types of POSS are those with one reactive site only, often referred to as mono-functional, however, the whole range of polar structures and functional groups can be bonded to POSS cages which allows the design of miscible materials with the hosting polymer.

Four types of POSS-epoxy hybrids can be distinguished (Matejka, 2014):

- Pendant POSS - mono-functional POSS bound to the epoxy network at the chain termination.
- Bead POSS - bi-functional POSS bound to the epoxy network at two sites.
• Star POSS - multi-functional POSS bound to the epoxy network in three or more (usually eight) places which acts like a cross-linker.

• Nonreactive POSS - physically dispersed within the epoxy network, without covalent bonding to a matrix. The smallest known size of silica, with dimensions in the range of 1-3 nm (Pielichowski et al., 2006).

The presence of organic groups on the surface of POSS nano-cages enables compatibility with polymer materials, and because of this, POSS is presumably a better modifier for polymers than purely inorganic silica or metal oxides. The functionality of POSS changes its appearance, depending on the number and chemistry of its substituents, POSS is available as solid (white powder), semi-solid or viscous liquid. However, the chemical affinity between the selected type of POSS and the polymer matrix is critical and the avoidance of phase separation and aggregation of POSS strongly depends on it. The interparticle interactions are often strong and even a good level of physical blending is not enough to prevent the formation of POSS-domains that can reach the size of several micrometers. These POSS-rich regions behave as defects or stress concentrators and weaken the material, which can be observed through declining mechanical properties (Ayandele et al., 2012). It will be demonstrated in the following sections of this chapter how morphology correlates with particular properties of nanocomposites.

**Mono-functional POSS**

Mono-functional POSS possesses a single polymerizable functional group, with the remaining vertices bearing inert organic groups. Mono-functional POSS (a crystalline solid) is often not practical for obtaining single-phase composites, especially when added in higher concentrations due to its phase separation tendency and creation of brittle POSS-rich regions within the material (Frank et al., 2012; Rashid et al., 2009). This POSS acts more like a pendant group, creating a linear organic-inorganic polymer which reduces the polymer’s mobility and consequently slightly increases the glass transition temperature.

Epoxy- and amino-POSS have attracted significant interest as potential modifiers for epoxy resins. POSS terminated with an epoxy or amine group is expected to blend well with the hosting resin, since those groups are already present along the polymeric epoxy or amine chains, however, it was shown by Constantin et al. (2013) that due to steric hindrance amino-POSS caused large agglomerates when blended with the DGEBA type of epoxy. This suggests that each epoxy-POSS pair might demonstrate its own set of properties.
2.3. Modification of epoxy resins with silicon derivatives

Multi-functional POSS

POSS bearing eight epoxy groups was first synthesized by Zhang and Laine (1996) with an aim to develop soluble, liquid POSS cubes that can be readily polimerizable. This type of POSS acts more like a crosslinker, decreasing the packing of the epoxy network and the glass transition temperature. The advantage of this type of POSS is an improved miscibility with the polymeric host, however, some thermal-mechanical properties are often reduced together with the crosslinking density. Nevertheless, it has been reported that octa-functional POSS was successfully used to obtain thermoplastic and thermosetting polymers with high surface areas, novel mechanical properties and enhanced thermal stability (Pielichowski et al., 2006).

2.3.3 POSS/Epoxy Hybrids

Research so far has been concentrated on the modification of DGEBA-like epoxy resins with various types of POSS, selected examples including the work of Barkoula et al. (2008); Boček et al. (2011); Constantin et al. (2013); Hamerton et al. (2015, 2016); Lungu et al. (2016); Matejka et al. (2004); Strachota et al. (2007); Takala et al. (2008). The addition of POSS to epoxy resins allows the development of materials with specially designed properties for space exposure such as resistance to AO and UV together with enhanced thermal stability.

Dispersion in POSS/epoxy nanocomposites

The creation of POSS/epoxy nanocomposites involves incorporation of already synthesized POSS nanoparticles into the epoxy matrix, which might lead to phase separation and nanoparticle agglomerations. The structure and morphology of the hybrids depend on the type of POSS used and the interfacial interactions between POSS and the epoxy networks. These interactions are the necessary condition for good dispersion of the nanoadditive. The distribution of the nanoparticles can be observed with a scanning or transmission electron microscope, or through investigation of thermal-mechanical properties.

Studies on improving the molecular level of dispersion were carried out by Frank et al. (2012). Two ways of decreasing the level of agglomeration were proposed. In one approach POSS is pre-reacted with DGEBA in order to enhance its solubility in the resin part and in another, the epoxy resin is cured at higher temperatures to increase the reaction rate of POSS and prevent phase segregation. The conclusion of this study was that both of the suggested methods significantly decrease the size of agglomerates and the most optimal approach was to use a low concentration of POSS (up to 10 wt%), POSS pre-reaction with the hosting matrix, and a high-temperature
Another suggested approach to improve the dispersion of mono-POSS within the epoxy resin matrix was proposed by Florea et al. (2015), which involves the addition of polydimethylsiloxane (PDMS) in small concentrations. The long, flexible chains of PDMS act like spacers between the bulky POSS molecules and aid in obtaining homogeneous, single-phase nanocomposites. It has been observed that PDMS slightly influences the properties of epoxy resins by increasing the mobility of polymeric chains and consequently decreasing the glass transition temperature. Increased spacing between polymeric chains also results in lower crosslinking density and as a result lower mechanical properties, which was confirmed by the DMTA analysis of Florea et al. (2015).

In another study, Florea et al. (2016) conducted an extensive comparison between POSS bearing one and eight reactive groups which showed that the number of reactive moieties is closely correlated with the level of dispersion and consequently governs the whole curing process. It was also shown that mono-POSS tends to agglomerate at the surface more than the octa-POSS type. The surface dispersion of POSS will likely affect uniform formation of silica protective layer under AO bombardment and protection from UV induced degradation, therefore it is essential to select the type of POSS that uniformly disperses with the epoxy matrix and creates a silicone-rich surface layer.

**Thermal stability of POSS/epoxy nanocomposites**

The rigid structure of the POSS nano-cage and the higher dissociation energies of silicon containing bonds in comparison with the corresponding carbon bonds, are the reasons for using these materials to improve the usually poor thermal stability of polymer materials. The higher dissociation energy of the Si-O bond is directly related to thermal stability. Several other properties of POSS, such as the concentration of POSS within the epoxy matrix, the level of dispersion and the type of POSS functional groups also affect the thermal stability. Studies of the thermal degradation of POSS bearing different types of substituents showed that with an increasing alkyl length, the weight loss onset shifts to higher temperatures (Fina et al., 2006). Phenyl-substituted POSS shows higher thermal stability than alkyl-substituted POSS due to a more complex thermal-degradation mechanism which requires breaking stable hexagonal rings.

Another study of POSS/epoxy thermal stability was performed by Boček et al. (2011) who reported an improvement of 30°C when compared to the neat epoxy, however, they also reported that in blends with poorly distributed POSS, the thermal stability worsened.
2.3. Modification of epoxy resins with silicon derivatives

**Thermo-mechanical properties of POSS/epoxy nanocomposites**

POSS reagents can either increase or decrease the glass transition temperature, depending on their chemical conformation. Mono-functional POSS with only one reactive site, acts like a pendant group, which effectively reduces chain mobility and increases the $T_g$. Increasing the complexity of an epoxy resin system by the addition of nanoparticles is likely to reduce the polymerization rate, which was observed by Florea et al. (2016).

Multi-functional types of POSS demonstrate a different type of behaviour. They act as cross-linkers and spacers between the epoxy chains - increasing flexibility and making them easier to flow, while decreasing the $T_g$. In the case of multi-functional POSS, the risk of incomplete curing is greater, and with a higher degree of cure and cross-link density, the $T_g$ is also higher. Therefore, the concentration of POSS should generally be kept low because an abundance of reactive POSS can actually lead to the deterioration of properties.
Chapter 3

Materials and methods

The chapter will discuss the material selection process for ultra-thin BRC structures. This project draws on the previous work of Fernandez (2015) in which the manufacturing method and material was selected for the purpose of the Gossamer deorbiter mission (Fernandez et al., 2011, 2014).

The material selection process is driven by two critical mission requirements. The first one considers the total boom thickness, which directly translates to the maximum radius of the boom in its coiled configuration and consequently the size of the boom deployer. The second requirement considers the structural behaviour of the BRC. As demonstrated by Fernandez and Viquerat (2014), to manufacture a long sample which is bistable over the whole length, the laminate must consist of several plies in a balanced configuration such as \([\pm \delta/0/\pm \delta]\), where \(\delta\) are plies of carbon fibre braid. The fibres orientation varies between \(\pm 50^\circ\) and \(\pm 35^\circ\). The unidirectional \(0^\circ\) ply between the braid plies provides additional stiffness to the long boom. Due to the high specificity of this non-standard manufacturing technique, it is not easy to introduce any modifications.

The developed manufacturing technique is based on hand lamination due to its novelty. The carbon fibre braid needs to be manually draped on a former in order to achieve a desired fibre orientation. After the preferred fibre angle is obtained, the braid can be impregnated with the resin. This is a very delicate procedure and in order not to distort the fibre angles and also to minimize the boom thickness the previous researchers chose to use a one-part epoxy resin film for this purpose. The detailed fabrication procedure is described in the Section 3.2 in which the novel modifications introduced by the author of this thesis are discussed.
3.1 Materials used in this study

Several approaches had been undertaken to select a material that will have better resistance to the LEO environment. As already mentioned, there are several critical requirements for BRC structures, therefore it was intended to develop a material strategy that can be easily transferred from the laboratory environment to industry. For this reason, only commercially available raw materials were selected and the proposed modification of the BRC structures focuses on blending the epoxy resin with selected nanoparticles in such a way that the individual components of the blend each contribute to combating the degrading effects of some of the factors present in LEO.

3.1.1 Aromatic epoxy resin system

The base material for this application was a one part epoxy resin film, TGDDM type provided by Cytec-Solvay (Wilton, UK), trade name MTM44-1. The chemical structure of this epoxy resin system is presented in Figure 3.1A. Because this epoxy was a prepreg, it was not possible to modify it with nanoparticles in the lab environment. The author of this thesis approached the manufacturer and seek the source of this material in a liquid form. Unfortunately the manufacturer was not able to provide the material as a two part uncured liquid, thus it was decided to approach another supplier and test the nanomodification on a different but chemically similar resin system. An important requirement for this resin was to be of low viscosity. Some initial studies of commercial DGEBA-like epoxy resin proved that dispersion of nanoparticles is virtually impossible in such a viscous liquid. However, epoxy resins containing reactive diluents offer reduced viscosity for the purpose of easier manufacturing, therefore this type of resin was sourced (Figure 3.1B). From the approached suppliers, Huntsman (Netherlands) offered to provide a suitable formulation of trade name XB6469 (epoxy)/Aradur 2954 (cycloaliphatic amine curing agent).

The author of this thesis made an attempt to manufacture a BRC using epoxy resin in a liquid form instead of using the MTM44-1 epoxy resin prepreg during her visit at the industrial partner’s manufacturing site. This proved to be a very difficult task, as the company did not have suitable equipment and was not used to using liquid resins in their daily work. Despite that, a short sample was manufactured.
but it was very difficult to achieve proper fibre alignment and the boom did not coil properly. Nevertheless, the thesis author decided to test properties of the XB/Amine epoxy resin modified with silicon nanoparticles in order to better understand how the resin would respond to such modification and whether appropriate curing and particle dispersion would be achieved. The results of this study are presented in Section 4.1.

3.1.2 Silicone/epoxy cycloaliphatic resin system

The main degrading factors for polymeric materials in LEO are atomic oxygen and ultraviolet radiation. AO affects all purely organic polymers by reactions with carbon and production of volatile components. This effect is significantly retarded in polymers containing inorganic elements such as silicon or fluorine. UV radiation also strongly affects epoxy resins but is much more detrimental to highly aromatic epoxies or any chemical that contains unsaturated chemical bonds since these parts of a molecule are strong UV absorbents.

Cycloaliphatic epoxy resins are characterized by mostly saturated chemical structures and lack of benzene rings in their backbones. For this reason they are a material of choice for electronic applications or those requiring operation in sunlight. It was concluded that a cycloaliphatic epoxy resin would be a more suitable material for ultra-thin CFRP masts given their operating environment. Therefore, an attempt was made to find a commercially available cycloaliphatic epoxy resin system with embedded silicon. Such a product, which is a combination of aliphatic epoxy and alkoxy silicone resin cured with amino alkoxy silane is offered by Evonik TEGO (Germany). According to the manufacturer this resin’s primary application is a coating for structures subjected to demanding environments involving salt water, sunlight or organic fouling on the outer surfaces.

An attempt was made to use the silicone/epoxy coating on a cured BRC, however given the curved geometry of this structure it was difficult to apply the coating uniformly. A second attempt was then made to manufacture the structure from a liquid resin, as described in Section 3.1.1. Both attempts were done during the same visit to the industrial partner’s manufacturing site, and the same kind of challenge with using liquid resins to manufacture a BRC structure was faced. Given that it was not possible to obtain a pre-braided carbon fibre fabric with a required varied angle at that time, the fabrication approach had to be changed.

The nature of shortwave UV radiation (UV-C) is such that it does not penetrate far within the material. AO only reacts with atoms on the surface, therefore it was suggested to only coat the outer layers of the structure with the cycloaliphatic silicone/epoxy resin. The aromatic MTM44-1 epoxy resin film (the base material) would be used only in the core of the structure and the outer surfaces would be
impregnated with the cycloaliphatic, siliconized epoxy. The coating and core resin systems would then be cured together on a cylindrical heating former.

This new technique is beneficial due to several factors:

- The manufacturing technique is not significantly changed, which is of benefit for the industrial partner who did not have to invest in equipment required for using liquid resin techniques such as moulds, vacuum bags and pumps among others.

- The outer layers of the structure are covered using siliconized cycloaliphatic epoxy and then the laminate is cured which means that the final product is manufactured in a single step. This is different to other protection techniques such as aluminizing that require additional surface cleaning preparation and collaboration with another industrial partner, generating additional cost.

- It is expected that the interface between the core epoxy resin and the modified surface will be stronger given that both materials are chemically similar. Stronger chemical bonds can be created between two polymer-based resins than a resin and a metallic coating.

A CFRP structure with silicone/epoxy cycloaliphatic resin as a coating was manufactured, however, after this modification a significant change in bistable behaviour was observed. It became apparent that the mechanical properties of the coating resin influence the structural parameters of the whole boom because the structure is so thin. After the modification, booms lost their bistable and deployment behaviour. Instead of a rapid snap from the coiled to extended configurations, the structure exhibited neutrally-stable behaviour which means that it is stable in every point between the coil and unfurled boom. Such behaviour was observed by Schultz et al. (2008) and was attributed to the resin stiffness. It became clear that due to the high silicon content in the coating resin, the CFRP structure was too flexible, which significantly reduced the boom stiffness. Although such behaviour can be advantageous for some applications, it was of concern that in case of long, extendible CFRP masts it would contribute to the structure buckling. Another concern with silicone/epoxy resin is that it is a room temperature curing system and the core resin requires elevated temperatures to achieve the appropriate level of crosslinking (up to 180 °C). It was of concern that this mismatch could cause deterioration of properties in the coating resin. This being the case, it was decided to seek another material, with higher mechanical properties and a more similar curing temperature regime to the core aromatic epoxy resin film.
3.1.3 Cycloaliphatic epoxy resin cured with amine

As already mentioned, cycloaliphatic epoxy resins offer enhanced UV stability due to their higher saturation and fewer UV absorption centres within a molecule. In order to further improve the UV stability it was decided to cure the cycloaliphatic epoxy in a non-standard way by using an amine hardener. The selected type was a cycloaliphatic amine recognised under a trade name Aradur 2954 and the selected type of cycloaliphatic epoxy was a bis-(epoxycyclohexyl)-methylcarboxylate recognised under the trade name CY 179, denoted further as CY-1. Both components were supplied by Huntsman Advanced Materials (Netherlands).

These two parts show lower chemical affinity, however, previous studies by González et al. (2011) show that cycloaliphatic epoxy can be cured with an amine, especially in high temperature regimes. However, the curing studies with DSC presented in Section 4.2.10, revealed that the developed system showed a non-standard curing behaviour and decomposition before the curing completed. Also, the CY-1/Amine resin system showed two distinctive, rather low T_g temperatures, which was interpreted as phase separation and problems with miscibility. For this reason the cycloaliphatic epoxy was changed for a CY 184 (cyclohexane-1,2-dicarboxylate, denoted further as CY-2) type which showed better compatibility with the amine hardener.

It was expected that the amine/cycloaliphatic blend would show better UV stability, which was indeed confirmed by lower mass loss in a UV-C radiation test. The results are presented in Section 5.8. Additionally, thermosets with a lower T_g might be a more suitable choice for applications involving thermal cycling. A lower T_g indicates a lower level of crosslinking which means that the polymeric chains can move more freely above the T_g which could prevent crack formation and resin embrittlement.

3.1.4 Cycloaliphatic epoxy resin cured with anhydride

Later it was also decided to evaluate the influence of nanoadditives on anhydride cured CY-1 epoxy resin systems. Anhydride cured epoxies show a much higher T_g and are more similar to the aromatic epoxy than the amine-cured one, which might make this resin system more appropriate for space applications. A comparative study of amine versus anhydride cycloaliphatic epoxy resins reinforced with three different types of nanoparticles: mono-POSS, octa-POSS and nanosilica is presented in Section 5.

Anhydrides are high temperature curing agents which do not react with epoxy resins at room temperature. The presence of a catalyst is required to aid fast curing of anhydride epoxies at elevated temperatures (usually in the range of 160-180 °C). Another advantage of anhydride hardeners is their lower viscosity and longer pot life, which should aid in nanoparticle dispersion and produce less shrinkage than amine
hardeners, which is expected to contribute to a smoother surface finish.

3.1.5 Cycloaliphatic epoxy resins with POSS

Polyhedral oligomeric silsesquioxanes (POSS) are a relatively new kind of additive, and are a very promising material for modification of epoxy resins for space applications for several reasons:

- POSS is commercially available in a variety of forms. Different types of chemical moieties can be selected to increase epoxy resin/POSS compatibility and facilitate the miscibility between epoxy and nanoparticles.

- POSS covalently bonds to an epoxy matrix in the formation of a new structure with a new set of properties. Cycloaliphatic epoxies (due to the lack of rigid benzene rings) exhibit lower thermal and mechanical properties than aromatic epoxies. Improvement in thermal-mechanical parameters of cycloaliphatic epoxy resin can be achieved by addition of POSS. This assumption was tested in Chapter 6.

- Under AO attack POSS undergoes cage opening and recombination with oxygen into a silica-like protecting layer. This statement is backed by the previous research and confirmed in Section 7.3.

Mono-functional POSS

Due to its relatively infrequent use in commercial applications, POSS is an expensive reagent. Although Hybrid Plastics, one of the leading POSS manufacturers worldwide, has an extensive number of POSS varieties in their portfolio, less popular varieties and customization of POSS reactive sides is very costly.

The first type of POSS used in this study was a mono-functional amino- or epoxy-terminated POSS, aminopropylisobutyl POSS (Figure 3.2A) and epoxycyclohexyllsobutyl (Figure 3.2B), respectively. This material was used by Hamerton et al. (2015) in the Department of Chemistry, University of Surrey for studies on reduction in water uptake in POSS/epoxy nanocomposites.

After initial studies presented in Section 4.1, it became apparent that mono-functional POSS would be difficult to disperse in the epoxy matrix. For this reason it was decided to blend mono-functional POSS with polydimethylsiloxane (PDMS) in equal ratios prior to addition to the cycloaliphatic epoxy in order to obtain a better level of dispersion.
3.2. Fabrication procedure of ultra-thin CFRP mast with surface protection

Octa-functional POSS

Octa-functional POSS has eight reactive groups, one at each vertex. Because of its enhanced reactivity, this type of POSS shows better miscibility with epoxy resins. It is also a viscous liquid rather than a powder, which makes it easier to mix with liquid epoxies. For this study, the selected type of octa-POSS was a glycidyl POSS (Figure 3.2C) terminated with eight epoxide groups.

3.1.6 Other silicon derivatives

Another silicone derivative used in this study was a 10-20 nm silicone dioxide nanopowder used similarly to POSS, supplied by Sigma Aldrich (USA). Nanosilica was used as a more affordable nano-modifier for cycloaliphatic epoxies.

Amino-terminated PDMS was supplied in a liquid form also by Sigma-Aldrich and used in combination with POSS as a dispersion agent.

3.2 Fabrication procedure of ultra-thin CFRP mast with surface protection

In this section, a manufacturing procedure of an ultra-thin epoxy resin based CFRP structure is presented. The fabrication procedure is based on the materials and methods developed for long deployable CFRP masts (Fernandez et al., 2014; Hillebrandt et al., 2014), such as those used in CubeSail (Lappas et al., 2011), InflateSail (Viquerat et al., 2016) and the RemoveDebris mission (Forshaw et al., 2016), with novel modifications that are aimed at advancement of LEO environment resistance.

In order to achieve better LEO resistance, outer layers of the composite were replaced with cycloaliphatic epoxy resin reinforced with silicon nanoparticles. The novelty of the developed resin blend lies in its enhanced UV stability due to the lower UV absorption of cycloaliphatic epoxies and the UV-blocking effects of silicon nanoparticles.

Figure 3.2: Three types of POSS nanoparticles used in this study: (A) amino-POSS, (B) epoxy-POSS, (C) octa-POSS.
nanoparticles, and the protection against AO and thermal extremes that some types of POSS nanoparticles (such as octa-POSS) also offer.

Figure 3.3 shows the schematic of the ultra-thin CFRP structure. Layup A presents the original structure developed in the earlier stages of this project while Layup B presents the structure with developments introduced by the author. The main difference between the two is that the outer layers of the base structure are replaced by siliconized, cycloaliphatic epoxy resin.

### 3.2.1 Stages of manufacturing

The fabrication procedure is presented in Figure 3.4 and includes the following main steps:

1. Preparing a wooden former covered in PTFE sleeve which is used as a carbon fibre braid support (Figure 3.4a).

2. Draping the CF braid over a wooden plate of the required width (Figure 3.4b). Different widths of the former may be used to obtained varied coiled diameters of the BRC structure.

3. Cutting the CF braid in half (Figure 3.4c) to obtain top and bottom plies of the laminate (Figure 3.4d).

4. Preparing the ply of unidirectional fibres that is used to provide extra torsional stiffness to the structure. The 2.56 cm wide UD tape is manually impregnated with the core aromatic epoxy resin film (Figure 3.4e).

5. CF braid strips cut to size (Figure 3.4d) are impregnated with the core aromatic epoxy resin film (Figure 3.4f).

6. Cycloaliphatic epoxy resin is mixed with nanoparticles (Figure 3.4g).
3.3. Characterization

7. The mixed resin is applied to the outer surfaces of the CFRP structure using standard techniques such as paint brushes (Figure 3.4h) and paint rollers (Figure 3.4i) in order to ensure total surface coverage and good wetting of CF.

8. The structure is covered in a perforated film (Figure 3.4j) and bleed cloth to absorb any resin excess and tightly wrapped on a cylindrical mandrel. The Kapton shrink tape is used to provide pressure and curvature (Figure 3.4k).

9. The final CFRP boom manufactured using the dual epoxy resin system is shown in Figure 3.4l.

Some tests (such as three point bending test or DMTA) require flat samples of rectangular geometry. In order to manufacture such samples, instead of curing the CFRP structures on a cylindrical mandrel under shrink tape, autoclave processing using a vacuum bagging method was implemented. Figure 3.5 shows an author during this manufacturing procedure.

3.3 Characterization

Curing studies DSC was performed on the uncured blends, using a TA Instruments Q1000 running TA Universal Analysis 2000 software, under a 50 ml/min nitrogen flow. Hermetically sealed aluminum pans, containing samples of approximately 6-6.5 mg, were subjected to a heat/cool/heat analysis. First, heating was performed from RT to 300°C at a rate of 20°C per minute to obtain the curing characteristics. A second heat, with the same heating rate was used to determine the glass transition temperature from the midpoint of the curve inflection.

Thermal stability TGA was performed on the cured blends using a TG Instruments Q500. Samples of approximately 8 mg were heated in an open platinum crucible from RT to 850°C with a ramp of 10°C per minute in flowing air or nitrogen at a 60 ml/min rate.

Surface chemistry XPS analyses were performed on a ThermoFisher Scientific Instruments K-Alpha spectrometer, using a monochromated Al Kα X-ray source (hν = 1486.6 eV) on an X-ray spot of ≈400 μm radius. Survey spectra were acquired by employing a Pass Energy of 200 eV. High resolution, core level spectra for all elements were acquired with a Pass Energy of 50 eV. All spectra were charge referenced against the C1s peak at 285 eV to correct for charging effects during acquisition. Quantitative surface chemical analyses were calculated from the high resolution, core level spectra.
3.3. Characterization

(a) PTFE sleeve  
(b) CF braid  
(c) CF braid cut  
(d) Top and bottom braid  
(e) UD impregnation  
(f) Braid impregnation  
(g) Surface resin  
(h) Impregnation  
(i) CF wetting  
(j) Perforated film  
(k) Wrapping  
(l) Final boom

Figure 3.4: Fabrication procedure of the ultra-thin CFRP structure with the developed surface treatment for improved LEO resistance.
following the removal of the non-linear (Shirley) background. The manufacturer’s Avantage software was used to analyse the data.

Contact angle measurement was performed according to the sessile drop method using a KRÜSS Easydrop-DSA20 apparatus and DSA1 dedicated Drop Shape Analysis software. Disposable syringes were used and the drop volume was approximately 1µl.

Surface spectroscopy was measured using Fourier transform Infrared (FTIR) spectroscopy in the Attenuated Total Reflectance (ATR) mode on an Agilent Cary600 spectrometer, 32 scans per sample, at a resolution of 4 cm\(^{-1}\) in absorbance mode. Spectra were acquired in the region 600-3800 cm\(^{-1}\) at room temperature. FTIR spectroscopy in ATR mode is sensitive to crystal contamination which produces negative absorptions in the 500-800 cm\(^{-1}\) wavenrange.

**Thermo-mechanical properties** Dynamic mechanical thermal analysis (DMTA) was performed using the DMA Q800 V7.5 Build 127 apparatus, using 30 × 15 × 0.3 mm rectangular specimens in a single cantilever bending mode. Tanδ was calculated as a function of temperature from 25°C to 230°C, using 5 K/min heating rate at 0.1% strain and 1 Hz frequency.

Flexural tests were carried out using an Instron bending machine in a simply supported mode, with a 10 mm distance between the supports. The sample dimensions were approximately 10 mm wide, 0.3 mm thick.
Surface roughness and morphology  Surface topography was analysed using a Zeiss LSM 700 laser scanning confocal microscope (LSC), and a dedicated ConfoMap Surface Imaging and Analysis Software for ZEISS microscopes. 3D images were produced from the scanned area of approximately $3 \times 3 \text{ mm}^2$, using a $10 \times$ objective. The average surface roughness was calculated from a minimum of 5 scans.

Studies of surface morphology and composition were carried out using a scanning electron microscope (SEM, JEOL 7100 F). Mapping of the silicon distribution over the scanned area was performed using energy dispersive X-ray spectroscopy (EDX) on the same SEM apparatus.
Chapter 4

Screening study of nanoparticle candidates

4.1 POSS/PDMS reinforced aromatic/amine epoxy resin

Modifications of two part epoxy resins with nanoadditives result in materials with a new set of properties that can be either superior or inferior in comparison with the unmodified material. Because of that, the first stage of analysis focused on studies of the compatibility between the epoxy resin system and different types of nanomodifier, and their influence on curing behaviour. The purpose of the nanoparticles is to increase the space adaptability of the epoxy resin, without significant deterioration in the properties (such as thermal and mechanical).

The first approach was to blend an aromatic epoxy resin cured with amine with a mono-functional amino-terminated POSS type, described in more detail in Section 3.1.5 in order to evaluate the dispersion of nanoparticles within the selected epoxy medium. Inspired by the work of Ayandele et al. (2012) and Frank et al. (2012) who concluded that a POSS loading of up to 10 wt% is beneficial for the polymer properties, it was decided to add up to 10 wt% of mono-POSS in three levels: 3, 5 and 10 wt%.

Nanoparticle dispersion within the epoxy after curing was analysed by EDX and the obtained scans are presented in Figure 4.1. It was observed that it was very difficult to achieve a uniform distribution of nanoparticles within the selected epoxy resin medium. It is also apparent that with an increasing POSS content phase separation is more likely to occur (Figure 4.1c). Such results were not considered satisfactory, because it is clear that the agglomeration will decrease the crosslinking density, resulting in an undercured epoxy. Despite implementing mixing techniques such as magnetic stirrers and sonication in an ultrasound bath, the interparticle interactions...
4.1. POSS/PDMS reinforced aromatic/amine epoxy resin

Figure 4.1: Dispersion of the mono-POSS added in 3, 5 and 10 wt% loadings to the aromatic/amine epoxy resin blends.

Figure 4.2: Synthesis route of aromatic epoxy/amine system with silicon additives. Amino-POSS blended with PDMS used as a dispersion factor in equal ratios prior to mixing with cycloaliphatic epoxy or added without PDMS. The ratio between mono-POSS and PDMS varied.

were too strong to overcome by physical means such as mixing. Hence it was decided to undertake another approach, inspired by the work of Florea et al. (2015). In the second trial, amino-terminated polydimethylosiloxane (PDMS) was added as a second reagent to the epoxy resin system, due to its very flexible polymeric backbone it can facilitate the dispersion of mono-POSS by acting as a spacer between POSS cages.

In order to check the effectiveness of PDMS as a dispersion agent, 5 wt% POSS/PDMS blends were prepared with a varying ratio of these two reagents. A schematic of the synthesis route is presented in Figure 4.2. EDX scans which show silicon dispersion are presented in Figure 4.3. It was observed that when POSS and PDMS are blended in the ratio 1:1, the phase separation occurrence is less visible, which is illustrated in Figure 4.3b. Based on the silicon dispersion maps, it was concluded that addition of PDMS is a promising approach to obtaining a more
homogeneous distribution of POSS nanoparticles.

Figure 4.3: Mono-POSS dispersion in aromatic epoxy resin after blending with PDMS in varying ratios.

This visual inspection was followed by the DSC studies which enable better understanding of the influence of additives on the curing behaviours of the epoxy resin blends (Figure 4.4). The aim of performing the DSC study on an uncured, modified epoxy resin blend was to learn about the system reactivity and homogeneity. It was found that increasing the system’s complexity by adding more than one reagent to the epoxy decreases its reactivity. This is confirmed by an increasing exotherm peak area (Figure 4.4a) which indicates a higher heat of cure and consequently that more energy is required to cure all the PDMS containing epoxy resin blends.

The flexible nature of the PDMS polymer could influence the $T_g$ by making the polymer network more loose and easier to flow, consequently decreasing the $T_g$. Figure 4.4b presents the second DSC heat scan which allows visual inspection of the $T_g$ shift. Table 4.1 summarizes the $T_g$ values taken at the midpoint of the glass transition curves. It can be observed that the epoxy blend with only PDMS as a reagent exhibits a lower $T_g$ by only 8°C. On the other hand, blends of both PDMS and POSS show higher $T_g$, because the bulky cages of POSS act like pendants and restrict chain mobility, counteracting the PDMS effect. Overall, it was concluded that addition of
4.2. POSS reinforced cycloaliphatic/amine epoxy resin

Figure 4.4: DSC curves for mono-POSS/PDMS reinforced aromatic/amine epoxy resin.

Table 4.1: Changes in glass transition temperature $T_g$, enthalpy of reaction (H) and surface roughness ($S_a$) for the aromatic epoxy blended with mono-POSS/PDMS reagents in varied ratios.

<table>
<thead>
<tr>
<th>PDMS content [%]</th>
<th>POSS content [%]</th>
<th>$T_g$ [°C]</th>
<th>H [J/g]</th>
<th>$S_a$ [µm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0</td>
<td>104</td>
<td>491</td>
<td>8.60±0.35</td>
</tr>
<tr>
<td>3.75</td>
<td>1.25</td>
<td>111</td>
<td>510</td>
<td>8.53±0.31</td>
</tr>
<tr>
<td>2.5</td>
<td>2.5</td>
<td>110</td>
<td>472</td>
<td>8.70±1.55</td>
</tr>
<tr>
<td>1.25</td>
<td>3.75</td>
<td>112</td>
<td>514</td>
<td>9.68±0.43</td>
</tr>
<tr>
<td>0</td>
<td>5</td>
<td>112</td>
<td>481</td>
<td>10.49±1.08</td>
</tr>
</tbody>
</table>

A small amount of PDMS does not significantly alter the $T_g$, therefore it could be viewed as a promising reagent to aid in mono-POSS dispersion within epoxy resin matrix.

Lastly, the relationship between surface roughness ($S_a$) and POSS content was studied by scanning the modified CFRP surfaces using LSM. Predictably, with increasing POSS content the $S_a$ also increases. However, the addition of PDMS decreases the surface roughness. It is desirable to minimize the $S_a$ in order to make the surface area smaller and therefore less prone to reactions in LEO with bombarding AO or various forms of radiation.

4.2 POSS reinforced cycloaliphatic/amine epoxy resin

After the initial studies of POSS dispersion within the aromatic epoxy resin blends and the nanoparticles’ effects on their curing behaviour, it was observed that monofunctional POSS is difficult to disperse within the aromatic epoxy resin. However, blending it with PDMS in equal ratios was found to improve the homogeneity of the
system. Following on from this work, it was decided to test whether the same kind of behaviour would also be observed in the cycloaliphatic type of epoxy resin.

It was decided to cure the cycloaliphatic epoxy with an amine hardener instead of a standard anhydride to further reduce the aromatic content within the polymer, which is supposed to further increase the UV resistance of this epoxy type. Following a similar approach to that presented in the previous Section (4.1), inorganic modification of 5 wt% POSS or a combination of POSS with PDMS (Figure 4.5) was performed.

Several types of POSS, from hundreds available commercially, had been considered as modifiers for the cycloaliphatic epoxy resins in order to improve their environmental resistance in LEO. The selected types are characterized by their chemical similarity with epoxy resins since they contain either amine or epoxide reactive groups.

The approach undertaken was to prepare a POSS or POSS/PDMS cycloaliphatic epoxy resin blend and test the material against some of the most hazardous space-like effects. Based on this screening study, the most promising type of POSS could be chosen. This would narrow down the number of material candidates in order to make it realistic to test them within the allocated time frame of this PhD programme.

4.2.1 Materials used in the screening study

To evaluate the effectiveness of a particular modification on thermal and radiation resistance, samples were exposed separately to shortwave UV radiation, and a temperature of 150°C for 72h in a vacuum chamber.

It was also attempted to simulate the combined effects of UV and thermal cycling, but at the time of testing the facility was not equipped with a heating accessory that could operate in vacuum conditions. Samples were first exposed to UV effects alone, and then moved to the thermal vacuum oven followed by cooling at -18°C. All samples spent 5h in the UV radiation chamber followed by 5h in the thermal chamber and finally 5h in the freezer for a total of three cycles.

Mass loss was recorded before and after the experiment using a four digit precision digital balance. After the exposure, samples were weighed within a maximum of 5 minutes of removing them from the testing facility. A detailed description of the simulation facility is given in Appendix A.

The following CFRP samples manufactured using different types of matrices were included in the study:

- Aromatic epoxy only - resin film used exclusively in the core of the structure and on outer surfaces (described in more detail in Section 3.1.1)
- Cycloaliphatic epoxy cured with amine, denoted further as CY-1/Amine - used
4.2. POSS reinforced cycloaliphatic/amine epoxy resin

Figure 4.5: Synthesis route of cycloaliphatic epoxy/amine system with silicon additives. Amino-POSS blended with PDMS in equal ratios prior to mixing with cycloaliphatic epoxy or added without PDMS as a dispersion factor. In different combinations epoxy-POSS and octa-POSS were used instead of amino-POSS.

- Cycloaliphatic epoxy cured with amine reinforced with 5 wt% of epoxy-POSS, denoted further as CY-1/Amine/epoxy-POSS - used on top and bottom of the structure only (the selected POSS type is described in more detail in Section 3.1.5).

- Cycloaliphatic epoxy cured with amine reinforced with 5 wt% of amino-POSS, denoted further as CY-1/Amine/NH$_2$-POSS - used on top and bottom of the structure only (the selected POSS type is described in more detail in Section 3.1.5).

- Cycloaliphatic epoxy cured with amine reinforced with 2.5 wt% of amino-POSS and 2.5 wt% of amino-PDMS, denoted further as CY-1/Amine/NH$_2$-POSS-PDMS - used on top and bottom of the structure only (the chemical structure of the selected PDMS type is depicted in Figure 4.5).

- Cycloaliphatic epoxy cured with amine reinforced with 5 wt% of octa-POSS, denoted further as CY-1/Amine/octa-POSS - used on top and bottom of the structure only (the selected POSS type is described in more detail in Section 3.1.5).
4.2.2 Thickness measurements

Preserving the small thickness of an ultra-thin CFRP structure is one of the main concerns when modifying them with any kind of surface treatment. The averaged thickness measurements taken with a micrometer of the modified CFRP samples are presented in Table 4.2.

After the application of silicon reinforced cycloaliphatic epoxy, a higher thickness was observed for samples containing NH$_2$-POSS which might imply a tendency to form agglomerates, and that this type of POSS and aliphatic epoxy are not entirely compatible. The POSS molecules are too small to cause any kind of increase in surface thickness, however, in the resin systems with large agglomerations it was observed that the resin was difficult to apply and then flow upon curing, which could be the reason why the overall laminate thickness increased. In general, the proposed surface modification does not significantly increase the thickness and can also be reduced by more controlled resin application techniques.

Table 4.2: Thickness change with application of POSS/cycloaliphatic epoxy protective layer.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Thickness [mm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aromatic epoxy only</td>
<td>0.348±0.02 (original)</td>
</tr>
<tr>
<td>CY-1/Amine/epoxy-POSS</td>
<td>0.350±0.03 (+1%)</td>
</tr>
<tr>
<td>CY-1/Amine/NH$_2$-POSS</td>
<td>0.421±0.04 (+21%)</td>
</tr>
<tr>
<td>CY-1/Amine/NH$_2$-POSS-PDMS</td>
<td>0.374±0.02 (+7%)</td>
</tr>
<tr>
<td>CY-1/Amine/octa-POSS</td>
<td>0.358±0.02 (+3%)</td>
</tr>
</tbody>
</table>

4.2.3 Moisture absorption

Moisture absorbed during the pre-launch period will remain in the matrix until the structure is deployed in the space environment, and even if the effects are limited by storing samples in clean rooms, they cannot be completely avoided. Upon deploying the structures in orbit, the dramatic reduction in atmospheric pressure may cause a violent removal of molecular water absorbed in the matrix, leading to delamination or small vibrations in rigid boom structures. For this reason, it is essential to reduce the water uptake of epoxy resins and based on the previous research it is understood that POSS is a suitable reagent for this purpose (Hamerton et al., 2015).

In order to evaluate the moisture absorption of POSS modified epoxy resins, samples were immersed in distilled water for 72h. After removing the excess water with an absorbent, the samples were weighed and compared to their initial mass. The results are presented in Table 4.3.

It can be observed that all samples gained approximately 1% of mass during the
Table 4.3: Changes in moisture absorption with application of POSS/cycloaliphatic epoxy protective layer.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mass change [%]</th>
<th>Mass % of aromatic epoxy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aromatic epoxy only</td>
<td>+0.98</td>
<td>reference point</td>
</tr>
<tr>
<td>CY-1/Amine/epoxy-POSS</td>
<td>+1.12</td>
<td>+13%</td>
</tr>
<tr>
<td>CY-1/Amine/NH₂-POSS</td>
<td>+0.83</td>
<td>-16%</td>
</tr>
<tr>
<td>CY-1/Amine/NH₂-POSS-PDMS</td>
<td>+0.92</td>
<td>-7%</td>
</tr>
<tr>
<td>CY-1/Amine/octa-POSS</td>
<td>+0.83</td>
<td>-15%</td>
</tr>
</tbody>
</table>

immersion study. A slightly higher mass gain was observed in case of the epoxy-POSS modified cycloaliphatic epoxy which is probably due to the poor material quality. In all other cases the moisture absorption was decreased, with a maximum of 16% for the CY-1/Amine/NH₂-POSS configuration.

4.2.4 Thermal stability - TGA

Aromatic epoxies are characterized by high thermal stability, which is directly related to the presence of large benzene rings that require more thermal energy to break. The absence of these structures in aliphatic polymers makes them less stable, which can be clearly observed from the TGA curves (Figure 4.6).

![TGA curves comparing thermal stability of aromatic epoxy resin versus epoxy-POSS reinforced cycloaliphatic/amine epoxy in air.](image)

Figure 4.6: TGA curves comparing thermal stability of aromatic epoxy resin versus epoxy-POSS reinforced cycloaliphatic/amine epoxy in air.

Table 4.4 presents a comparison of thermal-degradation values for an aromatic versus epoxy-POSS reinforced cycloaliphatic resin, which indicates that the aromatic epoxy can be safely used up to 300°C whereas the aliphatic one should only be used up to 190°C. The temperature profiles in LEO should not exceed 150°C therefore both resin systems are suitable. However, for spacecraft facing the Sun at all times or
in case of any unexpected solar activity thermal stability must be ensured and silicon
derivatives have been proved to be beneficial for thermal-stability purposes (Chruściciel
and Leśniak, 2014).

Table 4.4: TGA data comparing thermal stability of aromatic epoxy with epoxy-POSS
reinforced cycloaliphatic epoxy resin.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_{d5%}$ [°C]</th>
<th>$T_{d150^\circ C}$ [%]</th>
<th>$T_{d300^\circ C}$ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aromatic epoxy only</td>
<td>320</td>
<td>0.36</td>
<td>3.75</td>
</tr>
<tr>
<td>CY-1/Amine/epoxy-POSS</td>
<td>190</td>
<td>1.22</td>
<td>20.16</td>
</tr>
</tbody>
</table>

Silicones typically exhibit high thermal stability which is directly related to the
high dissociation energy of the Si-O bond. By introducing these strong bonds to
the structure of a weaker aliphatic epoxy/amine system, the thermal stability can be
improved. It is beneficial for both thermal stability and UV resistance to strengthen
the polymer with silicon containing bonds because by applying the siliconized layer
of epoxy, the weaker bonds such as C-O and C-N are shielded from direct exposure
to sunlight, which is expected to increase the structure’s survivability.

Nevertheless, thermal stability can be decreased by nanoparticles if the type of
modifier used is not entirely compatible with the epoxy system and hinders crosslink-
ing reactions. Silicon rich regions block the reactive epoxide and amino groups from
each other, and consequently these unreacted monomers can be released more easily
as volatiles due to thermal exposure. Table 4.5 presents the mass loss of the cy-
cloaliphatic epoxy resin cured with amine and reinforced with different types of POSS.
From the selected types of POSS, it was observed that only the octa-functional vari-
ant actually improved the thermal stability of the cycloaliphatic epoxy/amine system.
On the other hand, samples containing the mono-POSS types showed lower thermal
stability than the untreated cycloaliphatic/amine epoxy. It was observed that in-
creasing the resin system complexity by adding both NH$_2$-POSS and NH$_2$-PDMS
results in the lowest thermal performance which is probably attributable to reduced
crosslinking density.

Table 4.5: Thermal stability of the POSS/cycloaliphatic epoxy protective layer after
storage at 150° for 72h.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mass loss [%]</th>
<th>Mass % of original</th>
<th>Mass % of aromatic epoxy (reference point)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CY-1/Amine</td>
<td>1.91</td>
<td>original</td>
<td>-85%</td>
</tr>
<tr>
<td>CY-1/Amine/epoxy-POSS</td>
<td>2.11</td>
<td>-10%</td>
<td>-104%</td>
</tr>
<tr>
<td>CY-1/Amine/NH$_2$-POSS</td>
<td>3.14</td>
<td>-65%</td>
<td>-204%</td>
</tr>
<tr>
<td>CY-1/Amine/NH$_2$-POSS-PDMS</td>
<td>3.39</td>
<td>-78%</td>
<td>-230%</td>
</tr>
<tr>
<td>CY-1/Amine/octa-POSS</td>
<td>1.20</td>
<td>+37%</td>
<td>-16%</td>
</tr>
</tbody>
</table>
4.2.5 Mass loss due to UV radiation

The cycloaliphatic epoxy resin system selected for the surface coating is less thermally stable than the aromatic system as presented in Section 4.2.4. Coincidentally, it shows greater resistance to UV degradation due to a lower number of chromophores (the principal centres of UV absorption) present within the molecules. To confirm this assumption for the selected candidate materials, all samples were exposed to UV-C radiation. Table 4.6 presents the recorded mass changes.

It can be observed that the aromatic epoxy lost 16% more mass on average due to UV radiation than the aliphatic one. A significant loss was recorded for the sample modified with NH$_2$-POSS, however, other types of POSS had a positive effect on improving UV resistance. The lower mass loss was recorded for cycloaliphatic epoxy reinforced with POSS than in the case of the unmodified cycloaliphatic epoxy which indicates that POSS also contributes to combating the UV induced degradation by acting as a UV scattering agent.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mass loss [%]</th>
<th>Mass % of original</th>
<th>Mass % of aromatic epoxy</th>
</tr>
</thead>
<tbody>
<tr>
<td>CY-1/Amine</td>
<td>0.1520</td>
<td>original</td>
<td>+16%</td>
</tr>
<tr>
<td>CY-1/Amine/epoxy-POSS</td>
<td>0.0979</td>
<td>+35%</td>
<td>+46%</td>
</tr>
<tr>
<td>CY-1/Amine/NH$_2$-POSS</td>
<td>0.2732</td>
<td>-80%</td>
<td>-52%</td>
</tr>
<tr>
<td>CY-1/Amine/NH$_2$-POSS-PDMS</td>
<td>0.1129</td>
<td>+25%</td>
<td>+37%</td>
</tr>
<tr>
<td>CY-1/Amine/octa-POSS</td>
<td>0.1477</td>
<td>+3%</td>
<td>+18%</td>
</tr>
</tbody>
</table>

4.2.6 Superposition of the effects of temperature and UV

Figure 4.7 presents the mass loss due to UV and temperature effects acting separately, and to the combination of them acting sequentially. It can be observed that the exposure for the same time period to temperature caused more significant degradation than the exposure to UV radiation alone in all samples. For the case of exposing materials to the combination of effects, samples spent approximately half the time in the oven and the other half in the radiation chamber. Because of this the recorded mass loss is lower than in case of temperature only exposure, however, the same trend is observed in all configurations - the materials with the greatest recorded mass loss contained the NH$_2$-POSS. From the mono-functional POSS types, epoxy-POSS demonstrates a significantly higher compatibility with the cycloaliphatic/amine epoxy resin compared to amino-POSS, yet the octa-functional POSS shows the best performance from all tested samples, especially with regard to improvement in thermal stability.
4.2. POSS reinforced cycloaliphatic/amine epoxy resin

Figure 4.7: Mass loss induced by separate environmental effects: UV radiation (UV), thermal cycling (TC) and both effects combined (TC+UV).

4.2.7 Surface topography and morphology - LSM/EDX

During the course of the analysis, it was discovered that the original samples developed in the previous stages of this project have very rough surfaces. The selected ultra-thin epoxy film does not seem to cover the carbon fibre braid, even after applying double layers, which can be observed in Figure 4.8A. However, the application of the surface protection epoxy in a liquid form caused dramatic reductions in surface roughness from 83.4 µm to 8.08 µm (4.8B).

Low surface roughness is beneficial for space applications. A positive correlation between surface roughness and surface active area exists which increases the probability of reactions between the surface and the incoming photons or energetic particles impinging on a material in LEO. It can be observed in Table 4.7 that on average, addition of nanoparticles to the hosting CY-1/Amine epoxy resin only increases the $S_a$ value by $\approx 5\%$, and again PDMS tends to lower the surface roughness.

Table 4.7: Changes in the average surface roughness after applying the POSS/cycloaliphatic epoxy resin protective layer.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Average surface roughness [$\mu$m]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CY-1/Amine</td>
<td>9.45±0.7</td>
</tr>
<tr>
<td>CY-1/Amine/NH$_2$-POSS</td>
<td>10.58±0.9</td>
</tr>
<tr>
<td>CY-1/Amine/NH$_2$-POSS-PDMS</td>
<td>9.09±1.1</td>
</tr>
<tr>
<td>CY-1/Amine/octa-POSS</td>
<td>10.14±1.2</td>
</tr>
</tbody>
</table>

In order to evaluate how silicon is distributed in the CFRP samples coated with POSS reinforced cycloaliphatic epoxy layer, EDX mapping of the cross-section was
4.2. POSS reinforced cycloaliphatic/amine epoxy resin

Figure 4.8: Surface topography by laser scanning microscopy, aromatic epoxy resin CFRP structure without surface modification (A), the same structure coated with POSS reinforced cycloaliphatic epoxy resin (B).

performed (Figure 4.9). It can clearly be observed that silicon is present on the CFRP surface, and that the thickness of this protective layer is approximately 10 µm. Given that UV-C (the most damaging portion of the UV radiation) only affects the surface of polymeric materials (Dever et al., 2012), the protective layer is expected to be a sufficient protection strategy against UV radiation.

Figure 4.9: EDX spectroscopy mapping of the CFRP cross-section. Distribution of elements: carbon, oxygen and silicon in the CFRP structure covered with the POSS/cycloaliphatic epoxy protective layer.
4.2.8 Surface composition - XPS

Surface composition of the candidate materials was evaluated by XPS analysis which provides the surface composition of elements in a layer 5-10 nm from the surface. This method is very sensitive to contamination, therefore the results must be carefully analysed. The obtained data is presented in Table 4.8.

Table 4.8: Surface elemental composition [at.\%] by XPS studies for POSS reinforced cycloaliphatic/amine epoxy resins versus aromatic epoxy used for reference.

<table>
<thead>
<tr>
<th>Sample</th>
<th>C1s</th>
<th>F1s</th>
<th>N1s</th>
<th>O1s</th>
<th>Si2p</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aromatic epoxy only</td>
<td>64</td>
<td>27</td>
<td>2</td>
<td>6</td>
<td>TRAC.</td>
</tr>
<tr>
<td>CY-1/Amine</td>
<td>74</td>
<td>12</td>
<td>3</td>
<td>10</td>
<td>TRAC.</td>
</tr>
<tr>
<td>CY-1/Amine/epoxy-POSS</td>
<td>65</td>
<td>3</td>
<td>2</td>
<td>21</td>
<td>10</td>
</tr>
<tr>
<td>CY-1/Amine/NH\textsubscript{2}-POSS</td>
<td>67</td>
<td>9</td>
<td>3</td>
<td>16</td>
<td>5</td>
</tr>
<tr>
<td>CY-1/Amine/NH\textsubscript{2}-POSS-PDMS</td>
<td>64</td>
<td>0</td>
<td>1</td>
<td>23</td>
<td>12</td>
</tr>
<tr>
<td>CY-1/Amine/octa-POSS</td>
<td>66</td>
<td>7</td>
<td>2</td>
<td>17</td>
<td>7</td>
</tr>
</tbody>
</table>

TRAC. - traceable amount

Firstly, one may observe the presence of fluorine in almost all samples, which is a contamination that originates from using PTFE sheets in the manufacturing process as a release film. In order to remove this contamination either a different release film material should be used or surfaces could be cleaned prior to impregnation of the outer epoxy, for example with light argon sputtering plasma. The former would require changing the manufacturing method and the thesis author only discovered the latter in the later stages of her research.

Carbon and nitrogen contents are similar in all POSS reinforced cycloaliphatic epoxy samples. From the point of view of this project, the silicon content on the surface is the most interesting parameter. It is of interest to create a silicon rich surface because Si-containing bonds have a higher dissociation energies than their carbon equivalents. By shielding the C-bonds with Si-bonds, it is expected to enhance surface resistance to degradation by atomic oxygen or energetic photons. In non-modified aromatic and cycloaliphatic epoxies silicon is predictably not present on the surfaces. In the case of modified samples, the most silicon abundant is the NH\textsubscript{2}-POSS-PDMS containing one. It is difficult to analyse the data for mono-functional POSS types because they tend to form agglomerates, therefore the scan areas might not be representative of the whole surface. Octa-POSS reinforced epoxy shows a relatively silicon-rich surface of 7 at.\%.
4.2.9 Relationship between surface properties and degree of degradation

The mass loss caused by UV radiation can be correlated with surface properties, such as roughness (Figure 4.10, right), and the elemental content of silicon/oxygen (Figure 4.10, left). A positive correlation between increasing surface roughness and mass loss (correlation coefficient = 0.87) can be observed. This can be explained by the fact that the higher surface roughness indicates greater active surface area that can react with incoming photons or energetic particles, and consequently leads to an increase in erosion yield and mass loss.

It may be stated that lower surface roughness is also associated with the resin system reactivity. Octa-functional POSS produced an average surface roughness value of 10.14 µm, and an even lower value was obtained for a sample of NH₂-POSS-PDMS, where highly flexible PDMS chains help with smoothing the surface (Table 4.9). A 16% (10.58 µm) higher value was observed for the system containing only NH₂-POSS, which resulted in an increase in mass loss of 2.5 times.

![Figure 4.10: Mass loss change due to UV radiation in a function of Si/O surface content (left) and surface roughness (right).](image)

![Table 4.9: Mass loss change due to UV radiation compared with the Si/O surface content and surface roughness (Sₘ).](table)

<table>
<thead>
<tr>
<th>Sample: Cy-1/Amine +NH₂-POSS</th>
<th>epoxy-POSS</th>
<th>octa-POSS</th>
<th>NH₂-POSS-PDMS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sₘ</td>
<td>10.58</td>
<td>11.45</td>
<td>10.14</td>
</tr>
<tr>
<td>Si/O</td>
<td>21.45</td>
<td>30.09</td>
<td>24.72</td>
</tr>
<tr>
<td>% mass loss</td>
<td>0.27</td>
<td>0.1</td>
<td>0.15</td>
</tr>
</tbody>
</table>
Additionally, a negative correlation between the surface content of silicon and oxygen was discovered (correlation coefficient = -0.86, Figure 4.10, left). The lowest value of mass loss was recorded for a resin system containing epoxy-POSS with a combined percentage of silicon and oxygen elements of 30.9%. This is probably due to agglomeration which scattered a significant portion of the UV radiation. Samples with a Si/O content below 25% showed significantly higher mass loss than those with a Si/O content above 30%. Since Si-O bonds are stronger than C-O or C-N bonds that primarily build the structure of the cycloaliphatic epoxy/amine system, it is beneficial for reducing the erosion yield to shield the weaker bonds with the stronger ones and select the types of POSS which tend to migrate towards the surfaces.

4.2.10 Curing studies - DSC

Glass transition temperature is one of the most relevant parameters for thermoset polymers as it indicates the transition from solid and brittle to a more rubbery material. In thermoset polymers this transition is not as clear as in thermoplastics, because the crosslinked polymers do not melt and the molecules are locked in relatively fixed positions. There is a positive correlation between the extent of crosslinking and the $T_g$ because if the molecule movements are restricted by the presence of crosslinks, greater energy is required to cause their movement and consequently the $T_g$ is observed in a higher temperature regime.

Examination of $T_g$ is therefore an useful method to evaluate the crosslinking dentistry in a polymer. It is understood that higher crosslinking density means a higher level of arrangement in the polymer and therefore presumably a better resistance to environmental damage. However, highly crosslinked polymers are brittle and stiff, which is not always beneficial for applications requiring flexibility such as deployable structures.

In this screening study $T_g$ was evaluated in three modes, firstly by curing the liquid epoxy in the DSC pans, and secondly by testing already cured resins. In the second configuration samples are further subdivided into those cured with a maximum speed of 20°C/min (denoted as cured) and those cured with a heating ramp of 3°C/min (denoted as cured with ramp). The obtained data is presented in Table 4.10.

Table 4.10: Glass transition temperature [°C] of the CY-1/Amine/mono-POSS resin systems.

<table>
<thead>
<tr>
<th>Sample:</th>
<th>$T_g$ (uncured)</th>
<th>$T_g$ (cured)</th>
<th>$T_g$ (cured with ramp)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CY-1/Amine:</td>
<td>75</td>
<td>56, 79</td>
<td>71</td>
</tr>
<tr>
<td>CY-1/Amine/NH$_2$-POSS:</td>
<td>89</td>
<td>67</td>
<td>74, 93</td>
</tr>
<tr>
<td>CY-1/Amine/NH$_2$-POSS-PDMS:</td>
<td>76</td>
<td>74</td>
<td>76</td>
</tr>
<tr>
<td>CY-1/Amine/octa-POSS:</td>
<td>56</td>
<td>83</td>
<td>93</td>
</tr>
</tbody>
</table>
In the case of the cycloaliphatic/amine epoxy resin system, \(T_g\) (taken as a mid-point of the glass transition curve) is observed in the range of 70-80°C. This would imply that this is a lightly crosslinked resin system. The addition of POSS into this resin blend may influence the \(T_g\) in two ways: either it can decrease it by increasing the volume between polymer chains (making the resin flow more easily) or it can increase it by expanding the crosslinking density or acting as a fish-hook that reduces the epoxy mobility. The former is observed in the case of rapidly curing the octa-POSS modified sample and the latter in the \(\text{NH}_2\)-POSS containing one. However, when cured samples were tested, lower \(T_g\) was observed in the mono-POSS sample, which is probably due to phase separation. Allowing the resins time to cure by heating them with a ramp resulted in elevated \(T_g\) for the samples reinforced with octa-POSS. Occasionally, a double \(T_g\) was observed which indicated phase separation and problems with miscibility between POSS and the hosting epoxy resin. From the obtained DSC data it might be deducted that PDMS is a good dispersion agent, since \(T_g\) is almost identical in all cases. Epoxy-POSS reagent was not available at the time of running this study therefore it was not included in the analysis.

From the DSC data (Figure 4.11), it can be learnt that the CY-1/Amine resin system is not entirely compatible. The reason for this is the asymmetric exothermic peak, which indicates that the enthalpy of vaporization (represented by an endothermic peak) is included in the exothermic peak causing its asymmetry. Therefore it can be concluded that the resin system decomposes before it is fully cured. The complimentary TGA data (Table 4.11) confirms that this resin system is not stable up to 300°C.

Because of the relatively low \(T_g\) of the CY-1/Amine resin system, and a non-
standard curing behaviour it was decided to select a different type of cycloaliphatic epoxy to cure with this type of amine. The second selected epoxy is described in Section 3.1.3 and denoted as CY-2. A DSC curve for the new CY-2/Amine epoxy resin blend is presented in Figure 4.12. This resin system exhibits a $T_g$ between 80-100°C while cured in the DSC pan, which is much greater than the previously tested CY-1 containing epoxy and also the exothermic peak returns to the baseline indicating the completion of curing reaction (Figure 4.12).

![DSC curves of the CY-2/Amine cycloaliphatic epoxy resin.](image)

Figure 4.12: DSC curves of the CY-2/Amine cycloaliphatic epoxy resin.

### 4.2.11 Curing agent influence on thermal-stability - TGA

It has been shown in the previous section that changing the type of cycloaliphatic epoxy to blend with an amine from CY-1 type to CY-2 type had a profound effect on the curing behaviour and the glass transition temperature. It was also suspected that the resin/curing agent combination will influence the thermal stability. TGA analysis was performed to confirm this (Figure 4.13) on CY-1/Amine, CY-2/Amine and CY-1/Anhydride samples reinforced with 10 wt% of octa-POSS.

It was decided to include an anhydride cured epoxy resin system in the analysis because they typically have higher thermal stability than the corresponding amine cured blends. It can be observed in Table 4.13 that changing the type of cycloaliphatic epoxy from CY-1 to CY-2 in the amine cured system shifts the $T_{d5\%}$ from 249°C to 261°C, but then the degradation progresses at a faster rate, reaching 10% ($T_{d10\%}$) loss 20°C earlier. The thermal-degradation mechanism differs significantly between the amine- and anhydride cured resins, where in the former one can observe three degradation steps in contrast to a single step in the latter.
4.2. POSS reinforced cycloaliphatic/amine epoxy resin

Figure 4.13: TGA curves indicating thermal stability of octa-POSS reinforced cycloaliphatic epoxy based on curing either with amine or anhydride as a hardener.

Table 4.11: TGA results for cycloaliphatic epoxy hybrid systems cured with anhydride or diamine reinforced with 10 wt% of octa-POSS.

<table>
<thead>
<tr>
<th></th>
<th>CY-1/Diamine</th>
<th>CY-2/Diamine</th>
<th>CY-1/Anhydride</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_{d5%}$ [°C]</td>
<td>249</td>
<td>261</td>
<td>296</td>
</tr>
<tr>
<td>$T_{d10%}$ [°C]</td>
<td>303</td>
<td>282</td>
<td>317</td>
</tr>
<tr>
<td>Mass loss at 150°C [%]</td>
<td>1.1</td>
<td>1.1</td>
<td>0.9</td>
</tr>
<tr>
<td>Mass loss at 300°C [%]</td>
<td>10</td>
<td>17</td>
<td>6</td>
</tr>
<tr>
<td>$T_{onset}$ [°C]</td>
<td>252</td>
<td>270</td>
<td>302</td>
</tr>
</tbody>
</table>

4.2.12 Resistance to corrosion by atomic oxygen

The first study on resistance of the ultra-thin CFRP structures was performed by exposing samples to an RF oxygen plasma source for 2h, at a flow speed of 15 sccm (3 sccm oxygen, 12 sccm argon) and RF power of 200 W. The testing facility is described in more detail in Appendix A.4. Based on the mass loss of a reference Kapton sample the AO flux was calculated to be $1.32 \times 10^{16}$ atoms/cm²s.

At the time of running the first AO exposure screening test, due to limited facility availability, only two samples were analysed: one which was a purely aromatic epoxy resin CFRP and another which was impregnated with a siliconized aliphatic epoxy resin surface protective layer (described in more detail in Section 3.1.2). The main goal of this primary test was to verify how the aliphatic epoxy resin type with embedded silicon will respond to the highly oxidative plasma environment.

The comparison between a structure manufactured of a purely aromatic epoxy
4.2. POSS reinforced cycloaliphatic/amine epoxy resin

Figure 4.14: Visual comparison between a purely aromatic CFRP structure (left) and one protected with silicone/epoxy resin (right). Erosion due to AO exposure is clearly observed in the former case while no degradation with was observed in the latter.

and one with a surface protection after AO exposure can be macroscopically observed in Figure 4.14 and microphotographs are presented in Figure 4.15. It is apparent that the purely aromatic epoxy undergoes more profound changes and erodes to a higher extent. A border between the exposed and shielded sides can be seen in Figure 4.15a, while exposed fibres and matrix oxidation are clearly depicted in Figures 4.15b and 4.15c. On the other hand, noticeable changes were not observed in the protected CFRP structures, which suggests that silicon containing aliphatic epoxy resins are an effective strategy for improving AO resistance of organic structures.

Figure 4.15: SEM microphotographs presenting an AO erosion comparison between the purely aromatic (a,b,c) CFRP structure and one with silicone/epoxy resin protection layer (d,e,f).
4.3 Summary of the screening study

The presented screening study tested the response of nanocomposites against some space-like degrading factors, including UV radiation, temperature extremes, and atomic oxygen. Changes in curing behaviour of cycloaliphatic epoxies due to modification with nanoparticles were also tested, together with an evaluation of the surface morphology, composition and nanoparticle dispersion.

Based on the analyses performed it was concluded that:

- Surface modification of ultra-thin CFRP masts with POSS reinforced cycloaliphatic/amine resin is viewed as a promising strategy to extend the useful life of these structures in LEO.

- From the selected candidates of POSS, the octa-functional POSS is the most promising reinforcing agent because it has been shown this it might improve both UV resistance and thermal stability. The primary reason for that being that it disperses well in the epoxy matrix without formation of agglomerates, which does not significantly disturb the epoxy network.

- POSS has a positive effect on reducing moisture absorption of the epoxy matrix.

- Epoxy resin blends with amino-POSS or amino-POSS/PDMS in most cases caused deterioration of properties, therefore it was decided to exclude those modifiers from further analysis.

- It has been discovered that a correlation between surface roughness and Si/O content and mass loss due to UV degradation exists. In general, samples with lower surface roughness and higher Si/O content showed lower mass loss.

- Slow curing enables better blending between epoxy and POSS, which results in higher $T_g$ and consequently higher crosslinking density.

- A curing study revealed that the selected type of amine and cycloaliphatic epoxy are not compatible. This was confirmed by low or double $T_g$ that indicate low crosslinking density and phase separation. Additionally, the asymmetric exothermic peak indicates that the enthalpy of vaporization is included in the enthalpy of curing, therefore the degradation starts before the curing is completed. However, replacing the CY-1 cycloaliphatic resin type with the CY-2 increases the system’s compatibility with amine and results in improved curing behaviour and thermal-stability.

- The siliconized aliphatic epoxy resin system shows much higher AO resistance than a purely aromatic epoxy, indicating that embedding silicone to aliphatic epoxies is an effective protection strategy against AO erosion.
Chapter 5

Resin characterization studies

Based on the screening study presented in the previous chapter, it was decided to reduce the type of nanoparticles considered to just octa-functional POSS, and epoxy-terminated POSS. From an industrial point of view, POSS is not an ideal additive because it is a rather expensive reagent, therefore silica nanoparticles were added as a third type of additive in order to compare this more commercially available material with the new family of POSS reagents.

The purpose of this chapter is to demonstrate the properties of novel nanocomposites based on cycloaliphatic epoxy resin reinforced with silicon-containing nanoparticles. It was decided to compare two very different resin systems, both cycloaliphatic in their chemical nature and reinforced with silicon nanoparticles, but one cured with amine and the other cured with anhydride. The advantages of each are listed in Section 3.1.3 and 3.1.4. This chapter discusses the influence of modification on thermal stability, curing behaviour, morphology, surface chemistry, and topography.

5.1 Materials used in this study

The chemical structures of the cycloaliphatic resin systems with the corresponding curing agents and the nanomodifiers selected based on the screening study are presented in Figure 5.1. Each resin system was modified with 5 wt% of nanoparticles, so a total of six samples were prepared for analysis.

5.2 Curing studies - ATR-FTIR

Figure 5.2 presents the ATR-FTIR spectra of octa-POSS reinforced cycloaliphatic epoxies cured with either anhydride or amine. ATR-FTIR is a useful technique to determine the extent to which the curing reactions had progressed. Some of the most distinctive signs to confirm the progression of crosslinking reactions in the CY-
1/Anhydride/octa-POSS resin system are:

- the decrease in a band at 788 cm\(^{-1}\) associated with the opening of an epoxy group attached to a cyclohexane ring

- the disappearance of bands at 1780 and 1850 cm\(^{-1}\) confirming the reaction between anhydride and epoxy, associated with the asymmetric and symmetric carbonyl stretch of an anhydride ring

- the increase in the absorption region (1100-1300 cm\(^{-1}\)), assigned to coupled ester stretch, which indicates formation of ester linkages between the epoxy and anhydride

In the case of CY-2/Amine/octa-POSS systems the principal signs of a progressing curing reaction are:

- the increase in the hydroxyl stretching band at around 3300-3600 cm\(^{-1}\), which indicates generation of -OH groups following the epoxy ring opening reaction

- the decrease in the epoxy ring breathing band at 915 cm\(^{-1}\)

- the decrease in the 3006 cm\(^{-1}\) band associated with the C-H vibration in the strained, three-membered epoxy ring.

Prior to mixing the epoxy part with the hardener part, the nanomodifiers were pre-mixed with the curing agents because it has been reported in literature (Zucchi et al., 2007) that such premixing can aid in nanoparticles dispersion. To test whether any pre-reactions do indeed occur, additional ATR-FTIR spectra were taken after mixing the nanomodifiers with curing agents, but prior to adding the epoxy component. It was concluded by scan analysis (Figure 5.2, curves number 4) that obvious signs of
pre-reaction were not detected, probably because the nanomodifiers were added in such a small concentration.

The ATR-FTIR spectra also reveal the presence of Si-O-Si inorganic POSS cages in a strong absorption band at around 1085 cm$^{-1}$ in the pure octa-POSS. Due to the fact that POSS is added in low concentrations, its absorption within the final blend is relatively low, however, it is still detectable. Although ATR-FTIR is a surface sensitive method, in order to confirm the silicon presence, the analysis should be complemented by XPS studies, which can provide the information about concentration of elements within 20 nm from the surface.

5.3 Curing studies - DSC

It has already been mentioned that DSC is a useful technique to observe the curing behaviour of a resin (Section 4.2.10). The influence of adding nano-modifiers to cycloaliphatic epoxies was investigated by dynamic DSC and the obtained curves are presented in Figure 5.3. The DSC data that was of particular interest included: changes in maximum polymerization temperature, and the glass transition temperature (determined from the rescan, also known as second heat).

Figure 5.3a presents the first heating DSC scan for the CY-1/Anhydride epoxy resins reinforced with mono-POSS, octa-POSS or nanosilica. It is observed that the material modified with octa-POSS is the most reactive, given the high degree of epoxide functionality. The polymerization reaction starts at a lower temperature, and the maximum peak of the reaction exotherm occurs at 153$^\circ$C which is 7$^\circ$C degrees sooner than the unmodified epoxy. The addition of mono-POSS moves the maximum temperature of polymerization to 172$^\circ$C, which indicates that the polymeric chains are restricted and the modifier hinders the polymerization rate. The effects of nanosilica addition are similar to those of mono-POSS, however, it might be concluded that the polymeric network is less restricted in this case because the polymerization reactions start sooner.

Figure 5.3b presents the curves obtained during the first heating scan for the CY-2/Amine epoxy resins reinforced with either mono-POSS, octa-POSS or nanosilica. As one may observe, changing the configuration of the cycloaliphatic epoxy and replacing the anhydride with an amine dramatically affects the crosslinking behaviour. This is because the maximum polymerization temperature is strongly dependent on the nature of the curing agent and its reactivity towards the epoxy. The modified CY-2/Amine systems behave in the same fashion as CY-1/Anhydride ones. The octa-POSS reinforced epoxy is the most reactive, whereas the one with mono-POSS is the least reactive.

It can be concluded that the shifting of the polymerization temperature into
(a) 1-octa-POSS, 2-CY-1 only, 3-anhydride, 4- anhydride+octa-POSS, 5-CY-1/anhydride/octa-POSS cured

(b) 1-octa-POSS, 2-CY-2 only, 3-amine, 4-amine+octa-POSS, 5-CY-2/amine/octa-POSS cured

Figure 5.2: ATR-FTIR spectra of cycloaliphatic epoxy resin modified with octa-POSS.
a higher temperature regime and a lower heat of reaction is an indication that the added nano-modifier is hindering the crosslinking reactions. This shift is observed particularly in epoxy/nanoparticle blends with a tendency to agglomerate. Additional insight into the resin systems reactivity can be gained by the analysis of the conversion plots presented in Figure 5.4. As can be observed, modification with octa-POSS increases the reactivity of both amine and anhydride cured samples in comparison with the mono-POSS or nanosilica modified ones. The biggest influence of a nanomodifier is observed in the CY-1/Anhydride/octa-POSS and CY-1/Anhydride/mono-POSS samples, as the former apparently achieves full conversion some 42°C sooner than the latter. In the case of the CY-2/Amine system which is less chemically compatible than the CY-1/Anhydride, the addition of any type of POSS slows down the reaction rate.

## 5.4 Glass transition temperature observations - DSC

Looking at the DSC data summarized in the Table 5.1, it is apparent that both the hardener and the modifier influence resin curing characteristics and $T_g$. Glass transition temperature is strongly dependant on the selected hardener type while the nano-modifier only slightly shifts it, depending on whether it acts as a pendant group or a crosslinker.

Mono-functional types of POSS which posses only one reactive site act as a pendant groups, behaving like a "fish-hook" and catching any molecule nearby upon the polymer chains flowing due to elevated temperature. Indeed, both anhydride and amine cured resin systems modified with mono-POSS show a slight increase in the value of $T_g$. On the other hand, octa-POSS modified resins show lower $T_g$, which is caused by the fact that those molecules are bigger, with wide branches which makes
5.4. Glass transition temperature observations - DSC

Figure 5.4: Total conversions vs. temperature for 1-CY-2/Amine/SiO$_2$, 2-CY-1/Anhydride/octa-POSS, 3-CY-2/Amine/octa-POSS, 4-CY-2/Amine/mono-POSS, 5-CY-1/Anhydride/SiO$_2$, 6-CY-1/Anhydride/mono-POSS.

Table 5.1: DSC curves (2nd heat) for cycloaliphatic resin systems cured with anhydride or amine and modified with mono-POSS, octa-POSS or nanosilica.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_g$</th>
<th>$T_{\text{max}}$</th>
<th>$E^{**}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CY-1/Anhydride</td>
<td>197</td>
<td>161</td>
<td>296</td>
</tr>
<tr>
<td>CY-1/Anh/SiO$_2$</td>
<td>194</td>
<td>165</td>
<td>384</td>
</tr>
<tr>
<td>CY-1/Anh/mono-POSS</td>
<td>199</td>
<td>172</td>
<td>316</td>
</tr>
<tr>
<td>CY-1/Anh/octa-POSS</td>
<td>189</td>
<td>154</td>
<td>349</td>
</tr>
<tr>
<td>CY-2/Amine</td>
<td>83, 109</td>
<td>139</td>
<td>381</td>
</tr>
<tr>
<td>CY-2/Amine/SiO$_2$</td>
<td>71</td>
<td>141</td>
<td>245</td>
</tr>
<tr>
<td>CY-2/Amine/mono-POSS</td>
<td>80,111</td>
<td>137</td>
<td>270</td>
</tr>
<tr>
<td>CY-2/Amine/octa-POSS</td>
<td>76,112</td>
<td>142</td>
<td>376</td>
</tr>
</tbody>
</table>

* Temperature [°C] **Enthalpy [J/g]

them act more like spacers or crosslinkers, decreasing the polymer chain packaging efficiency and enabling easier flow at elevated temperatures.

During this study, two completely different resin systems have been developed. The CY-1/Anhydride resin system has a high $T_g$ (about 195°C), whereas the CY-2/Amine system displays a much lower $T_g$ (in the range of 70-80°C). In the case of amino-cured samples, two glass transitions are visible, which is an indication of phase separation and non-uniform dispersion. As shown in Section 4.2.10, such behaviour might be overcome by a slower curing ramp than 20°/min during the DSC scan. Nevertheless, it is evident that the compatibility of amine cured systems is lower than anhydride ones which exhibit a more defined $T_g$.

Selecting the system with a lower $T_g$ might be beneficial for applications where
a structure undergoes thermal cycling, since above the $T_g$ the mobility of chain segments is greater, the resin is more flexible, and can accommodate for dimensional changes. This might avoid the surface cracking of a more brittle, high $T_g$ epoxy with lower compliance.

5.5 Thermal stability - TGA

Thermal stability of the hybrid cycloaliphatic resins was evaluated with TGA in air and in an inert nitrogen atmosphere. The curves obtained are presented in Figure 5.5 and the data is summarized in Table 5.2. In the case of the CY-1/Anhydride system, the addition of octa-POSS does not change the thermal-degradation pattern with respect to the raw sample, which is an indication of good miscibility. The temperature at which 5% mass loss occurs ($T_{d5\%}$) is shifted 45°C higher for this system, which is a very significant improvement. On the other hand, nanosilica and mono-POSS modified samples behave almost identically to one another, but very differently to the raw material, showing three well resolved degradation steps. Such behaviour is probably associated with particle agglomeration and formation of phases which all have different peaks of degradation.

It can be observed that addition of cycloaliphatic nanomodifiers to the CY-2/Amine system has a smaller effect on the degradation characteristics than when added to a CY-1/Anhydride system. CY-2/Amine system degrades in the same fashion in all cases, regardless of the type of silicon nanoparticles, which indicates no significant influence on the thermal-degradation mechanism. $T_{d5\%}$ is slightly improved for the system modified with octa-POSS and in the higher temperature regime, the resin system modified with mono-POSS shows the highest mass loss which is probably associated with particle agglomeration because the nanoparticle-rich regions hinder the crosslinking density and make the unreacted parts of the polymer more volatile.

Looking at the mass loss at specific temperatures (Table 5.2) it is observed that at up to 150°C, the maximum mass loss of the tested samples is 1.2%. It can be stated that at lower temperatures the effect of the addition of nanoparticles is not evident, however, it is clearly observed at higher temperatures. The effects of nanoparticles on thermal-degradation are less apparent in case of the CY-2/Amine system than in the case of CY-1/Anhydride, where in the latter the resin resistance to elevated temperatures was improved by approximately 33% using mono-POSS, 52% using nanosilica and by 77% using octa-POSS as modifiers.

Looking at all samples reveals that physical modification with nanosilica is less effective than chemical modification with POSS, but the operating temperatures for the structure should determine the selection of POSS or nanosilica.
5.6 Surface morphology and silicon dispersion - SEM/EDX

Visual inspection by SEM and EDX mapping reveals the silicon distribution within the modified epoxies. It is apparent that mono-POSS shows a tendency to form agglomerates, especially in the anhydride cured epoxy (Figure 5.6a, picture b). It can be stated that nanosilica blends well with both epoxies, occasionally forming silicon-rich regions up to 10 µm in size. By far the best level of dispersion is shown by octa-POSS blended into the cycloaliphatic epoxy resins in which case perfect and homogeneous distribution of silicon was achieved (Figure 5.6ac and 5.6bc).

5.7 Surface composition and topography - LSM/XPS

The application of a new protective layer on the surfaces of CFRP structures changes the surface topography depending on the type of nanoparticles used. In order to obtain the surface profiles, samples were scanned with the LSM (Figure 5.7) and the averaged surface roughness data is presented in Table 5.3. The following trend
Table 5.2: TGA data for cycloaliphatic resin systems cured with anhydride or amine and modified with mono-POSS, octa-POSS or nanosilica.

<table>
<thead>
<tr>
<th></th>
<th>T_{d5%} [°C]*</th>
<th>T_{150°C} [%]</th>
<th>T_{300°C} [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>in air</td>
<td>in N₂</td>
<td>in air</td>
</tr>
<tr>
<td>CY-1/Anhydride</td>
<td>266</td>
<td>265</td>
<td>0.4</td>
</tr>
<tr>
<td>CY-1/Anh/SiO₂</td>
<td>252</td>
<td>296</td>
<td>1.2</td>
</tr>
<tr>
<td>CY-1/Anh/mono-POSS</td>
<td>287</td>
<td>271</td>
<td>0.6</td>
</tr>
<tr>
<td>CY-1/Anh/octa-POSS</td>
<td>311</td>
<td>311</td>
<td>0.8</td>
</tr>
<tr>
<td>CY-2/Amine</td>
<td>259</td>
<td>256</td>
<td>0.4</td>
</tr>
<tr>
<td>CY-2/Amine/SiO₂</td>
<td>260</td>
<td>266</td>
<td>0.9</td>
</tr>
<tr>
<td>CY-2/Amine/mono-POSS</td>
<td>257</td>
<td>255</td>
<td>0.8</td>
</tr>
<tr>
<td>CY-2/Amine/octa-POSS</td>
<td>266</td>
<td>262</td>
<td>1</td>
</tr>
</tbody>
</table>

* T_{d5\%} - temperature at which 5% mass loss occurs

(a) CY-1/Anhydride resin systems reinforced with: a) nanosilica, b) mono-POSS, c) octa-POSS.

(b) CY-2/Amine resin systems reinforced with: a) nanosilica, b) mono-POSS, c) octa-POSS.

Figure 5.6: Morphology and silicon distribution maps of cycloaliphatic epoxy resin systems cured with anhydride or amine and modified with mono-POSS, octa-POSS and nanosilica.

is observed in all modified samples: the ones with the lowest value of S_a are those containing nanosilica. This can be explained by the fact that nanosilica particles and bigger and heavier than POSS and tend to migrate deeper within the material. In the case of the octa-POSS reinforced samples, a slight increase in S_a is shown. The highest surface roughness was observed in the samples modified with mono-POSS, regardless of the hardener type.
Table 5.3: Average surface roughness [µm] of cycloaliphatic resin systems modified with mono-POSS, octa-POSS and nanosilica.

<table>
<thead>
<tr>
<th></th>
<th>+ SiO₂</th>
<th>+ octa-POSS</th>
<th>+ mono-POSS</th>
</tr>
</thead>
<tbody>
<tr>
<td>CY-1/Anhydride</td>
<td>4.57</td>
<td>5.35</td>
<td>6.64</td>
</tr>
<tr>
<td>CY-2/Amine</td>
<td>4.25</td>
<td>4.97</td>
<td>8.97</td>
</tr>
</tbody>
</table>

Figure 5.7: Surface topography of CFRP structures coated with a cycloaliphatic epoxy resins reinforced with either POSS or nanosilica.

As can be observed in Figure 5.7 the applied surface layers are far from perfect. Pits, defects and surface irregularities can be observed, which will inevitably contribute to higher environmental degradation. For the sake of surface roughness characterization these regions were excluded, however, there is a need to improve the application method. It is also believed that using the PTFE release agent which leaves the surfaces highly contaminated in fluorine (which will be discussed further in this section) makes the surface hydrophobic which makes it difficult to properly wet the fibres. For this reason surfaces should be cleaned prior to applying the outer cycloaliphatic epoxy layer.

XPS was used to determine the surface elemental composition for anhydride and amine cured epoxy resin systems. The XPS depth profiles obtained presenting the surface composition within a surface layer of approximately 5 nm are shown in Figure 5.8. The most detectable elements were carbon, oxygen and fluorine, however, fluorine should be treated as contamination and not an integral part of the formulation as
Silicon nanoparticles were added in low concentration, therefore it is clear that there is no silicon abundance on the surfaces. One can observe that mono-POSS shows a much higher concentration than octa-POSS or nanosilica (7.2 at.% in anhydride and 5.4 at.% in amine-cured resins) which indicates the tendency of mono-POSS to migrate towards the surfaces. On the other hand, nanosilica is hardly detectable on the surface (<1 at.%) which is probably a signal caused by silicon cross contamination rather than from embedded nanoparticles. This shows a tendency of nanosilica to penetrate deeper into the material. The comparison of surface composition between the CY-1/Anhydride and the CY-2/Amine systems with different nanomodifiers can be seen in Table 5.4.

Before requesting the XPS analysis, the author was not aware of the strong fluorine contamination. Apparently, PTFE which is used in the manufacturing process as a release film, leaves a strong trace on the surface. In order to reveal true surface compositions, samples of CY-1/Anhydride/octa-POSS and CY-1/Anhydride/nanosilica were lightly etched with an argon plasma. Because the XPS was performed externally, only two samples could be selected for analysis. The data obtained is presented in Table 5.5. From the XPS data it can be concluded that octa-POSS shows a greater tendency to migrate towards the surfaces than the heavier nanosilica particles that
Table 5.4: Surface elemental composition [at.%] by XPS studies for POSS reinforced cycloaliphatic/amine epoxy resins versus aromatic epoxy used for reference.

<table>
<thead>
<tr>
<th>Sample</th>
<th>C1s</th>
<th>F1s</th>
<th>N1s</th>
<th>O1s</th>
<th>Si2p</th>
</tr>
</thead>
<tbody>
<tr>
<td>CY-1/Anhyride/mono-POSS</td>
<td>63</td>
<td>11</td>
<td>0.5</td>
<td>19</td>
<td>7</td>
</tr>
<tr>
<td>CY-1/Anhyride/SiO₂</td>
<td>70</td>
<td>13</td>
<td>1</td>
<td>14</td>
<td>1</td>
</tr>
<tr>
<td>CY-1/Anhyride/octa-POSS</td>
<td>55</td>
<td>32</td>
<td>1</td>
<td>9</td>
<td>3</td>
</tr>
<tr>
<td>CY-2/Amine/mono-POSS</td>
<td>63</td>
<td>14</td>
<td>2</td>
<td>15</td>
<td>5</td>
</tr>
<tr>
<td>CY-2/Amine/SiO₂</td>
<td>60</td>
<td>28</td>
<td>2</td>
<td>9</td>
<td>1</td>
</tr>
<tr>
<td>CY-2/Amine/octa-POSS</td>
<td>58</td>
<td>30</td>
<td>2</td>
<td>8</td>
<td>0.5</td>
</tr>
</tbody>
</table>

are incorporated deeper within the surface and not detected in the 5 nm surface layer.

Table 5.5: Surface elemental composition [at.%] by XPS studies for cycloaliphatic epoxy resins cured with anhydride and reinforced with octa-POSS and nanosilica before and after plasma contamination removal. The composition of purely aromatic epoxy is presented for reference.

<table>
<thead>
<tr>
<th>Sample</th>
<th>F1s</th>
<th>O1s</th>
<th>N1s</th>
<th>C1s</th>
<th>Si2p</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aromatic</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>As received</td>
<td>3.7</td>
<td>10.2</td>
<td>3.7</td>
<td>82</td>
<td>0.5</td>
</tr>
<tr>
<td>Etched</td>
<td>0</td>
<td>7.6</td>
<td>4.7</td>
<td>87.8</td>
<td>0</td>
</tr>
<tr>
<td>CY-1/Anh/octa-POSS</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>As received</td>
<td>15.4</td>
<td>12.8</td>
<td>0.9</td>
<td>70.3</td>
<td>0.6</td>
</tr>
<tr>
<td>Etched</td>
<td>0</td>
<td>11.7</td>
<td>2.5</td>
<td>85.6</td>
<td>0.2</td>
</tr>
<tr>
<td>CY-1/Anh/SiO₂</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>As received</td>
<td>11.4</td>
<td>12.6</td>
<td>0.6</td>
<td>73.8</td>
<td>1.6</td>
</tr>
<tr>
<td>Etched</td>
<td>0</td>
<td>12.2</td>
<td>3.8</td>
<td>84</td>
<td>0</td>
</tr>
</tbody>
</table>

5.8 Exposure to UV radiation and temperature

The primary reason for including the amine cured cycloaliphatic resin in this analysis was because it was believed that by decreasing the number of unsaturated chemical bonds in the epoxy resin monomer, the UV resistance will be enhanced. The presence of chromophores such as aromatic rings, carbonyl groups and other double bonds causes intensive absorption of UV radiation.

During the crosslinking reactions, two anhydride molecules react with one molecule of CY-1 cycloaliphatic epoxy. Each anhydride bears two carbonyl groups and each epoxy bears one which results in a total of five carbonyl groups per monomer. In the case of the cycloaliphatic epoxy of type CY-2 which bears two carbonyl group and reacts with amine that does not possess any carbonyl groups, the number of -C=O groups per monomer is reduced to two. This theoretical assumption was tested by exposure of the cycloaliphatic epoxies reinforced with either mono or octa-POSS to the effects of UV radiation and temperature. The recorded mass loss after a period of 40h is presented in Figure 5.9. As can be observed, both POSS reinforced cycloaliphatic
epoxies show lower mass loss by about 50% in the case of anhydride cured epoxies and by about 60% in the case of the amine cured ones. Unfortunately, the reference SiO$_2$ containing sample got damaged and a reliable weight could not be measured. However, it was confirmed by observation of the other samples that substituting the hardener type for a fully saturated one increases the UV radiation resistance.

![Figure 5.9: Mass loss due to UV radiation and temperature for corresponding cycloaliphatic epoxy resins cured with anhydride or amine and reinforced with 5 wt% of octa- or mono-POSS.](image)

### 5.9 Summary of the resin characterization study

The main conclusions from this chapter are as follows:

- Curing the cycloaliphatic epoxy with anhydride produces highly crosslinked resin with high $T_g$. On the other hand, curing the system with amine produces a lightly crosslinked polymeric network with much lower $T_g$.

- Octa-POSS increases the resin system’s reactivity and shows a very satisfactory level of miscibility with both types of cycloaliphatic epoxies.

- From the selected modifiers octa-POSS significantly improves thermal-stability of anhydride cured epoxy. In the case of the amine cured system it is less effective but still shows a reinforcing effect. Mono-POSS and nanosilica are less significant in terms of thermal-stability, with nanosilica being the least effective.

- POSS nanocages tend to migrate towards the surface of CFRP structures, which is confirmed by higher surface roughness and silicon elemental content.
From the selected nanomodifiers only octa-POSS shows perfect dispersion in the epoxy matrix. Nanosilica disperses well, forming only occasional silicon-rich regions and mono-POSS proved to be an incompatible reagent that formed large agglomerates.

Based on the analysis performed, octa-POSS was selected as the primary nanoadditive for blending with the cycloaliphatic epoxies to improve their LEO resistance. Nanosilica proved to be less effective, however, due to its commercial availability it should not be excluded entirely from further analysis as an additive candidate. Mono-POSS was found to be incompatible with the selected types of cycloaliphatic epoxy resins and therefore excluded completely from further analysis.
Chapter 6

Nanocomposites with increasing octa-POSS content

In the previous chapter three types of silicon nanoparticles in combination with two types of cycloaliphatic epoxies and curing agents were compared. By analysing some of the material properties which are of interest for space applications, it was concluded that octa-functional POSS is the most promising modifier either in combination with anhydride or amine cured system depending on the particular application.

This chapter will discuss how the cycloaliphatic epoxy resin properties change based on an increasing loading of octa-POSS. It was of interest to examine how much of the additive is beneficial from a thermal-mechanical point of view. Due to time and budget constraints both anhydride and amine cured epoxy resin systems with 0, 5, 10, 15 and 20 wt% octa-POSS were only analysed by TGA, DMTA and ATR-FTIR. A complementary curing analysis by DSC and mechanical three point bending testing was performed only for the CY-1/Anhydride/octa-POSS combination.

6.1 Thermal stability - TGA

The influence of an increasing octa-POSS content on thermal stability of the cycloaliphatic epoxy resin systems was investigated by TGA. The data obtained for the CY-1/Anhydride/octa-POSS system is presented in Figure 6.1 and the parameters of interest are given in Table 6.1.

As can be observed, the addition of octa-POSS to the cycloaliphatic epoxy cured with anhydride blend significantly improves thermal stability. It is also apparent that the properties of the 5 wt% modified sample are superior to the non-modified epoxy, while the differences between the subsequent POSS loadings are much less evident. Such behaviour can be linked to the fact that an increasing content of octa-POSS reduces crosslinking density. Due to steric hindrance and octa-POSS being
Figure 6.1: TGA curves for the CY-1/Anhydride epoxy resin system reinforced with varying amounts of octa-POSS (a) and the corresponding first derivative curve (DTA, b) and conversion curve (c).
Table 6.1: TGA parameters for the CY-1/Anhydride epoxy resin system reinforced with varying amounts of octa-POSS.

<table>
<thead>
<tr>
<th>CY-1/Anhydride +</th>
<th>0%</th>
<th>5%</th>
<th>10%</th>
<th>15%</th>
<th>20%</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_{d5%}$ $[^\circ C]$</td>
<td>265</td>
<td>312</td>
<td>300</td>
<td>316</td>
<td>308</td>
</tr>
<tr>
<td>$T_{d10%}$ $[^\circ C]$</td>
<td>295</td>
<td>327</td>
<td>319</td>
<td>329</td>
<td>326</td>
</tr>
<tr>
<td>Mass loss at 150$^\circ C$ [%]</td>
<td>0.9</td>
<td>0.8</td>
<td>1.1</td>
<td>0.6</td>
<td>0.8</td>
</tr>
<tr>
<td>Mass loss at 300$^\circ C$ [%]</td>
<td>11</td>
<td>4</td>
<td>5</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>$T_{onset}$ $[^\circ C]$</td>
<td>295</td>
<td>333</td>
<td>328</td>
<td>332</td>
<td>329</td>
</tr>
<tr>
<td>$T_{peak}$ $[^\circ C]$</td>
<td>353</td>
<td>355</td>
<td>354</td>
<td>358</td>
<td>357</td>
</tr>
<tr>
<td>Area [%·-min/$^\circ C$]</td>
<td>353</td>
<td>355</td>
<td>354</td>
<td>358</td>
<td>357</td>
</tr>
</tbody>
</table>

a bulky molecule, crosslinking with epoxy and anhydride is made difficult, hence the unreacted parts of the polymeric chains are more volatile and more easily removable at elevated temperatures. It can be concluded that the addition of a small amount of octa-POSS is the most beneficial, since the 5% weight loss was shifted from 265$^\circ C$ for an untreated sample to 312$^\circ C$ for the one with 5 wt%.

The onset temperature denotes the point at which the weight loss begins and is a universal parameter for the evaluation of thermal stability. In all the samples the onset of degradation increased to approximately 330$^\circ C$. The peak temperature of the first derivative ($T_{peak}$) is an indication of the maximum change of the TGA curve. For all samples that temperature is around 355$^\circ C$ (Figure 6.1b), which is associated with degradation of the epoxy part. The area under this peak determines the amount of the compound that decomposed, and as can be observed, samples with a higher POSS content show smaller peak areas, which indicates that the inorganic part remains as ash within the sample.

Conversion plots have been calculated using Equation 6.1, where $m_0$ denotes the initial mass, $m_T$ is the mass at a certain temperature, and $m_1$ is the final mass. As can be observed in Figure 6.1c increasing POSS content slows down the reaction rate.

$$\alpha(T) = \frac{m_0 - m_T}{m_0 - m_1}$$ (6.1)

The same kind of thermal analysis was repeated for amine cured cycloaliphatic epoxy. The data obtained is presented in Figure 6.2 and summarized in Table 6.2. In this case, a positive correlation between POSS content and thermal performance is more clearly observed, and in contrast to the anhydride cured system, it seems like a higher POSS content is beneficial in this case. It is especially satisfactory to observe that mass loss at 150$^\circ C$ and 250$^\circ C$ reduces by 25% when compared the samples with 5 wt% and 20 wt% of octa-POSS (Table 6.2). Slight incremental, but not very significant improvements can be noticed in all studied parameters. Following the TGA first derivative curves (Figure 6.2b) indicates two equally significant maximums.
6.1. Thermal stability - TGA

Figure 6.2: TGA curves for the CY-2/Amine epoxy resin system reinforced with varying amounts of octa-POSS (a) and the corresponding first derivative curve (DTA, b) and conversion curve (c).
Table 6.2: TGA parameters for the CY-2/Amine epoxy resin system reinforced with varying amounts of octa-POSS.

<table>
<thead>
<tr>
<th>CY-2/Amine +</th>
<th>0%</th>
<th>5%</th>
<th>10%</th>
<th>15%</th>
<th>20%</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_{d5%}$ [°C]</td>
<td>257</td>
<td>263</td>
<td>264</td>
<td>268</td>
<td>277</td>
</tr>
<tr>
<td>$T_{d10%}$ [°C]</td>
<td>284</td>
<td>283</td>
<td>284</td>
<td>287</td>
<td>292</td>
</tr>
<tr>
<td>Mass loss at 150°C [%]</td>
<td>0.6</td>
<td>1</td>
<td>1</td>
<td>0.8</td>
<td>0.8</td>
</tr>
<tr>
<td>Mass loss at 300°C [%]</td>
<td>15</td>
<td>18</td>
<td>17</td>
<td>16</td>
<td>13</td>
</tr>
<tr>
<td>$T_{onset}$ [°C]</td>
<td>282</td>
<td>276</td>
<td>275</td>
<td>279</td>
<td>281</td>
</tr>
<tr>
<td>$T_{peak}$ [°C]</td>
<td>337,404</td>
<td>303,407</td>
<td>308,400</td>
<td>311,407</td>
<td>313,402</td>
</tr>
<tr>
<td>Area [%·min/°C]</td>
<td>9.6</td>
<td>9.2</td>
<td>9.1</td>
<td>9.1</td>
<td>8.9</td>
</tr>
</tbody>
</table>

of degradation: the first around 300°C and the second around 400°C. Similarly to the anhydride cured system, increasing octa-POSS content slows down the reaction rate (Figure 6.2c).

For applications requiring operation in LEO, temperatures up to approximately 150°C are expected, however, the key parameter for the polymers is the $\alpha/\epsilon$ ratio. For components of the spacecraft that face the Sun at all times, or in the case of unexpected solar activity, thermal stability must be ensured. Because of this the mass loss in the region of 150°C - 300°C is of highest interest. All samples experienced 1% or lower mass loss up to 150°C, which was a very satisfactory result. The anhydride cured cycloaliphatic epoxy resin system reinforced with 5 wt% octa-POSS is suitable for use in extreme temperatures, up to 300°C.

## 6.2 Curing behaviour - ATR-FTIR/DSC

ATR-FTIR is a useful technique to determine the chemistry of the modified resin system. This inexpensive and very fast analysis method can be used to determine whether crosslinking reactions have progressed. Because it is a surface sensitive technique it indicates whether POSS is present in the surface region which is of interest for space applications. The depth of penetration for a standard DGEBA epoxy resin calculated based on the refractive index of epoxy (approximately $n=1.3-1.5$) and a germanium crystal in the range of 3600-700 cm$^{-1}$ is between 0.5-3 µm (Mailhot et al., 2005).

ATR-FTIR scans were taken on samples cured with an increasing octa-POSS content and on an uncured epoxy of the same kind for comparison (Figure 6.3). All spectra were normalized before analysis in order to properly compare the intensity of the bands. The epoxy ring band in cycloaliphatic epoxies is shifted in comparison with the aromatic epoxy and is visible at 788 cm$^{-1}$. The disappearance of that band can be viewed as an indication of the completed crosslinking reaction. The presence of POSS is revealed by the appearance of a new band at 1085 cm$^{-1}$, which predictably
increases with increasing POSS content. In order to clearly see this, the region of interest is zoomed and presented in Figure 6.4.

![ATR-FTIR spectra for (a) CY-1/Anhydride and CY-2/Amine resin systems with increasing octa-POSS loadings and a pure resin system as a reference. Arrows point at Si-O-Si (1085 cm\(^{-1}\)) and epoxy ring (788 cm\(^{-1}\)) bands.](image)

**Figure 6.3:** ATR-FTIR spectra for (a) CY-1/Anhydride (b) and CY-2/Amine resin systems with increasing octa-POSS loadings and a pure resin system as a reference. Arrows point at Si-O-Si (1085 cm\(^{-1}\)) and epoxy ring (788 cm\(^{-1}\)) bands.

In the case of the anhydride cured cycloaliphatic epoxy, a complementary DSC analysis was performed to evaluate the influence of octa-POSS on the curing behaviour (Figure 6.5a). As one may observe, the addition of octa-POSS shifts the \(T_{\text{peak}}\) towards lower temperatures, making the resin more reactive. For the samples with octa-
6.2. Curing behaviour - ATR-FTIR/DSC

Figure 6.4: Zoomed in ATR-FTIR spectra for CY-1/Anhydride (a) and CY-2/Amine (b) resin systems with increasing octa-POSS loadings and a pure resin system as a reference. Arrows point at Si-O-Si (1085 cm\(^{-1}\)) and epoxy ring (788 cm\(^{-1}\)) bands.

POSS content in the range of 5-15%, this change is not substantial (a maximum shift of 10°C). In the case of the 20% modified sample the curing behaviour changes profoundly. The \(T_{\text{peak}}\) is observed 25°C sooner than in the unmodified epoxy and the peak itself is much broader which indicates that the polymerization reaction is spread over much a broader temperature range.

The glass transition temperature is also affected by the octa-POSS presence (Figure 6.5b). The general trend is that \(T_g\) decreases with increasing octa-POSS content. This indicates a lower crosslinking density, and higher mobility of the polymer which is disorganised by the presence of octa-POSS. A lower \(T_g\) together with a lower enthalpy of reaction are probably signs of an under-cured epoxy (Table 6.3). Again, up to 15 wt% octa-POSS content the change in \(T_g\) is not significant.

Figure 6.5: DSC curves for CY-1/Anhydride epoxy resin system reinforced with increasing content of octa-POSS.
Table 6.3: DSC data for CY-1/Anhydride epoxy resin system reinforced with increasing content of octa-POSS.

<table>
<thead>
<tr>
<th></th>
<th>$T_g$ [°C]</th>
<th>$T_{\text{peak}}$ [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CY-1/Anhydride</td>
<td>198</td>
<td>161</td>
</tr>
<tr>
<td>CY-1/Anhydride/5 wt% octa-POSS</td>
<td>184</td>
<td>156</td>
</tr>
<tr>
<td>CY-1/Anhydride/10 wt% octa-POSS</td>
<td>178</td>
<td>155</td>
</tr>
<tr>
<td>CY-1/Anhydride/15 wt% octa-POSS</td>
<td>163</td>
<td>155</td>
</tr>
<tr>
<td>CY-1/Anhydride/20 wt% octa-POSS</td>
<td>83,104</td>
<td>136</td>
</tr>
</tbody>
</table>

6.3 Thermo-mechanical properties - DMTA

DMTA analysis was performed on rectangular specimens, approximately 40 mm long, 15 mm wide and 0.5 mm thick, in order to compare the thermal-mechanical properties of the cycloaliphatic epoxies with varying content of octa-POSS. The measured storage modulus and tan delta curves are presented in Figure 6.6.

In general, mechanical properties are strongly affected by the presence of nanoparticles which disturb the alignment of the epoxy network. In theory, the addition of stiffer components, such as particles should increase the materials modulus, and such behaviour has been observed in the case of some nanoadditives such as nanoclays (Njuguna and Pielichowski, 2003). However, it is also possible that the presence of nanoparticles in a two part epoxy will hinder the crosslinking reactions and disturb the alignment of the polymeric chains. The first analysis of samples reinforced with varying contents of octa-POSS did not reveal any obvious correlation between the POSS loading and storage modulus, neither for anhydride nor for amine cured resins.

Because crosslinking density is affected by the presence of nanoparticles, so is the glass transition temperature. In the case of the anhydride cured system it has been observed that $T_g$ remains unaffected by the increasing POSS content up to 15 wt% and shows at approximately 189°C (Figure 6.6a, lower plot). For the case of the 20 wt% POSS sample the maximum value of tan $\delta$ (indicating the $T_g$) decreases to 175°C. Such behaviour shows that 20 wt% loading of a bulky POSS molecule reduced crosslinking and increased chain mobility by acting like a spacer. Nevertheless, in all cases, a single and well-defined $T_g$ is displayed, which is an indication of good miscibility between components and a homogeneous epoxy resin system. In the case of the amine cured resin system it can be observed that $T_g$ increases slightly with the higher POSS content, but the increase is too small to be significant (Figure 6.6b, lower plot).

It can be stated that octa-POSS loading up to 15 wt% in both resin systems does not significantly affect the glass transition temperature of the base epoxy, which is an important indication that octa-POSS is a suitable modifier for the selected epoxy types.
Figure 6.6: DMTA curves for cycloaliphatic resin systems reinforced with an increasing content of octa-POSS.

6.4 Mechanical properties - three point bending test

A complementary mechanical analysis had been performed for anhydride cured cycloaliphatic epoxy with different octa-POSS loadings. Tested samples were approxi-
mately 0.5 mm thick, 15 mm wide and the distance between supports was set to 30 mm. In order to examine the influence of nanoparticles on mechanical parameters, samples with an increasing octa-POSS content: 0, 5, 10, 15, 20 wt% were manufactured by autoclave processing, cut to rectangular pieces and subjected to a three point bending testing. The averaged data are presented in Table 6.7c.

<table>
<thead>
<tr>
<th>Aromatic</th>
<th>Flexural strength [MPa]</th>
<th>Flexural modulus [GPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aromatic</td>
<td>0</td>
<td>200</td>
</tr>
<tr>
<td>Aromatic</td>
<td>5%</td>
<td>400</td>
</tr>
<tr>
<td>Aromatic</td>
<td>10%</td>
<td>600</td>
</tr>
<tr>
<td>Aromatic</td>
<td>15%</td>
<td>800</td>
</tr>
<tr>
<td>Aromatic</td>
<td>20%</td>
<td>1000</td>
</tr>
</tbody>
</table>

Figure 6.7: Flexural properties of the cycloaliphatic epoxy resin cured with anhydride with increasing octa-POSS content versus aromatic epoxy used as a reference.

As one may observe, the cycloaliphatic/anhydride resin system has a higher strength and modulus than the base aromatic epoxy, however, the incorporation of 5 wt% of nanoparticles drops these values to the level of aromatic epoxy. It can be stated that such a small addition of nanoparticles does not offer any reinforcing effect on the structure, and causes a disturbance in the polymeric network resulting in a decrease in the mechanical properties. With the increasing POSS content, both strength and modulus rise when compared to the 5 wt% modified sample, so it might be observed that a higher concentration of nanoparticles has a reinforcing effect on the epoxy resulting in enhanced properties compared to those of the pure cycloaliphatic/anhydride resin system. In the case of the 20 wt% modified sample, a dramatic reduction in properties is observed. Such behaviour can be linked to the fact that octa-POSS is a branched, bulky molecule that in such a high concentration profoundly changes the crosslinking density and instead of acting as a reinforcement, behaves more like a defect within the material.

DMTA analysis performed on the same set of samples (originating from the same batch) confirms the aforementioned trend (Figure 6.8). In general, addition
of any content of octa-POSS nanoparticles decreases the mechanical performance of the structure. However, POSS loadings in the range of 10-15% provide reinforcement and the sample’s mechanical parameters are close to the non-reinforced cycloaliphatic/anhydride epoxy. As can be noticed, the data from the second manufactured batch is not in agreement with the one presented in Figure 6.6a. Based on this fact, it can be stated that octa-POSS should not be treated as a reinforcing agent because such behaviour is strongly dependant on the manufacturing process and the thermal history of a particular sample. It is more probable that the second DMTA analysis is more valid because more care had been put into the surface finish of the manufactured samples, and also the author was more experienced in using the apparatus. Nevertheless, octa-POSS should not be considered as a mechanically reinforcing additive, and in exchange for the environmental resistance that it offers, mechanical performance of the epoxy resin is likely to be sacrificed.

6.5 Chapter summary

This chapter discussed influence of an increasing POSS content on the thermal-mechanical properties of the anhydride or amine cured cycloaliphatic epoxy resins. Based on the analysis it can be stated that:

- 5 wt% addition of octa-POSS significantly improves thermal stability of anhydride cured cycloaliphatic epoxy.
• With an increasing octa-POSS content, thermal stability slightly, but not significantly increases in the amine cured cycloaliphatic epoxy.

• ATR-FTIR scans recorded for all samples indicate completed curing reactions and successful incorporation of POSS into the epoxy matrices, which is confirmed by the appearance of the characteristic Si-O band at 1085 cm$^{-1}$.

• A more detailed DSC analysis performed for the anhydride cured system reveals that the curing process is not significantly disturbed by a POSS loading up to 15wt%, however, crosslinking density clearly decreases, which is in agreement with lower $T_g$ for modified systems.

• DMTA analysis confirms a significant decrease in $T_g$ for the anhydride cured sample with 20 wt% octa-POSS content. No obvious correlation signs between the increasing POSS content and storage modulus were found in the case of the samples tested from the first batch.

• A complementary three point bending test and DMTA for anhydride cured cycloaliphatic epoxy revealed that the addition of nanoparticles decreases the strength of samples when compared to the untreated cycloaliphatic epoxy, however, with increasing octa-POSS content up to 15 wt%, the mechanical properties improve. Therefore it was concluded that a small addition of octa-POSS provides some reinforcement, but in high concentrations such as 20 wt%, the polymeric network gets highly disturbed and a dramatic reduction in properties is observed.
Chapter 7

Exposure to a space simulation environment

Following on from the resin characterization studies and evaluation of some of the material properties which are important for space applications, the modified cycloaliphatic resin systems were subjected to an environmental study in a space-like simulation facility.

This chapter will discuss the response of the resin systems to the degrading effects of UV radiation and atomic oxygen, in particular with respect to changes in surface chemistry and thermal-mechanical properties. An erosion yield in calculated together with an approximate life span prediction.

A detailed description of the testing facility, which was constructed solely for the purposes of this project is described in Appendix A.

7.1 Materials used in this study

Based on the resin characterization study and the studies of increasing octa-POSS content within the cycloaliphatic epoxy (Chapters 5 and 6), it was decided to select the anhydride cured resin system for environmental analysis. It was expected that the material’s response to AO is mostly governed by the interactions between AO and the octa-POSS embedded in the epoxy, therefore it was decided to narrow down the number of samples tested to five, including: a purely aromatic CFRP used as a reference, and a CFRP with 5, 10, 15 and 20 wt% octa-POSS reinforced cycloaliphatic epoxy cured with anhydride used on the outer layers.

7.2 Resins degradation due to UV radiation

A detailed description of the UV testing procedure is described in Appendix A.3.
7.2. Resins degradation due to UV radiation

7.2.1 Mass loss due to UV

The mass loss due to exposure to UV radiation and elevated temperature (85-100°C) is presented in Figure 7.1, which shows the effectiveness of using cycloaliphatic epoxy/octa-POSS blends in combating UV-induced chain scissioning and the consequent mass loss. As can be seen, a dramatic reduction in mass loss for all cycloaliphatic epoxy/octa-POSS was detected when compared to the purely aromatic epoxy. Samples were subjected to outgassing prior to UV testing in order to ensure that any mass loss was caused by the radiation. It was found that cycloaliphatic epoxy/octa-POSS blends also show much lower mass loss due to outgassing in high vacuum which is beneficial for space applications.

7.2.2 Surface chemistry change due to UV - ATR-FTIR

Surface chemistry spectra obtained by ATR-FTIR spectroscopy were recorded before and after the UV radiation test and are presented in Figure 7.2. It is apparent that the UV-C radiation considerably changes the chemistry of purely aromatic epoxy resins (Figure 7.2a) while no measurable changes in octa-POSS/cycloaliphatic epoxy were noticed.

The most distinctive signs of aromatic epoxy degradation which can be observed in the acquired spectra are: the decrease in the hydroxyl group at 3396 cm\(^{-1}\) and at 1000-1300 cm\(^{-1}\) which is assigned to -C-O and -C-H groups, indicating chain scissioning in this region. The -OH groups are the weakest and most probable cleavage site in the aromatic epoxy, and based on the recorded FTIR it can be stated that the epoxy
monomer is indeed broken in this place. This causes the appearance of the carbonyl band at 1725 cm\(^{-1}\) and a decrease in both -C-O and -OH regions.

Figure 7.2: Changes in surface chemistry measured by ATR-FTIR due to UV radiation. Aromatic epoxy used as reference (a) versus CY-1/Anhydride epoxy resin system reinforced with 5 wt\% octa-POSS (b).
7.3 Exposure to Atomic oxygen (AO)

Atomic oxygen etching was simulated by a radio-frequency (RF) plasma generator. Plasma was generated from a mixture of 1.5 sccm oxygen and 4 sccm argon. The pressure was $1.65 \times 10^{-4}$ Torr during gas flowing into the main vacuum chamber and the exposure time was 24h at 50W RF power. The mass loss of a reference Kapton sample allowed to calculate the AO fluence as $3.56 \times 10^{19}$ atoms/cm².

7.3.1 Mass loss due to AO

Measurements of mass loss were performed on samples outgassed in a vacuum chamber for a minimum of 24 hours and stored in a desiccator prior to testing in order to make sure that any mass loss is associated with the effects of AO erosion. Total mass loss (TML) due to AO exposure was calculated using Equation 7.1 where $M_1$ is the initial sample mass and $M_2$ is the final one.

As can be observed in Table 7.1, the mass loss decreases with increasing octa-POSS content. This is because the inorganic phase does not form volatile components with the bombarding oxygen, but rather recombines with oxygen atoms and gradually covers the surface in ash, which makes it difficult for AO to react with underlying layers of organic and volatile epoxy.

$$TML[\%] = \frac{M_1 - M_2}{M_1} \times 100$$  \hspace{1cm} (7.1)

Table 7.1: Total mass loss (TML) due to AO of CY-1/Anhydride epoxy resin system reinforced with different amounts of octa-POSS, versus unmodified epoxy.

<table>
<thead>
<tr>
<th>Aromatic*</th>
<th>5%**</th>
<th>10%**</th>
<th>15%**</th>
<th>20%**</th>
</tr>
</thead>
<tbody>
<tr>
<td>TML [%]</td>
<td>4.19</td>
<td>3.57</td>
<td>2.87</td>
<td>2.80</td>
</tr>
<tr>
<td>% of original</td>
<td>85</td>
<td>69</td>
<td>67</td>
<td>64</td>
</tr>
</tbody>
</table>

*Reference (TGDDM epoxy), **CY-1/Anhydride cycloaliphatic epoxy

7.3.2 AO influence on surface chemistry - contact angle measurement

Water contact angle measurement is a simple technique to analyse changes in the oxygen content on the surface due to oxidation and erosion caused by atomic oxygen. The formation of oxides increases the polar nature of the surface which results in better wetting and lower contact angles. In contrast, higher water contact angles are characteristic of more hydrophobic surfaces, with a high level of alignment and low functionality such as graphite (Taherian et al., 2013).
7.3. Exposure to Atomic oxygen (AO)

Analysis of the contact angle can be used to evaluate whether silicon embedded in the epoxy resin medium has reacted with atomic oxygen and created a silica-like passivation layer. Glass materials exhibit perfect wettability and \( \alpha \approx 0^\circ \). Therefore, it was expected that surfaces exposed in the oxygen plasma environment would show lower contact angles when compared to the raw materials. The difference in surface wetting is illustrated in Figure 7.3, and the plot in Figure 7.4 depicts changes in the water contact angle between CY-1/Anhydride samples (exposed and unexposed) to the AO environment with increasing octa-POSS content.

![Figure 7.3: Contact angle measurement on the surface of CY-1/Anhydride epoxy resin reinforced with 20 wt% octa-POSS, before (a) and after AO treatment. (b)](image)

![Figure 7.4: Contact angle change due to atomic oxygen exposure for CY-1/Anhydride samples with varied octa-POSS content.](image)

The contact angle measurement shows that exposing samples to AO profoundly changes their surface functionality. The fact that the contact angle heads towards
zero may indicate the formation of a hydrophilic silica layer on the surface in the octa-POSS containing samples. In the case of purely aromatic epoxy that does not contain any silicon, the decreasing contact angle is an indication of the formation of polar, carbon-oxygen groups on the surface. In order to numerically validate the changes in surface elemental composition, a complementary XPS analysis is required.

7.3.3 AO influence on surface chemistry - XPS

XPS is a surface specific technique which allows quantified analysis of the elemental content in a region approximately 5-10 nm from the sample surface. CFRP structures coated with the octa-POSS reinforced cycloaliphatic epoxy were subjected to XPS analysis before and after AO exposure, and the results are presented in Table 7.2.

Table 7.2: Changes in surface composition by XPS analysis [at.\%] of CFRP structures coated in CY-1/Anhydride/octa-POSS resin due to AO exposure.

<table>
<thead>
<tr>
<th></th>
<th>C1s</th>
<th>O1s</th>
<th>N1s</th>
<th>Si2p</th>
<th>Others**</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aromatic - raw</td>
<td>77.4</td>
<td>14.6</td>
<td>4.4</td>
<td>-</td>
<td>3.5</td>
</tr>
<tr>
<td>Aromatic - AO</td>
<td>67</td>
<td>19.4</td>
<td>3.9</td>
<td>-</td>
<td>9.7</td>
</tr>
<tr>
<td>5 wt%* - raw</td>
<td>69.3</td>
<td>13.7</td>
<td>2.7</td>
<td>2.6</td>
<td>11.9</td>
</tr>
<tr>
<td>5 wt%* - AO</td>
<td>63.5</td>
<td>25.7</td>
<td>3.3</td>
<td>4.6</td>
<td>2.9</td>
</tr>
<tr>
<td>10 wt%* - raw</td>
<td>82.2</td>
<td>7.7</td>
<td>2.3</td>
<td>1</td>
<td>6.9</td>
</tr>
<tr>
<td>10 wt%* - AO</td>
<td>70.4</td>
<td>21.3</td>
<td>2.8</td>
<td>3.7</td>
<td>2.2</td>
</tr>
<tr>
<td>15 wt%* - raw</td>
<td>75</td>
<td>14.2</td>
<td>3</td>
<td>2.2</td>
<td>5.1</td>
</tr>
<tr>
<td>15 wt%* - AO</td>
<td>45</td>
<td>35.9</td>
<td>2</td>
<td>12.7</td>
<td>4.2</td>
</tr>
<tr>
<td>20 wt%* - raw</td>
<td>81.4</td>
<td>11.3</td>
<td>1.7</td>
<td>1.8</td>
<td>3.8</td>
</tr>
<tr>
<td>20 wt%* - AO</td>
<td>26.7</td>
<td>46.3</td>
<td>1.1</td>
<td>20.6</td>
<td>5.3</td>
</tr>
</tbody>
</table>

*CY-1/Anhydride epoxy/octa-POSS, **F1s, N1s, S2p, Ca2p

It can be observed that the unmodified, aromatic epoxy experienced a decrease in carbon content of 13% and an increase in oxygen content of 30%, which is an indication of surface oxidation and the development of an oxygen functionalized surface. Also, the modified samples show the same trend in which carbon content decreases while the oxygen content increases. However, mass loss is significantly lower for those samples in comparison to the aromatic epoxy (Table 7.1), which suggests that volatile species are not formed, but rather the surface undergoes rearrangement. This can be confirmed by analysis of the silicon peak and the shift in its binding energy, which is in the range of 103.2-104.5 eV for SiO$_2$ and 101.8-102.4 eV for siloxanes. Figure 7.5 presents the Si2p peak for octa-POSS reinforced cycloaliphatic epoxy before the AO exposure (siloxane) and after the AO exposure (SiO$_2$).
7.3. Exposure to Atomic oxygen (AO)

Figure 7.5: Si2p measured by XPS. Before the AO exposure the Si peak indicates the presence of siloxanes (black line), and after the AO exposure the Si peak shift indicates the creation of silica on the surface (red line).

7.3.4 AO influence on surface topography - LSM

Both unmodified and silicon modified samples are expected to be etched by the oxygen plasma. Oxygen radicals are very reactive with carbon and silicon, forming volatile components with the former and an SiO$_2$ layer with the latter. Because silicon was added in small concentrations to the cycloaliphatic epoxy medium, it might be expected that the epoxy part will get eroded to some extent. This was confirmed by the mass loss studies presented in Section 7.3.1.

The surfaces of the samples before and after AO exposure were scanned with LSM in order to evaluate changes in the surface roughness. Due to the fact that the surface layers are applied by a hand lamination technique, the coverage is not perfect, resulting in occasional patches of underlying aromatic epoxy. In order to realistically represent the surface roughness, obvious defects were excluded from calculations of the average surface roughness. At least five 3×3 mm$^2$ scans were taken in different places and averaged. The obtained results are presented in Table 7.3.

All samples modified with octa-POSS experienced a decrease in surface roughness. There are a number of explanations for this behaviour. Firstly, plasma tends to be used in order to remove contamination and impurities from surfaces. During the AO exposure, it is likely that several nanometers of material were removed, which evened out the surface and consequently decreased the $S_a$ value. Another possible
7.3. Exposure to Atomic oxygen (AO)

Table 7.3: Changes in surface roughness due to AO exposure of the CY-1/Anhydride epoxy resin system reinforced with different amount of octa-POSS, versus an unmodified epoxy.

<table>
<thead>
<tr>
<th></th>
<th>$S_a$ Unexposed [µm]</th>
<th>$S_a$ AO exposed [µm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aromatic epoxy</td>
<td>7.94</td>
<td>10.49</td>
</tr>
<tr>
<td>CY-1/Anhydride/5 wt% octa-POSS</td>
<td>8.43</td>
<td>6.21</td>
</tr>
<tr>
<td>CY-1/Anhydride/10 wt% octa-POSS</td>
<td>6.89</td>
<td>5.16</td>
</tr>
<tr>
<td>CY-1/Anhydride/15 wt% octa-POSS</td>
<td>10.05</td>
<td>2.78</td>
</tr>
<tr>
<td>CY-1/Anhydride/20 wt% octa-POSS</td>
<td>10.42</td>
<td>5.94</td>
</tr>
</tbody>
</table>

scenario is a reaction between silicon and the bombarding oxygen and a subsequent building of a new layer of glass-like material on the surface. Thus, it may be stated, that oxygen plasma orders the surface of silicon modified materials, while in case of unmodified samples such an effect was not observed. The pure aromatic epoxy showed an increase in surface roughness, so it may be deduced that etching and erosion are what causes the surface deterioration, and the sample experiences a physical removal of the surface matter which overall increases the $S_a$ parameter.

7.3.5 AO influence on mechanical properties - three point bending test

Flexural strength and modulus of CFRP samples coated with modified cycloaliphatic epoxy resin system was evaluated by performing a three point bending tests on rectangular specimens - approximately 10 mm wide and 0.3 mm thick. The distance between supports was set to 10 mm which was a minimum value possible because of the low thickness of the tested specimens.

To calculate the strength ($\sigma_{max}$) and elastic moduli ($E$), it was assumed that the samples behave like a simply supported beam. From beam theory, the maximum normal stress due to bending can be expressed by Equation 7.2 and the modulus by Equation 7.3.

$$\sigma_{max} = \frac{3FL}{2wt^2} \quad (7.2)$$

$$E = \frac{FL^3}{4dwt^3} \quad (7.3)$$

where:
- $F$ - acting force [N]
- $L$ - distance between supports [mm]
- $w$ - sample width [mm]
- $t$ - sample thickness [mm]
As one may observe in Figure 7.6, replacing the outer layers of the laminate with the nano-reinforced cycloaliphatic epoxy slightly increases both strength and modulus when compared to the purely aromatic CFRP structure. In the aromatic epoxy CFRP sample, strength was not significantly affected by AO treatment but the elastic modulus decreased by approximately 13%. This implies that the selected TGDDM aromatic epoxy is of very high mechanical parameters and the erosion of a surface layer and 4.2% mass loss experienced during the AO treatment did not cause a significant strength alteration.

In general, the AO treatment tends to soften the exposed materials resulting in a lower modulus of elasticity after the exposure. A slight increase in strength is observed in aromatic and 5 wt% octa-POSS reinforced cycloaliphatic epoxy, which might be due to additional crosslinking caused by elevated temperatures in the plasma tube. Interestingly, the drop in strength is lower in 15 wt% than in the 10 wt% octa-POSS modified samples, and cannot be observed at all in the sample with 20 wt% octa-POSS content. Thus, it was concluded that if the loading of nanoparticles is low (5 wt%), then the epoxy network is not significantly disturbed. However, the effect of
increasing the content of nano-phase is a significant decrease in both strength and modulus, which is probably associated with the fact that the polymer’s network gets disturbed and the epoxy curing is not complete. The undercured portions of the polymer are more easily removed by AO. Moreover, with the increasing octa-POSS content, the silicon concentration on the surface increases, and a silica protective layer gets formed as discussed in the Section 7.3.3. It is believed that the protective layer may partially absorb the load which contributes to the higher retention of mechanical parameters.

Based on the compression test data before and after AO treatment, it can be stated that the samples with 5 and 20 wt% octa-POSS show a very satisfactory maintenance of mechanical properties after AO exposure. In spite of the fact that nanoparticles can be very effective in combating the environmental degradation, they might also reduce the crosslinking density and consequently decrease mechanical properties.

### 7.3.6 AO influence on thermal-mechanical properties - DMTA

The changes in thermomechanical properties due to AO exposure were evaluated with DMTA (Figure 7.7). From observations of the glassy region portions of the storage modulus curve, it can be concluded that coating of the outer layers of a CFRP structure with octa-POSS modified cycloaliphatic epoxy increases the mechanical parameters and has a reinforcing effect on the structure. This result is yet another indication of the good miscibility between octa-POSS and the cycloaliphatic epoxy. The transition behaviour is similar for the unprotected and protected samples, and in the rubbery region the storage modulus is higher when compared to the unexposed samples.

![Figure 7.7: Changes in mechanical properties (storage modulus) and T_g (max of tanδ) due to AO etching.](image)

(a) Aromatic epoxy-uncoated. (b) CY-1/Anhydride/5 wt% octa-POSS.

The analysis of the tanδ curves before and after AO exposure shows that in the case of the aromatic, uncoated epoxy, the crosslinking reaction progresses during exposure,
resulting in a slight increase in stiffness and an elevated $T_g$ (Figure 7.7a). A similar situation is observed in the sample coated with CY-1/Anhydride/5 wt% octa-POSS, which also experienced an approximate 30°C shift in $T_g$ (Figure 7.7b). This result might suggest that the structure was either undercured prior to exposure or that the exposure conditions caused rearrangement of the polymer into the formation of a tighter network, which would result in an increase in $T_g$.

### 7.3.7 AO influence on morphology - SEM

Observation of changes in surface morphology provides visual, tangible proof of material degradation due to AO treatment. The surface of all samples prior to AO exposure was smooth, as might be observed in Figure 7.8a. Due to the AO exposure, all samples (those modified with nanoparticles and the base aromatic epoxy) showed signs of surface erosion. Craters reaching 20 µm in size were created on the surface of unmodified epoxy, and this sample was damaged to the greatest extent, which is also confirmed by the highest mass loss (Table 7.3.1). CFRP samples coated with octa-POSS reinforced cycloaliphatic epoxy were also etched, however, to a much lower degree. Comparing the surface morphology of samples with increasing octa-POSS content, it is apparent that a higher concentration of silicon provides a greater level of surface protection from the bombarding AO.

For comparison, a SEM image of the Kapton reference sample was taken. As can be seen in Figure 7.9, the surface morphology transforms from a smooth to a characteristic carpet-like pattern. This is an indication that the conditions created in the simulation facility during this study are comparable to those of other researchers, since a similar type of morphology was obtained (Bitetti et al., 2007; Duo et al., 2008; Kleiman et al., 1995a; Lv et al., 2015; Zhao et al., 2001).

### 7.4 Erosion yield determination

Erosion yield of any sample can be calculated using Equation 2.3, provided that the AO fluence and material density are known. AO fluence for a particular mission might be obtained from actual space measurements, modelling tools such as SPENVIS (Spenvis) or from a ground-based simulation facility through the mass loss of a Kapton reference sample and Equation 2.2.

AO erosion yield was calculated for the CFRP coupons, each of approximately 10 mm wide × 50 mm long × 0.3 mm thick. The density of all samples was in the range of 1-1.1 g/cm³. Based on the Kapton mass loss the AO fluence was calculated to be approximately $3.56 \times 10^{19}$ cm³/atom.

As can be observed in Table 7.4, replacing the outer layer of CFRP structure
7.4. Erosion yield determination

(a) Virgin material.
(b) Aromatic, unmodified epoxy.
(c) CY-1/Anh/10 wt% octa-POSS.
(d) CY-1/Anh/15 wt% octa-POSS.

Figure 7.8: Surface erosion of CFRP samples coated with a CY-1/Anhydride resin system reinforced with an increasing content of octa-POSS due to atomic oxygen etching.

(a) Virgin material.
(b) AO etched.
(c) CY-1/Anh/10 wt% octa-POSS.
(d) CY-1/Anh/15 wt% octa-POSS.

Figure 7.9: Surface morphology comparison of Kapton reference sample, (a) prior and (b) after atomic oxygen etching.

with 5 wt% octa-POSS reinforced cycloaliphatic epoxy, decreases the erosion yield value by 22% when compared to the purely aromatic epoxy. Further increasing the octa-POSS content reduces this value to 40% of the unmodified epoxy. Again, this is in agreement with the mass loss measurements presented in Table 7.1.
Table 7.4: Erosion yield calculations for CFRP structures covered with octa-POSS reinforced cycloaliphatic epoxy vs. purely aromatic epoxy used as reference.

<table>
<thead>
<tr>
<th>Material</th>
<th>Calculated $E_{\text{yield}} \times 10^{-23}$ [cm$^3$/atom]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aromatic epoxy</td>
<td>3.95</td>
</tr>
<tr>
<td>CY-1/Anhydride/5 wt% octa-POSS</td>
<td>3.11</td>
</tr>
<tr>
<td>CY-1/Anhydride/10 wt% octa-POSS</td>
<td>2.43</td>
</tr>
<tr>
<td>CY-1/Anhydride/15 wt% octa-POSS</td>
<td>2.44</td>
</tr>
<tr>
<td>CY-1/Anhydride/20 wt% octa-POSS</td>
<td>2.5</td>
</tr>
</tbody>
</table>

One may notice that the obtained results of epoxy erosion yield are an order of magnitude higher than the flight data measured during the MISSE 2 PEACE mission. This is because the number of impinging atoms per unit time is 6-10 times greater than in orbit, therefore the rate of erosion is also accelerated. This acceleration factor was calculated as follows:

- Based on the mass loss of the Kapton reference sample exposed in the simulation chamber, the AO fluence was calculated to be $3.56 \times 10^{19}$ atom/cm$^2$ for the 25h of exposure, therefore it can be estimated that the sample experienced an AO fluence of $1.42 \times 10^{18}$ atom/cm$^2$ every hour.

- Based on the mass loss of two Kapton reference samples that flew on the MISSE 2 PEACE mission, the AO fluence for a 4 year exposure was estimated as $8.43 \times 10^{21}$ atom/cm$^2$ which gives $2.4 \times 10^{17}$ atom/cm$^2$ per hour of exposure in LEO.

- Comparing the AO fluence simulation to the LEO values gives:

  $\frac{\text{AO fluence}_{\text{chamber}}}{\text{AO fluence}_{\text{LEO}}} = \frac{1.42 \times 10^{18}}{2.4 \times 10^{17}} = 6$

- Comparing the erosion yield obtained from the simulation chamber with the LEO value for epoxy resin gives:

  $\frac{E_{\text{MISSE}}}{E_{\text{chamber}}} = \frac{4.2 \times 10^{-24}}{3.95 \times 10^{-23}} = 9.5$

- Based on the AO fluence and erosion yields comparison, it can be stated that in the SSC simulation facility the ageing is accelerated by 6-10 times.

The efficacy of the proposed solution can be validated by predicting the life-spans of purely aromatic samples versus the one treated with octa-POSS reinforced cycloaliphatic epoxy from the Equation 7.4, where $\Delta t$ is the thickness loss in cm, $E$ is the erosion yield of the selected material in cm$^3$/atom and AO is the AO fluence calculated for a certain mission. Using the 4 year MISSE mission AO fluence and erosion yields for purely aromatic epoxy (denoted as $E_1$) versus a treated sample (denoted as $E_2$), the approximate life span can be calculated. Taking an omega
shaped CFRP boom developed by DLR as an example (Block et al., 2011) which has a total thickness of 0.1 cm, the life span can be calculated from Equations 7.5 and 7.6.

\[
\Delta t = E \times AO \quad (7.4)
\]

\[
\Delta t_1 = E_1 \times AO = 4.2 \times 10^{-24} \times 8.43 \times 10^{21} = 0.04 = 0.01 \text{ cm/year} \quad (7.5)
\]

\[
\Delta t_2 = E_2 \times AO = 2.5 \times 10^{-24} \times 8.43 \times 10^{21} = 0.02 = 0.005 \text{ cm/year} \quad (7.6)
\]

As can be seen, an epoxy based CFRP boom of 0.1 cm thickness is expected to erode completely within 10 years at the altitude of the ISS, but the loss of structural properties is likely to occur much sooner. Nevertheless, by replacing the outer layers of the boom with octa-POSS reinforced epoxy resin, the life span can be doubled. This is true if assuming that the erosion rate progresses with the same rate, however, given that in the siliconized samples the surfaces chemistry changes and the ash, silica-like residue forms on the surface, it is likely the value of erosion yield will decrease with time. This statement requires further investigation. However, looking at the XPS surface elemental composition before and after AO exposure, for all samples modified with octa-POSS, it can be seen that SiO₂ content increases and carbon content decreases. This is most distinctly seen in samples modified with 15 wt% and 20 wt% of POSS, in which carbon content decreases 1.6 times and 3 times respectively and the silicon content increases 6 times and 10 times, respectively. From this data it is possible to state that there is a point in time where most of the carbon present on the surface is shielded by SiO₂, which is expected to stop or significantly slow down the erosion yield and considerably extend the life span of those structures in comparison with purely aromatic CFRP samples.

7.5 Chapter summary

In this chapter the efficacy of replacing the outer layers of an ultra-thin CFRP structures with an octa-POSS reinforced cycloaliphatic epoxy resin for the purpose of increasing the LEO resistance was presented. The developed epoxy resin system was subjected to the space-like degradation effects of atomic oxygen bombardment and the simulation of sunlight (temperature and short UV radiation combined).

The performed analysis shows that the novel CFRP configuration decreases the UV/thermal degradation by \(\approx 80\%\) when compared to the purely aromatic epoxy resin that was initially used for this application. Also, the proposed modification significantly reduces the outgassing rate.

AO exposure studies revealed that in an increasing octa-POSS content is beneficial
for decreasing the structure’s mass loss. This is due to the higher ash content on the surface that retards the erosion yield.

Also, with an increasing octa-POSS content, the surface chemistry changes more profoundly and the surface energy rises which is caused by the silica-like formation in octa-POSS containing specimens, and due to surface oxidation in purely organic material.
Conclusions

The work presented in this thesis was the first attempt to address the issue of LEO resistance of ultra-thin bistable CFRP deployable structures. Although various sources report high susceptibility of organic materials to LEO, the BRC structures were initially manufactured and designed without taking the long-term environmental resistance into consideration.

The main aim of this project was to develop a low-cost protection strategy from the LEO-induced degradation of ultra-thin CFRP structures. The proposed approach involves replacing the highly aromatic epoxy resin on the outer surfaces of the structure by a cycloaliphatic nano-silicon reinforced one. Such modification offers enhanced UV (by 80%), AO (by 50%) and thermal (by 20%) resistance, without significant alteration in structural and mechanical properties.

During the course of this study a screening analysis was performed to select the best type of nanomodifier from many that could be considered for this application. The cycloaliphatic POSS/epoxy nanocomposites were tested against space-like degrading factors including, UV, AO and temperature which showed that octa-POSS and epoxy-POSS containing samples have superior properties to amino-POSS containing samples. Based on the screening analysis, three nanomodifiers were selected: epoxy-POSS, octa-POSS and nanosilica (added as a more affordable replacement for POSS). All three were cured with either anhydride or amine. Then the developed cycloaliphatic epoxy was thoroughly characterized, including the nanoadditive influence on curing behaviour, surface, and thermal properties. Based on this preliminary analysis, it was found that octa-POSS as a nano-modifier showed superior properties to mono-POSS and nanosilica in dispersion and thermal properties. Additionally, it was shown that curing the system with an amine further reduces the aromatic content and increases UV resistance.

Following on from the resin characterization studies, the influence of increasing octa-POSS content on thermal-mechanical properties was studied. It was found that the addition of a small amount of octa-POSS significantly boosts thermal stability. The DMTA and bending tests confirm that octa-POSS does not act as a mechanically reinforcing agent.

The cycloaliphatic resin system cured with anhydride and reinforced with an in-
increasing octa-POSS loading was subjected to environmental testing, including atomic oxygen etching and UV radiation. During the analysis it was confirmed by XPS that the embedded silicon reacts with bombarding oxygen in the formation of a SiO$_2$ protective layer which decreases the erosion yield. The efficacy of octa-POSS was confirmed by SEM, laser surface scanning and flexural tests before and after AO exposure. It was found that increasing the octa-POSS content reduced mass loss induced by both effects, however, the resin study showed that the resin thermal-mechanical properties are unaffected only up to 15 wt%. It can be concluded that the developed cycloaliphatic epoxy resin system cured with anhydride is a promising protection strategy to extend the useful life of ultra-thin CFRP structures when used as a surface protection resin.

**Future work**

Future work should focus on the improvement of the manufacturing process in order to ensure that an even and defect-free surface is obtained. This should further reduce the environmental degradation, because as shown in this research, a correlation between a smoother surface and mass loss exists. Also, as presented by NASA and various other research groups, defects in coatings or surface layers are the primary centres for atomic oxygen attack, and once an oxygen radical enters the defect its probability of reaction greatly increases, and causing more severe damage. Hence, there is a need to improve the application of outer epoxy layers, for example with vacuum assisted resin impregnation techniques.

It is also of interest to manufacture the whole CFRP structure using the cycloaliphatic/octa-POSS resin formulation. However, due to the nature of the manufacturing technique, it is necessary to prepare this material in a pre-impregnated form. This requires additional kinetic studies of the resin formulation, followed by re-evaluation of structural and deployment behaviour.

Additionally, environmental testing should be continued on a more statistically significant number of specimens to calculate the variance in sample behaviour. There is also a need to measure the AO-induced mass loss in situ, for example by using a crystal microbalance in order to more accurately understand how the mass loss progresses over time. Based on the preliminary results it is expected that the erosion yield will decrease in time due to ash formation on the exposed surfaces. In contrast to purely organic materials that erode linearly, the built up silica layer on
the surface retards the erosion rate over time which would cause the erosion yield to vary throughout the structure’s lifetime. This statement requires further investigation though.

From an engineering point of view, the developed simulation facility requires alterations in order to expose materials to the effects of atomic oxygen, UV radiation and thermal cycling simultaneously. Additionally, in order to be able to characterize the simulation facility, plasma diagnostics should be implemented, for example by emission spectroscopy measurements.

The developed protection strategy should undergo a flight testing campaign before it can be considered a hardware candidate. This should include a thermal-vacuum and vibration testing for a specific mission, and long term storage effects on the material such as creep behaviour.
Appendix A

Simulation facility

Figure A.1: The Surrey Space Centre simulation facility.

Figure A.1 presents the simulation facility which is located in the Plasma propulsion lab at the Surrey Space Centre, which was constructed solely for the purpose of the project presented in this thesis.

The SSC simulation facility includes:

- **A**: The main vacuum chamber
- **B**: Radio-frequency (RF 13.56 MHz), power generator - connected to the con-
trolling unit (C) and the matching network (D) which are run in an automatic mode.

- E: UV deuterium lamp power supply
- F: UV deuterium lamp mounted on a KF vacuum flange
- G: Cooling unit - used to cool both the UV lamp and the RF antenna which generates plasma inside the chamber
- H: Gas bottles: argon and oxygen
- I: Gas flow controller
- J: Power supply used to heat the silicon mat inside the vacuum chamber or other electronic devices such as the photodiode.
- K: gas inlet to the chamber
- L: Pressure gauge
- M: Vacuum turbo pumps

A.1 High vacuum

Pressure in LEO is classed as high (less than of $10^{-5}$ Torr, Han and Kim (2006)). The SSC simulation facility can reach a pressure of $6.5 \times 10^{-5}$ Torr. While the plasma is running, the main chamber pressure increases about one order of magnitude due to pumping the mixture of oxygen and argon.

A.2 Elevated temperatures

In LEO spacecraft usually experience thermal cycling between -80°C and 100°C. The SSC simulation facility is able to heat up the samples to approximately 80-85°C using a silicone heating mat. Although there were plans to include a cooling accessory into the facility, time and budget constrains meant that it was not pursued. The temperature inside the chamber is monitored by a thermocouple which is connected via a feedthrough to a temperature meter positioned outside the vacuum chamber. The silicon heating mat is connected via the same feedthrough to a 12 V power supply.
A.3 UV radiation

UV radiation is simulated by a deuterium lamp (Heraeus, model D200VUV) which generates photons primarily in the UVC range (100-280 nm). This portion of UV radiation is by far the most damaging for polymeric materials. In order to measure the lamp’s intensity, an AXUV100 EUV-UV photodiode was mounted inside the chamber. The total flux measured at the location of the specimen stage was 110 \( \mu \text{W/cm}^2 \).

The flux produced in the range of 100-200 nm by the deuterium lamp was found to be approximately 10\( \times \) the flux of the sun in this region. This approximation was done by integrating the lamp spectrum provided by the manufacturer and comparing with the ASTM E-490-00 Solar Irradiance (Table A.1).
Table A.1: UV-C Lamp Irradiance vs Solar ASTM E-490-00 Irradiance.

<table>
<thead>
<tr>
<th>Wavelength Range (nm)</th>
<th>Lamp Power ($\mu$W/cm$^2$)</th>
<th>Solar Power ($\mu$W/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>115-120</td>
<td>11</td>
<td>0</td>
</tr>
<tr>
<td>120-130</td>
<td>21</td>
<td>0.7</td>
</tr>
<tr>
<td>130-150</td>
<td>23</td>
<td>0.1</td>
</tr>
<tr>
<td>150-170</td>
<td>35</td>
<td>0.5</td>
</tr>
<tr>
<td>170-200</td>
<td>8</td>
<td>8.5</td>
</tr>
<tr>
<td>200-240</td>
<td>7</td>
<td>142</td>
</tr>
<tr>
<td>240-280</td>
<td>3</td>
<td>516.5</td>
</tr>
</tbody>
</table>

Figure A.3: Spectra in the UV region for the AXUV100 photodiode and Heraeus UV lamp. A comparison of UV spectra in the shortwave range of solar and the UV lamp is also given.

A.4 Atomic oxygen

Before the simulation facility (Figure A.1) was built, the author was allowed to work for one week in a different chamber in order to familiarize herself with RF plasma and learn about the factors that contribute to the AO production. The main conclusions from this work are:

- The most affordable way to produce atomic oxygen is to use RF plasma sources which are popular in the plasma industry. An RF generator was also available at the university, therefore it was decided to continue working with this technology.
A.4. Atomic oxygen

- RF plasma sources produce thermal atomic oxygen (0.01-0.1 eV) and an isotropic impingement of particles on exposed samples, while in LEO the AO is hyperthermal ($\approx 5$ eV). However, the upgrade to a hyperthermal source is very complex and costly therefore it was decided to use the thermal source as an approximation.

- It is very difficult to create RF plasma from pure oxygen. A lot of power is required to ignite the plasma, which caused the antenna overheating very quickly. Therefore, a carrier gas is required to facilitate the process. Argon is commonly used in plasma industry and its etching effects on polymers are negligible. This was confirmed by exposing Kapton to the pure argon and argon/oxygen mixtures and in the former case no mass loss was detected.

- The first setup used did not have the antenna cooling installed. Because of that the maximum period of exposure was approximately 30 min without overheating the antenna. For that reason, in the final setup, the antenna was manufactured from a hollow copper wire that enables running water inside the antenna which prevents it from overheating.

(a) Kapton sample during experiment  (b) AO exposed

Figure A.4: Kapton reference sample exposed to AO plasma environment, sample positioned in the plasma afterglow (a) and post-exposure (b). Exposed and shielded parts of the sample are clearly visible.

In the second stage of this project a dedicated simulation facility was built, inspired by the simulation facilities described in literature and lessons learnt from the previous work done in the different chamber. Atomic oxygen effects on materials were simulated by etching the samples with plasma created from a mixture of argon and oxygen, with argon used as a carrier gas that facilitates plasma ignition.

In the SSC facility, plasma is generated in a glass (pyrex) tube 7 cm in diameter and the samples are positioned in the plasma afterglow, approximately 1 cm from the tube end. The pressure in the main chamber was usually in the order of $10^{-4}$ Torr.
while a gas mixture of oxygen and argon was flowing into the chamber at 5 sccm (1.5 sccm oxygen and 4 sccm argon). In order to ignite plasma in the glass tube only and not in the whole chamber, it was found that low RF power (up to 50 W) had to be used. However, because the RF antenna was cooled at all times, it was possible to run plasma continuously for 24 h.

Figure A.2 presents the inside view of the experiment including: UV light inlet (A), RF water-cooled antenna (B, glass tube removed for clarity), the sample specimen stage made of glass fibre reinforced epoxy with a silicon heating mat attached (C), thermocouple (D), gas tube that feeds the gas mixture to the pyrex tube (E).

At the time of setting up the experiment, no suitable plasma diagnostics were available. It was attempted to use a Langmuir probe and emission spectroscopy to evaluate the plasma composition, however, it was discovered that Langmuir probes are difficult to use with RF plasma and the readings were incorrect. A double compensation probe which is designed to work with RF fields was not available. The emission spectroscope did not have any accessory included to position the optical fibre cable inside the chamber. Unfortunately the price of such accessory was too high. Nevertheless, the efficacy of the atomic oxygen production was measured by a Kapton mass loss standard method which is well recognised and popular due to its simplicity and low cost (Figure A.4). Additionally, by measuring the XPS spectra of siliconized samples after AO exposure, the SiO$_2$ layer was detected on the surface, which confirms that the effects simulated in the SSC facility are similar in nature to the LEO degradation and findings in other simulation facilities.
Bibliography


B. Banks, S. A., S. Miller, and D. R. Issues and consequences of atomic oxygen undercutting of protected polymers in low earth orbit. In *Proceedings of the VI Inter-


