

# **Composites with Controllable Stiffness**

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## **Declaration**

This dissertation is a description of the work carried out by the author in the Department of Aeronautics and Chemical Engineering, Imperial College London between September 2009 and September 2013 under the supervision of Prof Alexander Bismarck, Prof Paul Robinson and Dr Lorenzo Iannucci. Except where acknowledged, the material is the original work of the author and no part of it has been submitted for a degree at this or any other university.

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## **Abstract**

High performance carbon fibre reinforced composites with controllable stiffness could revolutionise the use of composite materials in structural applications. Described here are structural materials, the stiffness of which can be controlled on demand. Such materials could have applications in morphing wings or deployable structures. A significant challenge in the field of morphing aerostructures is the development of a stiff skin material that can withstand aerodynamic loads but that can be readily deformed with acceptable actuation forces. To overcome this, two designs of carbon fibre reinforced epoxy composites with controllable stiffness have been developed that contain either thermo-responsive interphases or interleaf layers. At elevated temperatures they undergo large reductions in flexural stiffness and fully recover when cooled, with no discernible damage or loss in properties. These composites, when optimised, could therefore be used as skin materials in morphing wings.

In the first design, composites containing thermo-responsive interphases were manufactured by continuously coating polystyrene onto carbon fibres followed by resin infusion with an epoxy resin. Dynamic mechanical thermal analysis and flexural tests showed that reductions in stiffness of up to 30 % could be achieved when the composites were heated above the  $T_g$  of the interphase. Composites containing polyacrylamide interphases were also analysed using DMTA. These composites underwent reductions in storage modulus of up to 79 % when the polyacrylamide interphase was partially hydrated and heated above its  $T_g$ . In an alternative approach, interleaved laminates containing plies of polystyrene between carbon fibre reinforced laminae were also manufactured. When heated to 120 °C,

above the  $T_g$  of polystyrene, these composites exhibited up to 98 % loss in flexural stiffness and could undergo large deformations. The process was reversible as the composites could be returned to their original configuration and their flexural stiffness restored to their full values with no damage observed.

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## List of Publications and Presentations

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### Oral Presentations

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**Maples, H.**, Gaite, O., Smith, S., Bismarck, A., Robinson, P. *Carbon fibre reinforced epoxy composites with variable stiffness for use in morphing aerostructures*, 19th International Conference on Composite Materials, 28th July – 2nd August 2013, Montreal, Canada.

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## List of Units and Symbols

|                                      |                                                      |                          |                                                                    |
|--------------------------------------|------------------------------------------------------|--------------------------|--------------------------------------------------------------------|
| $^{\circ}$                           | degree                                               | <b>eV</b>                | electron volt                                                      |
| <b>%</b>                             | percent                                              | <b>F</b>                 | force                                                              |
| <b><math>\alpha</math></b>           | thermal expansion<br>coefficient                     | <b>F<sup>SBS</sup></b>   | short beam shear<br>strength                                       |
| <b><math>\beta</math></b>            | beta transition                                      | <b>GPa</b>               | gigapascal                                                         |
| $\gamma_{lv}$                        | surface tension                                      | <b>g</b>                 | gram                                                               |
| <b><math>\theta</math></b>           | contact angle                                        | <b>g</b>                 | acceleration due to<br>gravity (approx. 9.81<br>m/s <sup>2</sup> ) |
| <b><math>\pi</math></b>              | pi                                                   | <b>h</b>                 | hour                                                               |
| <b><math>\sigma</math></b>           | maximum stress                                       | <b>h</b>                 | thickness of specimen                                              |
| <b><math>\sigma^*</math></b>         | apparent stress                                      | <b>h<math>\nu</math></b> | photon energy                                                      |
| <b><math>\tau_{max}</math></b>       | maximum interlaminar<br>shear strength               | <b>Hz</b>                | Hertz                                                              |
| <b><math>\phi_f</math></b>           | diameter of polyimide<br>film circular cut-out       | <b>J</b>                 | Joule                                                              |
| <b>A</b>                             | Ampere                                               | <b>kg</b>                | kilogram                                                           |
| <b>b</b>                             | width of specimen                                    | <b>kN</b>                | kilonewton                                                         |
| <b><math>^{\circ}\text{C}</math></b> | degree Celsius                                       | <b>kV</b>                | kilovolt                                                           |
| <b>cm</b>                            | centimetre                                           | <b>kW</b>                | kilowatt                                                           |
| <b>cm<sup>2</sup></b>                | square centimetre                                    | <b>L</b>                 | support span                                                       |
| <b>cm<sup>3</sup></b>                | cubic centimetre                                     | <b>L<sub>e</sub></b>     | embedded fibre length                                              |
| <b>d<sub>f</sub></b>                 | fibre diameter                                       | <b>L<sub>i</sub></b>     | loading span                                                       |
| <b>d<sub>h</sub></b>                 | hole diameter                                        | <b>M</b>                 | molar                                                              |
| <b>dL</b>                            | decilitre                                            | <b>MPa</b>               | megapascal                                                         |
| <b>dm<sup>3</sup></b>                | litre                                                | <b>m</b>                 | metre                                                              |
| <b>E'</b>                            | storage modulus                                      | <b>m</b>                 | mass                                                               |
| <b>E''</b>                           | loss modulus                                         | <b>m</b>                 | gradient                                                           |
| <b>E<sub>f</sub></b>                 | fibre modulus                                        | <b>m<sup>2</sup></b>     | square metre                                                       |
| <b>E<sub>f</sub></b>                 | flexural modulus                                     | <b>m<sup>3</sup></b>     | cubic metre                                                        |
| <b>E<sub>f</sub><sup>RT</sup></b>    | effective flexural<br>modulus at room<br>temperature | <b>mbar</b>              | millibar                                                           |
| <b>EI</b>                            | bending stiffness                                    | <b>mg</b>                | milligram                                                          |
| <b>E<sub>m</sub></b>                 | matrix modulus                                       | <b>min</b>               | minutes                                                            |
|                                      |                                                      | <b>ml</b>                | millilitre                                                         |
|                                      |                                                      | <b>mm</b>                | millimetre                                                         |

|                      |                                             |                         |                                                                  |
|----------------------|---------------------------------------------|-------------------------|------------------------------------------------------------------|
| <b>mN</b>            | millinewton                                 | <b>t<sub>f</sub></b>    | time required for pressing polystyrene films                     |
| <b>mmol</b>          | millimole                                   |                         |                                                                  |
| <b>mol</b>           | mole                                        |                         |                                                                  |
| <b>m<sub>p</sub></b> | mass of polystyrene pellets                 | <b>T<sub>g</sub></b>    | glass transition temperature                                     |
| <b>ms</b>            | millisecond                                 | <b>T<sub>g-t</sub></b>  | glass transition temperature of thermoplastic                    |
| <b>mV</b>            | millivolt                                   |                         |                                                                  |
| <b>M<sub>w</sub></b> | molecular weight                            | <b>T<sub>g-c</sub></b>  | glass transition temperature of fibre reinforced composite plies |
| <b>μm</b>            | micrometre                                  |                         |                                                                  |
| <b>N</b>             | Newton                                      | <b>T<sub>m</sub></b>    | melting temperature                                              |
| <b>P</b>             | applied force                               | <b>τ<sub>IFSS</sub></b> | interfacial shear strength                                       |
| <b>Pa</b>            | Pascal                                      |                         |                                                                  |
| <b>p<sub>f</sub></b> | pressure applied to press polystyrene films | <b>V</b>                | voltage                                                          |
| <b>P<sub>m</sub></b> | maximum applied force                       | <b>V<sub>f</sub></b>    | fibre volume fraction                                            |
| <b>s</b>             | second                                      | <b>W</b>                | Watts                                                            |
| <b>sec</b>           | second                                      | <b>wt. %</b>            | percent by weight                                                |
| <b>T</b>             | temperature                                 |                         |                                                                  |

### List of Abbreviations

|             |                                  |              |                                           |
|-------------|----------------------------------|--------------|-------------------------------------------|
| <b>AAW</b>  | Active Aeroelastic Wing          | <b>CFRP</b>  | Carbon Fibre Reinforced Polymer           |
| <b>ABA</b>  | 4-acetoxybenzoic acid            | <b>CRG</b>   | Cornerstone Research Group                |
| <b>ABS</b>  | Acrylonitrile Butadiene Styrene  | <b>DARPA</b> | Defense Advanced Research Projects Agency |
| <b>AC</b>   | Applied Current                  | <b>DC</b>    | Direct Current                            |
| <b>AFRL</b> | US Air Force Research Laboratory | <b>DMTA</b>  | Dynamic Mechanical Thermal Analysis       |
| <b>ANA</b>  | 6-acetoxy-2-naphthoic acid       | <b>DSC</b>   | Differential Scanning Calorimetry         |
| <b>APO</b>  | Atmospheric Plasma Oxidation     |              |                                           |

|              |                                           |             |                                           |
|--------------|-------------------------------------------|-------------|-------------------------------------------|
| <b>DVS</b>   | Dynamic Vapour Sorption                   | <b>PMMA</b> | Poly(methyl methacrylate)                 |
| <b>FMC</b>   | Flexible Matrix Composite                 | <b>PS</b>   | Polystyrene                               |
| <b>GFRP</b>  | Glass Fibre Reinforced Polymer            | <b>PTFE</b> | Polytetrafluoroethylene                   |
| <b>4-HBA</b> | 4-hydroxybenzoic acid                     | <b>PVC</b>  | Polyvinylchloride                         |
| <b>HNA</b>   | 6-hydroxy-2-naphthoic acid                | <b>PZT</b>  | Lead Zirconium Titanate                   |
| <b>HQ</b>    | Hydroquinone                              | <b>RFD</b>  | Radial Field Diaphragm                    |
| <b>HQDA</b>  | Hydroquinone diacetate                    | <b>RIFT</b> | Resin Infusion under Flexible Tooling     |
| <b>IFSS</b>  | Interfacial Shear Strength                | <b>RP</b>   | Carbon Fibre Reinforced Polystyrene Layer |
| <b>ILSS</b>  | Interlaminar Shear Strength               | <b>RPM</b>  | Revolutions per Minute                    |
| <b>LaRC</b>  | Langley Research Center                   | <b>RT</b>   | Residence Time                            |
| <b>LC</b>    | Liquid Crystalline                        | <b>RT</b>   | Room Temperature                          |
| <b>LCP</b>   | Liquid Crystalline Polymer                | <b>SBS</b>  | Short Beam Shear                          |
| <b>MAV</b>   | Micro Air Vehicle                         | <b>SEA</b>  | Sebacic acid                              |
| <b>MAW</b>   | Mission Adaptive Wing                     | <b>SEM</b>  | Scanning Electron Microscopy              |
| <b>MFC</b>   | Macro Fibre Composite                     | <b>SMA</b>  | Shape Memory Alloy                        |
| <b>NASA</b>  | National Aeronautics Space Administration | <b>SMP</b>  | Shape Memory Polymer                      |
| <b>NGC</b>   | Northrop Grumman Corporation              | <b>SUA</b>  | Suberic acid                              |
| <b>OP</b>    | Oxygen Plasma                             | <b>TGA</b>  | Thermogravimetric Analysis                |
| <b>PAAm</b>  | Polyacrylamide                            | <b>THF</b>  | Tetrahydrofuran                           |
| <b>PAN</b>   | Polyacrylonitrile                         | <b>UAV</b>  | Unmanned Air Vehicle                      |
| <b>PIP</b>   | Plasma Induced Polymerisation             | <b>UD</b>   | Unidirectional                            |
|              |                                           | <b>XP</b>   | X-ray Photoelectron                       |
|              |                                           | <b>XPS</b>  | X-ray Photoelectron Spectroscopy          |

## 1. Introduction

Composite materials with controllable stiffness could be used in applications such as morphing skins [1, 2] and wings [3, 4], deployable structures [5], vibration control (damping) [6] and customised shape tailoring [5]. The aim of this research project was to produce a composite with controllable stiffness for potential use as a morphing skin in aircraft structures. In the context of engineering, morphing can be described as continuous shape change [7] and there are numerous benefits associated with the use of such technology. Morphing wings could improve the efficiency of aircraft by lowering drag and conceivably reducing weight through having fewer components [8, 9]. The concept of a morphing wing could also be applied to wind turbine blades [10] and racing car components [11] to enhance performance. The more intractable problems associated with designing a skin material for a morphing wing, i.e. the need to counteract large aerodynamic loads, have proved difficult to overcome [3]. A stiff skin material is required that can withstand aerodynamic loads but that can be easily deformed on demand [4]. Carbon fibre reinforced composites with controllable stiffness could be suitable skin materials as they would offer high stiffness (up to 107 GPa in bending) prior to actuation and low stiffness (as low as 1 GPa in bending) and increased strain to failure at elevated temperatures (e.g. 120 °C) [2, 12, 13]. In order to significantly deform conventional carbon fibre reinforced composites, high actuation forces (e.g. >0.5 kN for 2 mm thick specimens tested in three point bending at 32:1 span-to-thickness ratio) are required that may cause the composite to fail before the required deformation has been achieved. Therefore, described here is the development of high performance composites with variable stiffness that can undergo large, reversible bending deflections (midspan deflections up to 17.8 mm at a span of 64 mm) at low actuation forces (<10 N) when heated to

elevated temperatures (120 °C) in an environmental chamber or by applying a direct current to the carbon fibre reinforcement. In this project the developments of two designs of composite with controllable stiffness are described.

In the first design, each fibre within a polymer matrix composite is coated with a thin thermoplastic or thermoset layer with a glass transition temperature lower than that of the composite matrix. Heating the fibre coatings until they soften allows the fibres to slide within the matrix. The coatings can be softened by passing a current through the carbon fibres, which act as electrical resistance heaters. This can greatly reduce the flexural stiffness of the composite by up to 88 % [2]. This process is reversible, with the stiffness returning to its original value once the coating has cooled down. The choice of fibre coating depends primarily on the thermal properties of the polymer. It is required to have a glass transition temperature ( $T_g$ ) or melting point ( $T_m$ ) below that of the matrix but above the maximum service temperature of the structure in which it is used. The matrix can be either a thermoset or a thermoplastic provided that its glass transition temperature is much higher than the  $T_g$  of the fibre coating. For this project, polystyrene (PS) was selected as suitable carbon fibre coatings. Another polymer selected for coating onto carbon fibres was polyacrylamide (PAAm). Tridech et al. [15] coated PAAm onto carbon fibres using a continuous electrocoating technique. PAAm is a suitable coating as it has a  $T_g$  at approximately 84 °C when partially hydrated (20 % moisture content). By altering the moisture content in the PAAm coating, the reduction in composite stiffness can be tailored to occur at different temperatures.

The benefit of using coated carbon fibre reinforced epoxy composites with controllable stiffness in morphing applications is that only a thin thermoplastic

coating is required ( $<1\ \mu\text{m}$ ), which can be heated quickly by passing a current through the carbon fibres. This allows the stiffness to be controlled on demand. Another advantage is that the matrix remains stiff when the carbon fibre coating has softened. The composite can therefore withstand loading at elevated temperature without the risk of fibre misalignment. Below the softening temperature of the fibre coating the composites also have very similar flexural stiffness values (up to 87 GPa) compared to those of unsized carbon fibre reinforced epoxy composites and are therefore suitable for high performance applications [2]. The disadvantage of using these composites is that the maximum deflection at elevated temperatures is limited to the maximum strain of the matrix material.

The second design is an interleaved carbon fibre reinforced epoxy composite. Heating the composite above the  $T_g$  of the interleaf material softens the interleaf layers and allows the reinforced plies to slide relative to each other. At this temperature the flexural stiffness of the composites can be reduced significantly (up to 98 %) and large bending deflections (midspan deflections up to 17.8 mm at a span of 64 mm) are achievable [12, 14]. For this design, the interleaf material must have again a glass transition temperature above the maximum service temperature of the structure in which it is used but well below the  $T_g$  of the matrix. Polystyrene was again chosen as the interleaf material as its  $T_g$  is around 100 °C. The matrix used in the reinforced plies can be a thermoset or a thermoplastic as long as its glass transition temperature is well above the  $T_g$  of the interleaf material.

The advantage of using interleaved composites in morphing applications is that very large deformations can be achieved (as stated earlier) once the interleaf material has fully softened. Although it was not quantified in this research, it could be expected

that the interleaved composites can undergo much larger deformations than the composites reinforced with coated fibres (first design), as each reinforced layer is effectively disconnected at elevated temperature. As with the coated fibre reinforced epoxy composites, the carbon fibres within the Carbon Fibre Reinforced Polymer (CFRP) plies can be used as heating elements although they are not in direct contact with the interleaf material. One way to overcome this is to place the carbon fibres into the interleaf layers. A potential disadvantage of interleaved composites is that delamination could occur under certain loading conditions and when interleaf materials with weak adhesion to the reinforced composite layers are used.

### 1.1 Aim and objectives

The overall aim of this research project was to produce composites with controllable stiffness and to analyse the extent to which the stiffness of the composites could be reduced and restored.

1) The first objective was to develop thermo-responsive polymer coated carbon fibre reinforced epoxy composites with controllable stiffness and to examine the influence of the polymer coating on the thermal and mechanical properties of the composites at different temperatures. To achieve this objective the following tasks were performed chronologically:

- The effect of moisture on the stiffness of PAAm coated carbon fibre reinforced epoxy composites at different temperatures was determined. [People involved: The author and C. Tridech who fabricated the composites]
- A model epoxy matrix composite reinforced with polystyrene coated metal wires was manufactured and analysed to show that polystyrene could be used as an

effective interphase in composites with controllable stiffness. [People involved: The author]

- Polystyrene was coated onto carbon fibres and high performance polystyrene coated carbon fibre reinforced epoxy composites with controllable stiffness were developed. The stiffness loss at elevated temperature was then determined. [People involved: The author]

2) The second objective was to establish whether interleaved carbon fibre reinforced epoxy composites could undergo reductions in stiffness and reversible deflections above the  $T_g$  of the interleaf material. The following task was performed:

- Manufacture polystyrene interleaved composites and analyse the mechanical properties of these laminates at room and elevated temperatures. [People involved: The author, G. Nereau and S. Smith]

## 1.2 Structure of the thesis

This thesis is comprised of five chapters. The first chapter describes the motivation, aims and objectives and outlines the approach taken to develop composites with controllable stiffness. The second chapter is a literature review covering the development of morphing wings and the skin materials used in these structures. The literature review also covers previous attempts at developing composites with controllable stiffness, routes taken to graft polymers onto carbon fibres and the development of interleaved composites. The third chapter describes the effect of moisture on the thermal properties and storage moduli of PAAm coated carbon fibre reinforced composites with controllable stiffness that were manufactured by Tridech [15]. This chapter also describes the production of a polystyrene coated copper wire reinforced epoxy composite with controllable stiffness. The coating of polystyrene

onto carbon fibres and the production of polystyrene coated carbon fibre reinforced composites is then discussed. The composites are tested to determine whether they exhibit a loss in stiffness at elevated temperature. The fourth chapter describes the production of polystyrene interleaved composites with different layup sequences. The mechanical properties of the composites are analysed using flexural, compression and tensile tests to determine the stiffness loss when heated to 120 °C. In the final chapter conclusions are drawn and suggestions for future work are made. The fabrication of Kynar coated wire reinforced epoxy composites along with the flexural property predictions for the unidirectional interleaved composites is described in the appendix. The attempt to develop LCP coated carbon fibre reinforced composites with controllable stiffness is also described and is included in the appendix as this work was largely unsuccessful.

## **2. Literature Review**

### **2.1 Introduction**

A morphing wing is in essence a unitary and seamless structure that has the capability of changing into a variety of shapes depending on flight requirements [3, 7, 16]. Morphing wings are being seen as a replacement for conventional designs that consist of a large number of traditional components, such as flaps and ailerons, hydraulically independent of one another. If a shape change is required in a morphing wing then it follows that the whole structure will deform and reform upon actuation. There are good reasons for replacing conventional designs with radical departures into morphing structures. A one-piece adaptive wing could experience lower drag, leading to reductions in fuel consumption and therefore resulting in the production of fewer polluting gases, vibration and noise [8, 9, 17]. Both aerodynamics and aeroelastic control could be improved with such wings, thus enhancing the manoeuvrability and the flight envelope of the aircraft viz: aspect ratio changes to suit varying flight speeds, as exemplified with the NextGen Batwing that is described in section 2.2 [18, 19].

A significant challenge in morphing wing design is the development of a skin material that can withstand aerodynamic loads but can deform on demand at relatively low actuation forces. This literature review covers the development of potential skin materials (including composites with controllable stiffness), actuation mechanisms and morphing wings.

## 2.2 Review of morphing wing technologies

The Wright Brothers have been credited with using the first primitive morphing (warping) wings in 1903. To control the aeroplane they used a series of pulleys and cables attached to the tips of the wings [20]. As aircraft technology advanced and planes became faster there was an increasing need to design wings that could withstand higher aerodynamic loads and as a result morphing wings were replaced by the more typical rigid wings [21].

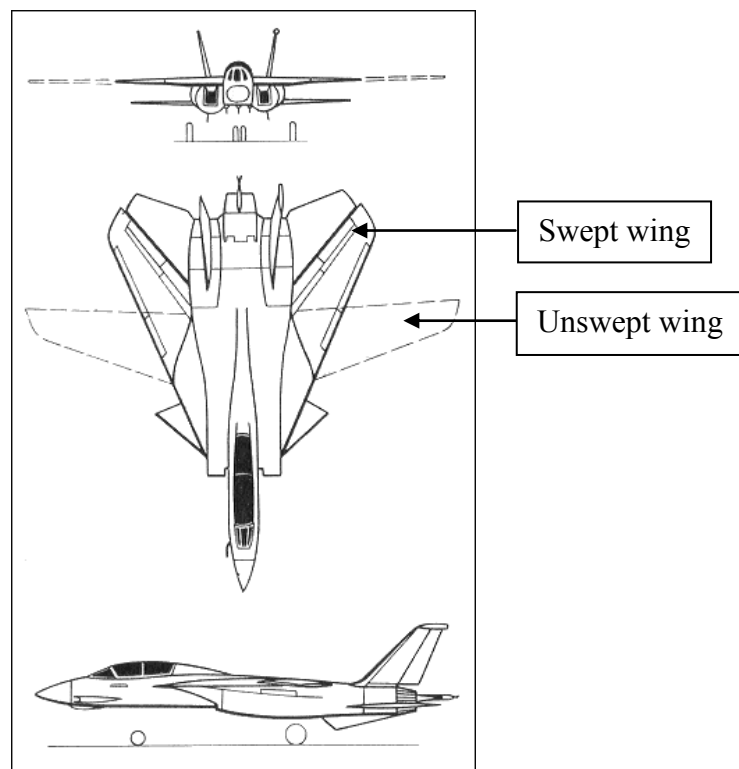


Figure 1: F-14 Tomcat with variable-sweep wings [22]

The Bell X-5 built in 1951 had sweeping (swing) wings that did not morph but moved back and forth via a series of pivots and rails [23]. Variable-sweep wing technology was later incorporated into the MiG-23, the F-14 Tomcat (see Figure 1) and the B-1B Lancer [17]. These pivoting mechanisms tend to be complex and difficult to install [24]. They are also heavy and require extensive maintenance. In

the author's opinion if morphing wing developments are ultimately successful then swing wing technology will become redundant due to reasons of aerodynamics, fuel consumption, maintenance and complexity.

In the mid-1980s the US Air Force Research Laboratory (AFRL) partnered with NASA on the Mission Adaptive Wing (MAW) programme [25]. A wing was built that contained a rigid link mechanism actuated using hydraulics (Figure 2).

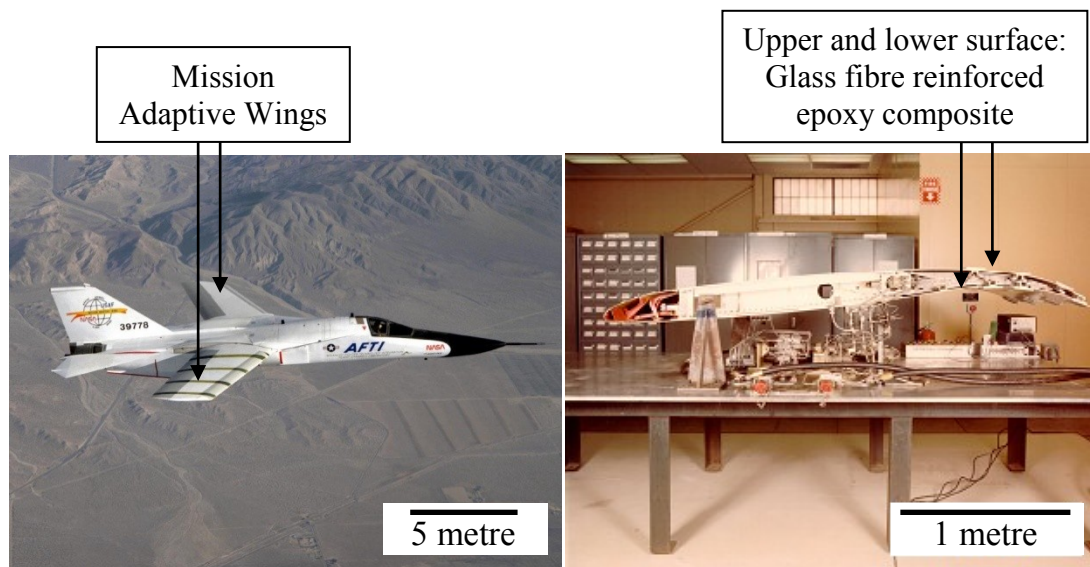


Figure 2: The Mission Adaptive Wing on an F111 aircraft (left) and a cross section of the wing (right) [26, 27]

Overlapping and sliding glass fibre reinforced epoxy composite panels were used on the lower aerofoil surface and a flexible glass fibre reinforced epoxy composite was used on the upper surface. The wing was installed on a F111 aircraft and made a number of successful flights between 1985 and 1988 but contrary to expectations the wing proved unsatisfactory as it was found to be too heavy and complex and this countered aerodynamic advantages and by 1989 it ceased to be used [3].

In 1996 the Active Aeroelastic Wing (AAW) research programme was started, led by the US Air Force Research Laboratory, Boeing Phantom Works and NASA Dryden Flight Research Center [18]. A wing was designed and tested on an F/A – 18 that contained leading and trailing edge control surfaces that could be deflected into the air stream to produce wing twist. In other words the energy of the airstream was being used to twist the wing, which allowed control of the aircraft during flight. The wing incorporated a thin carbon fibre reinforced epoxy composite skin with a honeycomb substructure that lowered the weight of the original F/A – 18 wing by approximately 30 kg. It was reported that the use of AAW technology in future aircraft systems will not only save weight but will also reduce aerodynamic drag [28]. Critically speaking this author considers that the AAW is technically not a morphing wing as it has leading control surfaces that move independently of one another, although the rest of the wing displayed morphing wing similarities.

The Smart Wing Program was a two phase project run between 1995 and 2001 by Defense Advanced Research Projects Agency (DARPA), NASA Langley Research Center (LaRC), AFRL and the Northrop Grumman Corporation (NGC) [29]. A highly effective hingeless morphing wing was developed and tested in the Langley Transonic Dynamic Tunnel [30]. NGC designed and built a control surface that utilised eccentuator arms actuated by piezoelectric lead zirconium titanate (PZT) ultrasonic motors. Deflections of up to  $\pm 20^\circ$  were achieved at relatively high rates ( $> 70^\circ/\text{s}$ ) at Mach numbers ranging from 0.3 to 0.8. Shape memory alloys (SMAs) were originally chosen as the actuators in the first phase of the program but were superseded by piezoelectric actuators, which were found to have a much greater bandwidth [29, 30]. The skin material consisted of a flexible honeycomb core bonded to an outer layer of high strain-to-failure silicone (elastomer). In this author's

opinion the outer silicon layer should be replaced with a more suitable skin material that has greater stiffness and is therefore capable of withstanding high aerodynamic loads. Ideally a material with controllable stiffness should be used that can resist these aerodynamic loads but can also be deformed at relatively low actuation forces when required.

NASA's Morphing Project was started in the late 1990s, led by LaRC [3, 31]. The aim of the project was to manage research efforts in the field of morphing in academic and government institutions. Firstly, one of the more notable achievements was the development of the NASA piezoelectric actuators such as the LaRC-MFC (Macro-Fiber Composite) [32]. These actuators were capable of producing large, directional, in-plane strains (approximately 2000 part-per-million). One application is to embed MFC actuators into flexible structures to cause deflections and allow vibration control [33-35]. MFC actuators were used previously to deform polystyrene interleaved composites at elevated temperature [12]. A single MFC actuator was bonded onto the upper surface of a polystyrene interleaved composite in a single cantilever type setup with a free length of 85 mm and a width of 20 mm and tip deflections of up 3.5 mm were achieved when the specimen was actuated at 120 °C. Secondly, yet another focus of NASA's Morphing Project was the development of biologically inspired technologies, but this is only of slight interest to this research and will not be referred to further [36].

In 2003 DARPA began its Morphing Aircraft Structures programme [19]. Until 2007 it supported three main contractors, Lockheed Martin Skunk Works, Raytheon Missile Systems and Hypercomp and NextGen Aeronautics, along with a number of university research groups. Each company formulated their own designs. Raytheon

aimed to build a telescopic wing for use on a US Navy Tomahawk cruise missile, although their design was dropped in 2007 [19]. Lockheed Martin Skunk Works developed a Z-wing morphing concept [17]. The wing could achieve out of plane morphing allowing the wing to form a number of different configurations (see Figure 3).

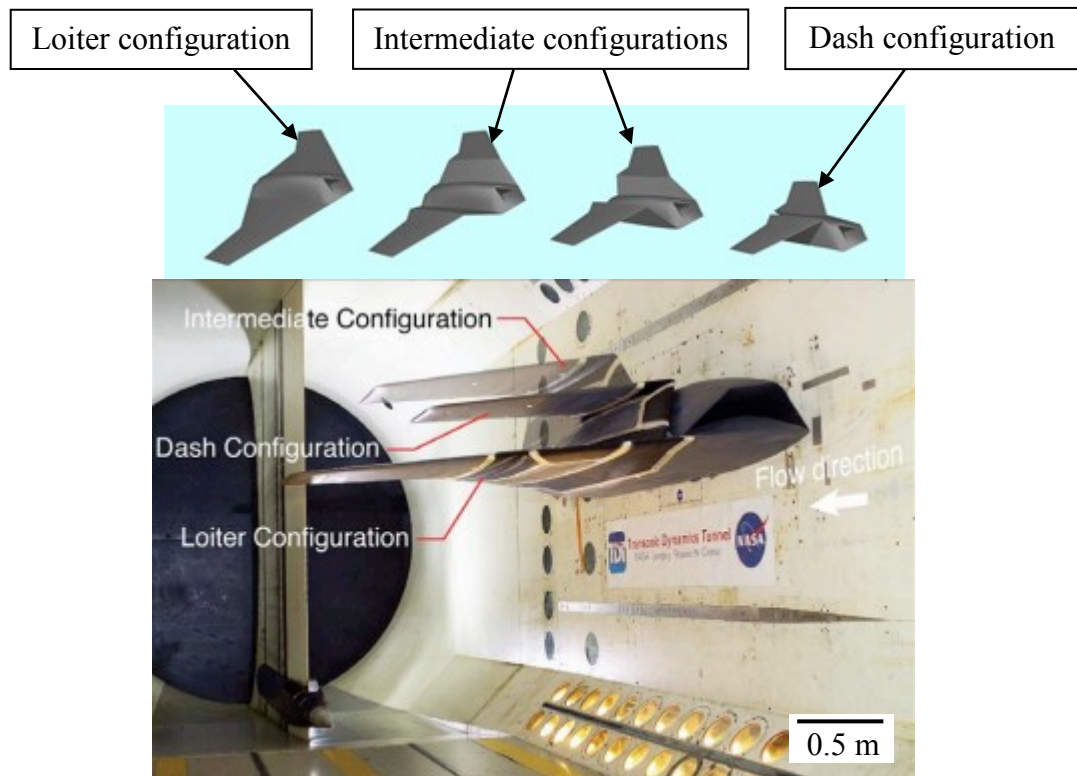


Figure 3: The Lockheed Martin Z-wing [17, 37]

It is envisioned that the morphing concept will be installed onto an Unmanned Air Vehicle (UAV) to increase the mission envelope of the aircraft. At higher speeds it is preferable to have a smaller wing span i.e. the wing morphs into its dash configuration. However, at lower speeds it is more favourable to have a wing with a larger surface area, this is possible in the loiter configuration. The model was tested in the Langley TDT at Mach numbers ranging between 0.2 and 0.9 and recreated altitudes between 10,000 and 50,000 feet. The wing contained a thermopolymer

smart actuator with a reinforced elastomeric skin. A vacuum system was required to hold the elastomeric skin flush against the internal structure of the wing in the loiter configuration. In the author's view this is a poor design as the morphing skin should be of sufficient stiffness to obviate the need for a vacuum. A shape memory polymer (SMP) designed by Cornerstone Research Group was originally selected for the skin material, however, there was a problem with the electrical resistive heating system. The SMP heating elements were composed of nichrome wires, which tended to break after a number of cycles. A new SMP skin has been designed [3, 17], although details were not published.

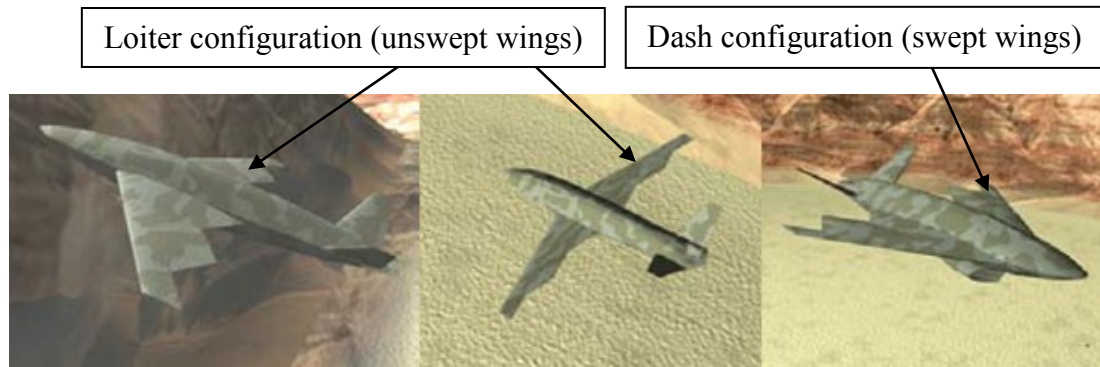


Figure 4: The NextGen Batwing design [19]

Hypercomp and NextGen Aeronautics have designed a morphing structure known as the Batwing that can undergo large in-plane shape changes and surface area reductions [3]. This allows the wing to change from loiter to dash positions (see Figure 4). The design of the wing can be seen in Figure 5. A kinematic sub-structure with an internal electro-mechanical actuation system was used, which enabled the wing to morph in a variety of directions. The wing consisted of multiple metal panels with elastomeric skins. The skin could undergo strains in excess of 100 % [26]. An underlying metallic ribbon structure was used to improve the out-of-plane stiffness of the skin. In the opinion of this author replacing the elastomeric skin with a

controllable stiffness material would be beneficial because such materials could offer improved stiffness prior to actuation and also offer, when required, lower stiffness and high strain-to-failure.

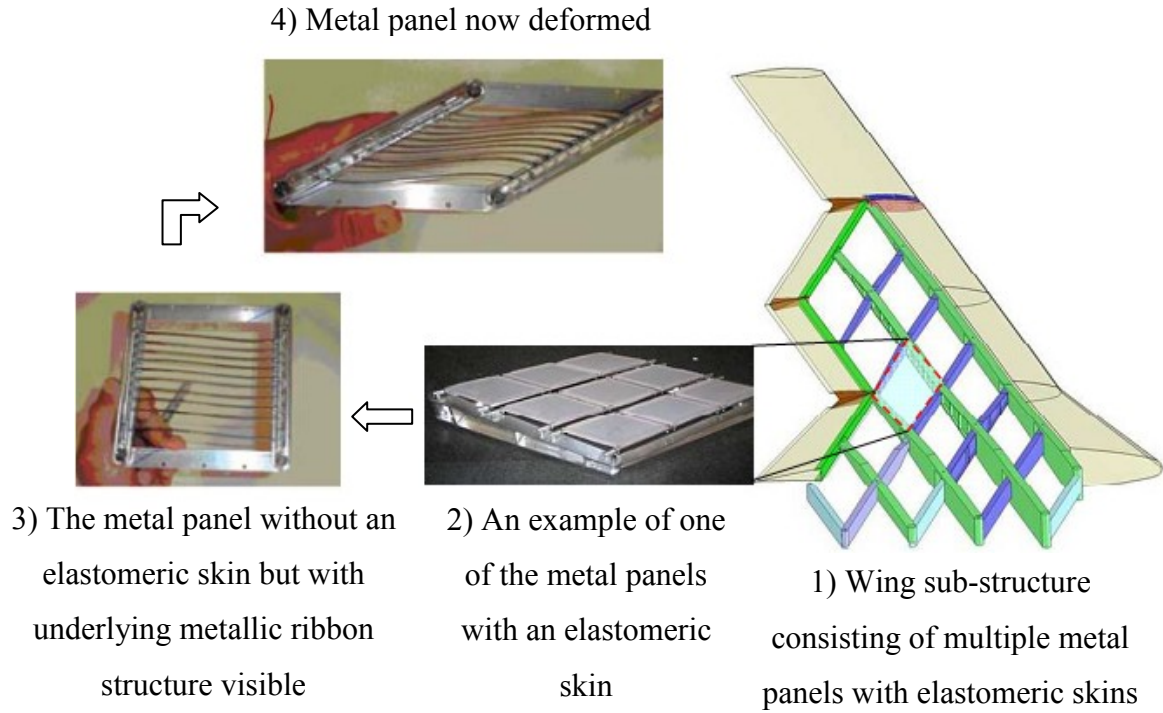


Figure 5: Underlying structure of the NextGen Batwing [26, 38]

When the wing moved from the loiter to the dash formation each constituent metal panel changed shape (deformed). A 45 kg UAV model was tested in August 2006. It was able to change its wing area by 40 % and its wing sweep from 15° to 35° in 5 to 10 seconds. In 2007 NextGen tested its second Morphing Technology Demonstrator UAV (MFX2). The aircraft (weighing 140 kg) managed to achieve a 40 % change in wing area, 73 % change in span and 177 % change in aspect ratio [3, 39].

Ramrakahyani et al. [40] developed an internal cellular truss structure for a morphing wing that contained shape memory alloy tendons providing actuation. A segmented skin was proposed that could be used in conjunction, which replicates the scales of a

fish i.e. overlapping plates [40, 41]. Morphing wings containing inflatable structures have also been designed [3, 42].

### **2.3 Potential morphing skin materials and actuation mechanisms**

The majority of morphing wing designs require a mechanical substructure that provides the change in shape. In order to maintain a smooth and continuous surface a skin material must be chosen that can deform and yet be able to transfer aerodynamic loads to the wing. The skin also needs the ability to deform quickly enough so as not to hinder the performance of the aircraft.

As has been mentioned already elastomers (rubbers) are potential materials for morphing skins [3]. Elastomers are a class of polymer that contain a low density of crosslinks which allow deformation but more importantly the ability to return to their original shape, after the load has been removed [43]. In 2003, Kikuta [20] tested a number of commercially available elastomers, including Tecoflex [44], Riteflex [45] and Arnitel [46]. Kikuta concluded that the elastomers analysed were not suitable for use in morphing wings as they could not withstand sustained high pressure loads. As mentioned before, Lockheed Martin used a silicone based elastomeric skin for the wing tunnel tests of their Z-wing design. The material performed poorly on account of a vacuum being required to hold the skin against the wing. Kikuta [20] also investigated a shape memory polymer. When an SMP is heated above its glass transition temperature ( $T_g$ ) it softens, which allows it to be deformed [47]. The polymer maintains its shape when cooled in the deformed state and then returns to its original shape once re-heated above its  $T_g$  without an applied load. One of the major drawbacks of shape memory polymers such as Veriflex (a commercially available SMP) is that they suffer from low strength and stiffness below the glass transition

temperature [3, 48]. As an example, the tensile strength and modulus of Veriflex below its  $T_g$  (62 °C) are 23 MPa and 1.2 GPa, respectively [48]. In this author's opinion SMPs and elastomers on their own would be unsuitable as morphing skins due to their low rigidity. However, these materials could potentially be used as interphase or interleaf materials in composites with controllable stiffness.

Shape memory alloys are another interesting and viable material for use in morphing wings [49]. They are most commonly used as actuators but they could also be utilised as reinforcement in composite skins to provide a shape memory effect [50]. A major problem with incorporating actuators into composite materials is that they always increase the volume and weight of the composite. Yet another problem is the often weak adhesion between the actuator and the matrix that will not only adversely affect the mechanical properties of the composite but also abate the work of the actuator [4]. One of the most widely used SMAs is Nitinol (NiTi) [51]. There are two major crystal structures (phases) associated with NiTi. At low temperatures the alloy is in its martensite phase and at high temperatures it transforms to its austenite phase. The temperatures at which these phases occur depend on the Ni:Ti ratio in the compound. It is possible to change the shape of the martensite phase by heating the alloy to around 500°C whilst maintaining the new configuration [52]. There are two types of SMAs, one-way and two-way [50]. A one-way shape memory alloy can be deformed easily at room temperature then returned to its original configuration once heated to its austenite phase. A two-way shape memory alloy is a material that has a shape memory effect at both high and low temperatures i.e. it remembers a shape when heated to its austenite phase and when cooled below [51]. To date there have been a number of successful attempts at incorporating shape memory alloys into wings. Nitinol strips have been used as actuators to twist an ABS (acrylonitrile

butadiene styrene) plastic wing up to  $5.5^\circ$  when the alloy straightened in its austenite phase [49]. The wing was a demonstrator model measuring 0.61 m in length. Sofla et al. [53-55] used SMAs as part of an antagonistic flexural cell unit. For this design a pair of one-way SMA strips was placed either side of a flexible inner core, which had large in-plane stiffness. By contracting and extending each strip separately the actuator moved up and down and this contraction of the strips could be achieved by heating the SMA to its austenite phase. A problem with these materials was that the actuator stroke was reduced after each deformation due to the accumulation of plastic strain. The degree of shape recovery was therefore limited. Another drawback of SMA actuators is their slow cooling rates, which reduces the response time of these materials for returning back to their original shape [4, 40]. In this author's opinion this technology could be employed as a leading or trailing edge assuming that the problems associated with post cyclical degradation and slow cooling rates can be resolved.

Piezoelectrics are materials in which an electrical charge is generated after a mechanical stress is induced within the material [56]. The process is reversible as an applied voltage will alter the shape of the material. The concept of using piezoelectric actuators in adaptive composite structures and aerospace applications is widespread [57-60]. Lim et al. [61] deformed the trailing edge of an aerofoil section by  $5^\circ$  using lightweight piezoelectric composite actuators sandwiched between glass fibre reinforced epoxy and carbon fibre reinforced epoxy composites. However, this deformation was achieved in a load free condition and if the aerofoil section were subjected to aerodynamic load, the achievable deflection would likely reduce.

Self-deforming composites could potentially be used as morphing skins. Trakakis et al. [62] developed a hybrid composite with upper plies of unidirectional (UD) glass fibre/epoxy and lower plies of UD carbon fibre/epoxy. To bend the composite they heated the laminate by applying a current to the carbon fibres, taking advantage of electrical resistance heating and the different thermal expansion coefficients of glass and carbon fibres ( $\alpha = 4.9 \times 10^{-6} \text{ K}^{-1}$  and  $-0.41 \times 10^{-6} \text{ K}^{-1}$ , respectively). The composite works on the same principle as bimetallic strips, which consist of two metals with different coefficients of thermal expansion that bend when heated [63]. The composite was analysed using three point bending tests. An electrical current of 6 A was applied for 400 s and a maximum deflection of 3.4 mm (230 mm span) was observed after 250 s. The rate of deflection as a function of temperature was 0.038 mm/ °C. A higher input current could have been used to increase the deflection, although if the temperature had been too high it would have softened the epoxy matrix. In this author's opinion the problem with the design is that once the epoxy around the electrically heated carbon fibres has softened the composite will no longer deflect and will return to its original shape. The maximum deflection is therefore likely to be very restricted and consequently these composites may not be suitable for use in applications where large deflections are required.

Sousa et al. [64] designed bistable carbon fibre reinforced laminates. The composites were bistable as they contained two adjacent regions with symmetric and unsymmetric stacking sequences. The composite could be snapped between its two stable configurations using an external force, such as a PZT actuator. To reduce stress concentrations in the resin rich boundary between the two adjacent stacking sequences, they proposed the use of curvilinear fibre paths.

## **2.4 Composites with controllable stiffness**

In recent years there has been considerable interest in the development of composites with controllable stiffness [3]. A composite with controllable stiffness could prove to be a viable skin material for use in morphing applications as it would offer high stiffness with increased compliance when required [14, 15]. Controllable stiffness materials may also find applications in deployable structures such as satellites [3]. These composites could make typical hinge mechanisms redundant.

Henry and McKnight [65] developed a form of variable stiffness composite consisting of a polyurethane shape memory polymer matrix with discontinuous steel reinforcement. The SMP was heated until it softened, which allowed the discontinuous elements to move relative to each other. This led to reductions in storage modulus of up to 99 % as measured using Dynamic Mechanical Thermal Analysis (DMTA). After deforming the composites at elevated temperature, the original shape of the specimens was recovered using the SMP as an actuator. However, in some cases the actuation forces it could produce were too small to enable full recovery, possibly due to irreversible plastic deformations occurring at large specimen deflections. Shape memory polymers can also be used as matrix materials in composites e.g. Veritex, which is a carbon fibre reinforced shape memory polymer composite [66]. The matrix can be heated through electrical resistance heating of the carbon fibres, which heats the SMP above its  $T_g$  and reduces the stiffness of the composite. A problem with designs such as these is that structural deformations can only occur when the matrix has softened. Therefore, when these composites are deformed at elevated temperature there is a possibility the

reinforcement could misalign, resulting in permanent damage and consequently in the author's opinion these materials are unsuitable for morphing applications.

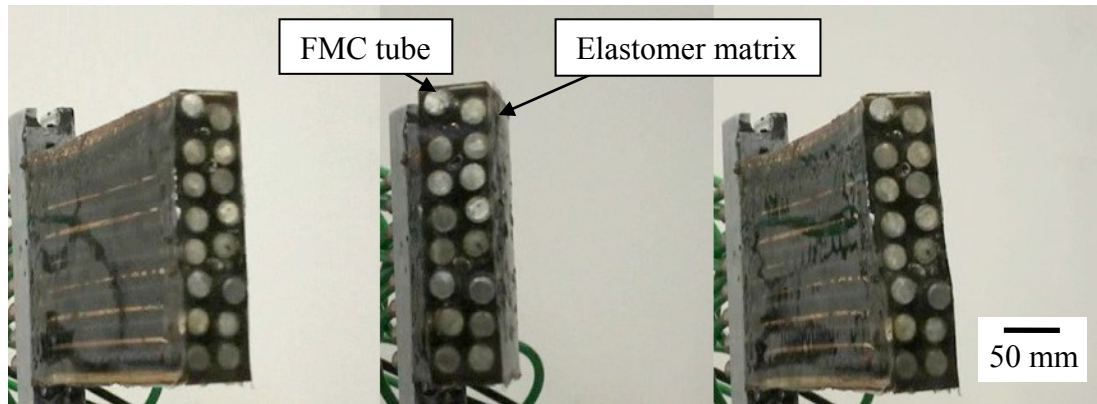


Figure 6: Unpressurised FMC tubes (left), out of plane bending – tubes on the left hand side are pressurised (middle) and twisted – top left and bottom right tubes are pressurised (right) [17]

Another form of controllable stiffness composite consists of braided flexible matrix composite (FMC) tubes within an elastomer matrix [17, 67]. When the tubes are pressurised with a fluid they either expand or contract depending on their design, leading to a change in composite shape and stiffness (Figure 6). As mentioned earlier the problem with using elastomers is that they cannot withstand high pressure loads. In the view of this author these composites are therefore unsuitable for use as morphing skins due to the low stiffness matrix and also due the requirements for carrying fluid to pressurise the FMC tubes.

A laminated beam with controllable stiffness, consisting of CFRP and glass fibre reinforced polymer (GFRP) layers, was designed for vibration damping applications [68]. The layers were not bonded together but an electric field was applied through the thickness (between the GFRP and CFRP elements) to prevent or allow relative

shear displacement between the adjacent layers. Experiments were performed to demonstrate that this approach could be used to adjust the flexural stiffness of such a beam to suppress vibration due to resonance. These beams were not designed to undergo large deflections and are therefore unsuitable for morphing applications in this author's opinion.

#### 2.4.1 Composites with controllable stiffness: Composites containing thermo-responsive fibre coatings

A particular design of controllable stiffness composite described in this study contains a thermo-responsive interphase. An interphase is a significant volume of material present between the fibre and matrix as opposed to an interface, which is a sharp boundary [69]. Interphases have been used to improve the interlaminar shear strength and fracture toughness of composites [70, 71]. An interphase can be created by coating a polymeric layer onto the surface of the reinforcement [71]. Tridech et al. [15] electrocoated carbon fibres with polyacrylamide. The coated fibres were then embedded into an epoxy matrix via resin infusion. This produced unidirectional epoxy composites reinforced by PAAm coated carbon fibres with controllable stiffness. The flexural moduli of the composites were determined at different temperatures using three point bending tests. The composites underwent an 88 % loss in flexural stiffness when heated from room temperature to 110 °C by passing a current through the carbon fibres. At this temperature the PAAm interphase had softened. The flexural stiffness was fully recovered when the composites were cooled to room temperature. Because of the significant reduction in stiffness at elevated temperature this design of controllable stiffness composite has good potential to be developed further for morphing skin applications. In another series of experiments Tridech [2] grafted poly(methyl methacrylate) (PMMA) and

poly(methyl methacrylate-co-acrylamide) p(MMA-co-AAm) onto fibres via continuous electrocoating, with the aim of producing composites with controllable stiffness. The coated fibres were then embedded in an epoxy matrix. When the composites were heated from room temperature to 130 °C, a 41 % and 54 % reduction in flexural stiffness was recorded for the composites containing PMMA and p(MMA-co-AAm) coated fibres, respectively. The flexural stiffness of these composites was also fully recovered when the specimens were cooled to room temperature.

#### 2.4.1.1 Polymer coating methods and fibre oxidation

When manufacturing composites with responsive fibre coatings there are many different polymer interphases (see section 2.4.1.2-3) and coating methods can be used. The surface of the carbon fibres may need to be treated prior to coating or polymer grafting to create a sufficient level of adhesion between the fibre and the interphase. Plasma oxidation can promote adhesion by increasing the surface free energy of the fibres through the introduction of oxygen containing functionalities [72, 73]. Covalent bonding is also possible between certain functional groups (such as carboxylic acids) on the fibre and the polymer coating [74]. Other oxidation routes have been developed although these have associated problems and therefore in this author's opinion are less suitable than plasma for oxidising fibres. Oxidative treatments can be carried out at elevated temperatures in air, however, this tends to lead to degradation of the carbon fibres as temperatures around 600 °C are required [75]. Oxidation performed in a pure oxygen environment still requires temperatures in excess of 400 °C, which could damage the fibres or lead to spontaneous combustion. A common wet oxidative treatment of carbon fibres uses boiling nitric acid. Compared to other oxidation processes plasma treatment is relatively safe as it

does not require corrosive chemicals and the temperature of the plasma does not exceed 400 °C [76]. Plasma also causes minimal damage to the fibres [77, 78].

There are a number of different methods for coating and/or grafting polymers onto carbon fibres. These include passing the fibres through a solution or dispersion of the polymeric material, i.e. solution or dispersion dip coating [71]. However, these result in a physical and not a chemical bond. Chemical bonding between the carbon fibre and the coating usually produces better adhesion and, therefore, improved stress transfer between the coating and the fibre [71]. There are different methods that can be used to covalently bond (graft) polymeric coatings onto carbon fibres including electropolymerisation [79, 80], plasma polymer deposition [81, 82] and in-situ chemical grafting reactions [83, 84] or interfacial polycondensation [85, 86]. In electropolymerisation, monomers are polymerised onto carbon in an electrolytic cell [71]. The advantage of using this process is that uniform layers of varying thickness can be grafted. It is also possible to control the polymer structure and, therefore, the properties of the fibre coating [71, 87]. In plasma polymerisation, a plasma source is used to initiate free radical polymerisation on the surface of the substrate [72]. It is typically used to coat thin, highly crosslinked polymer layers that have strong adhesion to the fibre surface [88]. For in-situ chemical grafting reactions, monomers are polymerised in the reaction mixture. The amount of grafting can be controlled by varying the amount of initiator. Tridech [2] described an electrocoating method in which a monomer is polymerised via free radical polymerisation in the vicinity of the carbon fibres. Free radical bulk polymerisation in the presence of carbon fibres can also be carried out [89]. In interfacial polycondensation reactions, a thin polymer film is rapidly formed at the interface of two unstirred, immiscible monomer solutions [86]. An advantage of using this technique to coat carbon fibres is that high

reaction rates can be achieved at room temperature. Another advantage is that the wetting of the fibres can be controlled by selecting appropriate solvents.

#### 2.4.1.2 Thermo-responsive fibre coating: Polystyrene (PS)

Polystyrene is a thermoplastic, vinyl polymer that is formed by polymerising the monomer styrene [90]. Polystyrene was first manufactured by Eduard Simon in 1839 and has been commercially available since 1925 [91]. Polystyrene is a common thermoplastic used in everyday items such as packaging. PS has a tensile modulus of approximately 3 GPa and a tensile strength around 50 MPa [90]. The chemical structure of polystyrene is shown in Figure 7.

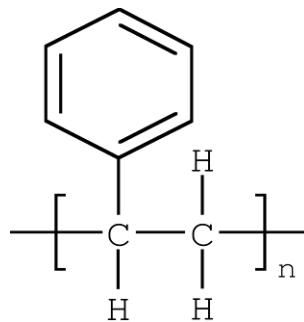


Figure 7: Polystyrene structure [92]

Polystyrene is a suitable candidate for use as a thermo-responsive coating in carbon fibre reinforced composites as it has a glass transition temperature at approximately 100 °C [93]. This is above the maximum operating temperature of an aircraft (90 °C) [94] and below the  $T_g$  of the epoxy matrix. Also, the storage modulus of polystyrene, recorded using DMTA, decreases dramatically above its  $T_g$  (Figure 8).

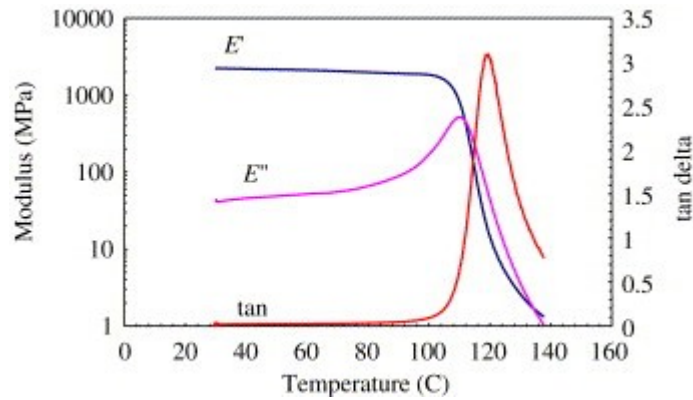


Figure 8: DMTA of polystyrene [93]

There are three configurations of polystyrene: atactic, syndiotactic and isotactic [95]. Atactic polystyrene is amorphous and, therefore, does not have a true melting point. Syndiotactic and isotactic polystyrene have crystalline structures and melting points around 270 °C and 240 °C, respectively.

➤ Coating polystyrene onto carbon fibres

Bismarck et al. [89] grafted polystyrene onto carbon fibres to try to improve the adhesion between carbon fibres and a polystyrene matrix. Soxhlet extraction showed that polystyrene had been covalently bonded onto the carbon fibres. Covalently bonding is preferred as it improves the adhesion between the relatively inert thermoplastic coating (polystyrene) and the carbon fibres [96]. From single fibre pull-out tests the polystyrene grafted fibres showed a 200 % improvement in adhesion to the polystyrene matrix when compared with the unmodified carbon fibres. The polystyrene was grafted using a batch bulk polymerisation in a nitrogen atmosphere. As this coating method was a batch process rather than a continuous process it would, in this author's opinion, be very difficult to use this method to coat long, continuous lengths of carbon fibres in sufficient quantities to manufacture a composite.

#### 2.4.1.3 Thermo-responsive fibre coating: Polyacrylamide (PAAm)

Polyacrylamide is a water soluble polymer formed by the polymerisation of acrylamide. PAAm is commonly used in water treatment as a flocculating agent [97].

The structure of PAAm is shown in Figure 9.

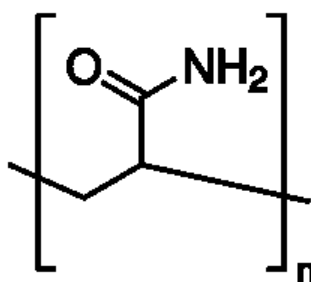


Figure 9: Polyacrylamide structure [98]

The glass transition temperature of anhydrous polyacrylamide is 165 °C [99]. By controlling the moisture content in the polymer the  $T_g$  can be adjusted and therefore PAAm is an interesting choice for use as a thermo-responsive fibre coating [100, 101].

##### ➤ Coating polyacrylamide onto carbon fibres

Tridech et al. [15] used a continuous electrocoating technique to graft 4 wt.% PAAm uniformly onto unsized carbon fibres. The carbon fibres were electrically contacted by passing them over stainless steel pins connected to the negative terminal of a power supply. The fibres were passed through a stainless steel tube (connected to the positive terminal) within a solution of acrylamide, DMF (solvent) and lithium perchlorate. The resulting PAAm grafted layer was 0.1 µm thick.

#### 2.4.2 Composites with controllable stiffness: Interleaved composites

The second design of controllable stiffness composites are interleaved laminates. There are five types of interleaving material as defined by Yasaee et al. [102]: “additional matrix resin, thermoset adhesive films, random short fibres, micro-sized polymer particulates and thermoplastic polymer films”. In previous studies interleaving has been used ostensibly to improve the damage tolerance of fibre reinforced composites [103, 104]. Unidirectional carbon fibre reinforced epoxy composites interleaved with the same matrix material were developed by Singh and Partridge [105]. Composites containing 50  $\mu\text{m}$  and 200  $\mu\text{m}$  thick central resin rich layers showed significant improvements in toughness when compared with non-interleaved composites of the same material. Up to 70 % increase in delamination resistance in mode I, 200 % in mode II and 100 % in mixed mode loadings (I/II) was recorded for the interleaved composites. Thermoplastic and thermoset interleaved carbon-epoxy composites were developed by Aksoy and Carlsson [106]. The interlaminar shear fracture (Mode II) of the interleaved composites was analysed. Both thermoset and thermoplastic interleaf materials increased the interlaminar fracture toughness of the composites by 450 % and 640 % respectively, when compared with the control sample (without interleaf layers). Lu et al. [107] analysed the instrumented drop weight impact response of a unidirectional carbon fibre-epoxy beam and a corresponding laminate interleaved with poly(ethylene-co-acrylic acid). The interleaved composites absorbed approximately 5 times more energy than the control sample at the initial point of fracture. The impact response of the interleaved beam was therefore significantly better than that of the control sample. Another potential use for interleaved composites is in damping applications [108]. The damping properties of interleaved composites containing polyurethane elastomers,

polyamide elastomers and polyethylene-based ionomers were studied by Kishi et al. [109]. From DMTA, composites interleaved with thermoplastic polyurethane had the highest damping properties due to the low stiffness of the thermoplastic polyurethane interleaf layers (storage modulus of 0.5 GPa at 25°C).

Interleaving has also been used to create composites primarily for use in morphing applications. For example the concept of a laminated material with controllable stiffness was studied by Gandhi and colleagues [110-112]. They developed structures containing three aluminium beams separated by layers of cast acrylic and polyvinyl chloride (PVC) type 1 material. Ultra-thin electric blanket heaters were embedded into the polymer layers in order to heat them through their glass transition temperatures. The flexural moduli of the beams at room temperature were between two and four times greater than at elevated temperature. A problem with this study in this author's opinion was that the experimental setup was poorly designed. The laminate was deformed in a single cantilever setup where only the central aluminium beam was clamped and deflected. The two outer aluminium beams were therefore only used as stiffening elements. If the inner beam were to be deflected significantly, the two outer aluminium beams would not deform as they should and would therefore eventually separate from the inner beam. McKnight et al. [113] patented the concept of a variable stiffness structure containing layers of constant and variable stiffness elements arranged in an alternating sequence. The patent also covered the possibility of variable stiffness elements with different shapes, for example, pillars, corrugation and honeycomb configurations.

A variable stiffness CFRP beam containing alternating layers of elastomer was reported by Raither et al. [14]. The elastomer was bonded to adjacent CFRP plies

using epoxy resin. The composite could be heated by passing a current through the carbon fibres within the central CFRP ply. The inner and outer CFRP layers had lamination angles of  $0^\circ$  and  $23^\circ$ , respectively. The different fibre orientations of the reinforced layers permitted adaptive bend-twist coupling of the laminated composite. The composite was tested in a single cantilever type setup, where only the inner (protruding) CFRP ply was deflected at the free end. When the elastomer was heated to  $80^\circ\text{C}$ , above its glass transition temperature of  $44^\circ\text{C}$ , the coupling stiffness was reduced by a factor of 10. A problem with this study is that the low  $T_g$  of the elastomer would limit the use of the composite in aerostructures, where the maximum operating temperature is  $90^\circ\text{C}$  [94]. However, the view of this author is that these composites could be an effective morphing skin provided an interleaf material with a higher  $T_g$  were to be selected.

A problem with interleaved composites is that the adhesion between the interleaf and matrix materials is often very weak, resulting in low toughness [114-117]. Some thermoplastic interleaf materials have low surface energies and this can lead to low adhesive strength at the interleaf-matrix interface. There are a number of ways to overcome this problem, including plasma and chemical treatment. Heness et al. [116] showed that plasma etching and chemical treatment could improve the adhesion of nylon interleaf films to an epoxy matrix. Nay et al. [114] used a plasma induced polymerisation (PIP) technique to deposit thin polyisoprene and polybutadiene layers onto polyimide interleaf films. These polymer layers improved the adhesion between the polyimide films and the matrix of interleaved carbon fibre reinforced epoxy composites. They also demonstrated that an argon plasma etch of the polyimide film prior to the PIP process further increased the adhesion within the interleaved composites.

## **2.5 Summary of literature review**

The design and fabrication of morphing wings is very much in its infancy. There are many concepts in development, the majority of which are not ready to replace conventional systems. However, the future of morphing wings looks promising and it is probable that with the necessary technological advancements these adaptive structures could be used in military and commercial aircraft. One of the major challenges in morphing wing design is the development of a suitable skin material. A number of potential skin materials have been conceived but most of these cannot be used in aerospace applications. Composites with variable stiffness could prove to be viable skin materials as they would offer high stiffness and yet flexibility when required. The subject of this PhD study covers the production of polymer coated carbon fibre reinforced epoxy composites and interleaved laminates with controllable stiffness that when optimised could be used as skin materials in morphing wings.

### 3. Polyacrylamide and Polystyrene Coated Fibre Reinforced Epoxy Composites

#### 3.1 Introduction

This chapter describes the production of coated carbon fibre reinforced epoxy composites with controllable stiffness. The composites contained thermo-responsive interphases that softened above their glass transition temperatures, which allowed the fibres to slide within the matrix (Figure 10). To actuate the stiffness change the carbon fibres were used as resistance heating elements by passing a current through the carbon fibres. When the fibre coating has softened, the ability of the interphase to transfer load to the fibres is reduced, greatly lowering the flexural stiffness of the composite.

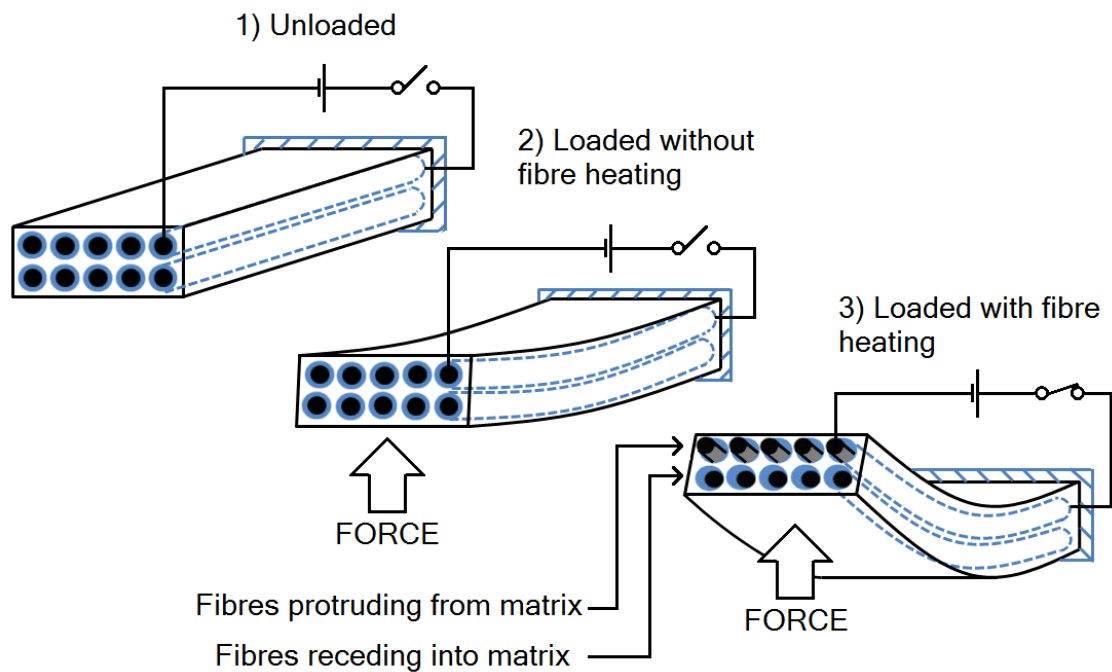


Figure 10: Concept of the controllable stiffness composite

The fibre coating was chosen so that its glass transition temperature ( $T_g$ ) was less than the  $T_g$  of the epoxy matrix but above room temperature. The fibre coating and the matrix can be either a thermoplastic or a thermoset. Polyacrylamide was chosen

as a fibre coating as it has a  $T_g$  of approximately 84 °C, when partially hydrated (20 % moisture content), which is well below the  $T_g$  of the epoxy resin (182 °C) used as the matrix (Table 1). Polystyrene was also chosen as a fibre coating as it has a  $T_g$  at approximately 100 °C, well below the  $T_g$  of the epoxy. In previous studies it has been shown that vinyl polymers including polystyrene could be grafted onto unsized carbon fibres via free radical polymerisation [89, 118, 119]. For the purposes of this study a coating method was chosen that would allow the individual fibres within a carbon fibre tow to be coated continuously with polystyrene.

### **3.2 Experimental details**

#### **3.2.1 Materials**

Unsize carbon fibres (AS4 12k HexTow™) were supplied by Hexcel Corporation (Duxford, Cambridge, UK). The aerospace grade resin system Araldite® LY556 and hardener XB3473 were purchased from Huntsman Advanced Materials Ltd. (Cambridge, UK). The epoxy was prepared using a resin to hardener mixing ratio of 100:23 by mass. Tinned copper wire (7125291) and silver-loaded electrically conductive paint (186-3600) were purchased from RS (Northants, UK), PS powder (ST316310) from Goodfellow (Cambridge, UK) and acetone (> 99 %) from VWR (Lutterworth, UK). 98 % sulphuric acid and n-dodecane (25.4 mN/m, 99 %) were purchased from Fisher Scientific (Loughborough, UK). Styrene ( $\geq$  99 %) and tetrahydrofuran ( $\geq$  99 %) were bought from Sigma Aldrich (Dorset, UK). The water-soluble azo initiator (VA-057) was purchased from Wako Chemicals (Neuss, Germany) and epoxy resin for microsections (Epoxicure) from Buehler (Coventry, UK).

### 3.2.2 Moisture content of PAAm coated carbon fibres

PAAm coated AS4 carbon fibres were prepared by Tridech [15]. The unsized and PAAm coated carbon fibres for DVS analysis were conditioned for 10 days at 20 °C and at 80 % relative humidity prior to characterisation to ensure the PAAm coating was hydrated. Dynamic Vapour Sorption (DVS Advantage, SMS, Middlesex, UK) was used to determine the moisture content of the PAAm coated and unsized fibres. The samples were dried for 24 h at 40 °C and 0 % relative humidity.

### 3.2.3 Conditioning of pure epoxy resin and PAAm coated carbon fibre reinforced composites

Prior to characterisation, the pure epoxy samples (preparation described in section 3.2.4.2) along with the unsized and PAAm coated carbon fibres composite specimens (manufactured by Tridech) were conditioned. Samples were either dried in a vacuum oven at 80 °C for 12 h, conditioned for 10 days at 20 °C (80 % relative humidity) or fully submerged into water for 36 h. This allowed the effect of moisture content on the  $T_g$  of the PAAm interphase to be studied. For this investigation the specimens are known as ‘dry’, ‘hydrated’ and ‘fully hydrated’, depending on the degree of conditioning. The weight before and after conditioning was measured using a microbalance.

### 3.2.4 Manufacturing copper wire reinforced epoxy composites

#### 3.2.4.1 Coating copper wires with polystyrene

Tinned copper wire (diameter = 600  $\mu\text{m}$ ) was used to reinforce epoxy matrix composites. The PVC sheathing around the wire was removed using a pair of wire strippers and the bare wire washed in acetone. The wire was then cut into 80 mm

long pieces using scissors. In order to coat the metal wires, each wire was individually dipped into a solution of PS in acetone (1:5 weight ratio) using tweezers as shown in Figure 11. The coated wires were then dried overnight at 60 °C to remove any residual solvent. The amount of polystyrene coating per length of copper wire was approximately 0.41 mg/cm.

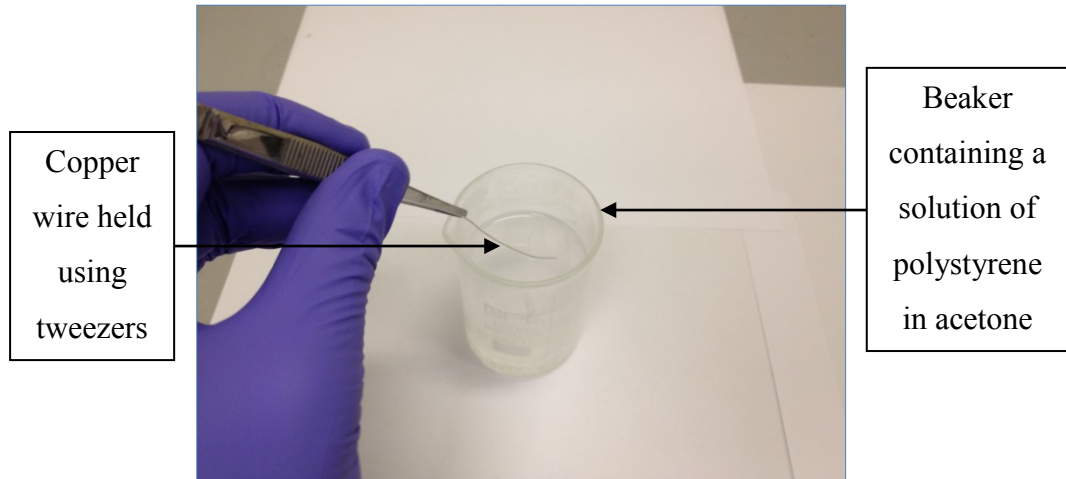


Figure 11: Method for coating copper wires with polystyrene

#### 3.2.4.2 Fabrication of pure epoxy samples and copper wire reinforced epoxy composites

Pure epoxy specimens were prepared by pouring the resin system into a stainless steel mould (80 mm × 50 mm × 2 mm) covered in release fabric (FF03PM, Aerovac, West Yorkshire, UK). The resin was degassed and then cured at 120 °C for 2 h and 180 °C for 4 h inside a vacuum oven. Cured DMTA specimens (40 mm × 5 mm × 2 mm) were prepared using a water cooled diamond bladed cutter (Diadisc 4200, Mutronic, Rieden, Germany).

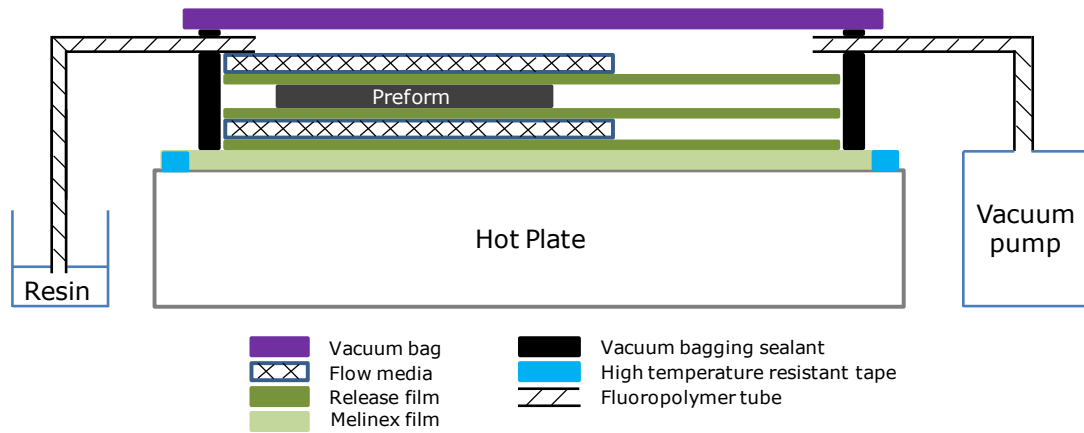


Figure 12: Diagram of resin infusion setup (RIFT)

The uncoated and PS coated copper wires were wrapped by hand around a release film (FF03PM, Aerovac, West Yorkshire, UK) covered metal plate (150 mm × 50 mm × 1 mm). Each preform consisted of two unidirectional layers of the same wire. Resin Infusion under Flexible Tooling (RIFT) was then used to infuse, consolidate and cure the specimens (the experimental setup is shown in Figure 12). To prepare the bagging setup for the resin infusion process, a polyester film (450 × 800 mm, Melinex®, PW 122-10 50-RL, PSG group, London, UK) was taped onto a heating plate (460 mm × 920 mm, Wenesco, Inc., Illinois, USA) using high temperature resistant tape (Flashtape 1, Aerovac, West Yorkshire, UK). A release fabric (360 × 700 mm, FF03PM, Aerovac, West Yorkshire, UK) was placed onto the Melinex® film, followed by a layer of polyester flow media (360 × 500 mm, Resin Diffuse Membrane®, 1507B, Newbury Engineer Texile, Berkshire, UK). The wire preforms were then placed between two layers of the release fabric. A layer of the Resin Diffuse Membrane® was placed on top of that. Two Legris fluoropolymer tubes (6 mm internal diameter, RS Components, Northants, UK) were positioned either end of the set-up. The inlet was bent several times in order to prevent air getting into the system when the vacuum was applied. The outlet was connected to a vacuum pump

(Island Scientific, Isle of Wight, UK). The system was sealed using vacuum bagging film (600 mm  $\times$  1000 mm, Capran 518 heat stabilised Nylon 6 blown tubular film, Aerovac, West Yorkshire, UK) and sealant tape (SM5127, Aerovac, West Yorkshire, UK). A vacuum was then applied to remove air from the vacuum bag. The inlet tube was placed into the resin container once the required pressure had been reached. The resin was allowed to flow over the sample at 40 °C and stopped once it had completely passed through the wire preforms. The curing cycle (2 h at 120 °C and 4 h at 180 °C) was programmed using a temperature controller (Wenescio, Inc., Illinois, USA). The cured specimens were cut into DMTA samples using a water cooled diamond bladed cutter. The dimensions of the uncoated and PS coated wire reinforced epoxy composite specimens were 40 mm  $\times$  5.4 mm  $\times$  1.19 mm and 40 mm  $\times$  6.8 mm  $\times$  1.26 mm, respectively. These composites were not conditioned prior to testing.

### 3.2.5 Coating polystyrene continuously onto carbon fibres

Polystyrene was coated continuously onto carbon fibres via an in situ polymerisation process. This method was chosen as it permitted the fibre tow to spread during the coating procedure thereby allowing individual fibres to be coated. Another attempt was also made to continuously coat carbon fibres with polystyrene, however this was unsuccessful. Carbon fibres were passed continuously through a bath of polystyrene dissolved in tetrahydrofuran (THF). This resulted in an un-spread carbon fibre tow having only been coated on the outer surface with the internal fibres being unaffected and remaining dry. For the in situ polymerisation described in this section (3.2.5), thirty metres of AS4 unsized carbon fibres were wound onto a custom made PTFE roller and pretension of 580 g applied. The fibres were passed through a glass bath (92 mm width, 370 mm and 88 mm height, IKEA, London, UK) containing two

custom made PTFE rollers. A  $1.76 \text{ mol/dm}^3$  styrene in water emulsion was added to the bath and then heated to  $50^\circ\text{C}$ . The mixture was stirred vigorously using a hotplate with a magnetic stirrer to stop it from separating.  $3.18 \text{ g/dm}^3$  ( $0.01 \text{ mol/dm}^3$ ) of water-soluble azo initiator was added. The carbon fibres were used as heating elements during the polymerisation process. The carbon fibres were heated to  $85^\circ\text{C}$  via two hollow stainless steel pins (6 mm diameter, 1 mm wall thickness, 316L, FTI Ltd., East Sussex, UK) before and after the bath to which 1.4 A were applied using a power supply (TYP 3218, Statron, Fürstenwalde, GDR). The temperature of the carbon fibres was measured using a thermocouple. The carbon fibres were collected onto a cardboard drum (83 mm diameter, 3 mm wall thickness) using a custom-built fibre winding unit with a brushless DC Motor (FBLM5120W-GFB/ GFB5G200, VEXTA, Oriental Motor Co., Hampshire, UK) at a speed of 0.14 m/min. The coated fibres were placed in drying oven at  $60^\circ\text{C}$  for 24 h. The setup for the continuous coating of polystyrene onto carbon fibres can be seen in Figure 13. The coating process was conducted inside a fume hood as styrene was being used.

Soxhlet extraction was performed on 2 m of the polystyrene coated fibres using THF as the solvent. This was to find out whether the polystyrene had been chemically bonded to the carbon fibres. The results of this experiment showed that polystyrene had not been chemically bonded (section 3.3.6) and therefore the remaining polystyrene coated carbon fibres were not washed to prevent the removal of any coating.

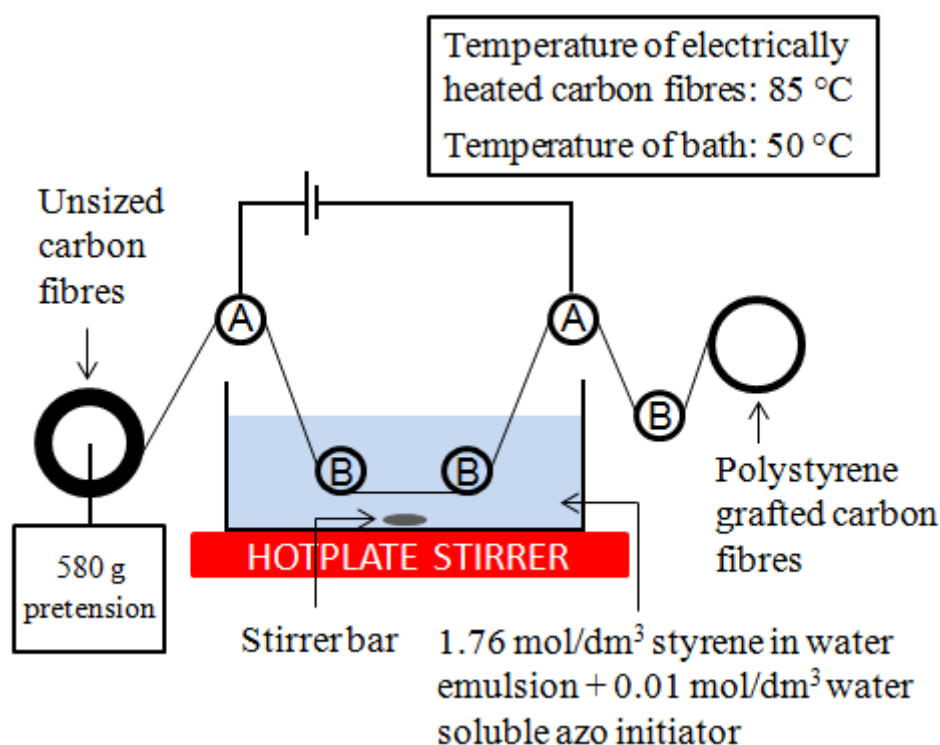


Figure 13: Setup for continuous coating of polystyrene onto carbon fibres, where (A) are stainless steel pins and (B) are PTFE rollers.

### 3.2.6 Characterisation of coated carbon fibres

#### 3.2.6.1 DSC analysis of PS coated carbon fibres

The thermal behaviours of the unsized (as-received) and PS coated carbon fibres were analysed using Differential Scanning Calorimetry (DSC) on a DSC Q2000 V24.4 Build 116 (TA Instruments, Delaware, USA). The samples were heated from – 25 °C to 225 °C, cooled to – 25 °C and then reheated to 225 °C in a nitrogen atmosphere and at a heating and cooling rate of 10 °C/ min. This heating and cooling regime was used to measure the  $T_g$  of polystyrene and the thermal transitions of any impurities on the fibre surface (although no other transitions were present). For each specimen five samples were tested.

### 3.2.6.2 Thermogravimetric analysis of PS coated carbon fibres

The amount of PS-coating on the carbon fibres was quantified using thermogravimetric analysis (TGA) on a TGA Q500 V6.7 Build 203 (TA Instruments, Delaware, USA). Measurements were taken in air from 30 °C to 600 °C at a heating rate of 10 °C/ min. For each specimen five samples were tested.

### 3.2.6.3 Surface composition of PS coated carbon fibres

The surface chemistry of the unsized and PS-coated carbon fibres was studied using X-ray Photoelectron Spectroscopy. The XPS spectra were obtained using a Thermo VG Scientific Sigma Probe spectrometer equipped with a monochromated Al K<sub>α</sub> X-ray source (hν = 1468.6 eV; power: 140 W). For the high-resolution spectra, the pass energy was set at 50 eV. An electron gun was used for charge compensation. The Advantage v.4.53 software was used to analyse the wide scan spectra and deconvolute the high resolution spectra.

### 3.2.6.4 Diameter of PS coated carbon fibres

The diameters of the carbon fibres were determined using the modified Wilhelmy-technique and calculated using equation 1.

$$d_f = \frac{m.g}{n.\pi.\cos\theta.\gamma_{lv}} \quad (1)$$

where  $d_f$  is fibre diameter,  $n$  the number of fibres (5),  $m$  the mass difference after emersion and immersion of carbon fibres in n-dodecane (recorded using a 4504 MP8 Sartorius Ultra-microbalance [resolution 0.0001 mg], Surrey, UK),  $\theta$  the contact angle (in this case zero) and  $\gamma_{lv}$  the surface tension of n-dodecane (25.4 mN/m). All

measurements were taken at room temperature. The fibres were well separated during the tests (approximately 1 mm spacing between each fibre).

#### 3.2.6.5 Morphology of PS coated carbon fibres

The carbon fibre surface was analysed using a Hitachi S-3400N Variable Pressure SEM at an accelerating voltage of 5 kV. The ends of the fibres and the SEM stub were painted with silver-loaded conductive paint (186-3600, RS Components, UK) to prevent charging.

#### 3.2.6.6 Interfacial shear strength between PS coated carbon fibres and the epoxy matrix

Single fibre pull-out tests were performed to determine the interfacial shear strength ( $\tau_{IFSS}$ ), a measure of practical adhesion, between the carbon fibres (unsized and PS-coated) and the epoxy resin matrix. The equipment used to prepare and analyse the test specimens was designed and built by Dr G. Kalinka and R. Sernow of the Federal Institute for Materials Research and Testing (BAM, Berlin, Germany). A test specimen was prepared by gluing the end of a single carbon fibre (approximately 10 mm in length) onto a washer (189-620, RS component, UK) using double sided tape (Scotch, 3M, USA). The washer was positioned onto the magnetic strip of the custom made embedding apparatus (Figure 14). A droplet of the epoxy/hardener mixture was placed into the hollow recess of an Allen key screw (BZP cap screw, M3x6, RS component, UK). The screw was then placed into the heater shown in Figure 14. The free end of the carbon fibre suspended from the washer (approximately 7 mm in length) was embedded into the epoxy/hardener mixture to a length of 30-60  $\mu\text{m}$  by lowering the pivoting arm of the embedding apparatus using the screw mechanism. The epoxy was then partially cured at 150 °C using the heater.

The carbon fibre was then cut from the washer to leave a free length of approximately 7 mm. The screw was removed from the heater and the epoxy fully cured at 160 °C for 12 h in a vacuum oven.

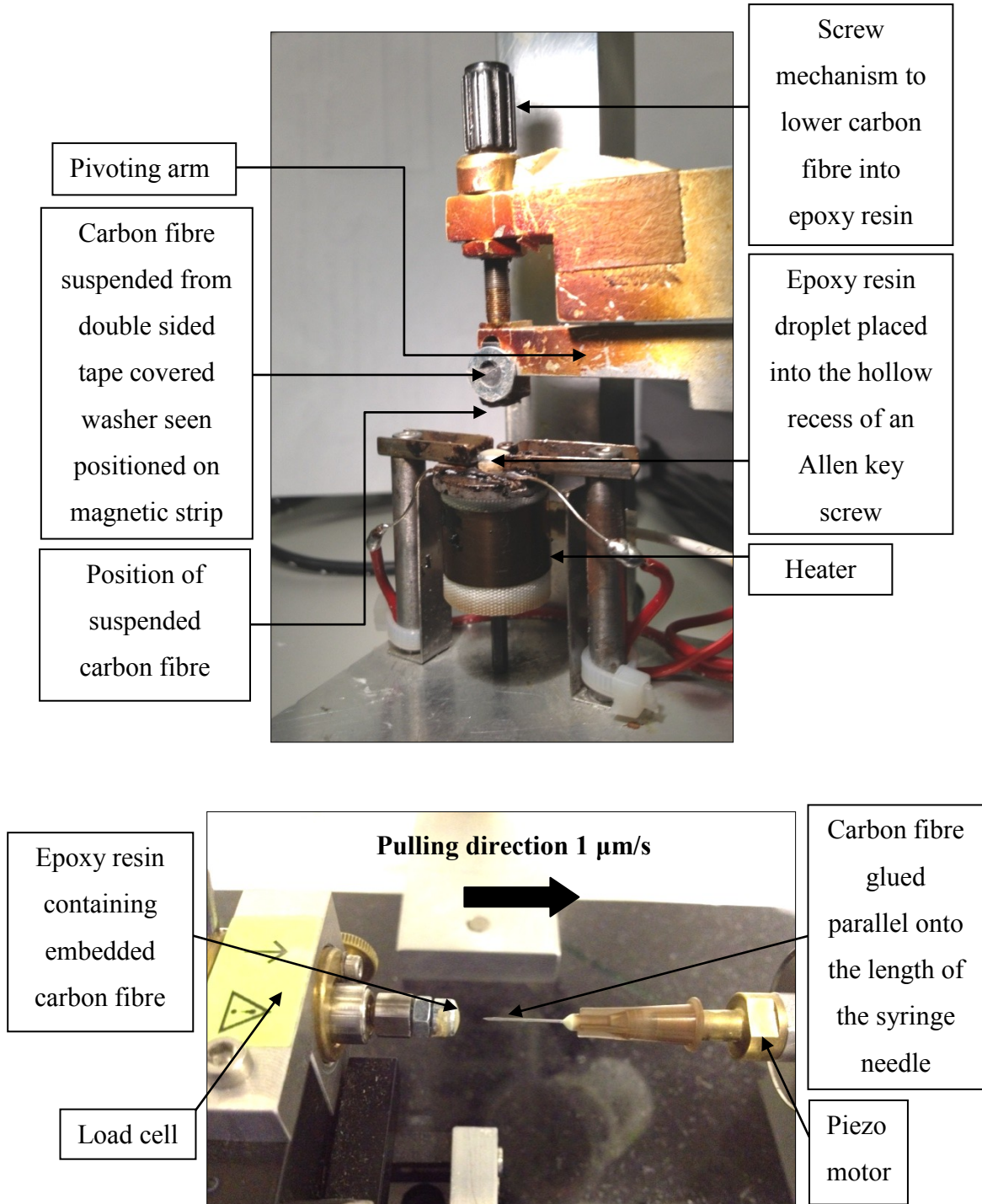


Figure 14: Single fibre pull-out test equipment: Embedding apparatus (above) and fibre pull out apparatus (below)

The cured specimen was then tested using the fibre pull-out apparatus (Figure 14). The screw containing the carbon fibre within the epoxy resin was screwed horizontally onto a load cell. A syringe needle (0.5 inch, 26 gauge, Microlance, Fisher, UK) was attached horizontally onto a piezoelectric motor. The free end of the carbon fibre was then laid alongside the length of the syringe needle and glued using cyanoacrylate adhesive (CN, Tokyo Sokki Kenkyujo, Japan). A piezo-motor was used to pull the fibre out of the matrix at a speed of 1 µm/s. The force was recorded using a load cell and logged by a computer. The interfacial shear strength was calculated using equation 2:

$$\tau_{IFSS} = \frac{P_m}{\pi \cdot d_f \cdot L_e} \quad (2)$$

where  $d_f$  is the fibre diameter,  $P_m$  the maximum force and  $L_e$  the embedded fibre length. The average interfacial shear strength was calculated from 8 measurements.

### 3.2.7 Filament winding carbon fibres to manufacture fibre preforms

A diagram of the experimental setup used to filament wind carbon fibres onto a metal plate is shown in Figure 15. The cardboard tube onto which the fibres were wound was placed onto a tension control machine (CTS setting panel, Izumi international, Osaka, Japan). The fibres were then placed over a force detector (DTH 6120, Izumi international, Osaka, Japan) and 120 g tension applied. The fibres were wound onto a release fabric (FF03PM, Aerovac, West Yorkshire, UK) covered aluminium plate (75 mm width, 200 mm length and 3 mm thickness) at 10 rpm using a filament winding machine (Kolelectric, Middlesex, UK). The fibres were guided onto the plate using a single, custom made, PTFE roller. Two layers of carbon fibres

were wound to manufacture the fibre preform. The epoxy resin was brushed onto the release fabric before the first layer was wound and was then brushed again between the first and second layers of carbon fibres to ensure complete infusion of the epoxy during the resin infusion step (section 3.2.8). The release fabric and the ends of the fibre tows were taped to the metal plate using high temperature resistant tape (Flashtape 1, Aerovac, West Yorkshire, UK). This process was repeated for the unsized carbon fibres.

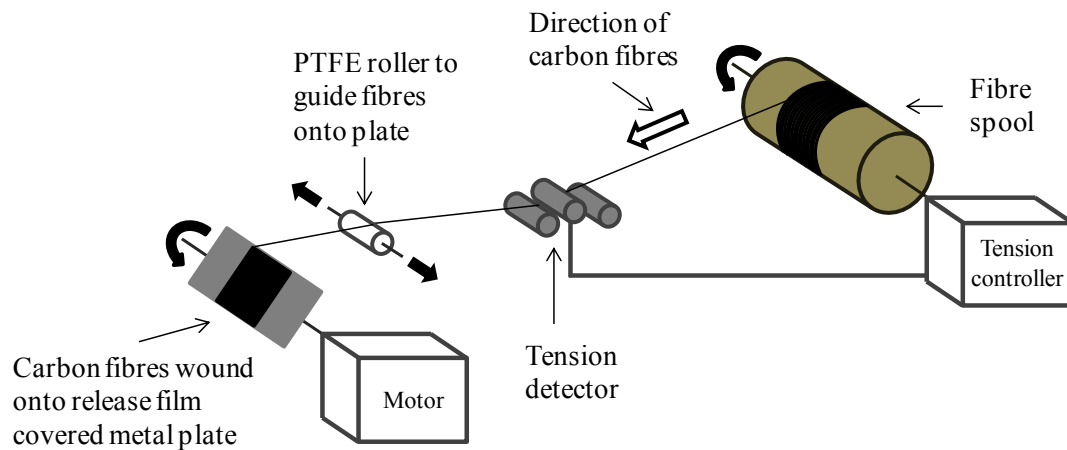


Figure 15: Diagram of the setup used to filament wind carbon fibres onto a metal plate

### 3.2.8 Manufacturing carbon fibre reinforced epoxy composites

The method used to resin infuse the carbon fibre preforms (RIFT) is described in section 3.2.4.2. The cured composites were cut into 40 mm × 5 mm test specimens for DMTA and 40 mm × 10 mm coupons for flexural testing using a water cooled diamond bladed cutter. The unsized and PS-coated carbon fibre reinforced composites were not conditioned prior to testing. The fibre volume fractions ( $V_f$ ) and void content ( $V_v$ ) of the composites was determined using acid digestion following procedure B described in ASTM D3171-99.

### 3.2.9 Preparation of microsection specimens of the wire and carbon fibre reinforced composites

Optical microscopy specimens (microsections) of the wire and carbon fibre reinforced composites were prepared in order to analyse the cross-sections of the composites. The composite samples were embedded in an epoxy resin and cured for 8 h at room temperature. The samples were polished using a grinder-polisher (MetaServ/ MetaPol, Buehler, Coventry, UK). Four sand papers with varying grit sizes were used initially (Si P120, P320, P800 and P2500) followed by three diamond based dispersions (6 $\mu$ m, 3 $\mu$ m and 1 $\mu$ m). The samples were then imaged using an optical microscope (BX51M/ DP70, Olympus, Tokyo, Japan).

### 3.2.10 Viscoelastic properties of the pure epoxy and the wire and carbon fibre reinforced composites

The viscoelastic behaviour of the pure epoxy and of the wire and carbon fibre reinforced composites was investigated using DMTA on a Tritec 2000 (Triton Technology Ltd., Keyworth, UK). Three point bending testing (unclamped) was performed using a gauge length of 15 mm. Heating rates of 5 °C/ min from -100 °C to 230 °C at a frequency of 1 Hz were used to determine the storage modulus ( $E'$ ) and loss modulus ( $E''$ ) of the composite samples. DMTA was used as a screening process for the composites containing PS-coated fibres and therefore only single tests were performed. Single measurements were also performed for the composites containing PAAm coated carbon fibres as these composites had been manufactured by Tridech who had tested the majority of them to failure and therefore there were only a limited number left available and suitable for testing.

### 3.2.11 Flexural tests

The flexural properties of epoxy matrix composites containing unsized and PS-coated carbon fibres were determined using three point bending tests at both ambient and elevated temperatures according to ASTM D7264-07. The tests were carried out on an Instron 4505 (Bucks, UK) equipped with a 1 kN load cell. A span-to-thickness ratio of 32:1 was used. The diameter of the loading nose and supports was 6 mm and a crosshead speed of 1 mm/ min was used. For one series of tests, specimens were loaded to a maximum deflection of 1 mm at room temperature (RT1) and then unloaded. The tests were then repeated at 120 °C in an environmental chamber (SFL, Eurotherm, West Sussex, UK) and then again at room temperature (RT2). The flexural strength was determined at room temperature by loading previously untested samples to failure. For some specimens of the unsized and PS-coated carbon fibre reinforced composites, a direct current was passed through the carbon fibres as an alternative method of heating. Both the upper and lower surfaces at each end of the samples were sanded down with sand paper and painted with silver conductive paint. Copper tape was then wrapped around the silver paint and the loose ends of the tape connected to a power supply (HY3003-3, Digimess, Derby, UK). To heat a specimen to 120 °C in 30 seconds, approximately 1.9 A and 2.8 V was needed for the unsized carbon fibre reinforced composites and 1.9 A and 2.5 V for the composites containing PS-coated carbon fibres. More extensive studies, including the effect of time on the temperature of the composites at different voltages, were not undertaken. The reason for this is that heating the composites with an applied current was treated as a preliminary experiment only.

The flexural modulus  $E_f$  of the specimens was calculated using equation 3, where  $L$  is support span,  $b$  the beam width,  $h$  the beam thickness and  $m$  the gradient of the

linear portion of the load - displacement curve between zero and 1 mm displacement. To calculate the average flexural modulus of the composites, five specimens of each sample were tested.

$$E_f = \frac{L^3 m}{4bh^3} \quad (3)$$

The flexural strength was calculated using equation 4, where  $\sigma$  is the maximum stress at the outer surface at the mid-span of the specimen (MPa) and P the applied force at failure (N). The flexural strength was determined by loading five specimens to failure.

$$\sigma = \frac{3PL}{2bh^2} \quad (4)$$

### 3.3 Results and discussion

The composites described in section 3.3.4, consisting of unidirectional unsized and PAAm coated carbon fibres within an epoxy resin, were manufactured by Tridech [15]. These composites had previously been tested in three point bending from room temperature to 130 °C but not loaded to failure. The characterisation of the PAAm coated carbon fibres (except for the DVS analysis) was performed by Tridech along with the fibre volume fraction tests. The rest of the analysis in this chapter was carried out by the author.

#### 3.3.1 Quantity of PAAm coating

As determined by TGA, 4 wt.% PAAm coating had been deposited onto the carbon fibres. Fibre diameters were determined gravimetrically using the modified Wilhelmy-technique. The diameter of the unsized carbon fibres was  $7.3 \pm 0.1 \mu\text{m}$ . The diameter of the PAAm coated fibres increased to  $7.5 \pm 0.1 \mu\text{m}$ . This is consistent with the weight increase determined from TGA and shows the presence of a thin fibre coating.

#### 3.3.2 Moisture content of PAAm coated fibres

Dynamic vapour sorption was used to analyse the moisture content of the hydrated PAAm fibre coating. The unsized and PAAm coated fibres lost 0.03 wt.% and 0.8 wt.% moisture, respectively, when dried for 24 h. The moisture content of the PAAm coating was therefore calculated to be 19.3 %.

#### 3.3.3 Viscoelastic properties of epoxy matrix

Dry and hydrated epoxy samples were analysed using DMTA (Figure 16).

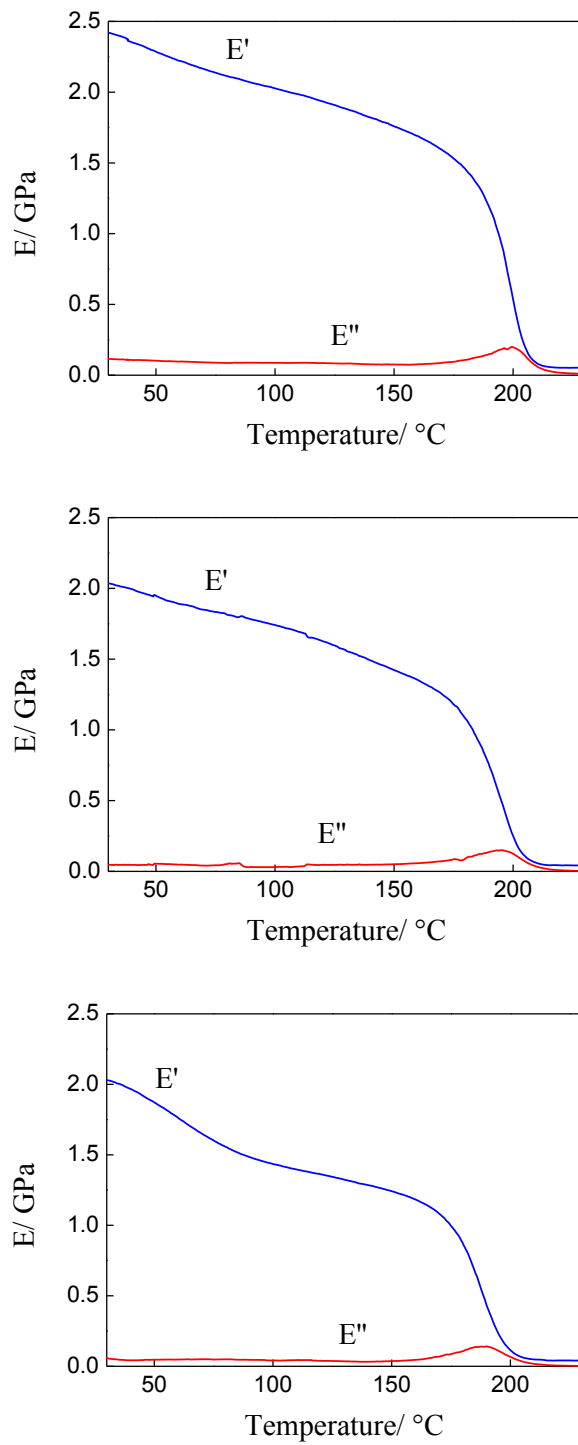


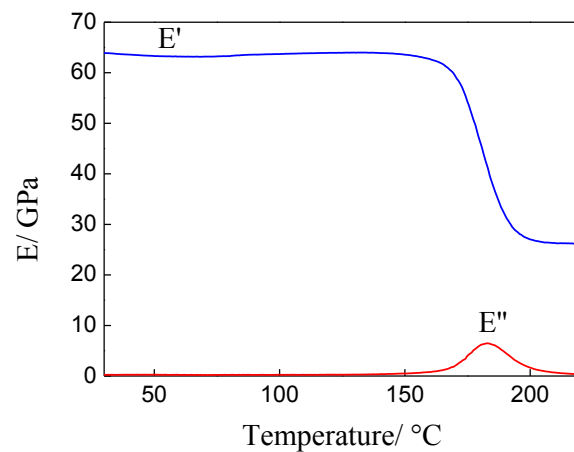
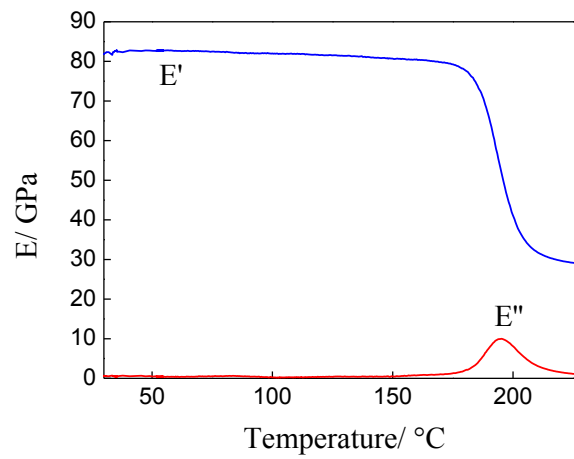
Figure 16: Storage modulus ( $E'$ ) and loss modulus ( $E''$ ) of the cured epoxy resin dry (top), the cured epoxy resin conditioned at 20  $^{\circ}\text{C}$  and 80 % relative humidity (middle) and fully moisture saturated cured epoxy resin by water immersion (bottom) as a function of temperature

The hydrated cured epoxy resin was conditioned for 10 days at 20 °C (80 % relative humidity) and the fully hydrated sample was conditioned by submerging it into water for 36 h prior to analysis. The moisture content in the hydrated and fully hydrated sample was 0.7 % and 0.8 %, respectively. The  $T_g$  taken as the peak temperature in the loss modulus (see Figure 16), of the dry epoxy sample was determined to be 199 °C. The  $T_g$  of the hydrated sample decreased to 193 °C due to the presence of water. The  $T_g$  of the fully hydrated sample was lower still lower at 187 °C. The moisture content and glass transition temperatures of the specimens are summarised in Table 1. At 30 °C the storage moduli of the dry, hydrated and fully hydrated samples were 2.4 GPa, 2 GPa and 2 GPa, respectively. The storage modulus of all three samples dropped by >98 % when heated to 230 °C. As each of the epoxy samples behaved similarly below the glass transition temperature, it can be concluding that the contribution of the hydrated matrix in lowering the modulus of composites containing PAAm coated carbon fibres was insignificant.

#### 3.3.4 Fibre volume fraction, void content and viscoelastic properties of PAAm coated fibre reinforced composites

The fibre volume percentages of composites containing unsized and PAAm coated carbon fibres, determined following ASTM D 3171-99, were  $48 \pm 2$  % and  $52 \pm 1$  %, respectively. Acid digestion also revealed that relatively low void percentages (approximately 0.2 %) were present in both composites. The viscoelastic properties of the composites containing unsized carbon fibres were determined using DMTA (Figure 17). At 30 °C the storage modulus of the dried composite was 82 GPa. The  $T_g$  of the epoxy was recorded to be 194 °C from the peak in the loss modulus (Figure 17). The moisture content in the hydrated and fully hydrated composites containing unsized carbon fibres was 0.3 % and 0.6 %, respectively (Table 1). The hydrated

unsized fibre reinforced composite (conditioned for 10 days at 20 °C and at 80 % relative humidity) had a single  $T_g$  at 182 °C, corresponding to the epoxy resin. Below this temperature the storage modulus remained at approximately 63 GPa. The overall loss in stiffness from 30 °C to 230 °C was 59 %. The  $T_g$  of epoxy in the fully moisture saturated unsized carbon fibre reinforced composite was measured to be 180 °C. The storage modulus of both hydrated samples increased at elevated temperature. This may be due to thermal expansion of the composites.



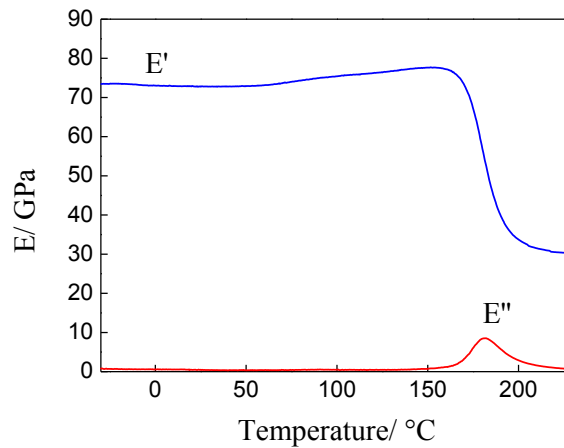


Figure 17: Storage modulus ( $E'$ ) and loss modulus ( $E''$ ) of a dried (top), hydrated (middle), and fully hydrated unsized carbon fibre reinforced epoxy composite (bottom) as a function of temperature

Composites containing PAAm coated carbon fibres were also analysed using DMTA (Figure 18). A PAAm coated fibre reinforced composite conditioned at 20 °C and 80% relative humidity was dried in a vacuum oven at 80 °C for 12 h. The  $T_g$  of the PAAm coating was 155 °C, which is close to the  $T_g$  of anhydrous PAAm (165 °C) [99]. A 91 % drop in storage modulus from 74 GPa to 7 GPa was recorded when the dried PAAm coated fibre reinforced epoxy composite was heated from 30 °C to 230 °C. This drop in stiffness was caused by the softening of both the dried PAAm and the epoxy. However, because of the close proximity of the PAAm and epoxy glass transition temperatures it is difficult to discern the effect of the coating on the stiffness loss alone. The moisture content in the hydrated PAAm coated fibre reinforced composite (conditioned for 10 days at 20 °C and at 80 % relative humidity) was 1.3 % (Table 1). At 30 °C the storage modulus of the composite was 66 GPa. At 130 °C the storage modulus dropped by 71 % to 19 GPa. The PAAm coating within the composite exhibited a broad  $T_g$  around 84 °C that can be

attributed to plasticization of the PAAm by adsorbed water in the partially hydrated polymer [100, 101]. The overall loss in stiffness from 30 °C to 230 °C (including the contribution from the softened epoxy) was 88 %.

Table 1: DMTA results and moisture content of conditioned epoxy, unsized and PAAm coated carbon fibre reinforced epoxy composites

| Specimen                                  | Conditioning of specimen <sup>†</sup> | Moisture content of specimen/% | T <sub>g</sub> PAAm/ °C | T <sub>g</sub> epoxy/ °C | % loss in storage modulus at T <sup>‡</sup> , where T <sub>g</sub> (PAAm) < T < T <sub>g</sub> (epoxy) |
|-------------------------------------------|---------------------------------------|--------------------------------|-------------------------|--------------------------|--------------------------------------------------------------------------------------------------------|
| Pure epoxy                                | Dried                                 | 0                              | -                       | 199                      | -                                                                                                      |
|                                           | Hydrated                              | 0.7                            | -                       | 193                      | -                                                                                                      |
|                                           | Fully hydrated                        | 0.8                            | -                       | 187                      | -                                                                                                      |
| Unsize carbon fibre reinforced epoxy      | Dried                                 | 0                              | -                       | 194                      | -                                                                                                      |
|                                           | Hydrated                              | 0.3                            | -                       | 182                      | -                                                                                                      |
|                                           | Fully hydrated                        | 0.6                            | -                       | 180                      | -                                                                                                      |
| PAAm coated carbon fibre reinforced epoxy | Dried                                 | 0                              | 155                     | -                        | *                                                                                                      |
|                                           | Hydrated                              | 1.3                            | 84                      | -                        | 79                                                                                                     |
|                                           | Fully hydrated                        | 10.7                           | 1                       | -                        | 71                                                                                                     |

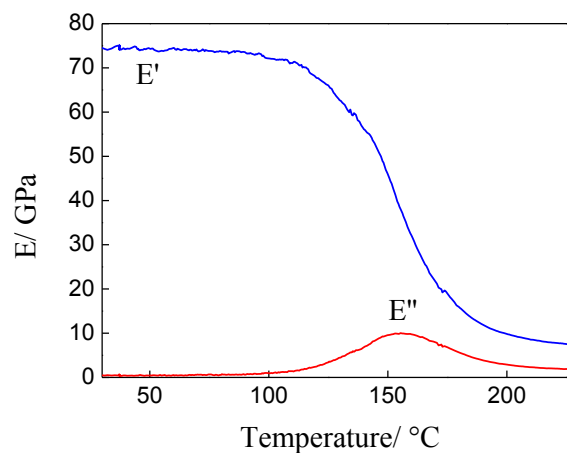
<sup>†</sup> ‘Dried’ specimens were placed in a vacuum oven at 80 °C for 12 h, ‘hydrated’ specimens conditioned for 10 days at 20 °C and at 80 % relative humidity and ‘fully hydrated’ specimens were completely submerged into water for 36 h

<sup>‡</sup> T (Temperature)

\* Difficult to discern the effect of PAAm on the stiffness loss alone due to the close proximity of the PAAm and epoxy glass transition temperatures

The T<sub>g</sub> of the epoxy resin is only seen in the DMTA curves of the unsized fibre reinforced composite. This is because the storage modulus of these composites at the T<sub>g</sub> of the epoxy (e.g. 42 GPa at 182 °C for the hydrated specimen) is higher than the E' of the PAAm coated fibre reinforced composites at this temperature. The

composites containing hydrated and dried PAAm coated fibres had therefore softened to an extent where the epoxy  $T_g$  could no longer be detected. A composite containing PAAm coated carbon fibres was submerged into water for 36 h. The moisture content in this fully hydrated composite was 10.7 %. The  $T_g$  of the PAAm coating had dropped significantly to 1 °C due to moisture uptake. At -30 °C the storage modulus of the composite containing fully hydrated PAAm coated carbon fibres was 67 GPa. When this composite was heated through the  $T_g$  of the PAAm coating, from -30 °C to 30 °C, the storage modulus of the composite dropped by 79 % to 14 GPa. A similar value (71 %) was observed for the composite containing the partially hydrated PAAm coated fibres that was conditioned for 10 days at 20 °C and at 80 % relative humidity. Therefore, hydrating the PAAm coating around the carbon fibres in the composites allowed the  $T_g$  of the PAAm to be adjusted, which in turn enabled the composite stiffness to be reduced at temperatures well below the  $T_g$  of the epoxy resin. The storage modulus of the fully moisture saturated composite containing PAAm coated fibres increased at temperatures exceeding 130 °C. This could be due to moisture evaporating from the composite or sample expansion above the boiling point of water in the specimen.



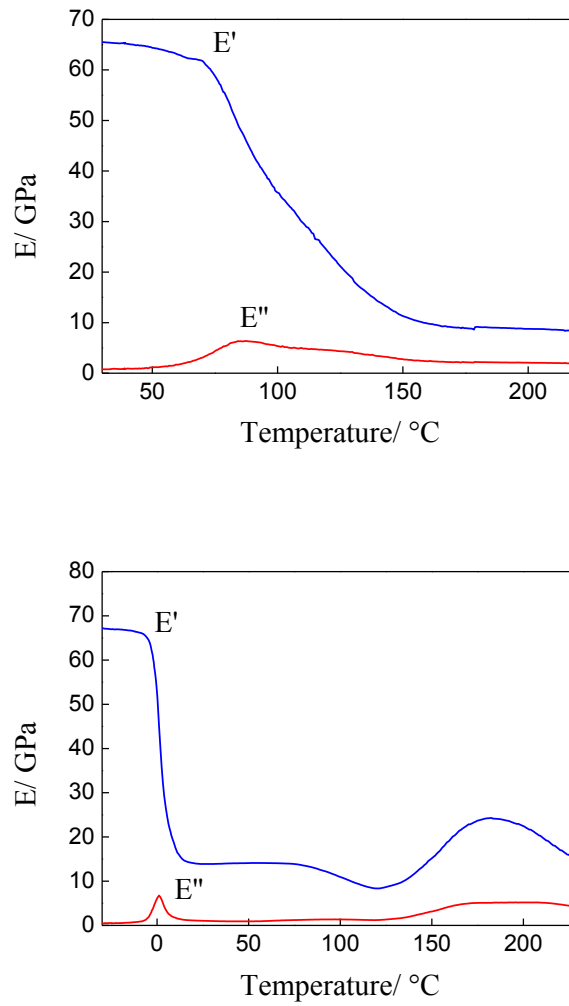


Figure 18: Storage modulus ( $E'$ ) and loss modulus ( $E''$ ) of a dried (top), hydrated (middle), and fully hydrated PAAm coated carbon fibre reinforced epoxy composite (bottom) as a function of temperature

Five heating/cooling cycles from 30 °C to 140 °C were performed on a composite containing partially hydrated PAAm coated carbon fibres using DMTA. No loss in performance was observed over the 5 cycles (Figure 19). This indicates that none of the constituents degraded and that the moisture content must have remained constant in the PAAm coating.

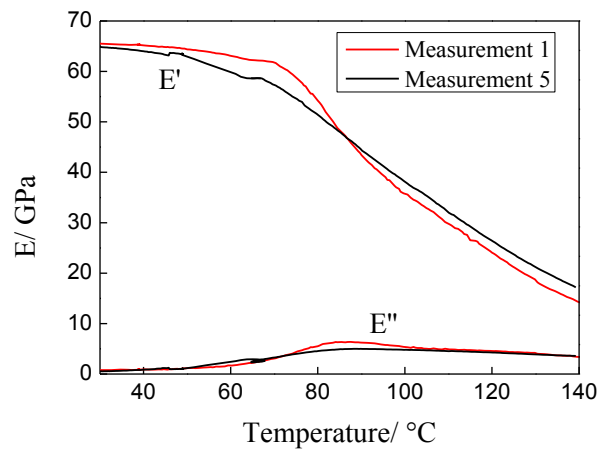


Figure 19: DMTA curves of hydrated PAAm coated fibre reinforced epoxy composite subjected to 1 and 5 heating cycles

Tests were carried out to observe fibres sliding within the composite containing PAAm coated fibres at elevated temperature. To image the ends of the bent composites, to see whether the fibres were sliding, the composites had to be polished, as the ends of the cut composites were too rugged to see any differences between straight and bent samples. The composites were deflected to 1 mm (in 3 point bending) at 130 °C within an environmental chamber. The specimens were then cooled in the deformed state. However, it was found that polishing “smeared” the composite surface and so the fibres, PAAm coating and matrix were indistinguishable and apparently fused, which constrained the fibre ends. Unfortunately, fibre sliding was not observed but instead the samples bent to a shape expected when the fibre ends were constrained. It is also likely that the PAAm coating had chemically bonded to the epoxy [120]. This would have limited the distance the fibres could slide within the composite. However, when a deformed composite sample containing PAAm coated carbon fibres that was bent in flexure at 130 °C to 1 mm, was heated unconstrained with a heat gun it could clearly be seen to straighten out and return to its original shape.

However, in order to illustrate that the fibres do slide in “composites” containing coated fibres above the  $T_g$  of the coating, a polyvinylidene fluoride ( $T_g = -40\text{ }^{\circ}\text{C}$ ) coated copper wire reinforced epoxy model composite was manufactured (see appendix A.2). When the specimen was bent at room temperature the metal wires slid within the wire coating adhering to the resin matrix because of the weak coating/wire interface. Images of the specimen were taken before and after bending (Figure 80, left and right, respectively). Prior to bending the composite the ends of the wires are in alignment with the epoxy matrix. When composites were bent by hand, the wires on the compression side of the composite can be seen protruding from the specimen. The wires on the tensile side are receding slightly, although this is not as obvious in these optical micrographs.

### 3.3.5 Predicted and measured mechanical properties of polystyrene coated wire reinforced epoxy composites

A polystyrene coated copper wire reinforced epoxy composite was manufactured along with a control sample containing uncoated copper wires.

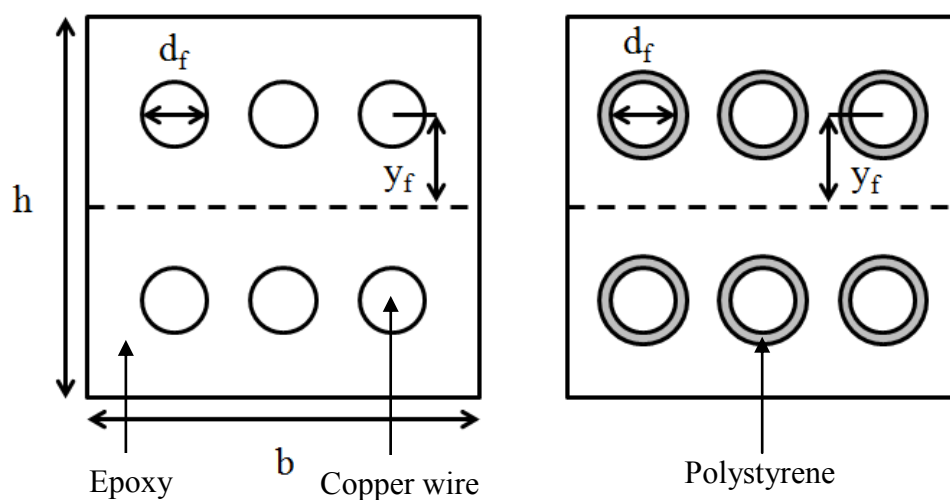


Figure 20: Cross sectional diagram of uncoated (left) and polystyrene coated wire reinforced epoxy composite (right)

Cross sectional diagrams of the composites are shown in Figure 20. A reduction in the stiffness of the composite containing PS-coated copper wires was achieved by heating the composite to 130 °C which is above the glass transition temperature the PS-coating (115 °C). For the composites containing the uncoated wires, the stiffness was not affected at this temperature. Heating both composites above the epoxy matrix  $T_g$  of 199 °C also resulted in a loss in stiffness as expected. Cross-sectional images of the composites containing PS-coated wires composite show the presence of a uniform PS coating around the wires (Figure 21). The thickness of the PS coating measured from microsection images was approximately 40  $\mu\text{m}$ .

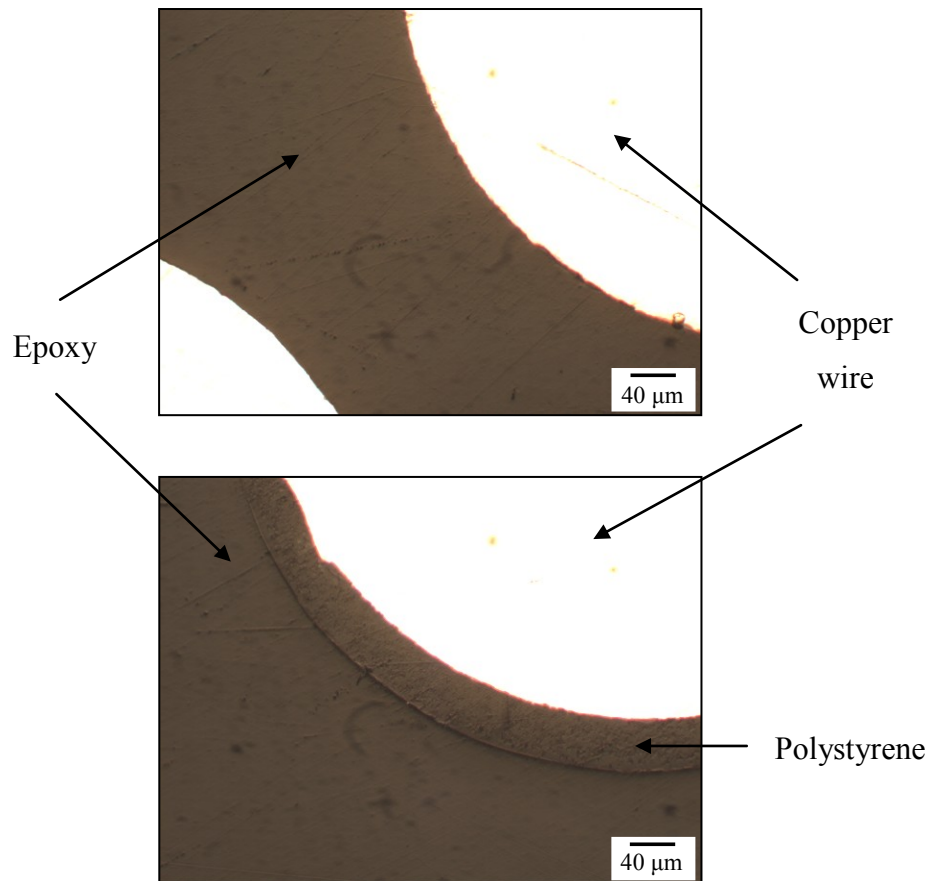


Figure 21: Cross section of uncoated wire reinforced composite (left) and polystyrene coated wire reinforced composite (right) at 20  $\times$  magnification

The viscoelastic properties of the pure epoxy resin can be seen in Figure 16. The  $T_g$  was recorded to be 199 °C from the peak in the loss modulus. At 30 °C, the storage modulus was 2.4 GPa. The storage modulus dropped by 98 % to 0.05 GPa when heated to 230 °C. The viscoelastic properties of the composites containing uncoated and PS-coated wires are shown in Figure 22.

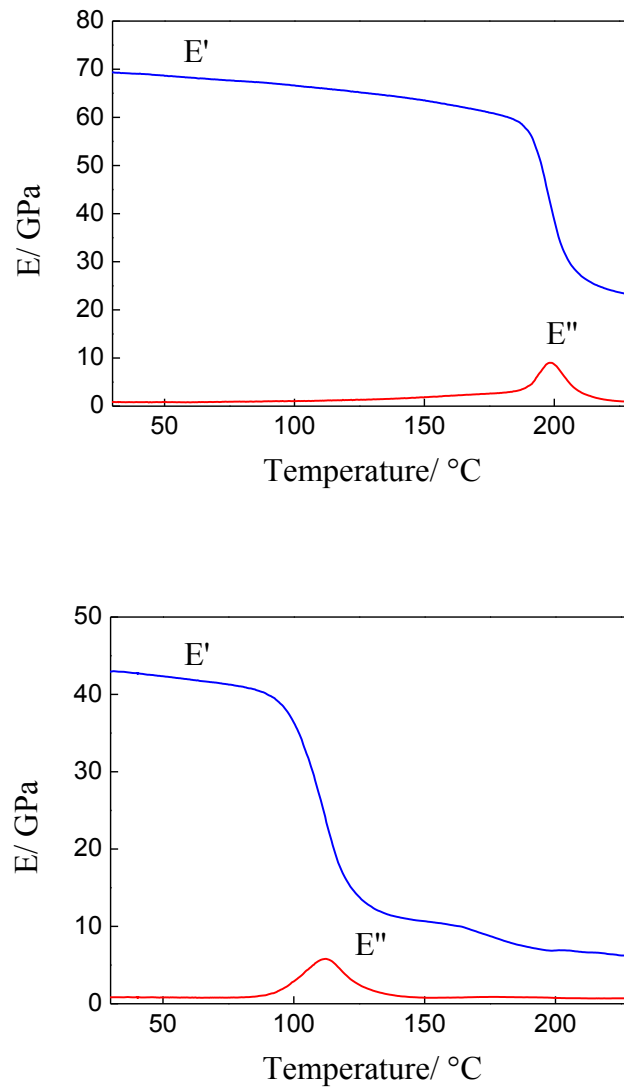


Figure 22: DMTA curves of the uncoated (above) and PS coated wire reinforced epoxy composite (below)

The storage modulus of the uncoated wire reinforced composite was 69 GPa at 30 °C. At 130 °C this dropped by 6 % to 65 GPa. Above the  $T_g$  of the epoxy resin (199 °C) at 230 °C the storage modulus was 23 GPa. The storage modulus of the composites containing PS-coated wires at 30 °C was 43 GPa. The difference in stiffness between the composites containing uncoated and PS-coated wire reinforced composite at room temperature is due to the different fibre volume fractions ( $V_f$ ). The  $V_f$  for the composites containing uncoated and PS-coated wires was 0.62 and 0.43, respectively. The average  $T_g$  of polystyrene in the coated wire reinforced composite was recorded at 115 °C from the peak in the loss modulus. Above the  $T_g$  of PS at 130 °C the storage modulus of the composite dropped by 70 % to 13 GPa.

The effective flexural Young's modulus of the uncoated and polystyrene coated wire reinforced composites at different temperatures (30 °C, 130 °C and 230 °C) was predicted. Firstly, the predicted bending stiffness (EI) of the specimen, assuming it only consisted of epoxy matrix, was determined using equation 5, where b is the width of the composite (uncoated wire composite: 5.4 mm, PS coated wire composite: 6.8 mm) h is the thickness (uncoated wire composite: 1.19 mm, PS coated wire composite: 1.26 mm). The modulus of the matrix ( $E_m$ ) was taken as the storage modulus of the pure epoxy from DMTA.

$$EI|_{\text{matrix}} = \frac{E_m b h^3}{12} \quad (5)$$

The additional contribution of the fibres to the bending stiffness was then calculated using equation 6. The modulus of the copper wires ( $E_f$ ) was assumed to be 120 GPa [121] and was not expected to change with temperature. The fibre diameter of the wires ( $d_f$ ) was 0.6 mm. The term  $y_f$  is the distance between the mid-plane of the composite and the mid-point of each wire (see Figure 20) and is 0.30 mm and 0.31

mm for the uncoated and PS-coated wire composites, respectively. The term  $d_h$  is the diameter of the holes in the matrix at 130 °C (which is  $d_h$  plus twice the coating thickness).

$$EI|_{\text{fibres}} = \sum_{\text{all fibres}} \left( \underbrace{E_f \frac{\pi}{4} \left( \frac{d_f}{2} \right)^4}_{(i)} - \underbrace{E_m \frac{\pi}{4} \left( \frac{d_h}{2} \right)^4}_{(ii)} \right. \\ \left. + \underbrace{E_f \pi \left( \frac{d_f}{2} \right)^2 y_f^2}_{(iii)} - \underbrace{E_m \pi \left( \frac{d_h}{2} \right)^2 y_f^2}_{(iv)} \right) \quad (6)$$

The combined stiffness of the fibres and matrix was then determined (equation 7).

$$\text{Total EI} = EI|_{\text{matrix}} + EI|_{\text{fibres}} \quad (7)$$

Finally, the predicted (effective) flexural Young's modulus of the composite was calculated using equation 8.

$$E_{\text{effective}} = \frac{\text{Total EI} \times 12}{bh^3} \quad (8)$$

These values were then compared against the values determined using DMTA. For simplicity when calculating the predicted stiffness, the PS was considered to be part of the matrix (i.e. with the same Young's modulus) and the adhesion between each constituent was assumed to be perfect. At 30°C, below the  $T_g$  of polystyrene, the load transfer between the matrix and the reinforcement was assumed to be the same for both composites and all parts of eq. 6 were used. Above the  $T_g$  of PS, at 130 °C, it was assumed the coating had softened and there was no longer any load transfer between matrix and PS-coated wires in the composite. At this temperature the

stiffness of the composite containing PS-coated wires was that of the matrix (with holes), plus the stiffness of each individual wire i.e. part (iii) of eq. 6 was not used and  $d_h$ , the diameter of the holes, was taken as the fibre diameter,  $d_f$ , plus twice the coating thickness. At 230 °C, the matrix was assumed to have completely softened. The effective modulus of both composites at 230 °C depends only on the stiffness of the reinforcement. Table 2 summarises these conditions in the calculations of the effective flexural modulus.

Table 2:  $E_m$  values and the use of equation 6 in calculations of effective Young's modulus of copper wire reinforced composites

| Temp/<br>°C | $E_m$ /<br>GPa | Equation 6 <sup>†</sup> |       |        |       |       |               |       |        |       |         |
|-------------|----------------|-------------------------|-------|--------|-------|-------|---------------|-------|--------|-------|---------|
|             |                | Uncoated fibres         |       |        |       |       | Coated fibres |       |        |       |         |
|             |                | Pt i                    | Pt ii | Pt iii | Pt iv | $d_h$ | Pt i          | Pt ii | Pt iii | Pt iv | $d_h$   |
| 30          | 2.4            | ✓                       | ✓     | ✓      | ✓     | $d_f$ | ✓             | ✓     | ✓      | ✓     | $d_f$   |
| 130         | 2.4            | ✓                       | ✓     | ✓      | ✓     | $d_f$ | ✓             | ✓     | ×      | ✓     | $d_f^*$ |
| 230         | 0              | ✓                       | ×     | ×      | ×     | -     | ✓             | ×     | ×      | ×     | -       |

\* plus twice the coating thickness

<sup>†</sup> Pt i, ii, iii and iv refer to parts of equation 6, ✓ and × indicate whether a part of the equation was used or not,  $d_h$  is the diameter of the holes in the matrix at 130 °C and  $d_f$  is the fibre diameter

The measured Young's modulus values at room temperature are in good agreement with the predicted values (Table 3). As stated earlier, to calculate the predicted stiffness of the composites containing PS-coated wires, the PS was considered as part of the matrix and the difference in adhesion between the constituents was not taken into account. As the measured and predicted values are similar, it can therefore be assumed that the polystyrene coating did not adversely affect the stiffness of the composite. At 130 °C the stiffness of the composite containing uncoated wires was

expected to remain unchanged. There was however a 6 % drop in stiffness from 69 GPa to 65 GPa. This could be associated with a slight relaxation of the polymer network when heated to this temperature.

Table 3: Predicted and measured stiffness values of uncoated and polystyrene coated wire reinforced epoxy composites at different temperatures

| Reinforcement                             | E predicted/ GPa |        |        |        | E measured/ GPa <sup>†</sup> |        |        |        |
|-------------------------------------------|------------------|--------|--------|--------|------------------------------|--------|--------|--------|
|                                           | 30 °C            | 130 °C | % loss | 230 °C | 30 °C                        | 130 °C | % loss | 230 °C |
| Uncoated wire (14) <sup>‡</sup>           | 71               | 71     | 0      | 11     | 69                           | 65     | 6      | 23     |
| Polystyrene coated wire (13) <sup>‡</sup> | 49               | 12     | 76     | 10     | 43                           | 13     | 70     | 6      |

<sup>†</sup> Storage modulus values from DMTA

<sup>‡</sup> Number of reinforcing wires

The measured and predicted modulus of the composite containing PS-coated wires at 30 °C was 43 GPa and 49 GPa, respectively. At 130 °C the measured and predicted modulus for this composite was 13 GPa and 12 GPa, respectively. The similarity of these results validates the mechanism of stiffness loss assumed in the prediction calculation (i.e. that fibres can slide within the epoxy matrix). At 230 °C the measured values from DMTA are higher than the predicted values. This is due to the matrix not fully softening above its glass transition temperature (see Figure 16) unlike the assumption for the predicted stiffness calculations.

### 3.3.6 Solvent extraction of polystyrene carbon fibre coating

Soxhlet extraction was performed on 2 m of the PS-coated carbon fibres (0.885 g/m). The weight of the fibres after washing (0.856 g/m) was approximately that of unsized AS4 fibres (0.858 g/m). The coating had therefore been removed as it was not chemically bonded.

### 3.3.7 Polystyrene coated carbon fibre morphology

SEM images of the unsized and PS-coated AS4 carbon fibres can be seen in Figure 23. The PS coating on the fibres is not uniform and appears to have agglomerated on the fibre surface. The inhomogeneous nature of the PS coating may be due to poor spreading of the fibres as they passed through the monomer bath.

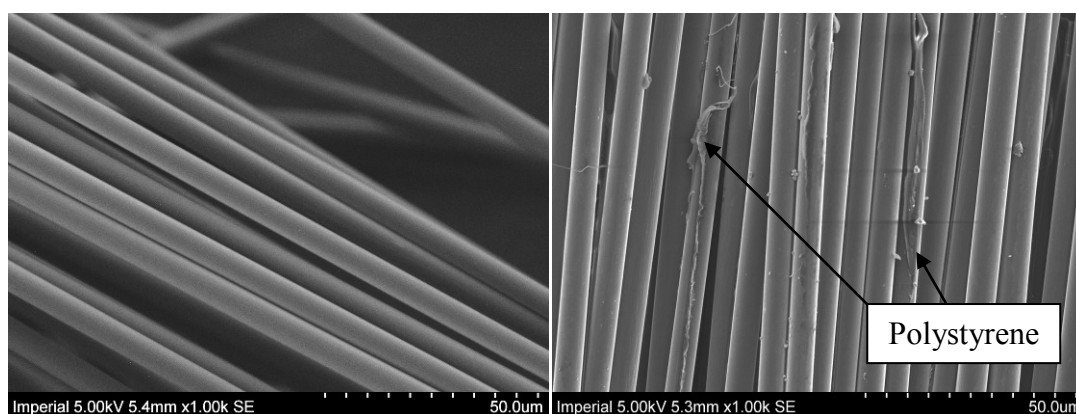


Figure 23: SEM images of unsized (left) and polystyrene coated carbon fibres (right)

It was difficult to achieve even fibre spreading during the coating step as a limited number of spreading pins could be used. This was due to size restrictions within the fume hood, where the coating process was carried out.

### 3.3.8 Surface composition of polystyrene coated carbon fibres

The atomic composition of the unsized fibres, from the wide scan spectrum, was 85 % carbon, 13 % oxygen and 2 % nitrogen (Table 4). The O:C ratio was 0.15. The atomic composition of the PS-coated fibres was 91 % carbon, 6 % oxygen and 3 % nitrogen (O:C ratio of 0.07). The high percentage of carbon on the PS-coated fibres suggested the fibres had been coated. The presence of oxygen and nitrogen could be due to a non-uniform coating on the fibres or the presence of impurities such as the products from the breakdown of the initiator.

Table 4: Surface atomic composition of the unsized and polystyrene coated carbon fibres

| Sample                     | Surface composition, atomic % |    |   |      |
|----------------------------|-------------------------------|----|---|------|
|                            | C                             | O  | N | O:C  |
| Unsize AS4 fibres          | 85                            | 13 | 2 | 0.15 |
| Polystyrene coated fibres  | 91                            | 6  | 3 | 0.07 |
| Polystyrene (pure polymer) | 100*                          | -  | - | -    |

\* Theoretical value for pure polystyrene assuming there are no impurities

The peak fitted (deconvoluted) high-resolution C 1s XP spectra of the unsized and PS-coated carbon fibres are shown in Figure 24. For the unsized but industrially oxidised carbon fibres the associated functional groups at the corresponding peaks were assigned according to XPS spectra reported by Yue et al. [122] and Erden et al. [76].

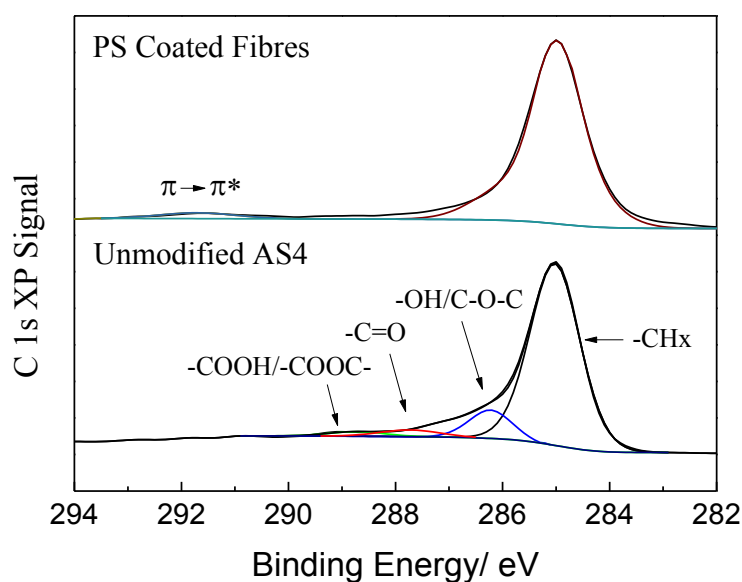


Figure 24: High resolution C 1s XP spectra of unsized and polystyrene (PS) coated carbon fibres

There is a CH<sub>x</sub> peak at 285 eV and the broad peak at approximately 286.3 eV corresponds to a single carbon-oxygen bond, e.g. alcohols or ethers. A carbonyl group was assigned to the peak at 287.7 eV and a carboxylic acid group or an ester bond to the peak at 289.1 eV. For the PS-coated carbon fibres, there are two deconvoluted peaks that confirm the presence of PS on the fibre surface. The large peak at 285 eV corresponds to the carbon atoms in the phenyl rings and the aliphatic backbone [123, 124]. The peak at 291.6 eV corresponds to the  $\pi \rightarrow \pi^*$  shake-up peak from the phenyl rings [125, 126].

### 3.3.9 Fibre diameter and interfacial shear strength measurements

The fibre diameters of the unsized and PS-coated carbon fibres, measured using the modified Wilhelmy-technique, are summarised in Table 5. The fibre diameter of the unsized AS4 fibres was  $7.10 \pm 0.01 \mu\text{m}$ . The fibre diameter of the PS coated fibres increased to  $7.26 \pm 0.08 \mu\text{m}$  suggesting the presence of a thin layer of PS on the fibre surface. The large error for the coated fibres could be attributed to a non-uniform coating.

Table 5: Fibre diameters and interfacial shear strengths of polystyrene coated carbon fibres to an epoxy resin

| Sample                    | Fibre Diameter/ $\mu\text{m}$ | Interfacial Shear Strength/ MPa |
|---------------------------|-------------------------------|---------------------------------|
| Unsized AS4 fibres        | $7.10 \pm 0.01$               | $101.2 \pm 2.6^b$               |
| Polystyrene coated fibres | $7.26 \pm 0.08$               | $100.4 \pm 7.0$                 |

<sup>b</sup> [2]

The interfacial shear strength (IFSS) of the unsized and PS-coated fibres to the epoxy matrix was determined using single fibre pull-out tests. The IFSS for each

fibre was approximately the same (Table 5). This shows that after modifying the fibre surface, the adhesion between the carbon fibres and the epoxy resin was unaffected.

#### 3.3.10 Thermal analysis of polystyrene coated carbon fibres

The glass transition of the PS coating on the carbon fibres was recorded at  $99 \pm 3$  °C using DSC. The  $T_g$  of polystyrene reported here is lower than the  $T_g$  of polystyrene reported in section 3.3.5. This is most likely due to differences in the molecular weights of the polymers as a result of different polymerisation times (degree of polymerisation). As expected no transitions could be seen for the unsized carbon fibres. Thermal gravimetric analysis (TGA) revealed that the unsized carbon fibres remained thermally stable in air up to 500 °C, after which they start to degrade significantly (Figure 25). The unsized carbon fibres underwent a 0.58 wt.% loss when heated to 500 °C. There was a 1.62 wt.% loss when the PS-coated fibres were heated to 500 °C. This degradation appeared to be a two-step process. The first step at approximately 130 °C corresponded to the evaporation of unreacted styrene. This could be prevented by washing the fibres after coating, however as the coating was not covalently bonded (section 3.3.6), washing the fibres could have removed the polystyrene. The unreacted styrene should evaporate or polymerise during the composite manufacturing process (RIFT) so it is unlikely to be present in the composite. The second degradation step at approximately 310°C corresponded to the degradation of PS.

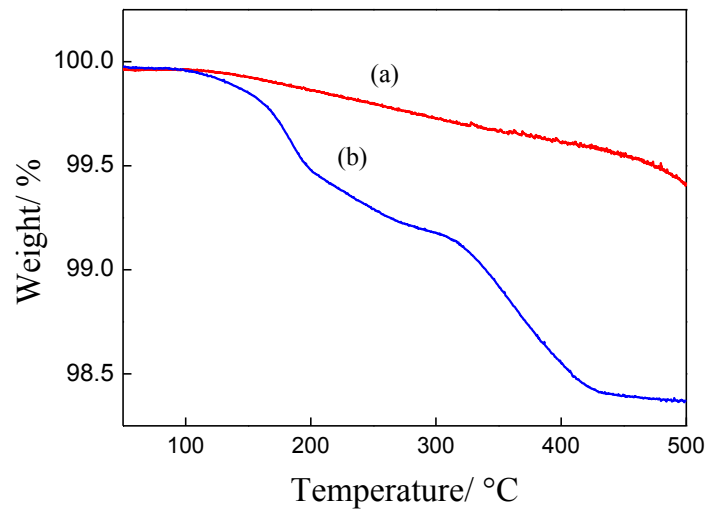


Figure 25: Representative TGA curves for unsized (a) and polystyrene coated carbon fibres (b) measured in air

### 3.3.11 Cross sectional images of composites containing unsized and polystyrene coated carbon fibres

Cross-sections of the composites containing unsized and PS-coated carbon fibres can be seen in Figure 26. There is an even distribution of fibres throughout the control sample. In comparison, the composites reinforced by PS-coated fibres contained a large number of voids. It is likely that the fibre coating restricted the infusion of the epoxy resin during the manufacturing process. The fibre volume percentage and void content of the composite reinforced by PS-coated fibres was  $56 \pm 1$  % and  $5.6 \pm 0.5$  %, respectively. For the composites reinforced using unsized carbon fibres the fibre volume percentage was  $56 \pm 2$  % and the void content was  $1.2 \pm 1.1$  %.

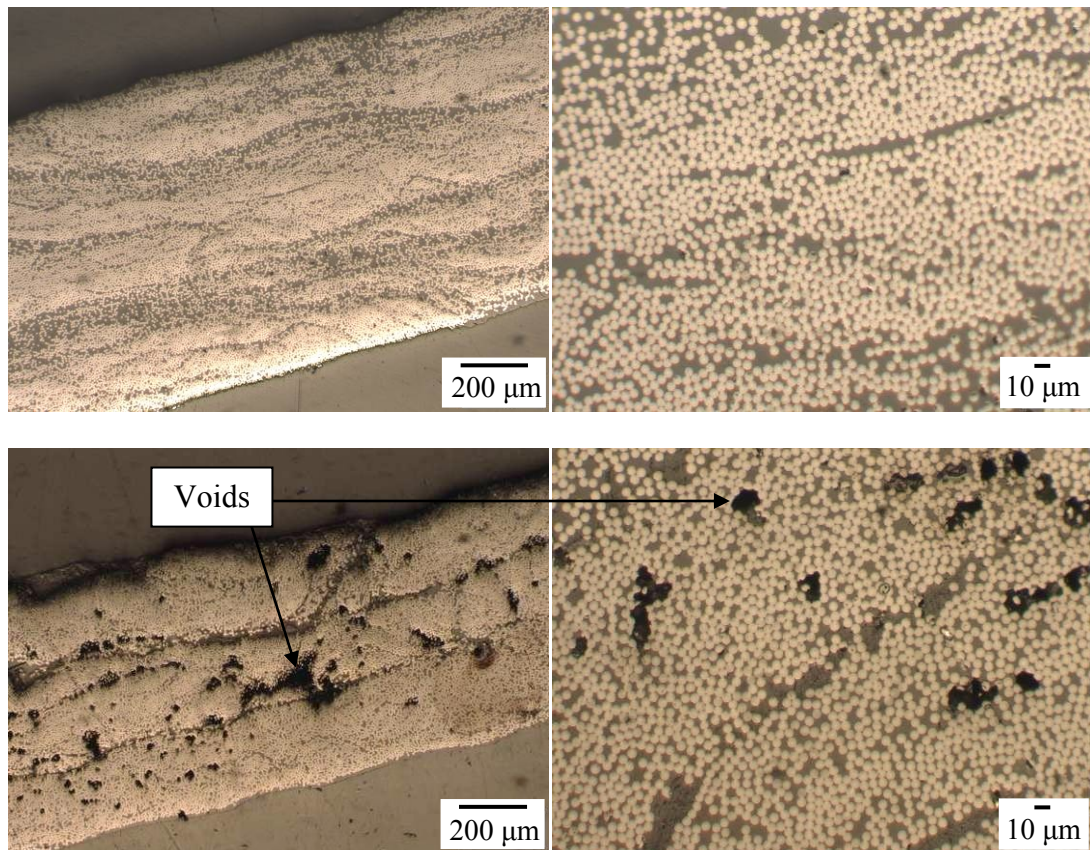


Figure 26: Cross sections of unsized (top) and polystyrene coated carbon fibre reinforced composites (bottom) [at 5× magnification (left) and 20× magnification (right)]

### 3.3.12 Viscoelastic properties of polystyrene coated fibre reinforced composites

The DMTA curves for the composites containing unsized carbon fibres showed a single transition at 174°C, corresponding to the  $T_g$  of the epoxy (Figure 27). The  $T_g$  of the epoxy in the composite is much lower than the  $T_g$  of the epoxy described in section 3.3.5 (199 °C). This is probably due to [unintentional] differences in the curing temperatures [127].

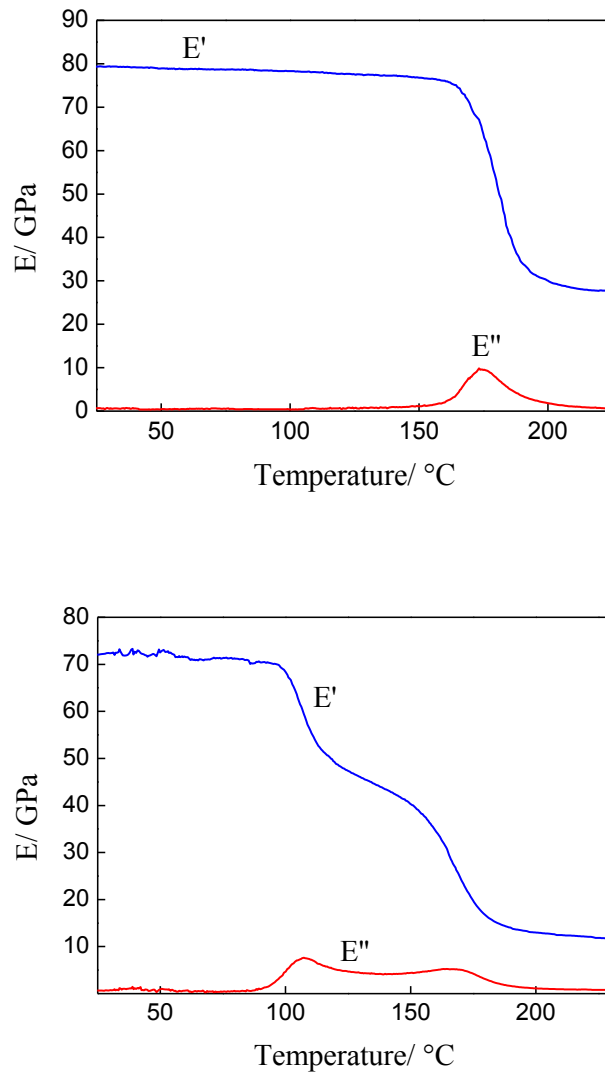


Figure 27: DMTA curves showing the storage modulus ( $E'$ ) and loss modulus ( $E''$ ) for the unsized (top) and the polystyrene coated carbon fibre reinforced epoxy composite (bottom) as a function of temperature

A 32 % decrease in the storage modulus, from 72 GPa to 49 GPa, was observed when composites containing PS coated carbon fibres were heated from room temperature to 120°C. This relatively small loss in stiffness can be associated with an inhomogeneous coating of polystyrene on the carbon fibres. The  $T_g$  of the PS-coating within the composite was recorded at 110 °C from the first peak of the loss modulus. The  $T_g$  of polystyrene from DSC analysis of the PS-coated carbon fibres

was  $99 \pm 3$  °C. This difference could be due to constriction of polystyrene within the composite, leading to a loss in free volume and therefore an increase in the  $T_g$  of the polymer. As the composite was heated from 120 °C to 230 °C the storage modulus dropped by 76 % to 12 GPa, associated with the  $T_g$  of the epoxy matrix.

### 3.3.13 Flexural properties of polystyrene coated carbon fibre reinforced composites

The flexural properties of the composites containing unsized and PS-coated fibres were analysed using three point bending tests at room and elevated temperature. The composites were heated to 120 °C using either an environmental chamber or by passing a current through the carbon fibres, which act as microheating elements for the composites. Representative load-displacement curves for the composites containing unsized and PS-coated fibres heated by applying a current are shown in Figure 28.

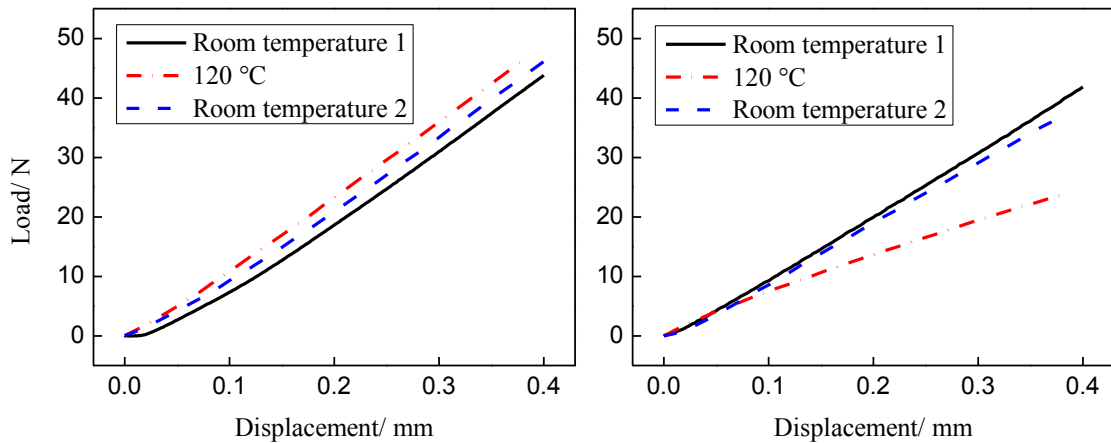


Figure 28: Representative load displacement curves of unsized (left) and polystyrene coated carbon fibre (right) reinforced composites at room temperature and 120 °C  
[heated using an applied current]

The gradients of the curves were approximately the same when the composites containing unsized carbon fibres were heated to 120 °C using an applied current. For these control samples the gradients of the load-displacement curves initially at room temperature (1), secondly at 120 °C and lastly at room temperature (2), were  $109 \pm 5$  N/mm,  $117 \pm 6$  N/mm and  $113 \pm 5$  N/mm, respectively. The gradients of the load-displacement curves were reduced by 35 % when the PS-coated fibre reinforced composites were heated to 120 °C and then returned to their original value when the composites were re-tested at room temperature. For these PS-coated fibre reinforced composites the gradients of the load-displacement curves initially at room temperature (1), secondly at 120 °C and lastly at room temperature (2) were  $113 \pm 7$  N/mm,  $73 \pm 13$  N/mm and  $112 \pm 14$  N/mm, respectively. The flexural properties of the composites are shown in Table 6 and the flexural modulus values are also presented graphically in a bar chart in Figure 29. No significant change in stiffness occurred when the unsized carbon fibre epoxy composites were heated to 120 °C in an environmental chamber. This behaviour was expected as the testing temperatures were well below the  $T_g$  of the epoxy matrix. The composites containing PS-coated fibres had a 30 % lower flexural stiffness when heated in an environmental chamber to 120 °C. The reduction in bending stiffness was higher when the composites were heated by passing a current through the carbon fibres. When heated from room temperature to 120 °C using this technique the recorded flexural stiffness loss was 36 %. It is likely that the actual temperature around the carbon fibres was higher than the surface temperature of the composites (where the temperature was recorded) when using an applied current to heat the specimens.

Table 6: Flexural properties of unsized and polystyrene coated carbon fibre reinforced epoxy composites at room temperature (RT) and 120 °C

| Reinforcement           | Flexural Strength/ MPa | Flexural Modulus/ GPa |         |        |        |                 |        |        |        |
|-------------------------|------------------------|-----------------------|---------|--------|--------|-----------------|--------|--------|--------|
|                         |                        | Environmental Chamber |         |        |        | Applied Current |        |        |        |
|                         |                        | RT 1                  | 120 °C  | % loss | RT 2   | RT 1            | 120 °C | % loss | RT 2   |
| Unsize carbon fibres    | 1471 ± 22              | 81 ± 8                | 81 ± 10 | 0      | 82 ± 6 | 85 ± 6          | 91 ± 7 | 0      | 87 ± 6 |
| PS-coated carbon fibres | 1122 ± 14              | 81 ± 4                | 57 ± 5  | 30     | 85 ± 5 | 87 ± 3          | 56 ± 8 | 36     | 86 ± 9 |

The stiffness of the composite containing PS-coated fibres returned to its original value once the specimens were cooled to room temperature. This suggests that no permanent damage occurred due to the heating and cooling cycles. Both heating methods are therefore viable to reduce the flexural stiffness of these composites. The flexural strengths of the unsized and PS-coated carbon fibre reinforced composites were 1471 ± 22 MPa and 1122 ± 14 MPa, respectively. The lower flexural strength of the composite containing PS-coated carbon fibres is most likely due to its high void content.

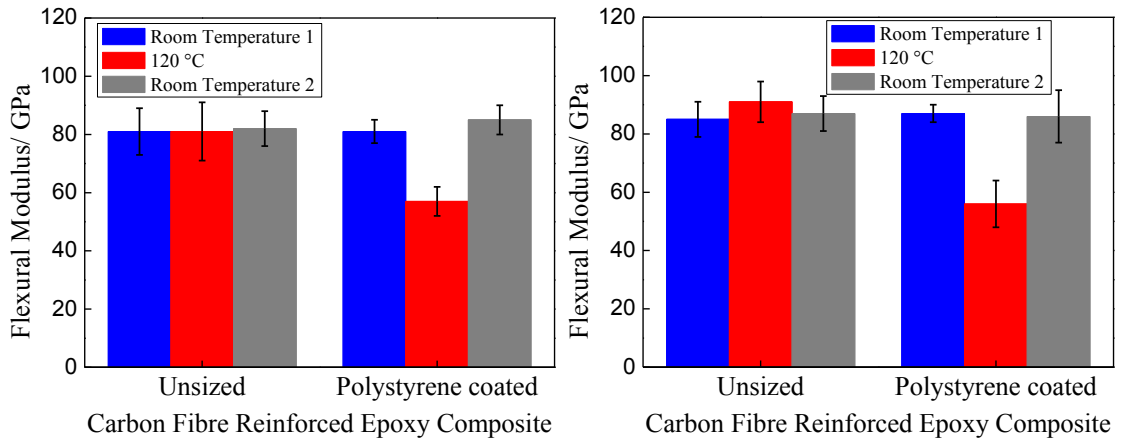


Figure 29: Flexural modulus of unsized and polystyrene coated carbon fibre reinforced epoxy composites at room temperature and 120 °C [composites heated using an environmental chamber (left) and an applied current (right)]

### 3.4 Summary

It was demonstrated that composites containing hydrated PAAm coated carbon fibres exhibited up to a 79 % reduction in storage modulus when heated above the  $T_g$  of the fibre coating. The temperature at which the composites underwent a loss in stiffness could be controlled by adjusting the hydration level in the PAAm coating surrounding the fibres.

A controllable stiffness composite containing PS-coated copper wires was fabricated and analysed using DMTA. When heated to 130 °C, above the  $T_g$  of PS, the composite underwent a 70 % reduction in storage modulus. A control sample reinforced with uncoated copper wires was also manufactured that only underwent a 6 % loss in storage modulus when heated to 130 °C. The stiffness was predicted at different temperatures and these values were in good agreement with the values measured using DMTA.

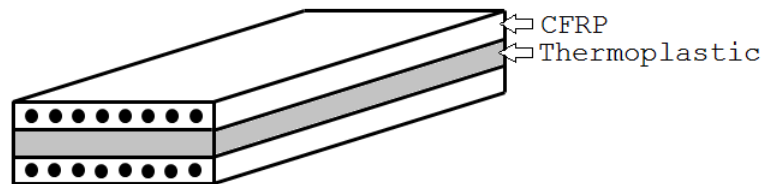
Polystyrene was continuously coated onto carbon fibres via an in situ polymerisation technique. Epoxy matrix composites containing the PS-coated fibres were then manufactured. A 32 % reduction in storage modulus was recorded when the composites containing PS-coated fibres were heated from 30 °C to 120 °C using DMTA. This relatively low drop in stiffness at elevated temperature was caused by a non-uniform polystyrene carbon fibre coating. No reduction in storage modulus occurred when the composites containing unsized fibres were heated to 120 °C. The flexural stiffness of the composites containing PS-coated fibres was also determined using three point bending tests. The composites underwent a 36 % reduction in flexural stiffness when heated from room temperature to 120 °C (by applying a current to the carbon fibres) and fully recovered when cooled.

## 4. Interleaved Composites with Controllable Stiffness

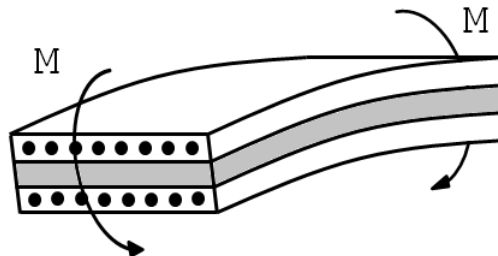
### 4.1 Introduction

This chapter describes the concept of interleaved composites with controllable stiffness. The interleaved composites contain plies of carbon fibre reinforced composite separated by layers of thermoplastic. The thermoplastic is chosen so that its glass transition temperature ( $T_{g-t}$ ) is below that of the fibre reinforced composite plies ( $T_{g-c}$ ).

1. No deflection at room temperature.



2. Composite deflected at room temperature. Exhibits high flexural stiffness.



3. Composite deflected at elevated temperature  $T$ ,  $T_{g-t} < T < T_{g-c}$ . Exhibits low flexural stiffness.

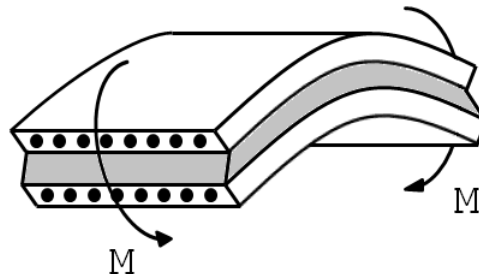


Figure 30: Concept diagram of an interleaved composite with controllable stiffness

When the thermoplastic is heated to a temperature  $T$ , where  $T_{g-t} < T < T_{g-c}$ , it softens and can undergo large shear deformations. This dramatically reduces the flexural stiffness of the composite by allowing the reinforced plies to slide relative to each other (Figure 30). The fibre reinforced matrix can be either a thermoplastic or a thermoset. For this study, polystyrene was chosen as the interleaf material as it has a  $T_g$  around 100 °C, well below the  $T_g$  of the epoxy at  $194 \pm 3$  °C, which was chosen for the fibre reinforced matrix. To manufacture polystyrene films for use in interleaved composites they have to be pressed from either polystyrene powder or pellets. Bioriented PS films can be bought from various suppliers, which will have been stretched during [film] manufacturing process [128]. When heated above the  $T_g$  of polystyrene the films exhibit a shape memory effect and shrink to their original size. Polystyrene films pressed from powder or pellets do not shrink at elevated temperature.

## **4.2 Experimental details**

### **4.2.1 Materials**

Carbon fibre-epoxy unidirectional prepreg (HexPly, 914C-TS-5-34%) was supplied by Hexcel (Cambridge, UK). PAN-based woven carbon fibres (HTA 5131, 3K, five harness satin weave, 200 g/m<sup>2</sup>) were purchased from Tissa Glasweberei AG (Oberkulum, Switzerland). Polystyrene pellets (ST316310) were purchased from Goodfellow (Cambridge, UK).

### **4.2.2 Fabrication of polystyrene films for flexure test specimens**

A predetermined mass,  $m_p$ , of polystyrene pellets were distributed evenly in a circular pattern (75 mm diameter) in the centre of a layer of polyimide release film (250 mm × 250 mm × 0.025 mm, Upilex-25S, UBE, Osaka, Japan). Two more

release film layers of the same size but containing a central circular cut-out, of diameter  $\phi_f$ , were aligned on top of the first film. Finally a complete layer of release film was placed on top to enclose the polystyrene pellets within the release film layers. The whole assembly was then placed between two stainless steel plates (250 mm  $\times$  240 mm  $\times$  3 mm) and put into a hot press (Model 4126 Manual, Hydraulic Press, Carver, Indiana, USA) for 10 mins at 250 °C without pressure. This fully dried the polystyrene and removed air bubbles. In previous attempts this procedure was followed but without heating the pellets to 250 °C without pressure. Consequently the films produced were of low quality because of the volume of air bubbles present. The films were then pressed at an elevated pressure,  $p_f$ , for a predetermined period,  $t_f$ . Polystyrene films with thicknesses of  $126 \pm 9$   $\mu\text{m}$ ,  $240 \pm 20$   $\mu\text{m}$ ,  $73 \pm 10$   $\mu\text{m}$  and  $113 \pm 25$   $\mu\text{m}$  were produced. The values of the processing parameters  $m_p$ ,  $\phi_f$ ,  $p_f$  and  $t_f$ , together with the resulting thickness of the films are given in Table 7.

Table 7: Processing parameters for manufacturing polystyrene films

| <b>Film for composite</b> | <b><math>m_p^\dagger</math> / g</b> | <b><math>\phi_f^\dagger</math> / cm</b> | <b><math>p_f^\dagger</math> / ton</b> | <b><math>t_f^\dagger</math> / min</b> | <b>Film thickness/ <math>\mu\text{m}</math></b> |
|---------------------------|-------------------------------------|-----------------------------------------|---------------------------------------|---------------------------------------|-------------------------------------------------|
| A                         | 5                                   | 190                                     | 3                                     | 40                                    | $126 \pm 9$                                     |
| A*                        | 10                                  | 220                                     | 3                                     | 40                                    | $113 \pm 25$                                    |
| B                         | 5                                   | 190                                     | 2                                     | 60                                    | $240 \pm 20$                                    |
| C                         | 2                                   | 190                                     | 3                                     | 40                                    | $73 \pm 10$                                     |

$^\dagger$   $m_p$  is the mass of polystyrene pellets,  $\phi_f$  is the diameter of the cut-out in the release film,  $p_f$  is the pressure during pressing and  $t_f$  is the time taken to press the PS film

A semicircular section of polystyrene film ( $73 \pm 10$   $\mu\text{m}$  thick) is shown in Figure 31. After pressing the films that are produced are always circular, however, this film had unintentionally split during handling. Nevertheless the photograph shows the films to be transparent and without air bubbles.

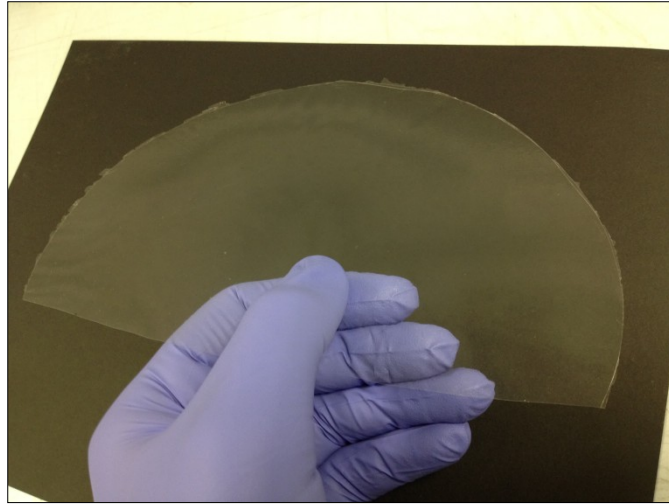


Figure 31: Semicircular section of polystyrene film

#### 4.2.3 Fabrication of woven carbon fibre reinforced polystyrene films

A woven carbon fibre matt (HTA 5131, 3K, five harness satin weave,  $200 \text{ g/m}^2$ , Tissa Glasweberei) was impregnated with polystyrene using a film infusion technique. The fabric was placed between two polystyrene films ( $126 \pm 9 \text{ }\mu\text{m}$ ) and then sandwiched between polyimide film covered stainless steel plates ( $250 \text{ mm} \times 240 \text{ mm} \times 3 \text{ mm}$ ). The sample was put in the hot press at 1 ton and  $250 \text{ }^\circ\text{C}$  for 1 hour. The resulting thickness of the lamina was  $285 \pm 13 \text{ }\mu\text{m}$ . The fibre volume fractions of the carbon fibre reinforced polystyrene films were approximately 0.56 (assuming there were no voids).

#### 4.2.4 Fabrication of interleaved composites

Four interleaved composites with unidirectional CFRP layers (**A**, **A\***, **B** and **C**) were manufactured. Composite **A** consisted of 8 layers of polystyrene ( $126 \pm 9 \text{ }\mu\text{m}$  thick) and 9 plies of unidirectional carbon fibre reinforced epoxy (HexPly, 914C-TS-5-34%, Hexcel, nominal cured ply thickness =  $126 \text{ }\mu\text{m}$ ) arranged in an alternating sequence. Composite **A\*** was manufactured for tensile testing and had the same

structure as Composite **A** but with fewer layers. It consisted of 3 layers of polystyrene ( $126 \pm 9 \mu\text{m}$  thick) and 4 plies of unidirectional carbon fibre reinforced epoxy ordered in an alternating sequence.

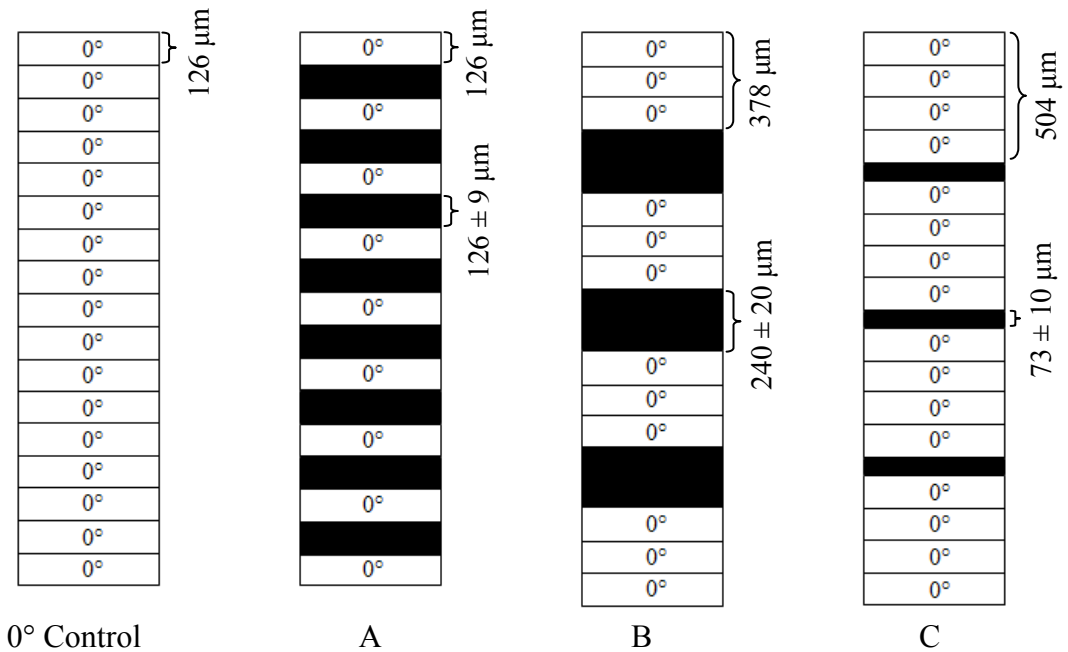


Figure 32: Layup sequence of the  $0^\circ$  control sample (left), Composite **A** (middle left), Composite **B** (middle right) and Composite **C** (right) [drawn to scale] – dark layers are polystyrene and white layers are unidirectional CFRP plies

Composite **B** contained three layers of polystyrene ( $240 \pm 20 \mu\text{m}$  thick) and four blocks of carbon fibre reinforced epoxy (each block consisting of 3 prepreg plies) arranged in an alternating sequence. Composite **C** consisted of three layers of polystyrene ( $73 \pm 10 \mu\text{m}$  thick) and four blocks of carbon fibre reinforced epoxy (each block consisting of 4 prepreg plies) also arranged in an alternating sequence. A control sample consisting of 17 unidirectional reinforced plies was also manufactured. A second control sample ( $0^\circ$  control\*) was prepared for tensile testing and was fabricated from 8 unidirectional reinforced plies. The layup configurations of these composites (except Composite **A**\* and  $0^\circ$  control\*) are shown in Figure 32.

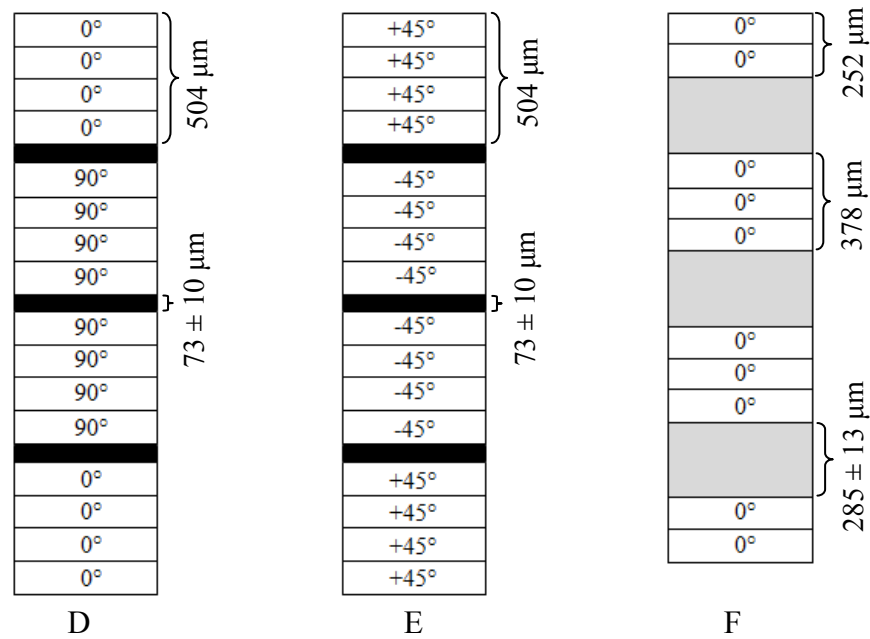


Figure 33: Layup sequence of Composite **D** (left), Composite **E** (middle) and Composite **F** (right) [drawn to scale] – dark layers are polystyrene, white layers are CFRP plies and grey layers are woven carbon fibre reinforced polystyrene layers

Two interleaved composites with multidirectional CFRP layers (Composite **D** and **E**) were fabricated. Both composites **D** and **E** contained three layers of polystyrene ( $73 \pm 10 \mu\text{m}$  thick) and four blocks of carbon fibre reinforced epoxy (each block consisting of 4 prepreg plies) arranged in an alternating sequence. For Composite **D** the inner CFRP blocks were placed at  $90^\circ$  to the two outer CFRP blocks. For Composite **E** the inner CFRP blocks were placed at  $-45^\circ$  and the outer blocks at  $+45^\circ$ . The layup sequence for both these laminates is shown in Figure 33. Two multidirectional control samples without polystyrene were also manufactured. The layup sequence of these composites were  $[0^\circ_4/90^\circ_4/90^\circ_4/0^\circ_4]$  and  $[+45^\circ_4/-45^\circ_4/-45^\circ_4/+45^\circ_4]$ , where  $0^\circ$ ,  $90^\circ$ ,  $+45^\circ$  and  $-45^\circ$  indicates the fibre direction of the CFRP layer. An interleaved composite with woven reinforced polystyrene layers (Composite **F**) was manufactured. This was because using carbon fibres to reinforce the polystyrene interleaf layers could potentially increase the flexural stiffness of the

interleaved composites at room temperature and also provide a way of quickly heating the polystyrene by passing a current through the woven carbon fibres. The stacking sequence of the composite was  $[0^\circ_2/\text{RP}/0^\circ_3/\text{RP}/0^\circ_3/\text{RP}/0^\circ_2]$ , where  $0^\circ$  is a unidirectional carbon fibres reinforced epoxy ply, and RP is a carbon fibre reinforced polystyrene layer (with the warp direction of the fabric parallel to the  $0^\circ$  direction). The layup configuration of Composite **F** is shown in Figure 33. This composite was manufactured and tested by G. Nereau under the supervision of the author [129].

A special interleaved laminate was developed in which the interleaf layers were only present in the central 28 mm of the flexure specimen. This length was equal to the beam span in order to maintain a span-to-thickness ratio of 32:1. Beyond the interleaved layers were CFRP plies. This laminate was termed ‘constrained’ as the CFRP plies were restricted from relative sliding at the ends of the flexure specimen. This laminate was developed as there may be applications in which the interleaved composites need to be clamped at elevated temperature without the risk of compressing the polystyrene layers or loading only the outer CFRP plies. This can be overcome by manufacturing interleaved composites with constrained interleaf layers and therefore creating a pure CFRP region at the end of the composite that can be clamped without incurring any problems. The specimen consisted of 3 polystyrene layers and 4 unidirectional carbon fibre reinforced epoxy plies arranged in an alternating sequence. The thickness of the polystyrene films was  $126 \pm 9 \mu\text{m}$ . The layup configuration of the constrained laminate is shown in Figure 34. This composite was prepared and tested by S. Smith under the supervision of the author [130].

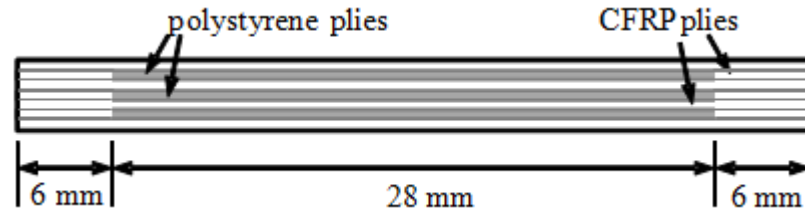


Figure 34: Layup sequence of the constrained laminate

All the composite plates were 100 mm long in the  $0^\circ$  fibre direction and 150 mm wide, except the tensile test specimen plates that were 210 mm long in the  $0^\circ$  fibre direction and 120 mm wide.

Table 8: Details of cured laminates

| Laminate               | Layup*                                                                   | Laminate thickness/mm | Mechanical testing method |
|------------------------|--------------------------------------------------------------------------|-----------------------|---------------------------|
| $0^\circ$ Control      | $[0^\circ_{17}]$                                                         | $2.14 \pm 0.06$       | Flexure/compression/SBS   |
| $0^\circ$ Control*     | $[0^\circ_8]$                                                            | $0.99 \pm 0.02$       | Tension                   |
| $0/90^\circ$ Control   | $[0^\circ_4/90^\circ_4/90^\circ_4/0^\circ_4]$                            | $2.02 \pm 0.03$       | Flexure/SBS               |
| $\pm 45^\circ$ Control | $[+45^\circ_4/-45^\circ_4/-45^\circ_4/+45^\circ_4]$                      | $2.04 \pm 0.03$       | Flexure/SBS               |
| A                      | $[(0^\circ/P^{109})_4/0^\circ/(P^{109}/0^\circ)_4]$                      | $2.00 \pm 0.04$       | Flexure/compression/SBS   |
| A*                     | $[0^\circ/P^{102}/0^\circ/P^{102}/0^\circ/P^{102}/0^\circ]$              | $0.81 \pm 0.02$       | Tension/flexural fatigue  |
| B                      | $[0^\circ_3/P^{196}/0^\circ_3/P^{196}/0^\circ_3/P^{196}/0^\circ_3]$      | $2.12 \pm 0.05$       | Flexure/SBS               |
| C                      | $[0^\circ_4/P^{68}/0^\circ_4/P^{68}/0^\circ_4/P^{68}/0^\circ_4]$         | $2.22 \pm 0.07$       | Flexure/SBS               |
| D                      | $[0^\circ_4/P^{38}/90^\circ_4/P^{38}/90^\circ_4/P^{38}/0^\circ_4]$       | $2.13 \pm 0.04$       | Flexure/SBS               |
| E                      | $[+45^\circ_4/P^{61}/-45^\circ_4/P^{61}/-45^\circ_4/P^{61}/+45^\circ_4]$ | $2.20 \pm 0.06$       | Flexure/SBS               |
| F                      | $[0^\circ_2/RP^{280}/0^\circ_3/RP^{280}/0^\circ_3/RP^{280}/0^\circ_2]$   | $2.10 \pm 0.05$       | Flexure                   |
| Constrained            | $[0^\circ/P^{109}/0^\circ/P^{109}/0^\circ/P^{109}/0^\circ]$              | $0.83 \pm 0.04$       | Flexure                   |

<sup>†</sup>  $0^\circ$ ,  $90^\circ$  and  $\pm 45^\circ$  indicate the fibre direction of a CFRP ply,  $P^t$  indicates a polystyrene layer of thickness  $t$   $\mu\text{m}$  and  $RP^t$  indicates a carbon fibre reinforced polystyrene layer of thickness  $t$   $\mu\text{m}$ .

<sup>‡</sup> SBS: Short Beam Shear.

Each laminate was cured in a hot press (G969, George E Moore and Sons, Birmingham, UK) at 175 °C and 100 psi for 1 h. The thicknesses of the cured laminates and the interleaves are shown in Table 8. The thicknesses of the polystyrene layers in the cured laminates were calculated assuming the thickness of a cured CFRP ply was 0.126 mm. The change in thickness of the polystyrene layers during curing is due to flow of the material at the high temperature and pressure causing leakage from the edge of the laminates.

#### 4.2.5 Preparation of DMTA, flexural and short beam shear tests specimens

The composites were cut into 80 mm × 10 mm coupons for flexural testing, 20 mm × 10 mm coupons for interlaminar shear testing and 40 mm × 5 mm coupons for DMTA using a water cooled diamond bladed cutter (Diadisc 4200, Mutronic, Rieden, Germany). The constrained specimens were cut into 40 mm × 10 mm coupons for flexural testing. For each composite the 0° direction was parallel to the longer dimension of the specimen.

#### 4.2.6 Preparation of tensile test specimens

Composite A\* (3 layers of polystyrene and 4 plies of unidirectional carbon fibre reinforced epoxy) was cut into a 200 mm × 100 mm plate using a water cooled diamond blade cutter. Four end tab plates (100 mm × 50 mm) with 45 ° chamfers were glued onto the grit blasted composite surface using epoxy glue (2014-1, Araldite, Huntsman, Duxford, UK). The epoxy was cured under vacuum for 24 h at room temperature. The resulting gauge length was 100 mm.

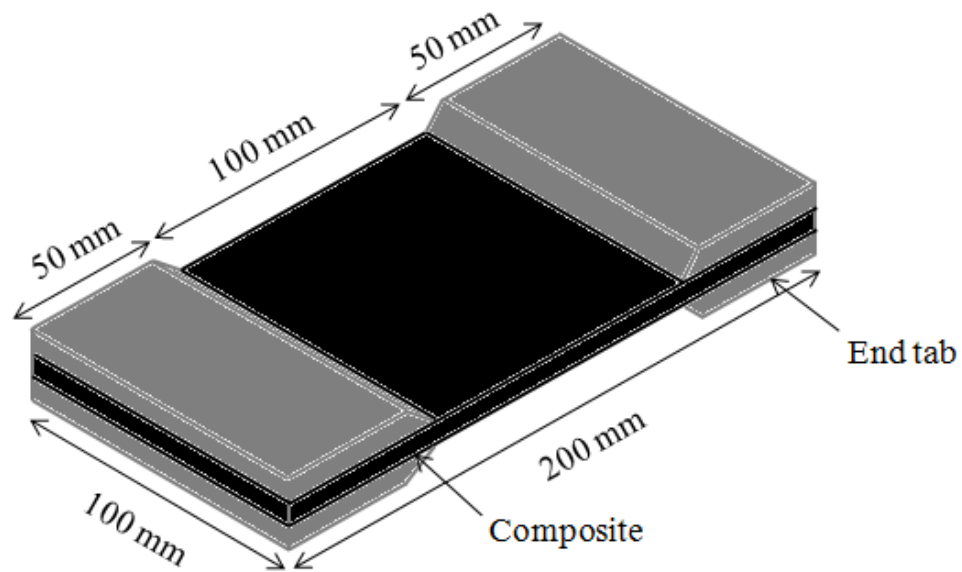


Figure 35: Diagram of tensile test plate during preparation

A diagram of the tensile test plate during preparation is shown in Figure 35. The composite plate was cut into 200 mm  $\times$  12 mm specimens using a water cooled diamond blade cutter. (The end tab plates were glued onto the composite panels prior to cutting into individual specimens and this was done to save time. Water from the cutting process did not affect the bond between the end tabs and the composite). Strain gauges (QFLA-2-11, Strain Gauges, Tokyo Sokki Kenkyujo Co., Tokyo, Japan) were glued onto one side of the composite at the centre of the gauge length using adhesive (NP-50, TML Strain Gauge Adhesive, Tokyo Sokki Kenkyujo Co., Tokyo, Japan).

#### 4.2.7 Preparation of compression test specimens

Composite A was cut to the required dimensions (150 mm  $\times$  91 mm) using a water cooled diamond blade cutter. Four end tab plates (150 mm  $\times$  40 mm) with inverse chamfers were glued onto the grit blasted composite surface using epoxy glue (2014-1, Araldite, Huntsman, Duxford, UK). To ensure the gauge length remained at 10

mm during the epoxy curing, a silicone rubber shim was placed along the length of the gauge area. After curing under vacuum for 24 h at room temperature the composite was ground to a width of 90 mm using a grinder.

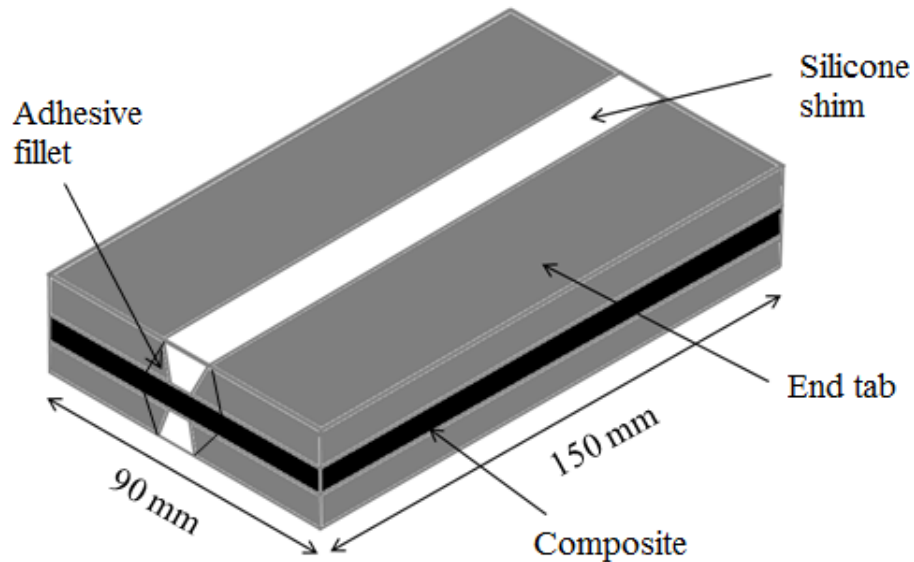


Figure 36: Diagram of compression test plate during preparation

A diagram of the compression test plate during preparation is shown in Figure 36. The shim was removed and the composite plate was then cut into 90 mm  $\times$  10 mm specimens using a water cooled diamond blade cutter. (Again, water from the cutting process did not affect the bond between the end tabs and the composite). Strain gauges (QFLA-2-11, Strain Gauges, Tokyo Sokki Kenkyujo Co., Tokyo, Japan) glued to both sides of the composite at the centre of the gauge length using adhesive (NP-50, TML Strain Gauge Adhesive, Tokyo Sokki Kenkyujo Co., Tokyo, Japan).

#### 4.2.8 Evaluation of viscoelastic properties of composites

The viscoelastic behaviour of the composites was investigated using DMTA. This method is described in section 3.2.10. DMTA was used as a screening process and

consequently for most specimens only single measurements were taken. However, for some specimens, to determine whether the loss in composite stiffness was completely reversible, three samples were tested.

#### 4.2.9 Mechanical testing

##### 4.2.9.1 Flexural testing

The flexural properties of the composites at both ambient and elevated temperatures were determined using three point bending tests according to ASTM D7264-07 (as described previously in section 3.2.11). The tests were carried out on an Instron 4505 (Bucks, UK) using a 1 kN load cell. A span-to-thickness ratio of 32:1 was used. The diameter of the loading nose and supports was 6 mm and a crosshead speed of 1 mm/min was used. Measurements were taken at room temperature and then at 120 °C using an environmental chamber (SFL, Eurotherm, West Sussex, UK). In the first test of a specimen at room temperature (RT1), the specimen was loaded to a maximum deflection of 1 mm and then unloaded. The test was then repeated at 120 °C in the environmental chamber and then again at room temperature (RT2). The flexural strength was determined at room and elevated temperature by loading pristine samples to failure. For some specimens of Composite A and the control sample a direct current was passed through the carbon fibres as an alternative method of heating. Both the upper and lower surfaces at each end of the samples were sanded down with sand paper and painted with silver conductive paint (186-3600, RS Components, Northants, UK). Copper tape was then wrapped around the silver paint and the loose ends of the tape connected to a power supply (HY3003-3, Digimess, Derby, UK). The experimental setup is shown in Figure 37. To heat a specimen to 120 °C in 30 seconds approximately 1.8 A and 3 V were needed for the

interleaved composite and 1.3 A and 4 V for the pure CFRP composite. To calculate the average flexural modulus of the composites, five specimens of each sample were tested.

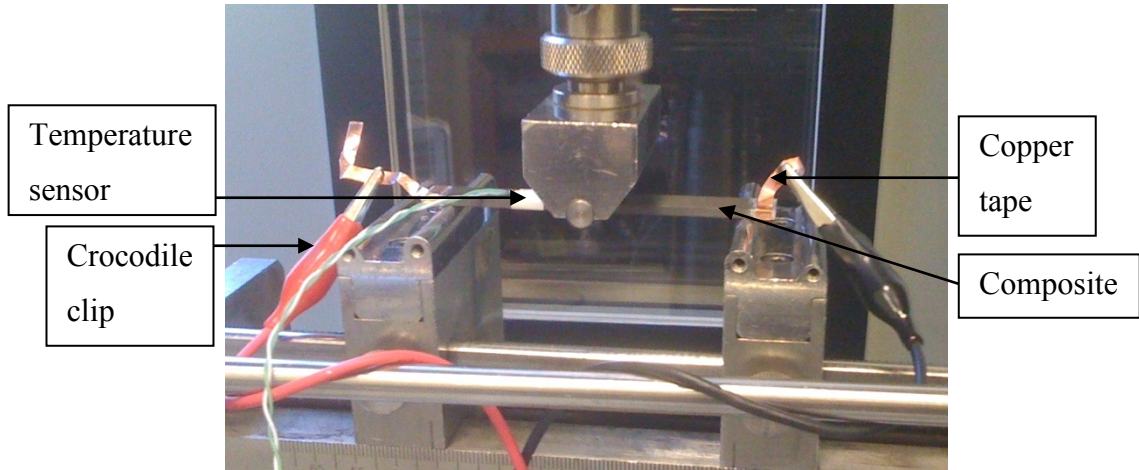


Figure 37: Experimental setup for heating a composite specimen with an applied current during a three point bending test

The apparent flexural modulus,  $E_f$ , of the specimens was calculated using equation 3 (section 3.2.11). The apparent flexural strength was calculated using equation 4. The flexural strength was determined by loading five specimens to failure. The maximum shear stress,  $\tau_{max}$ , in the flexural test specimens was calculated using equation 9.

$$\tau_{max} = \frac{P}{2(bh)} \cdot \frac{3}{2} \quad (9)$$

where  $P$  is the load at failure,  $b$  is the composite width and  $h$  is the composite thickness.

#### 4.2.9.2 Flexural fatigue testing

One interleaved laminate (Composite A\*) was tested in three point bending from room temperature to 120 °C (cycle 1) and back to room temperature (cycle 2) at 32:1 span to thickness ratio using the method described in section 4.2.9.1. At room temperature the composite was deflected by 1 mm and at 120 °C it was deflected by 10 mm. Altogether 40 heating and cooling cycles were performed. The stiffness at 120 °C was calculated using equation 3 for each cycle. The room temperature stiffness was checked at cycle 0, 20, 40. These tests were performed by S. Smith under the supervision of the author.

#### 4.2.9.3 Short beam shear testing

The interlaminar shear strengths (ILSS) of the composites were determined using short beam shear tests at both 25 °C and 120 °C. ASTM D2344-00 was followed. To calculate the average ILSS of the composites, five specimens of each sample were tested. The tests were carried out on an Instron 4505 (Bucks, UK) using a 10 kN load cell. A span-to-thickness ratio of 4:1 was used. The diameter of the loading nose and supports were 6 mm and 3 mm, respectively. A crosshead speed of 1 mm/ min was used. The environmental chamber was used to heat the composite to 120 °C. The ILSS was calculated using equation 9 (where P is the maximum load observed during the test). The strength of each composite was determined by loading five specimens to failure and the failure mode was checked using optical microscopy.

#### 4.2.9.4 Tensile testing

Tensile tests were performed at room temperature on an Instron 4505 (Bucks, UK) with a 100 kN load cell. The tests were carried out in accordance with ASTM

D3039-07. The testing speed was 2 mm/ min. The tensile strength and modulus was determined by loading five specimens to failure.

#### 4.2.9.5 Compression testing

Compression tests were performed at room temperature according to the Imperial College Compression Test method [131]. The tests were performed on an Instron 4505 (Bucks, UK) with a 100 kN load cell. The testing speed was 1 mm/ min. To calculate the average compressive strength and modulus five specimens were tested.

#### 4.2.10 Preparation of microsection specimens

Microsection specimens were prepared in order to analyse the cross sections of the composites. The method used to prepare these specimens is described in section 3.2.9.

### 4.3 Results and discussion

#### 4.3.1 Viscoelastic properties of interleaved composites

The storage modulus,  $E'$ , of the pure CFRP and interleaved composites at room temperature and 120 °C are shown in Table 9. As stated earlier DMTA was used as a screening process and therefore for most specimens only single measurements were conducted. However, in some cases more than one specimen was tested and the errors are shown in Table 9. The errors that are shown are indicative of the errors that would have been seen in those specimens that were tested only once. The average  $T_g$  of polystyrene from DMTA, taken as the peak in the loss modulus, was  $107 \pm 4$  °C.

Table 9: Storage moduli of interleaved composites and control samples at 30 °C and 120 °C determined using DMTA

| Composite            | Storage Modulus/ GPa |         | % loss |
|----------------------|----------------------|---------|--------|
|                      | 30 °C                | 120 °C  |        |
| 0° control sample    | 121 ± 4              | 120 ± 4 | 1      |
| 0/90° control sample | 91                   | 87      | 4      |
| ± 45° control sample | 13                   | 10      | 23     |
| A                    | 66 ± 11              | 2 ± 1   | 97     |
| B                    | 96                   | 10      | 90     |
| C                    | 102                  | 13      | 87     |
| D                    | 89                   | 8       | 91     |
| E                    | 13                   | 3       | 77     |
| F                    | 62                   | 16      | 74     |

The storage modulus of the 0° control sample at 30 °C and 120 °C was  $121 \pm 4$  GPa and  $120 \pm 4$  GPa, respectively. Above 130 °C the storage modulus decreased due to the  $T_g$  of the epoxy resin at  $194 \pm 3$  °C (Figure 38).

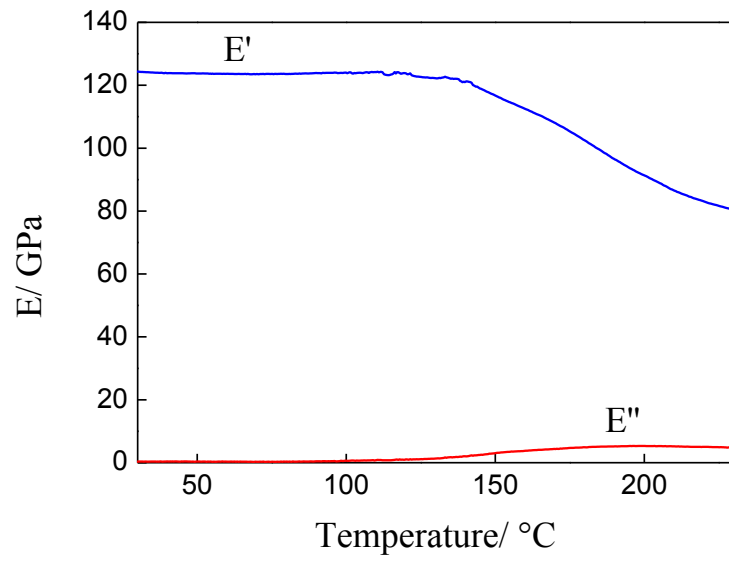


Figure 38: DMTA curves showing the storage modulus ( $E'$ ) and loss modulus ( $E''$ ) of the  $0^\circ$  control sample as a function of temperature

The storage modulus of the Composite **A** at  $30^\circ\text{C}$  was  $66 \pm 11$  GPa. Above the glass transition, at  $120^\circ\text{C}$ , the storage modulus dropped by 97 % to  $2 \pm 1$  GPa (Figure 39).

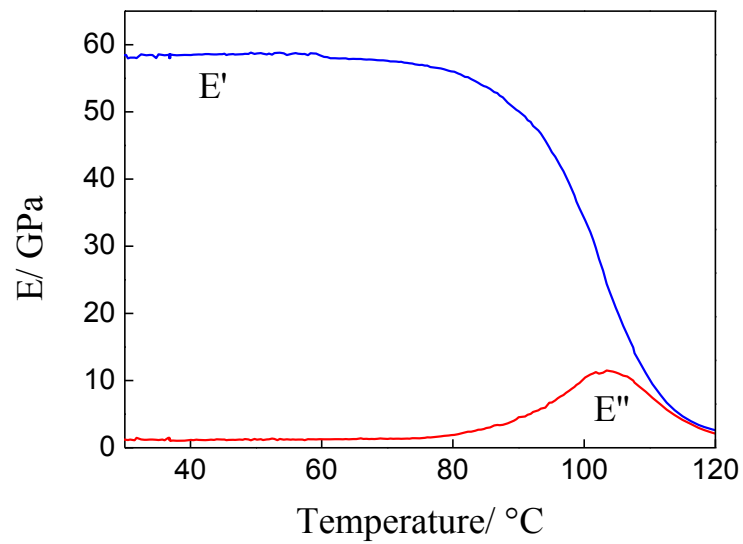


Figure 39: DMTA curves for Composite **A**

At room temperature the storage modulus of Composite **B** was 96 GPa (Figure 40). Compared to Composite **A** this modulus is 45 % higher and can be explained by the greater content of CFRP plies within Composite **B**. At 120 °C the storage modulus dropped by 90 % to 10 GPa.

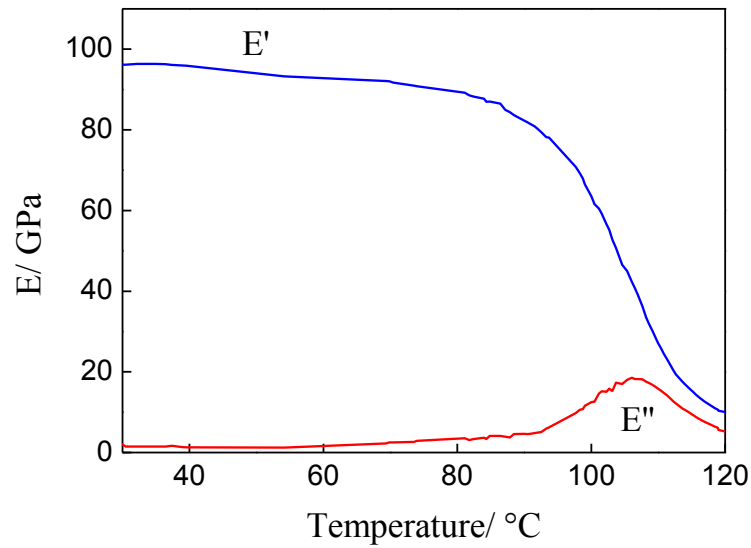


Figure 40: DMTA curves for Composite **B**

Composite **C** also underwent a significant loss in storage modulus when heated from room temperature to 120 °C. At 30 °C the storage modulus of Composite **C** was 102 GPa (Figure 41). At 120 °C the modulus dropped by 87 % to 13 GPa.

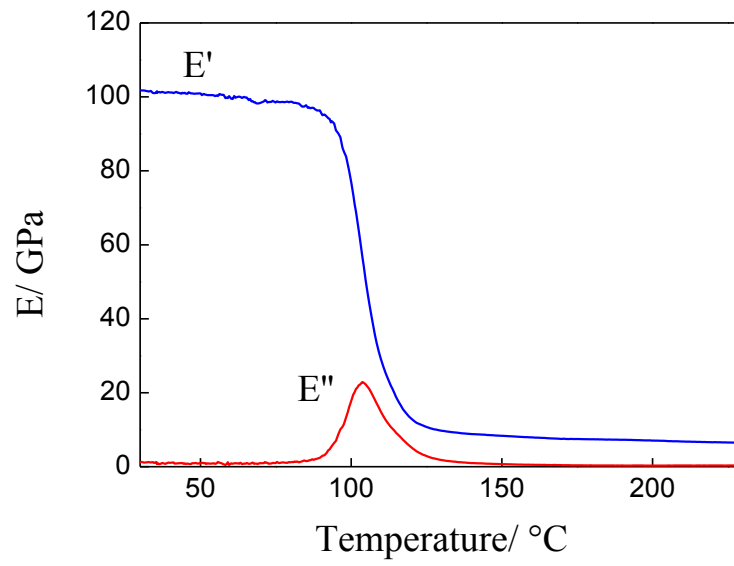


Figure 41: DMTA curves for Composite **C**

The DMTA curves of Composite **D** are shown in Figure 42. The storage modulus at 30 °C was 89 GPa and at 120 °C it dropped by 91 % to 8 GPa.

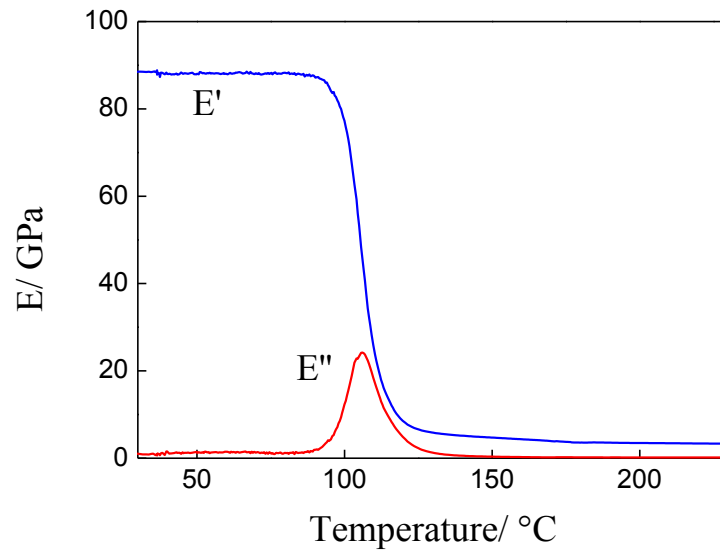


Figure 42: DMTA curves for Composite **D**

At 30 °C the storage modulus of Composite **E** was 13 GPa (Figure 43). When heated to 120 °C the modulus dropped by 85 % to 2 GPa.

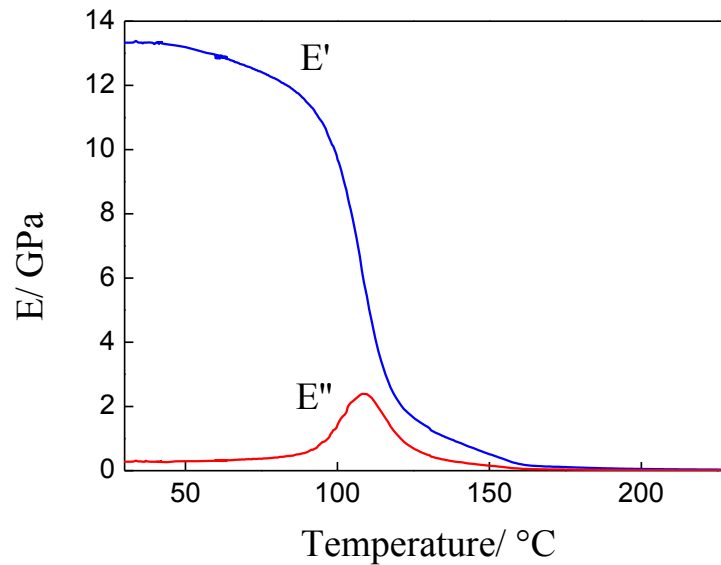


Figure 43: DMTA curves for Composite **E**

#### 4.3.2 Flexural properties of interleaved composites

##### 4.3.2.1 Flexural properties of unidirectional interleaved composites

As stated earlier, the flexural modulus of each sample was determined using three point bending tests at room temperature (RT 1), at 120 °C (using an environmental chamber) and again at room temperature (RT 2). Selected samples of the control composite and Composite **A** were heated to 120 °C by applying a direct current to the carbon fibres. Representative load-displacement curves for the 0° control sample are shown in Figure 44. The gradients of the lines are approximately the same despite the changes in temperature and heating technique. For the control samples tested at room temperature before being heated, using an environmental chamber and an applied current, the gradients of the load-displacement curves were  $150 \pm 5$  N/mm

and  $137 \pm 10$  N/mm, respectively. For the control samples heated to  $120^\circ\text{C}$  using the above heating methods the gradients of the load-displacement curves were  $143 \pm 4$  N/mm and  $134 \pm 5$  N/mm, respectively. Finally for the control samples retested again at room temperature after being heated using the same two heating methods, the gradients of the load-displacement curves were in turn  $151 \pm 4$  N/mm and  $138 \pm 4$  N/mm.

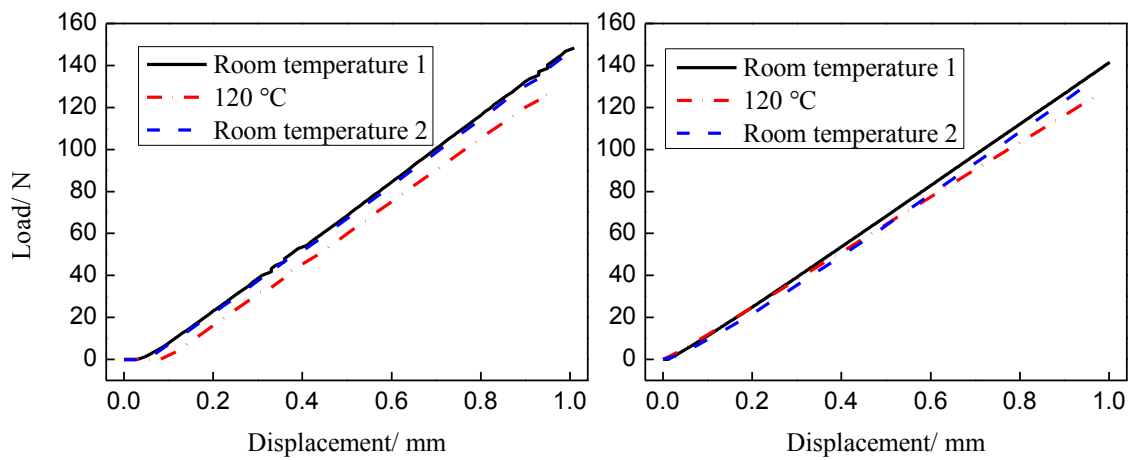


Figure 44: Representative load displacement curves of  $0^\circ$  control sample at room temperature and  $120^\circ\text{C}$  [composites heated using an environmental chamber (left) and an applied current (right)]

Load displacement curves for Composite A tested in three point bending can be seen in Figure 45. The gradient is significantly lower ( $>98\%$  lower) at  $120^\circ\text{C}$  than at room temperature and fully returns to its original value when cooled to  $25^\circ\text{C}$ . For the interleaved composites tested at room temperature before being heated, using an environmental chamber and an applied current, the gradients of the load-displacement curves were  $77 \pm 4$  N/mm and  $86 \pm 6$  N/mm, respectively. For the interleaved composites heated to  $120^\circ\text{C}$  using the above heating methods the

gradients of the load-displacement curves were identical at  $1 \pm 0.3$  N/mm. Finally for the control samples retested again at room temperature after being heated using the same two heating methods, the gradients of the load-displacement curves were in turn  $77 \pm 4$  N/mm and  $85 \pm 6$  N/mm.

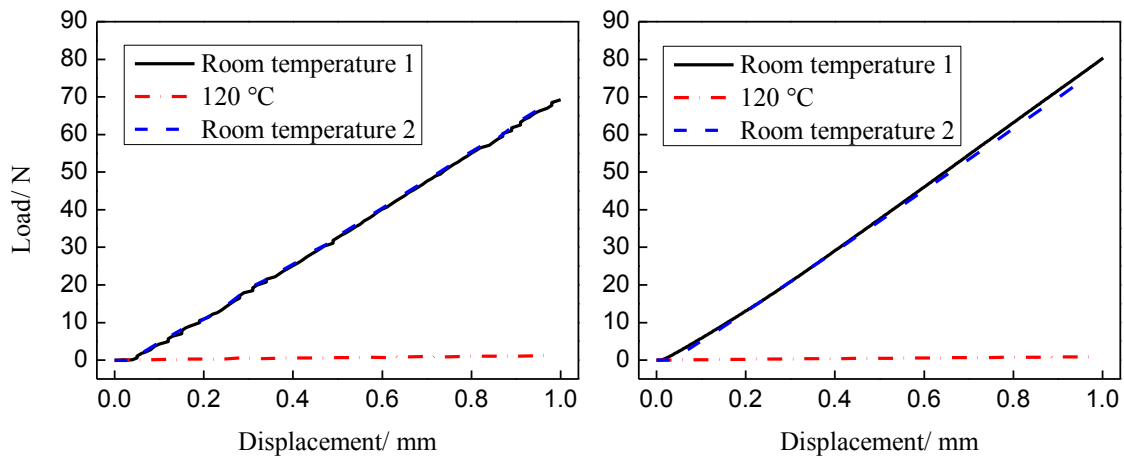


Figure 45: Representative load displacement curves of Composite **A** at room temperature and 120 °C [environmental chamber (left), applied current (right)]

Although a displacement of only 1 mm is shown, a maximum deflection of 17.8 mm was applied to one specimen at 120 °C without initiation of failure. An image of a deformed polystyrene interleaved laminate (Composite **A**) is shown in Figure 46. When this deformed sample was cooled to RT while under load and then unloaded the specimen retained the applied deformation. The composite then returned to its original shape (with <0.5 mm residual deflection) when heated back up to 120 °C without load. This occurred as the internal stresses in the deformed reinforced epoxy layers were released as a result of the polystyrene softening.



Figure 46: Straight and deformed polystyrene interleaved composites (80 mm in length)

Composites **B** and **C** were heated to 120 °C using the environmental chamber and not through an applied current. Both of these composites exhibited similar change due to temperature to that observed for Composite **A**.

Table 10: Flexural moduli of the pure unidirectional carbon fibre reinforced epoxy and interleaved composites at room temperature (RT) and 120 °C

| Composite  | Apparent Flexural Modulus/ GPa |                  |                |         |                 |         |        |         |
|------------|--------------------------------|------------------|----------------|---------|-----------------|---------|--------|---------|
|            | Environmental Chamber          |                  |                |         | Applied Current |         |        |         |
|            | RT 1                           | 120 °C           | % loss         | RT 2    | RT 1            | 120 °C  | % loss | RT 2    |
| 0° control | 118 ± 3                        | 112 ± 2          | 5.1            | 116 ± 3 | 113 ± 11        | 110 ± 8 | 2.7    | 114 ± 7 |
| A          | 65 ± 3<br>(71) <sup>†</sup>    | 1 ± 0.2<br>(0.3) | 98.5<br>(99.6) | 65 ± 4  | 68 ± 3          | 1 ± 0.2 | 98.5   | 66 ± 3  |
| B          | 90 ± 1<br>(97)                 | 4 ± 1<br>(3)     | 95.6<br>(97.3) | 90 ± 2  | - <sup>‡</sup>  | -       | -      | -       |
| C          | 107 ± 7<br>(112)               | 7 ± 0.02<br>(5)  | 93.5<br>(95.4) | 106 ± 3 | -               | -       | -      | -       |

<sup>†</sup> The predicted flexural modulus values are shown in brackets and were calculated using the equations in appendix A.3

<sup>‡</sup> Only the 0° control samples and Composite **A** were heated using an applied current

The flexural moduli of the composites are summarised in Table 10 and are graphically presented in bar charts in Figure 47. The flexural modulus of the pure carbon fibre reinforced composite was approximately 116 GPa at both room temperature and 120 °C. The flexural modulus of Composite A at room temperature was  $65 \pm 3$  GPa. At 120 °C, above the  $T_g$  of polystyrene, the modulus fell by 98 % to  $1 \pm 0.2$  GPa. When re-tested at room temperature no loss in flexural modulus could be seen.

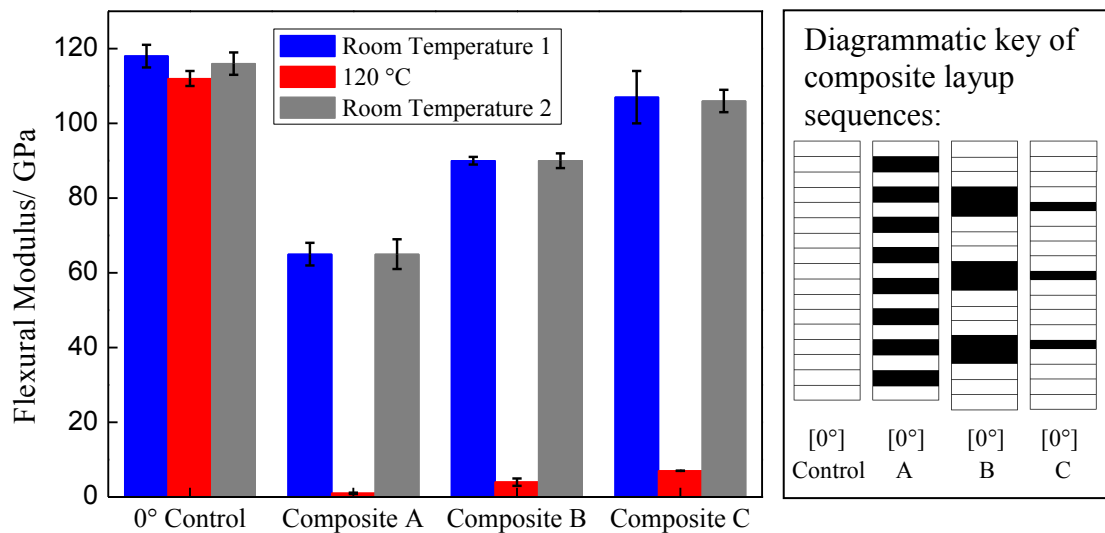


Figure 47: Flexural moduli of the pure unidirectional carbon fibre reinforced epoxy and interleaved composites [heated to 120 °C using an environmental chamber] (including diagrammatic key, where unidirectional CFRP plies are white and polystyrene layers are black)

The values of flexural modulus obtained from the environmental chamber and resistant heating are very similar suggesting that an applied current does not adversely affect the flexural stiffness of the composite. However, polystyrene could be seen flowing out at the ends of the Composite A where the electrical contacts

were connected. The temperature was significantly higher at the contacts than at elsewhere in the sample causing the polystyrene to melt. This problem did not occur when using the environmental chamber. The flexural modulus of Composite **B** at room temperature was 90 GPa. At 120 °C this fell by 96 % to 4 GPa and when re-tested at 25 °C returned to 90 GPa. The flexural stiffness of Composite **C** at room temperature was 107 GPa. When heated to 120 °C the stiffness dropped by 93 % to 7 GPa. The stiffness returned to its original value prior to heating once cooled to room temperature.

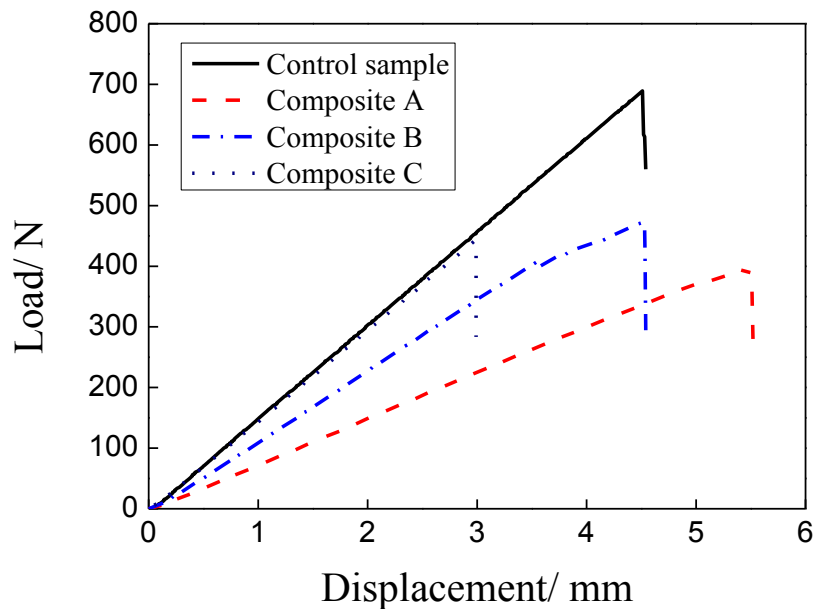


Figure 48: Load displacement curves of 0° control sample and interleaved flexural specimens **A**, **B** and **C** tested to failure at room temperature

Load displacement curves of the control sample and interleaved composites, tested to failure, can be seen in Figure 48. For Composite **B** the kink in the load displacement curve at approximately 400 N was taken as the point of failure. At room temperature the flexural strength of the 0° control sample was  $1550 \pm 11$  MPa and failed in

compression at the mid-span. The apparent flexural strength values are given in Table 11 and are graphically presented in a bar chart in Figure 52. The apparent flexural strengths of composites **A**, **B** and **C** were  $966 \pm 18$  MPa,  $894 \pm 12$  MPa and  $987 \pm 20$  MPa, respectively. The interleaved composites have lower flexural strength than the pure CFRP composite but this is because these specimens failed prematurely in interlaminar shear.

Table 11: Flexural strengths and interlaminar shear strengths of the interleaved and pure unidirectional carbon fibre reinforced epoxy composites

| Composite  | Flexural tests                     |                         |           | SBS tests <sup>†</sup>        |             |
|------------|------------------------------------|-------------------------|-----------|-------------------------------|-------------|
|            | Apparent Flexural Strength/ MPa    |                         |           | $\tau_{\max}$ at Failure/ MPa | ILSS/ MPa   |
|            | RT <sup>†</sup>                    | 120 °C                  | % loss    | RT                            | RT          |
| 0° control | $1550 \pm 11$                      | $636 \pm 25$            | 59        | $24 \pm 0.2$                  | $111 \pm 2$ |
| A          | $966 \pm 18$<br>(936) <sup>‡</sup> | - <sup>*</sup><br>(23)  | -<br>(98) | $15 \pm 0.3$                  | $71 \pm 6$  |
| B          | $894 \pm 12$<br>(1280)             | - <sup>*</sup><br>(81)  | -<br>(93) | $14 \pm 0.2$                  | $79 \pm 4$  |
| C          | $987 \pm 20$<br>(1474)             | - <sup>*</sup><br>(132) | -<br>(91) | $15 \pm 0.3$                  | $52 \pm 2$  |

<sup>†</sup> RT: Room temperature, SBS: Short beam shear

<sup>‡</sup> The predicted flexural strength values are shown in brackets and were calculated using the equations in appendix A.3

<sup>\*</sup> The flexural strength of the interleaved composites could not be measured at 120 °C since at large deflections the sides of the loading nose fixture came in contact with the composite

Table 11 includes the maximum interlaminar shear stress,  $\tau_{\max}$ , in each of the composites at failure. The consistently low value of  $\tau_{\max}$  in the interleaved specimens

indicated that the bond of the polystyrene to the epoxy composite is rather weak (delamination at the PS-epoxy interface can be seen in Figure 54). At 120 °C the flexural strength of the 0° control sample dropped by 59 % to  $636 \pm 25$  MPa. The control sample failed in compression at 120 °C as occurred at room temperature. The flexural properties of the 0° composites are therefore dominated by compressive properties. (Compression test results, reported later in section 4.3.6, showed that the 0° control sample underwent a dramatic loss in compressive strength from  $1264 \pm 132$  MPa to  $657 \pm 60$  MPa when heated from room temperature to 120 °C.) The flexural strength of the interleaved composites could not be measured at 120 °C since at large deflections the sides of the loading nose fixture came in contact with the composite.

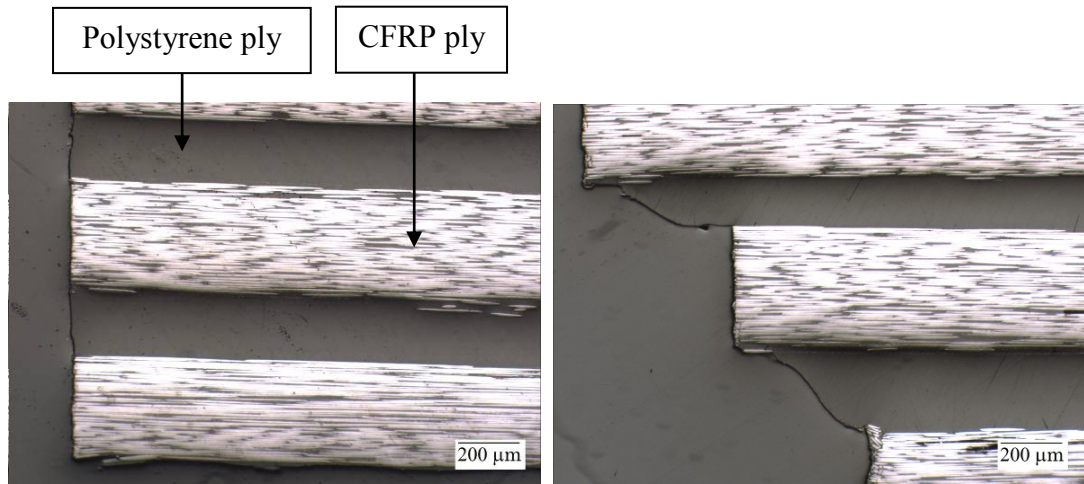


Figure 49: Cross section of Composite **B** before flexure testing (left) and in its deformed state after cooling under load (right) at  $20 \times$  magnification

Microscopy images of Composite **B** before and after flexural stiffness testing are shown in Figure 49. The separation of reinforced layers by polystyrene can clearly be seen and no delamination was observed. After testing at 120 °C (max load 6 N),

the ends of the composite are deformed as a result of the polystyrene softening and allowing the reinforced epoxy plies to slide relative to each other.

#### 4.3.2.2 Flexural properties of multidirectional interleaved composites

The flexural properties of the multidirectional reinforced composites are shown in Table 12 and flexural modulus values are graphically presented in Figure 50. At room temperature the flexural modulus of Composite **D**, with 0/90° fibre reinforced plies, was  $93 \pm 4$  GPa. The flexural stiffness of the 0/90° control sample, without polystyrene, at room temperature was  $96 \pm 2$  GPa. At 120 °C the flexural stiffness of Composite **D** dropped by 96 % to  $4 \pm 0.07$  GPa and returned fully when cooled back to room temperature. The flexural stiffness of the control sample did not change significantly at elevated temperature.

Table 12: Flexural properties and interlaminar shear strengths of multidirectional reinforced interleaved composites and control samples

| Composite              | Flexural tests        |              |        |            | SBS <sup>†</sup> tests |                               |            |
|------------------------|-----------------------|--------------|--------|------------|------------------------|-------------------------------|------------|
|                        | Flexural Modulus/ GPa |              |        |            | Flexural Strength/ MPa | $\tau_{\max}$ at Failure/ MPa | ILSS/ MPa  |
|                        | RT 1 <sup>†</sup>     | 120 °C       | % loss | RT 2       |                        |                               |            |
| 0/90° control          | $96 \pm 2$            | $94 \pm 3$   | 2      | $99 \pm 2$ | $1145 \pm 8$           | $18 \pm 0.1$                  | $44 \pm 4$ |
| D                      | $93 \pm 4$            | $4 \pm 0.07$ | 96     | $93 \pm 2$ | $709 \pm 12$           | $11 \pm 0.2$                  | $31 \pm 1$ |
| $\pm 45^\circ$ control | $15 \pm 0.7$          | $13 \pm 0.5$ | 13     | $15 \pm 1$ | $180 \pm 9$            | $3 \pm 0.2$                   | $30 \pm 5$ |
| E                      | $15 \pm 1$            | $1 \pm 0.1$  | 94     | $16 \pm 1$ | $137 \pm 15$           | $2 \pm 0.2$                   | $26 \pm 2$ |

<sup>†</sup> RT: Room temperature, SBS: Short beam shear

The flexural stiffness of Composite **E**, with  $\pm 45^\circ$  fibre reinforced layers, at room temperature was  $15 \pm 1$  GPa. The flexural stiffness of the  $\pm 45^\circ$  control sample, without polystyrene, was  $15 \pm 0.7$  GPa at room temperature. When heated from room temperature to 120 °C the flexural modulus of Composite **E** dropped by 94 %



composite ( $2 \pm 0.2$  MPa) was lower than that of the  $\pm 45^\circ$  control sample ( $3 \pm 0.2$  MPa) and this suggests there was a change in the type of failure.

#### 4.3.2.3 Predicted flexural properties of unidirectional interleaved composites

The predicted bending behaviour of the unidirectional interleaved composites at room temperature and  $120^\circ\text{C}$  was calculated using beam theory (see appendix A.3). The results are given in Table 10 and 11. The predicted loss in flexural stiffness for each composite was similar to the experimentally observed values. However, the predicted values of flexural stiffness at room temperature are higher than the measured values from flexural tests (see Figure 51).

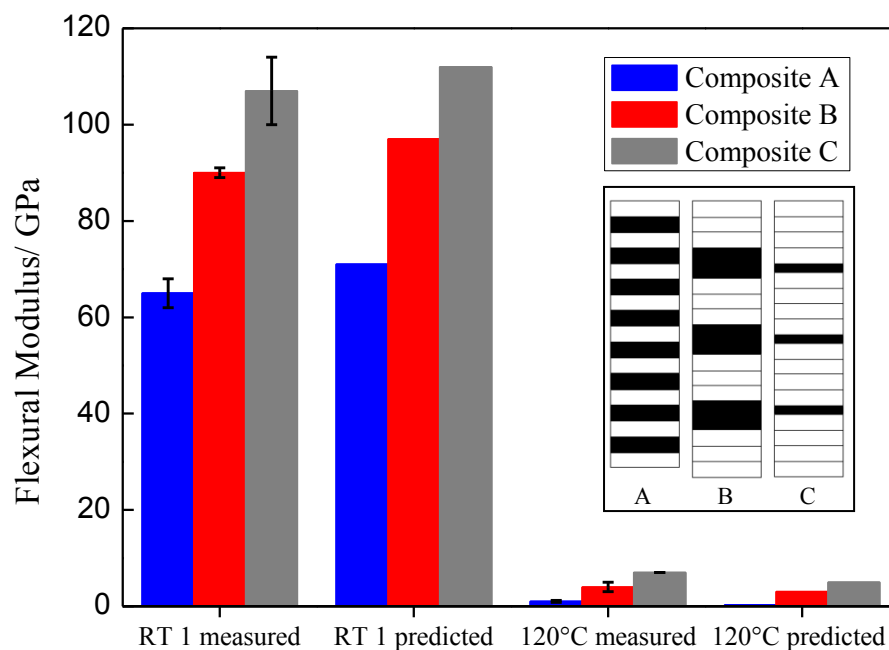


Figure 51: Measured and predicted flexural modulus values of unidirectional interleaved composites at room temperature (RT) and  $120^\circ\text{C}$  (including diagrammatic key, where unidirectional CFRP plies are white and polystyrene layers are black)

For example, the measured flexural stiffness of Composite **A** at room temperature was  $65 \pm 3$  GPa but the predicted value is 71 GPa. A possible explanation for this difference is that the theory does not include shear distortion of the polystyrene layers. There is also a contrast between the actual and predicted stiffness values at high temperature. The predicted values are lower than the measured values at 120 °C. For example, for Composite **A**, the measured flexural stiffness at 120 °C was  $1 \pm 0.2$  GPa and the predicted value was 0.3 GPa. This is because the theory disregards the residual shear stiffness of the softened polystyrene layers.

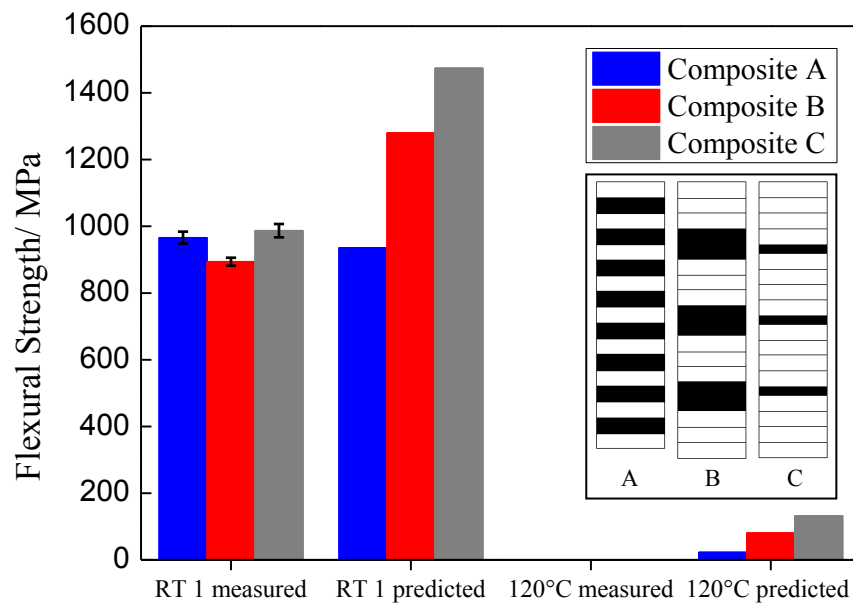


Figure 52: Measured and predicted flexural strength values of unidirectional interleaved composites at room temperature (RT) and 120 °C (including diagrammatic key, where unidirectional CFRP plies are white and polystyrene layers are black)

Figure 52 shows there are significant differences between the measured and predicted apparent flexural strength of the composite interleaved specimens **A**, **B** and

C. Here measured apparent flexural strength refers to the strength that is calculated from the failure load assuming the beam is homogeneous. For the predicted apparent strength the measured flexural strength of the  $0^\circ$  control sample is used to predict the failure load of the interleaved composites and from this the predicted apparent strength is calculated, again assuming the beam is homogeneous. However, as noted earlier, in all three cases the specimen failure mode was not flexure but was interlaminar shear. The values of  $\tau_{\max}$  given in Table 11 shows that the interlaminar shear stress in each of the interleaved specimens at failure was around 15 MPa and indicates that the PS-epoxy interface was relatively weak (delamination at the PS-epoxy interface is shown in Figure 54).

To demonstrate that higher flexural stresses could be achieved if the interlaminar shear stress was reduced a modified flexural specimen (see Figure 53) was manufactured from Composite C.

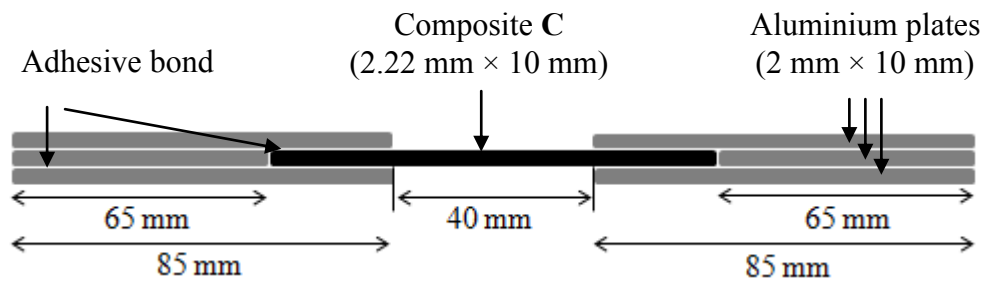


Figure 53: Diagram of extended flexural test specimen

The composite was bonded to aluminium plates at either end of the specimen to increase its length. This specimen was then tested in four point bending. The loading span (116 mm [support span 190 mm]) was larger than the length of the composite (80 mm) so as to eliminate shear stresses with the laminate. The strength of this extended specimen was 1107 MPa. This is closer to the predicted value (1474 MPa) showing that shear failure was responsible for the low flexural strength values in the

standard flexural specimens. The strength values for the interleaved composites at 120 °C could not be measured, due to limitations of the testing equipment at large specimen deflections, however the apparent strength is predicted to dramatically reduce at this temperature as expected. For example, the flexural strength of Composite **A** is predicted to reduce by 98 % from 936 MPa at room temperature to 23 MPa at 120 °C.

#### 4.3.3 Interlaminar shear strength of interleaved composites

The ILSS at room temperature of composites **A**, **B** and **C** were  $71 \pm 6$  MPa,  $79 \pm 4$  MPa and  $52 \pm 2$  MPa, respectively (Table 11). The ILSS of the 0° control sample was  $111 \pm 2$  MPa. The lower ILSS of the interleaved composites can be associated with weak adhesion at the polystyrene-epoxy interface, where delamination took place. From flexural tests the maximum shear stress ( $\tau_{\max}$ ) in the control sample was calculated as 24 MPa using equation 9 and no shear failure was observed, as expected. For composites **A**, **B** and **C** the maximum shear stress at failure of the flexural specimens was 15 MPa, 14 MPa and 15 MPa, respectively (Table 11). These values are much smaller than the measured ILSS values but for these laminates the failure mode, as noted in the previous section, in all cases was interlaminar shear. High ILSS values from short beam shear can be expected when considering this testing method only give the apparent ILSS, as compressive forces are known to contribute to the strength value [132, 133]. Cross sectional images of the control sample and Composite **A** at the mid-span after short beam shear testing are shown in Figure 54. Delamination can be seen at the interface between the polystyrene and CFRP layers.

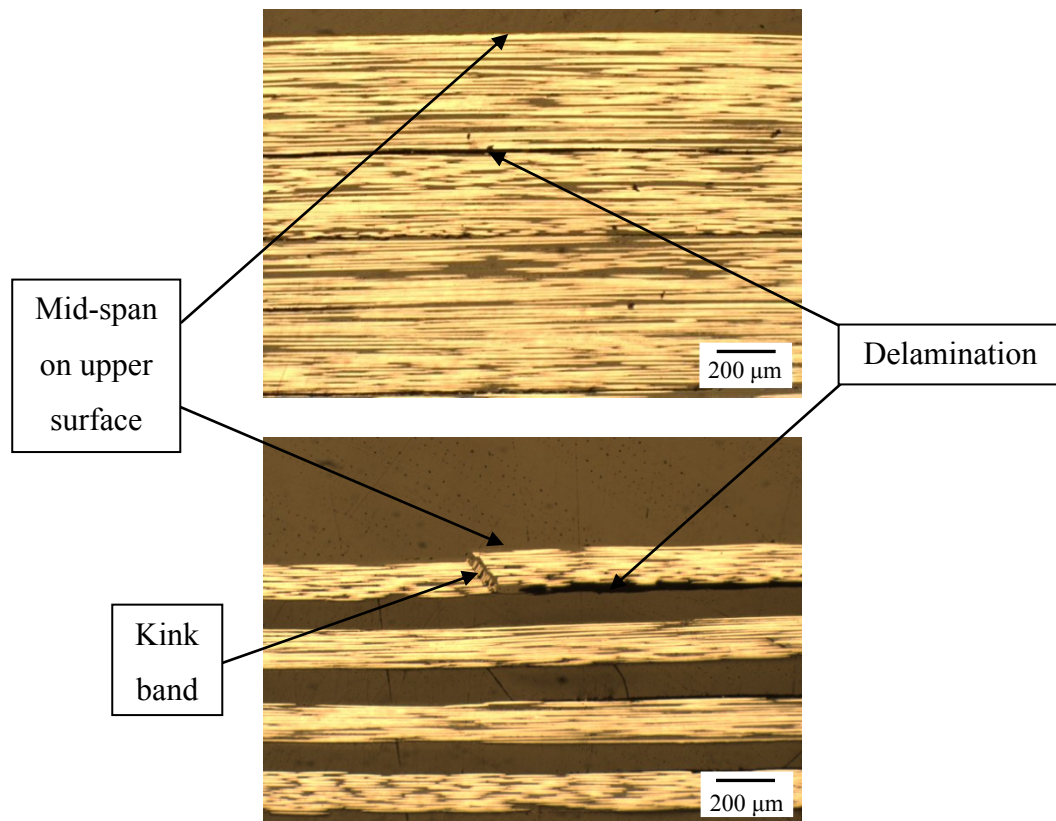


Figure 54: Cross sections of carbon fibre reinforced epoxy control composite (top) and Composite **A** (bottom) at the mid-span after short beam shear testing at room temperature

The ILSS of the 0/90° control sample and Composite **D** at room temperature was  $44 \pm 4$  MPa and  $31 \pm 1$  MPa, respectively (Table 12). At room temperature the ILSS of the  $\pm 45^\circ$  control sample and Composite **E** was  $30 \pm 5$  MPa and  $26 \pm 2$  MPa, respectively. These composites also failed in interlaminar shear.

ILSS testing was also performed on the interleaved composites at 120 °C. However, the composites did not fail but, due to the large deflections these specimens were compressed between the loading nose and the support pins. A strength value could therefore not be determined.

#### 4.3.4 Flexural fatigue performance of interleaved composite

Flexural fatigue tests were performed on Composite A\* to determine whether there was any reduction in flexural performance after multiple heating and cooling cycles. The results of the flexure tests are shown in Figure 55. At room temperature the flexural modulus of the composite was approximately 65 GPa and at 120 °C it fell to around 2 GPa. After 40 cycles the flexural modulus at both room temperature and 120 °C did not change significantly.

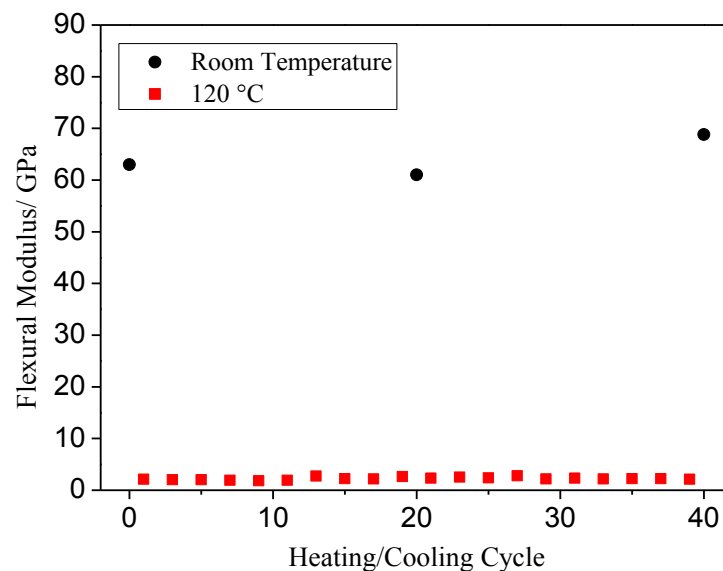


Figure 55: Flexural modulus of interleaved fatigue specimen (Composite A\*) after 40 heating and cooling cycles

To determine whether there was any damage within the composite after 40 cycles, cross sectional images were taken (Figure 56). Slight damage was visible at the ends of the specimen where voids had formed between the CFRP layers and the polystyrene.

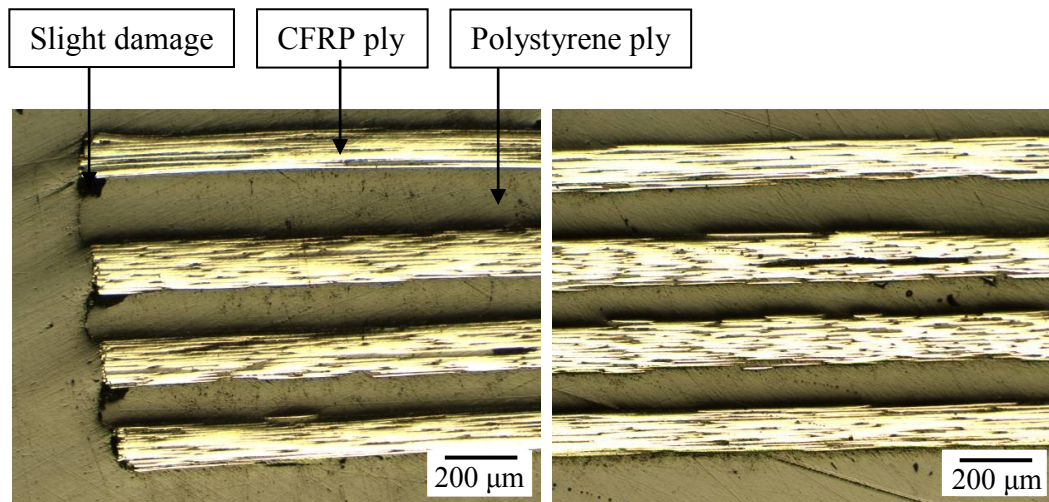


Figure 56: Cross sectional images of the end (left) and middle (right) of flexural fatigue specimen (Composite A\*) after 40 heating and cooling cycles ( $5 \times$  magnification)

There was also slight extrusion of the polystyrene at the ends of the specimen. The rest of the composite was undamaged, confirming that the process is completely reversible under these conditions. This suggests interleaved composites could be used in applications where large, reversible deflections are required over an extended lifetime. Images of the ends of the interleaved specimen after 0 cycle and 40 cycles (Figure 57) were overlaid, to determine whether the thickness of the composite or the polystyrene layers had changed after fatigue testing. The thickness of the composite and the polystyrene layers remained the same, despite slight extrusion of polystyrene at the ends of the specimen. The reason the thickness did not change is probably due to the lack of damage in the rest of the specimen.

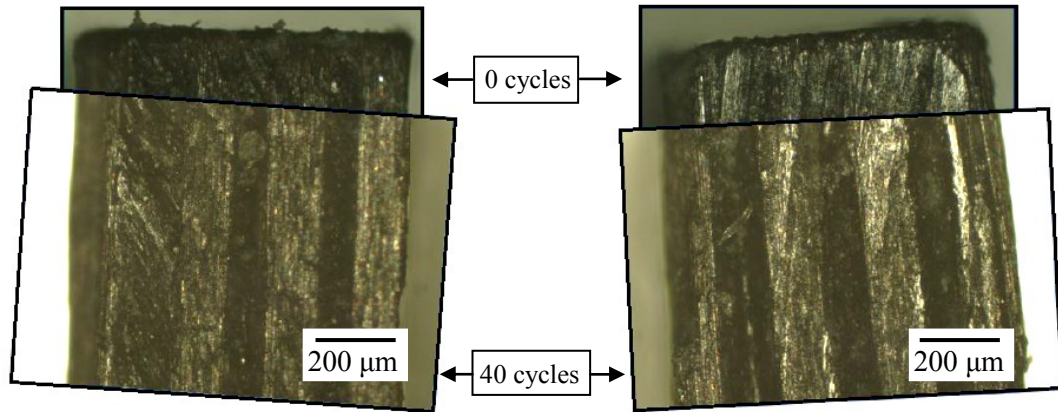


Figure 57: Images of the ends of the interleaved flexural fatigue specimen  
(Composite A\*) after 1 cycle and 40 cycles

#### 4.3.5 Tensile properties of interleaved composites

When tested in tension both the interleaved composites and 0° control samples failed within the gauge length at room temperature and exhibited brooming as a result of fibre fracture [134]. At 120 °C, the 0° control samples failed catastrophically within the gauge length as they did at room temperature. At 120 °C, only the outer CFRP plies of the interleaved composite failed as they carried the majority of the load. Failure of these plies occurred at the border between the end tab and the gauge length. The outer plies had then slid along with the attached end tabs. This type of failure mode could be considered invalid as only the outer CFRP plies have failed and not the entire specimen. However, these results are still useful as they provide information on how the interleaved composites behave under a different loading condition. A cross sectional image of the end of the failed interleaved tensile specimen tested at 120 °C is shown in Figure 58. The large clamping force of the grips had also caused the polystyrene and the CFRP layers to extrude from around the sides of the end tab in the interleaved specimens.

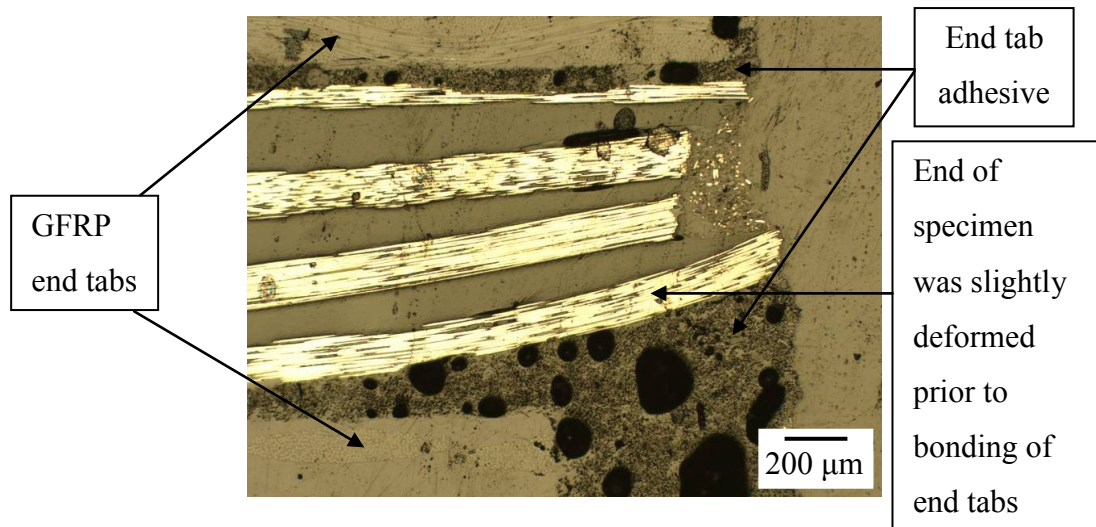


Figure 58: Cross section of the end of a deformed interleaved composite after tensile loading at 120 °C ( $5 \times$  magnification)

Representative tensile test curves of the interleaved composite (Composite A\*, consisting of 4 0° CFRP plies and 3 polystyrene interleaves) and the 4-ply 0° control sample) at room temperature and 120 °C are shown in Figure 59.

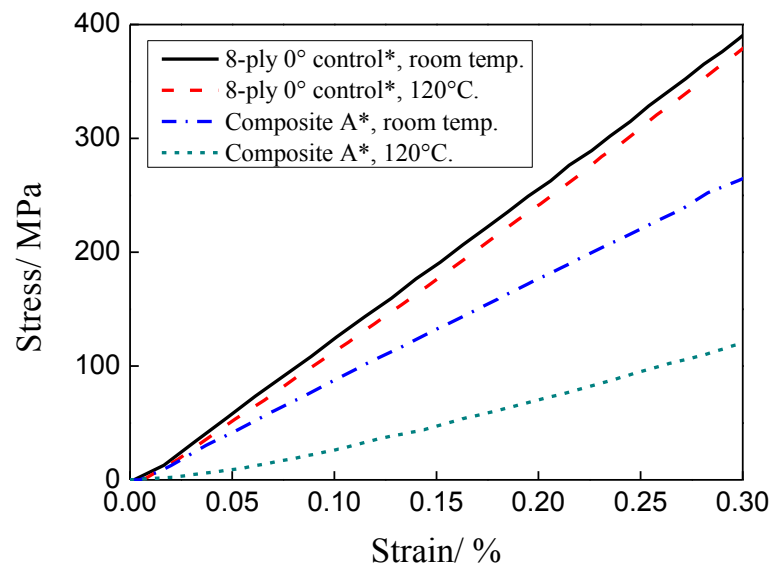


Figure 59: Representative stress-strain curves of the 0° control samples and interleaved composites that were tested in tension at room temperature and 120 °C

The tensile properties of the composites at room temperature and 120 °C are shown in Table 13 and are graphically presented in bar charts in Figure 60. At room temperature the Young's modulus of the interleaved composite (determined from a centrally positioned strain gauge) is 61 % of that of the control specimen which is very close to the theoretically expected value based on the 62 % volume fraction of CFRP plies in the interleaved composite. However the average tensile strength of the interleaved composite, at 52% of the average strength of the control sample, is lower than expected from simple theory. This may be due to variations in the quality of the interleaved composite as indicated by the significantly higher scatter in the strength data of this material. The tensile properties of the pure carbon fibre reinforced composite remained unchanged at elevated temperature as previously observed [135]. The strength of the interleaved composite at 120 °C dropped by 54 % of the room temperature value and this is because the inner CFRP plies were effectively disconnected when the polystyrene layers had softened. However, at 120 °C there was only a 38 % drop in Young's modulus of the interleaved composite compared to the room temperature case.

Table 13: Tensile properties of the interleaved and pure carbon fibre reinforced epoxy composites at room temperature (RT) and 120 °C

| Composite   | Modulus/ GPa |          | % loss | Strength/ MPa |           | % loss |
|-------------|--------------|----------|--------|---------------|-----------|--------|
|             | RT           | 120 °C   |        | RT            | 120 °C    |        |
| 0° control* | 145 ± 6      | 146 ± 13 | 0      | 1682 ± 67     | 1629 ± 94 | 3      |
| A*          | 88 ± 12      | 55 ± 6   | 38     | 867 ± 114     | 395 ± 62  | 54     |

As noted earlier, the modulus was determined using data from a central strain gauge, and the fact that the stiffness drop is less than 50 % indicates that at this distance from the specimen grips some load had transferred across the softened polystyrene

layers to the inner CFRP plies of the interleaved composite. (This also suggests that if longer flexural specimens were tested then the stiffness loss at elevated temperature may be less than predicted by the simple beam theory used here.)

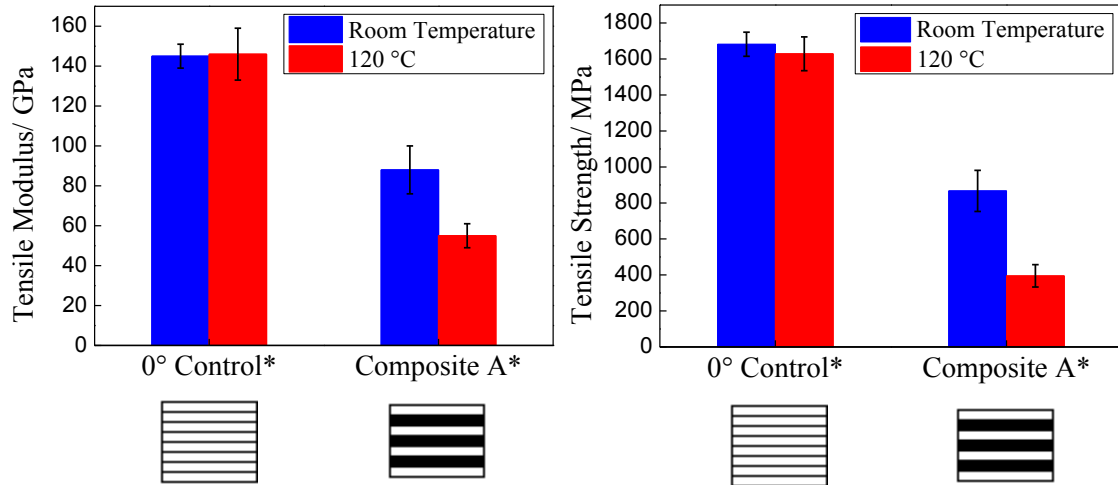


Figure 60: Tensile modulus and strength of the interleaved and pure carbon fibre reinforced epoxy composites at room temperature and 120 °C (including diagrammatic key suspended below respective bars, where unidirectional CFRP plies are white and polystyrene layers are black)

#### 4.3.6 Compression properties of interleaved composites

When tested under compression at room temperature both the 0° control sample and interleaved composite A failed catastrophically in the gauge length. At 120 °C the 0° control specimens again failed catastrophically in the gauge length but the interleaved specimens did not show any material failure and instead buckled immediately when loaded. Pictures of Composite A and the 0° control sample after testing at 120 °C can be seen in Figure 61.



Figure 61: Failed 0° control sample (left) and interleaved composite A (right) after compression testing at 120 °C

Representative compression test curves of 0° control samples and interleaved composite A at room temperature are shown in Figure 62. At 120 °C stress-strain curves for the interleaved composites could not be recorded as the specimens buckled immediately.

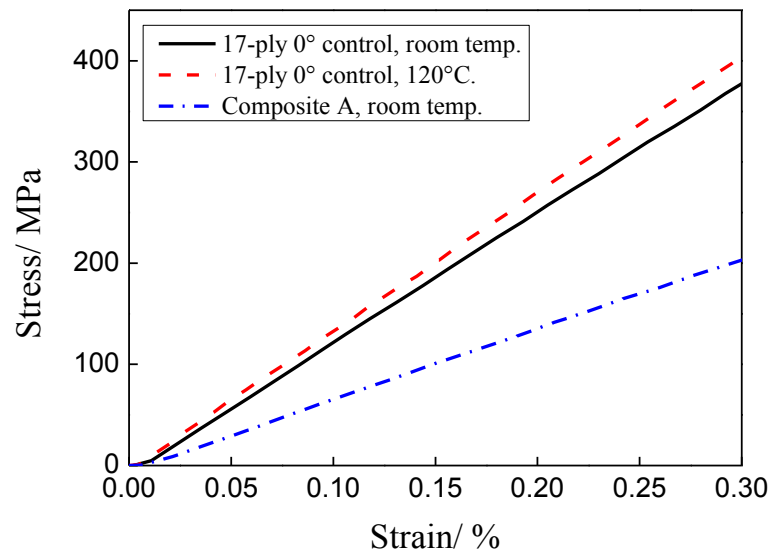


Figure 62: Representative stress-strain curves of the 0° control samples and interleaved composites that were tested in compression at room temperature and the 0° control samples that were tested at 120 °C

The measured properties of the composites are given in Table 14 and are graphically presented in bar charts in Figure 63. The compressive Young's modulus and strength at room temperature for the 0° control sample were  $127 \pm 3$  GPa and  $1264 \pm 132$  MPa, respectively and for the interleaved composite were  $66 \pm 1$  GPa and  $786 \pm 64$  MPa, respectively.

Table 14: Compressive properties of the interleaved and pure carbon fibre reinforced epoxy composites at room temperature (RT) and 120 °C

| Composite  | Modulus/ GPa |             | % loss | Strength/ MPa  |              | % loss |
|------------|--------------|-------------|--------|----------------|--------------|--------|
|            | RT           | 120 °C      |        | RT             | 120 °C       |        |
| 0° control | $127 \pm 3$  | $136 \pm 5$ | 0      | $1264 \pm 132$ | $657 \pm 60$ | 48     |
| A          | $66 \pm 1$   | -           | -      | $786 \pm 64$   | -            | -      |

The interleaved values of modulus and strength are 52% and 62% of the control sample values which, in view of the variability of the data, are reasonably close to the expected value of 57 % i.e. the volume fraction of CFRP plies in the interleaved specimen. At 120 °C the modulus of the 0° control sample remained similar but the strength decreased by 48 % to  $657 \pm 60$  MPa. This loss of strength is expected due to the temperature dependence of the matrix shear properties. This reduction in compressive strength at high temperature has been studied previously [135]. (A similar, but larger, strength reduction of 59 % was observed in the 120 °C flexural tests of the 0° control specimens which also exhibited a compressive failure mode [see Table 11].) As noted earlier the interleaved specimens did not exhibit any material failure but instead buckled. As a consequence no values for Young's modulus and strength were determined.

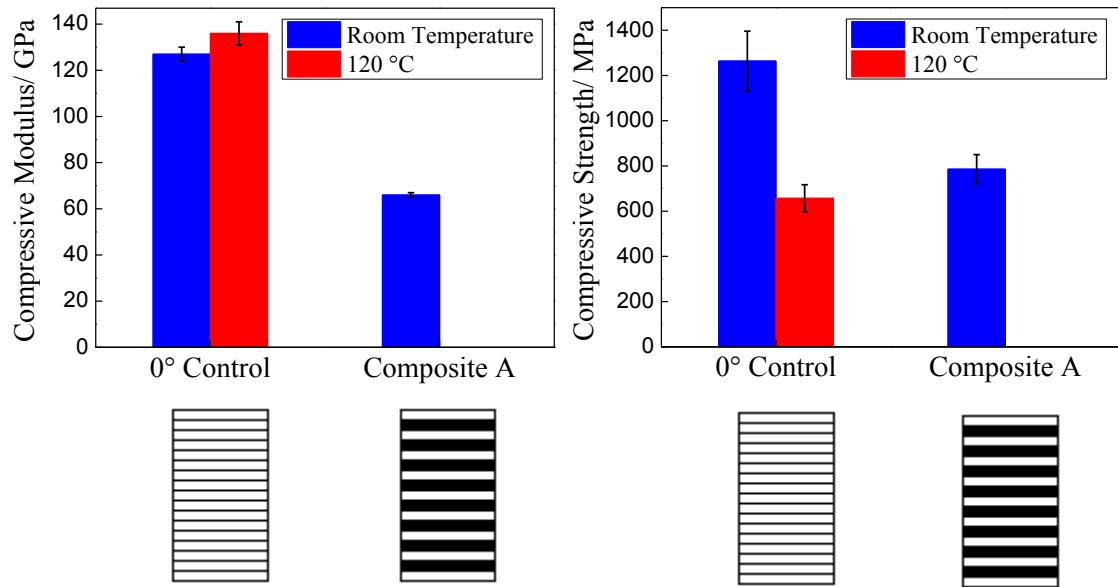


Figure 63: Compressive modulus and strength of the interleaved and pure carbon fibre reinforced epoxy composites at room temperature and 120 °C (including diagrammatic key suspended below respective bars, where unidirectional CFRP plies are white and polystyrene layers are black)

#### 4.3.7 Flexural properties of interleaved composite with reinforced interleaf layers

An interleaved composite with woven carbon fibre reinforced polystyrene layers, Composite F, was analysed using DMTA (Figure 64). At 30 °C, the storage modulus was 62 GPa. Above this temperature, at 120 °C, the stiffness dropped by 74 % to 16 GPa.

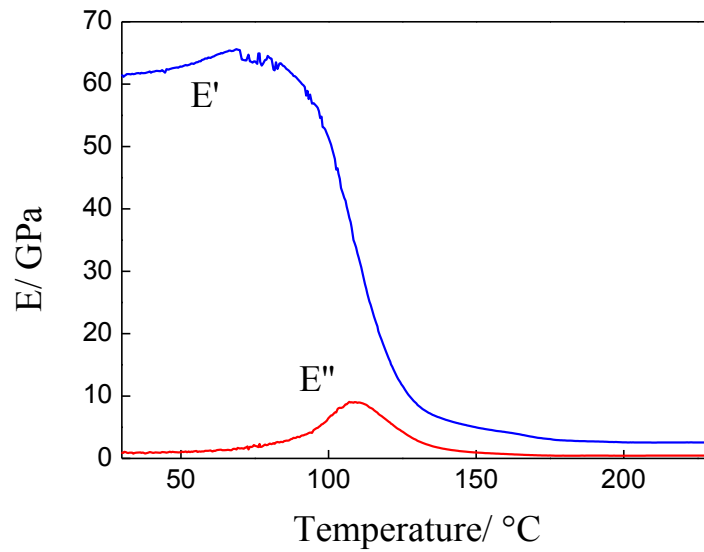


Figure 64: DMTA curves for Composite **F**

Composite **F** was also investigated using three point bending tests. The results are summarised in Table 15. The flexural modulus of the composite at room temperature was  $90 \pm 7$  GPa. According to beam theory calculations (see appendix A.3), the expected stiffness of the composite without reinforced interleaf layers was 80.1 GPa. Therefore reinforcing the polystyrene layers with woven fabric does improve the stiffness of the interleaved composites, in this case by 12 %. The woven fibres also provide a way of directly heating the polystyrene layers that will permit faster response times in real applications. At 120 °C the stiffness dropped by 92 % to 7 GPa. When cooled to room temperature the stiffness returned to its original value. At 120 °C, Composite **F** failed at approximately 2 mm displacement and can therefore not achieve the large deflections observed with the un-reinforced interleaved specimens.

Table 15: Flexural properties of interleaved composite with reinforced polystyrene layers at room temperature (RT) and 120 °C

| Composite | Apparent Flexural Strength/ MPa |                 |            | Apparent Flexural Modulus/ GPa |              |            |        |
|-----------|---------------------------------|-----------------|------------|--------------------------------|--------------|------------|--------|
|           | RT                              | 120 °C          | % loss     | RT 1                           | 120 °C       | % loss     | RT 2   |
| F         | 601 ± 36<br>(1052) <sup>†</sup> | 60 ± 21<br>(53) | 90<br>(95) | 90 ± 7<br>(80)                 | 7 ± 3<br>(2) | 92<br>(98) | 90 ± 6 |

<sup>†</sup> The predicted values are shown in brackets and were calculated using the equations in A.3 assuming the composite contained unreinforced polystyrene interleaf layers

A reason for this failure at elevated temperature could be due to a lack of polystyrene between the woven reinforcement and the unidirectional CFRP layers. A cross sectional image of the interleaved composite containing reinforced polystyrene plies can be seen in Figure 65. There is no distinct layer of polystyrene at the edge of the interleaf region and this would restrict the unidirectional CFRP layers from sliding with respect to each other; resulting in failure at elevated temperature. The apparent flexural strength of Composite **F** at room temperature was 601 ± 36 MPa. The predicted flexural strength for the composite without reinforced interleaved layers was much higher at 1052 MPa. This can be explained as the maximum interlaminar shear stress,  $\tau_{\max}$ , for Composites **F** was only 9 MPa. This was even lower than the shear stress of the standard interleaved composites (approximately 15 MPa) indicating there was a change in the type of failure. This may have been due the lack of polystyrene between the woven carbon fibres and CFRP layers, where failure occurred. The measured and predicted flexural strength at 120 °C are similar, however the prediction assumes failure occurs in the CFRP plies whereas at 120 °C failure occurred at the interface between the central interleaf layer and the adjacent unidirectional CFRP ply.

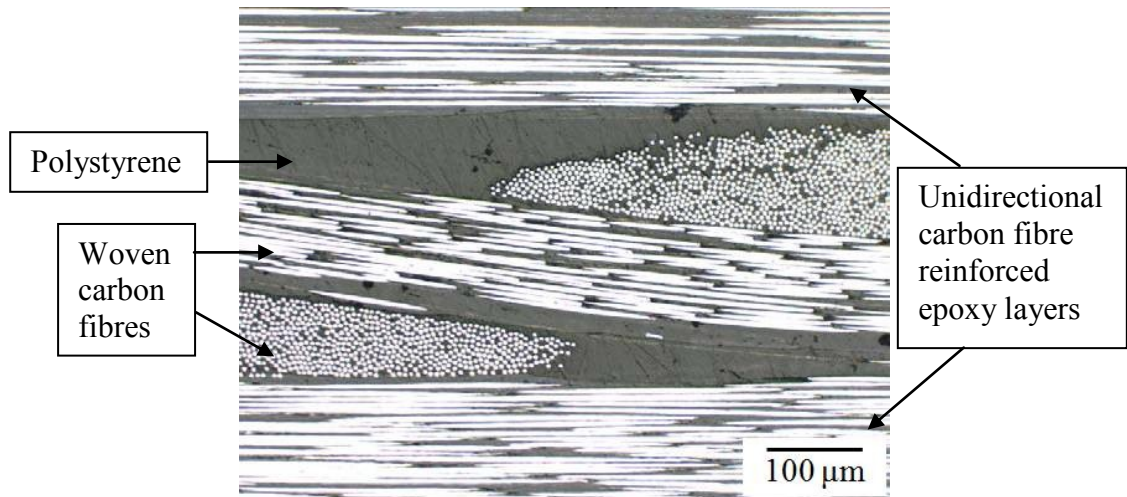


Figure 65: Cross section of the polystyrene interleaved composite containing woven carbon fibre reinforced interleaf layers at  $20 \times$  magnification

#### 4.3.8 Flexural properties of constrained interleaved composites

In some applications it may not be suitable to have polystyrene throughout the entire length of the specimen e.g. at a join with another component. Therefore interleaved composites with constrained ends were manufactured (Figure 34).

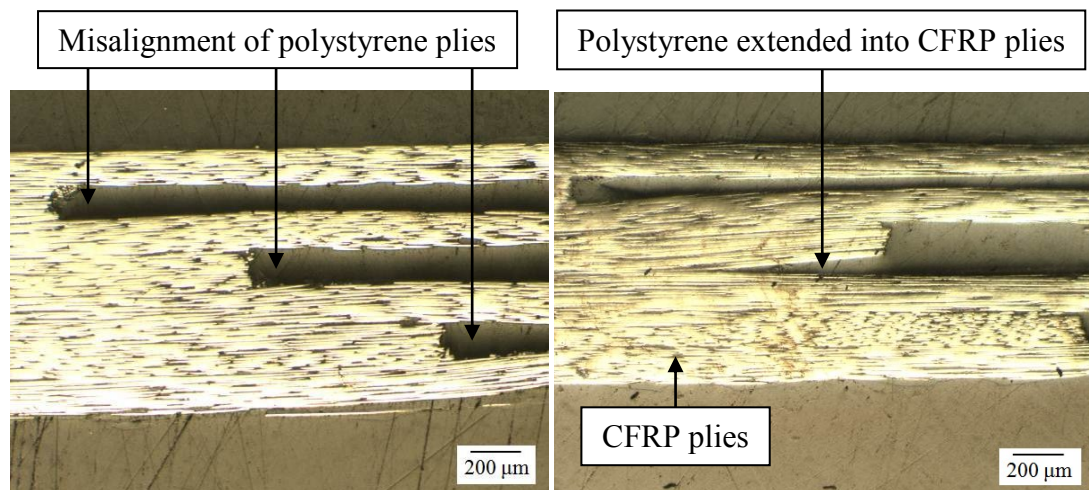


Figure 66: Cross sections of constrained polystyrene interleaved composites at the boundaries between the polystyrene and carbon fibre reinforced epoxy layers at  $5 \times$  magnification

Polystyrene was replaced at the ends of the composites with CFRP plies of the same thickness. Cross sectional images of the constrained laminate are shown in Figure 66. Although care was taken during lay-up, there was still misalignment of the interleaved regions. There were also areas within the composite where the polystyrene had extended into the CFRP layers. At room temperature the flexural strength and modulus of the constrained laminate was  $942 \pm 31$  MPa and  $69 \pm 6$  GPa, respectively (Table 16). These values are similar to the flexural properties of Composite A that consisted of single CFRP plies separated by unconstrained polystyrene layers. The maximum shear stress in constrained laminate (13 MPa) was also similar to that of Composite A (15 MPa) and both failed similarly in shear at room temperature. When the constrained laminate was heated to 120 °C, the stiffness of the composite was reduced by 90 % to  $7 \pm 0.4$  GPa. Composite A underwent a much larger loss in stiffness (98 %) when heated to 120 °C. This is because at elevated temperature each CFRP ply was independent over the entire length of the specimen. Upon cooling, the stiffness of the constrained laminate returned to its original value prior to heating. Unlike the unconstrained (standard) interleaved composites, delamination occurred when the constrained composites were deflected at elevated temperature.

Table 16: Flexural properties of the constrained interleaved composite at room temperature (RT) and 120 °C

| Composite   | Apparent Flexural Strength/ MPa |              |        | Apparent Flexural Modulus/ GPa  |                    |            |            |
|-------------|---------------------------------|--------------|--------|---------------------------------|--------------------|------------|------------|
|             | RT                              | 120 °C       | % loss | RT 1                            | 120 °C             | % loss     | RT 2       |
| Constrained | $942 \pm 31$                    | $122 \pm 23$ | 87     | $69 \pm 6$<br>(88) <sup>†</sup> | $7 \pm 0.4$<br>(6) | 90<br>(93) | $65 \pm 5$ |

<sup>†</sup> The predicted values are shown in brackets and were calculated using the equations given in reference [12].

The strength of the constrained laminates at elevated temperature was  $122 \pm 23$  MPa. Delamination occurred when the composites were deflected to 3 mm (span = 26.56 mm) at 120 °C. Due to the limited deflections of the constrained composites at elevated temperature, they could not be used in applications where large, reversible deformations are required. Images of the constrained composites after failure at 120 °C can be seen in Figure 67.

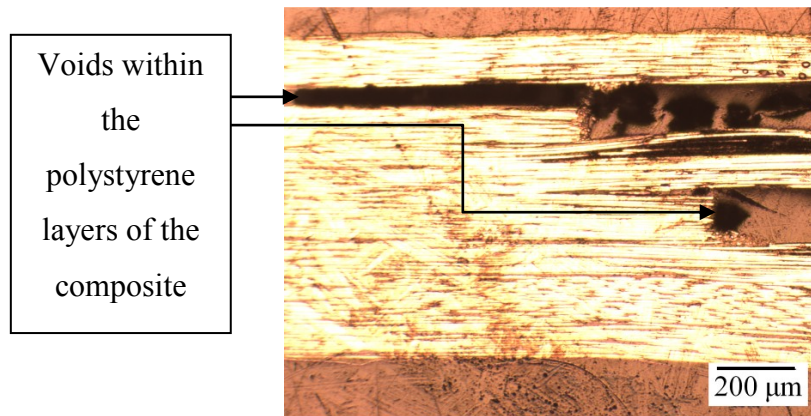


Figure 67: Cross sectional images of the failed constrained interleaved flexural specimen at the support at  $5 \times$  magnification

Damage had propagated throughout the entire length of the specimen and voids were present within the composite. There was also delamination of the CFRP layers beyond the support location. The failure mode at high temperature was different to that at room temperature. At high temperature, delamination at the support region resulted in the specimen kinking.

The apparent flexural modulus of the constrained composites at room and elevated temperature was predicted [12]. Once again the beam theory equations over predict the stiffness at room temperature presumably because the theory does not include shear distortion of the polystyrene layers and under predicts the modulus at high

temperature values because theory completely disregards the residual shear stiffness of the softened thermoplastic layers.

#### **4.4 Summary**

Polystyrene interleaved composites were manufactured and analysed to determine whether they could undergo a reversible loss in stiffness. DMTA results showed that a 97 % reduction in storage modulus could be achieved when the composites were heated from room temperature to 120 °C. Similarly, flexure tests showed that a loss in flexural stiffness of up to 98 % occurred when the composites were heated from 25 °C to 120 °C. When the temperature was maintained at 120 °C without an applied load, the composites returned to their original shape. When re-tested at room temperature, no loss in flexural stiffness was observed. These composites therefore have potential for applications in morphing wings, where a stiff material is required that can be deformed on demand with acceptable actuation forces. The compressive and tensile properties of the interleaved composites were also investigated. Compared to the pure carbon fibre reinforced epoxy composite at room and elevated temperature, there was a significant drop in stiffness and strength due to the presence of polystyrene.

Laminates with woven reinforced polystyrene layers and constrained interleaved regions were also manufactured. These laminates exhibited significant loss in flexural stiffness at elevated temperature but could not undergo large deformations when heated above the  $T_g$  of polystyrene. This may limit the use of these composites in applications where large deflections are required.

## 5. Conclusions and Suggestions for Future Work

### 5.1 Conclusions

A significant challenge in the design of adaptive structures, such as morphing wings, is the development of a stiff skin material that can be deformed on demand with acceptable actuation forces. To overcome this, the concept of carbon fibre reinforced epoxy composites with controllable stiffness was investigated. Two designs of controllable stiffness composite were described in this thesis. The composites contain either thermo-responsive interphases or interleaf layers, which are simply polymer coatings or layers with a  $T_g$  higher than the service temperature of the composites but much lower than the  $T_g$  of the composite matrix. These composites have acceptable flexural stiffness prior to activation and therefore with appropriate developments may have potential for use in aerospace applications. When heated above the  $T_g$  of the polymer interphase or interleaf, the flexural stiffness of the composites was reduced by up to 98 %. At this temperature the composites could undergo reversible deflections without delaminating. The composites were able to return to their original configuration and their flexural modulus restored to their full values. The conclusions from the findings of each design are listed below.

#### 5.1.1 Polymer coated fibre reinforced epoxy composites with controllable stiffness

- a) Carbon fibre reinforced epoxy composites containing thermo-responsive fibre coatings such as PAAm are capable of experiencing large reductions in storage modulus (up to 79 %) when heated above the  $T_g$  of the fibre coating.
- b) Water soluble fibre coatings like PAAm are unlikely to be suitable for use in high performance applications such as morphing wings due to their moisture dependence. The temperature at which PAAm coated carbon fibre reinforced

epoxy composites (manufactured by Tridech) experienced a reduction in stiffness was controlled by changing the moisture content in the PAAm coating.

- c) A beneficial consequence of using a water soluble fibre coating is that it gives the end user/consumer greater versatility to adapt the composite to the required stiffness by changing its moisture content.
- d) Polystyrene (a non-moisture dependent polymer) is a suitable candidate for use as a thermo-responsive interphase as it can lead to reductions in composite stiffness of up to 70 % above its  $T_g$ .
- e) Chemically bonded fibre coatings within composites are not essential to produce an effective loss in stiffness. This loss in stiffness can alternatively be achieved through physical bonding. When a polystyrene coated copper wire reinforced epoxy composite (in which the polystyrene had been physically coated) was tested in DMTA, the predicted and measured loss in stiffness, at elevated temperature, were in good agreement.
- f) Solution dip-coating can be used to effectively coat polystyrene onto metal wires. However, in the case of carbon fibres, unlike metal wires, it was not possible to efficiently separate the fibres so they could not be coated using this technique.
- g) The more uniform the fibre coating (interphase) within a composite, the greater will be the reduction in composite stiffness, at elevated temperatures. This is because the flexural stiffness of non-uniform polystyrene coated carbon fibre reinforced epoxy composites was only reduced by 36% when heated above the  $T_g$  of polystyrene. A greater loss in stiffness would have occurred if the polystyrene fibre coatings were more uniform but to determine the extent of this loss in stiffness would require further experimentation.

- h) Polystyrene interphases within carbon fibre reinforced composites can be effectively heated above their  $T_g$  by applying a current to the carbon fibres. This method of applying a current would be useful in morphing applications as it reduces complexity and cost and is likely to be less time consuming than other methods, such as external heating pads, when heating the fibre coating above its  $T_g$ , although precise time savings would need to be determined.

#### 5.1.2 Interleaved composites with controllable stiffness

- a) Polystyrene interleaved carbon fibre reinforced epoxy composites experienced large reductions in flexural stiffness (up to 98 %) when heated from room temperature to 120 °C.
- b) The interleaved composites underwent large, reversible deflections (midspan bending deflections up to 17.8 mm at a span of 64 mm) at elevated temperature and returned to their original configuration when the temperature was maintained at 120 °C and the load was removed. No loss in flexural stiffness occurred when these composites were cooled to room temperature.
- c) Hypothetically (pending further research) a reasonable working assumption is that the interleaved designs would be able to experience much larger deformations when compared to the first design of controllable stiffness composite (i.e. coated fibre reinforced epoxy composites). This because at elevated temperature each ply within the interleaved composite is effectively disconnected, whereas for the first design the maximum deformation at elevated temperature is limited to the maximum strain of the matrix material. Interleaved composites are therefore more likely to be suitable candidates for use in applications where large deflections are required.

- d) Simple beam theory can be used to predict the flexural modulus of the unidirectional interleaved composites at room and elevated temperature because these predicted values were in good agreement with the measured values from three point bending tests.
- e) Beam theory is not effective at predicting the flexural strength of polystyrene interleaved composites at room temperature as the predicted and measured strength values were not in agreement. This is because the interleaved composites underwent premature flexure failure at room temperature due to weak adhesion at the polystyrene - epoxy interface, where the failure occurred. If these composites were to be used in high performance applications this problem would need to be addressed.
- f) Polystyrene interleaved composites buckled and did not fail catastrophically when tested in compression at 120 °C and this attribute may be useful in applications e.g. aerospace where the avoidance of catastrophic failure following impact is paramount.
- g) Polystyrene interleaved composites with constrained interleaf regions experienced failure at low mid span deflections (at approximately 3 mm at a span of 26.56 mm) when tested in flexure at high temperature, unlike the standard interleaved composites. This could limit the use of these composites in applications where large deformations are required as in morphing wing structures. However, it is reasonable to draw the conclusion that by constraining the interleaf layers and creating a pure CFRP region at the end of the laminate these materials could be used in applications where the composite needs to be clamped at elevated temperature without the risk of compressing the polystyrene layers or loading only the outer CFRP plies.

- h) Reinforcing the interleaf layers with woven fibres increased the stiffness of an interleaved composite at room temperature by 12 %. This procedure would also permit the polystyrene interlayers to be heated quickly by passing a current through the woven carbon fibres.

## 5.2 Suggestions for future work

- Modifying the fabrication and testing of polymer coated carbon fibre reinforced epoxy composites

In order for the carbon fibre reinforced composites to exhibit a greater loss in flexural stiffness, the fibre coating process needs to be improved. In theory each individual fibre within the composite should be coated with a thin thermo-responsive polymer, which could be either thermosetting or thermoplastic. This may be achieved using different coating techniques, such as electropolymerisation, plasma polymerisation and interfacial polymerisation. Spreading the carbon fibres during the fibre coating process was a significant problem. As a result not all the fibres were coated and therefore improving the fibre spreading would be essential for any further studies. Different polymers could also be coated onto carbon fibres such as poly(acrylonitrile-butadiene-styrene) (ABS) and polyacrylonitrile. The effect of these polymers on the flexural properties of the composites must then be determined.

The relationship between applied voltage, current and composite temperature should be quantified for composite specimens of different sizes. This would determine the power requirements and whether this is a viable heating technique for large composite specimens. A study to establish the least time it takes to soften an interphase when using resistance heating could also be carried out. In morphing aerostructures this is important as shape change has to occur instantaneously. Finally, flexural fatigue testing is required to ensure that the composites do not fail after repeated heating and cooling cycles.

➤ Further developing interleaved composites

A study aiming to optimise the flexural strength and stiffness of the interleaved composites at room temperature, without compromising on the achievable stiffness loss, should be conducted. This study could include altering the position, thickness and number of the interleaf layers. One way to improve the flexural strength and potentially eliminate shear failure is to use different interleaf materials. Polymers such as syndiotactic or atactic PMMA, PEEK and polystyrene copolymers, such as ABS and Styrene Acrylonitrile (SAN), could be used. If the adhesion between these polymers and the CFRP layers is weak then plasma or chemical modification of the interleaf surface should be attempted. The flexural stiffness may be further improved by reinforcing the interleaf layers with unidirectional carbon fibres. Applying a direct current to the fibres would allow the interleaf material to be heated more rapidly. As with the previous design of controllable stiffness composite, extensive flexural fatigue testing is required. The composites should also be tested in different humidities to understand how moisture affects the mechanical properties of the laminates. The composites containing woven carbon fibre reinforced polystyrene layers should be remade ensuring there is a sufficient amount of polystyrene between the woven fabric and the CFRP ply. This may prevent the composites failing at low deflections at elevated temperature.

➤ Incorporating the composites into a morphing aircraft wing model

In order to use the composites as morphing skin materials, the composite would have to be incorporated into a model containing actuators and heating mechanisms. Preliminary tests have been carried out where MFC actuators and thin film Kapton heaters were bonded to the surface of an interleaved composite [12]. The next stage would be to use the composites as a skin material in a morphing wing model.

## 6. References

1. James, T., Menner, A., Bismarck, A., Iannucci, L. Morphing Skins: Development of New Hybrid Materials. *Proceedings of the 4th SEAS DTC Technical Conference*, Edinburgh, UK, 7-8 July, 2009.
2. Tridech, C. Smart Fibre Coatings: Stiffness Control in Composite Structures. Ph.D. Thesis, Imperial College London, December 2011.
3. Thill, C., Etches, J. Bond, I., Potter, K., Weaver, P. *Morphing Skins*. Aeronautical Journal, 2008, **112**(1129), 117-139.
4. Sofla, A.Y.N., Meguid, S.A., Tan, K.T., Yeo, W.K. *Shape Morphing of Aircraft Wing: Status and Challenges*. Materials and Design, 2010, **31**(3), 1284-1292.
5. Henry, C., McKnight, G. Deformable Variable-Stiffness Cellular Structures. U.S. Patent 7,678,440 B1, March, 2010.
6. Kornbluh, R.D., Prahlad, H., Pelrine, R., Stanford, S., Rosenthal, M.A., von Guggenberg, P.A. Rubber to Rigid, Clamped to Undamped: Toward Composite Materials with Wide-Range Controllable Stiffness and Damping. *Proceedings of SPIE 5388, Smart Structures and Materials 2004: Industrial and Commercial Applications of Smart Structures Technologies*, San Diego, CA, March 14, 2004.
7. Wiggins, L.D., Stubbs, M.D., Johnston, C.O., Robertshaw, H.H., Reinholtz, C.F., Inman, D.J. A Design and Analysis of a Morphing Hyper-Elliptic Cambered Span (HECS) Wing. *Proceedings of the 45th AIAA/ASME/ASCE/AHS/ASC Structures, Structural Dynamics and Materials Conference*, Palm Springs, CA, 19-22 April, 2004.
8. Spillman, J.J. *The Use of Variable Camber to Reduce Drag, Weight and Costs of Transport Aircraft*. Aeronautical Journal, 1992, **96**(951), 1-9.
9. Thuwis, G.A.A., Abdalla, M.M., Gurdal, Z. *Optimization of a Variable-Stiffness Skin for Morphing High-Lift Devices*. Smart Materials and Structures, 2010, **19**(12), 124010.
10. Puterbaugh, M., Beyene, A. *Parametric Dependence of a Morphing Wind Turbine Blade on Material Elasticity*. Energy, 2011, **36**(1), 466-474.
11. Zolfagharifard, E. *Morphing Materials Form the Shape of Wings to Come*. 2011 [cited 23th June 2013]; Available from: <http://www.theengineer.co.uk/in-depth/morphing-materials-form-the-shape-of-wings-to-come/1009061.article>.

12. Maples, H.A., Gaite, O., Smith, S., Bismarck, A. Robinson, P. Carbon Fibre Reinforced Epoxy Composites with Variable Stiffness for use in Morphing Aerostructures. *Proceedings of the 19th International Conference on Composite Materials (ICCM19)*, Montreal, Canada, 28 July – 2 August, 2013.
13. Kuder, I.K., Arrieta, A.F., Raither, W.E., Ermanni, P. *Variable Stiffness Materials and Structural Concepts for Morphing Applications*. Progress in Aerospace Science, 2013, <http://dx.doi.org/10.1016/j.paerosci.2013.07.001>.
14. Raither, W., Bergamini, A., Gandhi, F., Ermanni, P. *Adaptive Bending-Twist Coupling in Laminated Composite Plates by Controllable Shear Stress Transfer*. Composites Part A-Applied Science and Manufacturing, 2012, **43**(10), 1709-1716.
15. Tridech, C., Maples, H.A., Robinson, P., Bismarck, A. *High Performance Composites with Active Stiffness Control*. Applied Materials and Interfaces, 2013, **5**, 9111-9119.
16. Wilson, J.R. *Morphing UAVs Change the Shape of Warfare*. Aerospace America, 2004, **42**(2), 28-29.
17. Hinshaw, T.L. Analysis and Design of a Morphing Wing Tip Using Multicellular Flexible Matrix Composite Adaptive Skins. M.S. Thesis, Virginia Polytechnic Institute and State University, July 2009.
18. Voracek, D., Pendleton, E., Reichenbach, E., Griffin, K., Welch, L. *The Active Aeroelastic Wing Phase I Flight research Through January 2003*, 2003, NASA.
19. Weisshaar, T.A. *Morphing Aircraft Technology - New Shapes for Aircraft Design*, 2006, Purdue University.
20. Kikuta, M.T. Mechanical Properties of Candidate Materials for Morphing Wings. M.S. Thesis, Virginia Polytechnic Institute and State University, December 2003.
21. Barbarino, S., Bilgen, O., Ajaj, R.M., Friswell, M.I., Inman, D.J. *A Review of Morphing Aircraft*. Journal of Intelligent Material Systems and Structures, 2011. **22**(9), 823-877.
22. Aerospaceweb. *F-14 Tomcat Wing Diagram* [cited 20th January 2014]; Available from: <http://www.aerospaceweb.org/aircraft/fighter/f14/>.
23. NASA. *Project Description: X-5* [cited 21st October 2013]; Available from: [http://www.nasa.gov/centers/dryden/multimedia/imagegallery/X-5/X-5\\_proj\\_desc.html](http://www.nasa.gov/centers/dryden/multimedia/imagegallery/X-5/X-5_proj_desc.html)

24. Marks, P. *Aviation - The Shape of Wings to Come* [cited 13th May 2013]; Available from: <http://www.newscientist.com/article/dn7552-aviation--the-shape-of-wings-to-come.html>.
25. Kota, S., Hetrick, J.A., Osborn Jr. R.F. *Adaptive Structures: Moving Into The Mainstream*. Aerospace America, September 2006, 16-18.
26. Weisshaar, T.A. New Aircraft Systems Concepts - Towards New Horizons in Aeroelasticity. *NATO Research Technology Organization Research Symposium, RTO-MP-AVT-152*, Loen, Norway, 3-8 May, 2008.
27. NASA. *AFTI F-111* [cited 17th January 2014]; Available from: [http://www.nasa.gov/centers/dryden/multimedia/imagegallery/F-111AFTI/EC85-33205-07\\_prt.htm](http://www.nasa.gov/centers/dryden/multimedia/imagegallery/F-111AFTI/EC85-33205-07_prt.htm).
28. Pendleton, E. Back to the Future, How Active Aeroelastic Wings are a Return to Aviation's Beginnings and a Small Step to Future Bird-like Wings. *Proceedings of the 14th JSASS Aircraft Symposium*, Sendai, Japan, 11 October, 2000.
29. Kudva, J.N. *Overview of the DARPA Smart Wing Project*. Journal of Intelligent Material Systems and Structures, 2004, **15**(4), 261-267.
30. McGowan, A.R., Washburn, A. E., Horta, L. G., Bryant, R. G., Cox, D. E., Siochi, E. J., Padula, S. L., Holloway, N. M. Recent Results from NASA's Morphing Project. *Proceedings of the SPIE 9th Annual International Symposium on Smart Structures and Materials*, San Diego, CA, 17-21 March, 2002.
31. Valasek, J. *Morphing Aerospace Vehicles and Structures*; Wiley: Chichester, 2012; p. 9.
32. Smart Material. *Macro Fibre Composite (MFC) brochure* [cited 11th May 2013]; Available from: <http://www.smart-material.com/media/Datasheet/MFC-V2.0-2011-web.pdf>.
33. Wilkie, W., High, J., Bockman J. Reliability Testing of NASA Piezocomposite Actuators. *Proceedings of the 8th International Conference on New Actuators*, Bremen, Germany, 10-12 June, 2002.
34. Voracek, D., Reaves, M. C., Horta, L. G., Potter, S. Ground and Flight Test structural excitation using Piezoelectric Actuator, 2002, NASA.
35. Kovalovs, A., Barkanov, E., Gluhihs, S. Active Control of Structures Using Macro-Fiber Composite (MFC). *Journal of Physics: Conference Series*, 2007, **93**, 012034.

36. McGowan, A.R., Cox, D.E., Lazos, B.S., Waszak, M.R., Raney, D.L., Siochi, E.J., Paul Pao, S. Biologically Inspired Technologies in NASA's Morphing Project. *Proceedings of SPIE, Smart Structures and Materials*, San Diego, CA, 28 July 2003.
37. New Scientist. *The Next 100 Years of Flight – Part Two* [cited 5th February 2014]; Available from: <http://www.newscientist.com/articleimages/dn4484/1-the-next-100-years-of-flight--part-two.html>.
38. Asheghian, L., Street, J., Kudva, J., Olympio, K.R., Gandhi, F. Development of Bio-Mimetic Morphing Skins for Micro-UAVs. *Proceedings of PACAM XI, 11th Pan-American Congress of Applied Mechanics*, Foz do Iguaçu, PR, Brazil, 4-8 January, 2010.
39. Warwick, G. *NextGen's Shape-Changing UAV Morphs in Flight* [cited 21st Oct 2013]; Available from: <http://www.flightglobal.com/news/articles/nextgens-shape-changing-uav-morphs-in-flight-218799/>.
40. Ramrakahyani, D.S., Lesieutre, G.A., Frecker, M., Bharti, S. Aircraft Structural Morphing using Tendon Actuated Compliant Cellular Trusses. *Proceedings of the 45th AIAA/ASME/ASCE/AHS/ASC Structures, Structural Dynamics and Materials Conference*, Palm Springs, CA, 19-22 April, 2004.
41. Pennsylvania State University. *Airplane Wings That Change Shape Like a Bird's Have Scales Like a Fish*. [cited 5th January 2010]; Available from: <http://live.psu.edu/story/6497>.
42. Cadogan, D., Smith, T., Uhelsky, F., MacKusick, M. Morphing Inflatable Wing Development for Compact Package Unmanned Aerial Vehicles. *Proceedings of the 45th AIAA/ASME/ASCE/AHS/ASC Structures, Structural Dynamics and Materials Conference*, Palm Springs, CA, 19-22 April 2004.
43. McMurry, J. *Organic Chemistry*, 6th Edition; Brooks/Cole: London, 2004; p. 1169.
44. Lubrizol. *Tecoflex Product Information* [cited 4th February 2014]; Available from: <https://www.lubrizol.com/LifeScience/Products/Tecoflex.html>.
45. Celanese. *Riteflex Product Information* [cited 4th February 2014]; Available from: <http://www.celanese.com/engineered-materials/products/Riteflex-TPC-ET.aspx>.
46. DSM. *Arnitel Product Information* [cited 4th February 2014]; Available from: [http://www.dsm.com/products/arnitel/en\\_US/product-info.html](http://www.dsm.com/products/arnitel/en_US/product-info.html).
47. Cornerstone Research Group. *Shape Memory Polymer Overview* [cited 31st May 2013]; Available from: <http://www.crgroup.com/tech-center/shape-memory-polymer-overview>.

48. Rauscher, S.G. Testing and Analysis of Shape-Memory Polymers for Morphing Aircraft Skin Application, M.S. Thesis, University of Pittsburgh, April 2008.
49. Gonzalez, L. Morphing Wing Using Shape Memory Alloy: A Concept Proposal, 2005, Texas A&M University.
50. Hartl, D.J., Lagoudas, D. C. Aerospace applications of shape memory alloys. *Proceedings of the Institution of Mechanical Engineers, Part G: Journal of Aerospace Engineering*, April, 2007.
51. Saburi, T. Ti-Ni Shape Memory Alloys. In Shape Memory Materials; Otsuka, K., Wayman, C.M., Eds.; Cambridge University Press, Cambridge, 1998, p 49-96.
52. Stanford University. *Shape Memory Alloys and their Applications* [cited 14th January 2013]. Available from: <http://www.stanford.edu/~richlin1/sma/sma.html>.
53. Sofla, A.Y.N., Elzey, D.M., Wadley, H.N.G. *Two-Way Antagonistic Shape Actuation Based on the One-Way Shape Memory Effect*. Journal of Intelligent Material Systems and Structures, 2008, **19**(9), 1017-1027.
54. Sofla, A.Y.N., Elzey, D.M., Wadley, H.N.G. *Cyclic Degradation of Antagonistic Shape Memory Actuated Structures*. Smart Materials and Structures, 2008. **17**(2), 025014.
55. Elzey, D.M., Sofla, A.Y.N., Wadley, H.N.G. *A Shape Memory-Based Multifunctional Structural Actuator Panel*. International Journal of Solids and Structures, 2005, **42**(7), 1943-1955.
56. Gautschi, G. Piezoelectric Sensorics: Force, Strain, Pressure, Acceleration and Acoustic Emission Sensors, Materials and Amplifiers; Springer: Berlin, 2002; p. 6.
57. Franco Correia, V.M., Aguiar Gomes, M.A., Suleman, A., Mota Soares, C.M., Mota Soares, C.A. *Modelling and Design of Adaptive Composite Structures*. Computer Methods in Applied Mechanics and Engineering, 2000, **185**(2-4), 325-346.
58. Crawley, E.F. *Intelligent Structures for Aerospace - a Technology Overview and Assessment*. AIAA Journal, 1994, **32**(8), 1689-1699.
59. Bilgen, O. Macro Fiber Composite Actuated Unmanned Air Vehicles: Design, Development and Testing. M.S. Thesis, Virginia Polytechnic Institute and State University, October 2007.

60. Bilgen, O. *Summary of Available Publications for the Development of MFC Actuated UAVs Started by Dan Inman, Onur Bilgen and John Ohanian at Virginia Tech* [cited 11th May 2013]; Available from: [http://www.smartmaterial.com/media/Publications/MFC/Research\\_using\\_MFCs\\_Web-list.pdf](http://www.smartmaterial.com/media/Publications/MFC/Research_using_MFCs_Web-list.pdf).
61. Lim, S.M., Lee, S., Park, H.C., Yoon, K.J., Goo, N. S. *Design and Demonstration of a Biomimetic Wing Section Using a Light Weight Piezo-Composite Actuator (LIPCA)*. Smart Materials and Structures, 2005, **14**, 1799-1804.
62. Trakakis, G., Galiotis, C. *Development and Testing of a Self-Deformed Composite Material*. Composite Structures, 2010, **92**(2), 306-311.
63. Nave, R. *Bimetallic Strips* [cited 14th May 2013]; Available from: <http://hyperphysics.phy-astr.gsu.edu/hbase/thermo/bimet.html>.
64. Sousa, C.S., Camanho P.P., Suleman A. *Analysis of Multistable Variable Stiffness Composite Plates*. Composite Structures, 2013, **98**, 34-46.
65. McKnight, G., Henry, C. Variable Stiffness Materials for Reconfigurable Surface Applications. *Proceedings of SPIE 5761, Smart Structures and Materials 2005: Active Materials: Behavior and Mechanics*, San Diego, CA, 6 March, 2005.
66. Cornerstone Research Group. *Shape Memory Polymers* [cited 10th January 2013]; Available from: <http://www.crgroup.com/tech-center/veriflex-shape-memory-polymer>
67. Shan, Y., Philen, M., Lotfi, A., Li, S., Bakis, C.E., Rahn, C.D., Wang, K.W. *Variable Stiffness Structures Utilizing Fluidic Flexible Matrix Composites*. Journal of Intelligent Material Systems and Structures, 2009, **20**, 443-456.
68. Bergamini, A., Christen, R., Motavalli, M. *Electrostatically Tunable Bending Stiffness in a GFRP-CFRP Composite Beam*. Smart Materials and Structures, 2007, **16**(3), 575-582.
69. Jesson, D.A., Watts, J.F. *The Interface and Interphase in Polymer Matrix Composites: Effect on Mechanical Properties and Methods for Identification*. Polymer Reviews, 2012, **52**(3-4), 321-354.
70. Cantwell, W.J., Morton, J. *The Impact Resistance of Composite-Materials - A Review*. Composites, 1991, **22**(5), 347-362.
71. Labronici, M., Ishida, H. *Toughening Composites by Fiber Coating: A Review*. Composite Interfaces, 1994, **2**(3), 199-234.
72. Dilsiz, N. *Plasma Surface Modification of Carbon Fibers: A Review*. Journal of Adhesion Science and Technology, 2000, **14**(7), 975-987.

73. Bismarck, A., Kumru, M.E., Springer, J., Simitzis, J. *Surface Properties of PAN-Based Carbon Fibers Tuned by Anodic Oxidation in Different Alkaline Electrolyte Systems*. Applied Surface Science, 1999, **143**(1-4), 45-55.
74. Sastri, S.B. Novel Interphases: Synthesis, Molecular Orientation and Grafting of Liquid Crystal Polymers onto Carbon Fibres Ph.D. Thesis, University of Illinois, January 1990.
75. Donnet, J-B., Rebouillat, S., Wang, T.K., Peng, J.C.M. Carbon Fibers, 3rd Edition; Marcel Dekker: New York, 1998; p. 161-189.
76. Erden, S., Ho, K.K.C., Lamoriniere, S., Lee, A.F., Yildiz, H., Bismarck, A. *Continuous Atmospheric Plasma Oxidation of Carbon Fibres: Influence on the Fibre Surface and Bulk Properties and Adhesion to Polyamide 12*. Plasma Chemistry and Plasma Processing, 2010, **30**(4), 471-487.
77. Boudou, J.P., Paredes, J.I., Cuesta, A., Martinez-Alonso, A., Tascon, J.M.D. *Oxygen Plasma Modification of Pitch-Based Isotropic Carbon Fibres*. Carbon, 2003, **41**(1), 41-56.
78. Vautard, F., Fioux, P., Vidal, L., Dentzer, J., Schultz, J., Nardin, M., Defoort, B. *Modification of the Carbon Fiber Surface by Oxygen Plasma and its Influence on Adhesion Strength in Acrylate-Based Composites Cured by Electron Beam and Ultra Violet Light*. The Journal of Adhesion, 2013, **89**, 460-485.
79. Dujardin, S., Lazzaroni, R., Rigo, L., Riga, J., Verbist, J.J. *Electrochemically Polymer-Coated Carbon-Fibers - Characterization and Potential for Composite Applications*. Journal of Materials Science, 1986, **21**(12), 4342-4346.
80. Bismarck, A., Menner, A., Kumru, M.E., Sezai Sarac, A., Bistriz, M., Schulz, E. J. *Poly(carbazole-co-acrylamide) Electrocoated Carbon Fibers and their Adhesion Behavior to an Epoxy Resin Matrix*. Journal of Materials Science, 2002, **37**(3), 461-471.
81. Kettle, A.P., Beck, A.J., O'Toole, L., Jones, F.R., Short, R.D. *Plasma Polymerisation for Molecular Engineering of Carbon-Fibre Surfaces for Optimised Composites*. Composites Science and Technology, 1997, **57**, 1023-1032.
82. Kettle A.P., Jones, F.R., Alexander, M.R., Short, R.D., Stollenwerk, M., Zabold, J., Michaeli, W., Wu, W., Jacobs, E., Verpoest, I. *Experimental Evaluation of the Interphase Region in Carbon Fibre Composites with Plasma Polymerised Coatings*. Composites Part A-Applied Science and Manufacturing, 1998, **29**, 241-50.

83. Bismarck, A., Pfaffernoschke, M., Springer, J. *Grafted Carbon Fibers and their Physicochemical Properties. I. Grafting of Methacrylic Acid onto Carbon Fibers*. Journal of Applied Polymer Science, 1999, **71**(7), 1175-1185.
84. Koschinski, I., Reichert, K.H. *Preparation of Carbon-Fiber Reinforced Poly(Phenylene Sulfide) by In Situ Polymerization*. Makromolekulare Chemie-Rapid Communications, 1988, **9**(5), 291-298.
85. Varelidis, P.C., McCullough, R.L., Papaspyrides, C.D. *The Effect on the Mechanical Properties of Carbon/Epoxy Composites of Polyamide Coatings on the Fibers*. Composites Science and Technology, 1999, **59**(12), 1813-1823.
86. Cranmer, J.H., Tesoro, G.C., Uhlmann, D.R. *Chemical Modification of Carbon-Fiber Surfaces with Organic Polymer-Coatings*. Industrial and Engineering Chemistry Product Research and Development, 1982, **21**(2), 185-190.
87. Bismarck, A., Lee, A.F., Sezai Serac, A., Schulz, E., Wilson, K. *Electrocoating of Carbon Fibres: A Route for Interface Control in Carbon Fibre Reinforced Polymethylmethacrylate?* Composites Science and Technology, 2005, **65**(10), 1564-1573.
88. Kang, H.M., Kim, N.I., Yoon, T.H. *Plasma Etching and Plasma Polymerization Coating of Carbon Fibers. Part 1. Interfacial Adhesion Study*. Journal of Adhesion Science and Technology, 2002, **16**(13), 1809-1823.
89. Bismarck, A., Pfaffernoschke, M., Springer, J., Schulz, E. *Polystyrene-Grafted Carbon Fibers: Surface Properties and Adhesion to Polystyrene*. Journal of Thermoplastic Composite Materials, 2005, **18**(4), 307-331.
90. Goodfellow. *Polystyrene Material Information* [cited 5th April 2013]; Available from: <http://www.goodfellow.com/E/Polystyrene.html>.
91. Lokensgard, E. *Industrial Plastics: Theory and Applications*, 4th Edition; Delmar Learning: New York, 2004; p. 472.
92. *Polystyrene Structure* [cited 6th April 2013]; Available from: <http://en.wikiversity.org/wiki/File:Polystyrene.png>.
93. Spinks, G.M., Brown, H.R., Liu, Z. *Indentation Testing of Polystyrene Through the Glass Transition*. Polymer Testing, 2006, **25**(7), 868-872.
94. *Department of Defense Handbook, Global Climatic Data for Developing Military Products, Mil-HDBK-310*, 1997.
95. Wunsch, J.R. *RAPRA Review Report 112, Polystyrene: Synthesis, Production and Applications*, 2000.

96. Hull, D., Clyne, T.W. *An Introduction to Composite Materials*, 2nd Edition; Cambridge University Press: Cambridge, 1996; p. 140.
97. ZL Petrochemicals. *About Polyacrylamide* [cited 25th September 2013]; Available from: <http://www.zlpam.com/wp-content/uploads/2011/11/About-Polyacrylamide-Fact-Sheet.pdf>.
98. Sigma-Aldrich. *Polyacrylamide Structure* [cited 25th September 2013]; Available from: <http://www.sigmaaldrich.com/catalog/product/sigma/92560?lang=en&region=GB>
99. Fox, R.B. Glass Transition Temperature of Selected Polymers. In *CRC Handbook of Chemistry and Physics*, 93rd Edition; Haynes, W. M., Ed.; CRC Press, Boca Raton, 2012, 13-10.
100. Qutubuddin, S., Lin, C.S., Tajuddin, Y. *Novel Polymeric Composites from Microemulsions*. *Polymer*, 1994, **35**(21), 4606-4610.
101. Yuen, H.K., Tam, E.P., Bullock J.W. On the Glass Transition Temperature of Polyacrylamide. In *Analytical Calorimetry*; Johnson, J.F., Gill, P.S., Eds.; Springer: US, 1984; Vol. 5, p. 13-24.
102. Yasaee, M., Bond, I.P., Trask, R.S., Greenhalgh, E.S. *Mode I Interfacial Toughening Through Discontinuous Interleaves for Damage Suppression and Control*. *Composites Part A-Applied Science and Manufacturing*, 2012, **43**(1), 198-207.
103. Duarte A, Herszberg I, Paton R. Impact Resistance and Tolerance of Interleaved RTM Laminates. *Proceedings of the 12th International Conference on Composite Materials (ICCM12)*, Paris, France; 5-9 July, 1999.
104. Evans R, Hirschbuehler K. Thermoplastic Interleafed Resin Matrix Composites with Improved Impact Strength and Toughness, Patent US 4604319 A, June, 1984.
105. Singh, S., Partridge, I.K. *Mixed-Mode Fracture in an Interleaved Carbon-Fibre Epoxy Composite*. *Composites Science and Technology*, 1995, **55**(4), 319-327.
106. Aksoy, A., Carlsson, L.A. *Interlaminar Shear Fracture of Interleaved Graphite/Epoxy Composites*. *Composites Science and Technology*, 1992, **43**(1), 55-69.
107. Lu, W.H., Liao, F.S., Su, A.C., Kao, P.W., Hsu, T.J. *Effect of Interleaving on the Impact Response of a Unidirectional Carbon-Epoxy Composite*. *Composites*, 1995, **26**(3), 215-222.

108. Chandra, R., Singh, S.P., Gupta, K. *Damping Studies in Fiber-Reinforced Composites - A Review*. Composite Structures, 1999, **46**(1), 41-51.
109. Kishi, H., Kuwata, M., Matsuda, S., Asami, T., Murakami, A. *Damping Properties of Thermoplastic-Elastomer Interleaved Carbon Fiber-Reinforced Epoxy Composites*. Composites Science and Technology, 2004, **64**(16), 2517-2523.
110. Gandhi, F., Kang, S.G. *Beams with Controllable Flexural Stiffness*. Smart Materials and Structures, 2007, **16**(4), 1179-1184.
111. Murray, G., Gandhi, F. *Multi-Layered Controllable Stiffness Beams for Morphing: Energy, Actuation Force, and Material Strain Considerations*. Smart Materials and Structures, 2010, **19**(4), 045002.
112. Gandhi, F., Murray, G., Kang S.G. *Flexural Stiffness Control of Multilayered Beams*. AIAA Journal, 2009, **47**(3), 757-766.
113. McKnight, G.; Barvosa-Carter, W. Variable Stiffness Structure. U.S. Patent 7,892,630 B1, February, 2011.
114. Nay, J.C., Pitt, W.G., Armstrong-Carroll, E. *Improving Adhesion in Interleaf Composites Using Plasma Processing*. Journal of Applied Polymer Science, 1995, **56**(4), 461-469.
115. Riefler, R.S., Powers, J.W. Interleaf Layers in Fiber Reinforced Resin Laminate Composite, Patent US 4954382 A, September, 1990.
116. Heness, G., Stevens, M., Dossett, B. *The Effect of Surface Treatment on Delamination for a Nylon Interleaving Material*. Material Forum, 2007, **31**, 90-95.
117. Hojo, M., Matsuda, S., Ochiai, S., Murakami, A., Akimoto, H. The role of Interleaf/Base Lamina Interphase in Toughening Mechanisms of Interleaf-Toughened CFRP. Proceedings of the 12th International Conference on Composite Materials (ICCM12), Paris, France, 5-9 July, 1999.
118. Bismarck, A., Pfaffernoschke, M., Song, B., Springer, J. *Grafted Carbon Fibers and their Physico-Chemical Properties. Part II. Grafting of Liquid Crystalline Methacrylic Monomers onto Carbon Fibers and the Influence of an Applied Voltage to the Carbon Fiber Embedded in a Liquid Crystalline Matrix*. Journal of Applied Polymer Science, 1999, **71**(11), 1893-1904.
119. Selimovic, M., Bismarck, A., Pfaffernoschke, M., Springer, J. *Grafted Carbon Fibers and their Physico-Chemical Properties. Part IV: Grafting of Cyano-Biphenyl Containing Liquid-Crystalline Monomers onto Modified Carbon Fibers*. Acta Polymerica, 1999, **50**(4), 156-162.

120. Zhang, M.Q., Rong, M.Z., Yu, S.L., Wetzel, B., Friedrich, K. *Effect of Particle Surface Treatment on the Tribological Performance of Epoxy Based Nanocomposites*. *Wear* 2002, **253**, 1086–1093.
121. Toolbox, T.E. *Modulus of Elasticity - Young Modulus for Some Common Materials* [cited 15th June 2013]; Available from: [http://www.engineeringtoolbox.com/young-modulus-d\\_417.html](http://www.engineeringtoolbox.com/young-modulus-d_417.html).
122. Yue, Z.R., Jiang, W., Wang, L., Gardner, S.D., Pittman Jr, C.U. *Surface Characterization of Electrochemically Oxidized Carbon Fibers*. *Carbon*, 1999, **37**(11), 1785-1796.
123. Lock, E.H., Petrovykh, D.Y., Mack, P., Carney, T., White, R.G., Walton, S.G., Fernsler, R.F. *Surface Composition, Chemistry, and Structure of Polystyrene Modified by Electron-Beam-Generated Plasma*. *Langmuir*, 2010, **26**(11), 8857-8868.
124. Beamson, G., Briggs, D. *High Resolution XPS of Organic Polymers: The Scienta ESCA 300 Database*; Wiley: Chichester, 1992; p. 295.
125. Moustaghfir, A., Tomasella, E., Jacquet, M., Rivaton, A., Mailhot, B., Gardette, J.L., Beche, E. *ZnO/Al<sub>2</sub>O<sub>3</sub> Coatings for the Photoprotection of Polycarbonate*. *Thin Solid Films*, 2006, **515**(2), 662-665.
126. Yaghoubi, H., Taghavinia, N. *Surface Chemistry of Atmospheric Plasma Modified Polycarbonate Substrates*. *Applied Surface Science*, 2011, **257**(23), 9836-9839.
127. Menard, K.P. *Dynamic Mechanical Analysis: A Practical Introduction*; CRC Press; London, 2008.
128. Throne, J.L. *Technology of Thermoforming*; Hanser Gardner Publications: Cincinnati, 1996; p. 620.
129. Nereau, G. *Controllable Stiffness Composites for Use in Morphing Wings*. M.S. Thesis, Imperial College London, September 2012.
130. Smith, S. *Carbon Fibre Reinforced Epoxy Composites with Controllable Stiffness*. M.S. Thesis, Imperial College London, September 2012.
131. Häberle, J.G., Godwin, E.W. *The Imperial College Method for Testing Composite Materials in Compression*, Imperial College London, London, 1999.
132. Turner, S. *General Principles and Perspectives*. In *Mechanical Testing of Advanced Fibre Composites*; Hodgkinson, J.M., Ed.; Woodhouse Publishing: Cambridge, 2000; p. 27.

133. Feraboli, P.J., Kedward, K.T. In Search of the True Interlaminar Shear Strength. Proceedings of the 19th Joint American Society for Composites/American Society for Testing and Materials Committee D30, Atlanta, GA, 17-20 October, 2004.
134. ASTM, *Standard Test Method for Tensile Properties of Polymer Matrix Composite Materials*. vol. D 3039/D 3039M – 07 2007.
135. Ankara, A., Weisgerber, D., Vilsmeier, J. Influence of Moisture on the Mechanical Properties of Graphite Epoxy System. In: *Advanced Composite Materials and Structures*, Taipei, Taiwan; 19-23 May, 1986.
136. Demus, D. Phase Types, Structures and Chemistry of Liquid Crystals. In *Liquid Crystals*; Baumgartel, H., Franck, E.U., Grubein, W., Eds.; Springer: New York, 1994; p. 1-6.
137. Donald, A., Windle, A., Hanna, S. *Liquid Crystalline Polymers*, 2nd Edition; Cambridge University Press: Cambridge, 2006; p. 1-67.
138. Lange, S. *Lyotropic Liquid Crystals* [cited 7th June 2013]; Available from: [http://home.arcor.de/stefan.\\_lange/uni/in\\_rep\\_html/node2.html](http://home.arcor.de/stefan._lange/uni/in_rep_html/node2.html).
139. Chandrasekhar, S. *Liquid crystals*, 2nd Edition; Cambridge University Press: Cambridge, 1992; p. 1-6.
140. Bhama, S., Stupp, S.I. *Grafting of a Liquid-Crystal Polymer on Carbon-Fibers*. *Polymer Engineering and Science*, 1990, **30**(10), 603-608.
141. Carfagna, C., Acierno, D., Di Palma, V., Amendola, E., Giamberini, M. *Composites Based on Carbon Fibers and Liquid Crystalline Epoxy Resins, 1 Monomer Synthesis and Matrix Curing*. *Macromolecular Chemistry and Physics*, 2000, **201**(18), 2631-2638.
142. Lebonheur, V., Stupp, S.I. *Grafting of a Functionalized Side-Chain Liquid-Crystal Polymer on Carbon-Fiber Surfaces - Novel Coupling Agents for Fiber Polymer Matrix Composites*. *Chemistry of Materials*, 1993, **5**(9), 1287-1292.
143. Lebonheur, V., Stupp, S.I. *Coupling Carbon-Fibers to Epoxy Matrices with Grafted Side-Chain Liquid-Crystal Polymers*. *Chemistry of Materials*, 1994, **6**(10), 1880-1883.
144. Prichard, W.W. *Hydroquinone Diacetate*. *Organic Syntheses*, 1955, **3**, 452.
145. De Ruijter, C., Bos, J., Boerstoel, H., Dingemans, T.J. *Novel Thermotropic Esters-Based Polymers with Broad Nematic Processing Windows*. *Journal of Polymer Science Part A-Polymer Chemistry*, 2008, **46**(19), 6565-6574.

## **Appendix**

### **A.1 Liquid crystalline polymer coated carbon fibre reinforced epoxy composites**

#### **A.1.1 Introduction**

Attempts were made to manufacture epoxy matrix composites containing liquid crystalline polymer grafted carbon fibres. LCPs were originally chosen as fibre coatings as they typically exhibit more than one phase transition i.e. switching stages. This allows more control over the stiffness of the composites at different temperatures. To manufacture the coated fibre reinforced epoxy composites with variable stiffness, firstly the LCP had to be synthesised as no suitable commercially available LCPs could be found. An attempt was made to covalently bond the main chain LCP onto carbon fibres to improve the adhesion between the fibres and the coating. In order to do this the fibres had to be oxidised to introduce carboxylic acid groups onto the fibre surface that would allow esterification reactions to occur between the LCP and the fibre. After the fibre coating process, the coated fibres were then embedded into an epoxy matrix via resin infusion. These composites did not undergo a loss in stiffness above the  $T_g$  of the LCP fibre coating. This suggests that the LCP was not successfully coated onto the carbon fibres.

##### **A.1.1.1 Background information: Liquid crystalline polymers**

Thermotropic liquid crystalline polymers (LCPs) could be used as carbon fibre coatings in composites with controllable stiffness as they typically exhibit a higher number of phase transitions i.e. switching stages, compared with other polymers. Liquid crystals can be described as molecules that can form crystalline regions in the liquid state [136]. Liquid crystals were first discovered by Reinitzer in 1888 [137]. He noticed two melting points in esters of cholesterol. When heated above their first

$T_m$  a cloudy liquid was observed that exhibited birefringence and iridescent colours that turned clear above its second apparent  $T_m$ . Birefringence is a phenomenon where light is split into two different waves by an optically anisotropic medium. The rigid part of a molecule or polymer that gives rise to the liquid crystalline range (mesophase) is known as the mesogen [137]. The mesogen has anisotropy in both attractive and repulsive forces, which contributes to the mesophase formation.

The two major classifications for liquid crystals are thermotropic and lyotropic [137]. Materials, which exhibit a mesophase over specific temperature range are known as thermotropic, whereas those compounds which only show a mesophase in a solvent are called lyotropic. Lyotropic liquid crystals are built up of amphiphilic molecules, i.e. molecules that contain hydrophilic and hydrophobic groups [138]. The Friedelian classes identified by Friedel in 1922 are nematic, cholesteric and smectic [137, 139]. These classes indicate the positioning and orientation of the mesogens. Liquid crystalline polymers are those polymers that exhibit a mesophase above their melting point or, if one is not present, the glass transition temperature [137]. There are two main types of LCP, main chain and side chain. The names denote where the mesogens are located [137]. An example of a main chain LCP is Vectran (Figure 68), which is a commercial polymer composed of 73% 4-hydroxybenzoic acid (4-HBA) and 27% 6-hydroxy-2-naphthoic acid (HNA).

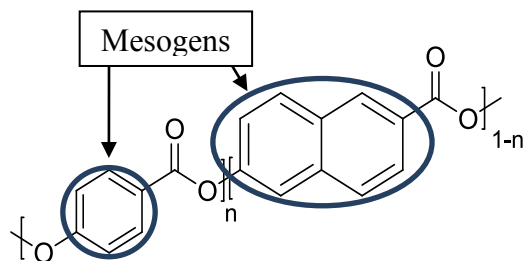


Figure 68: Main chain LCP (Vectran)

In side chain LCPs the mesogen is attached to the polymer backbone. An example of a cyano-biphenyl containing side chain LCP synthesised by Semilovic et al. [119] is shown in Figure 69.

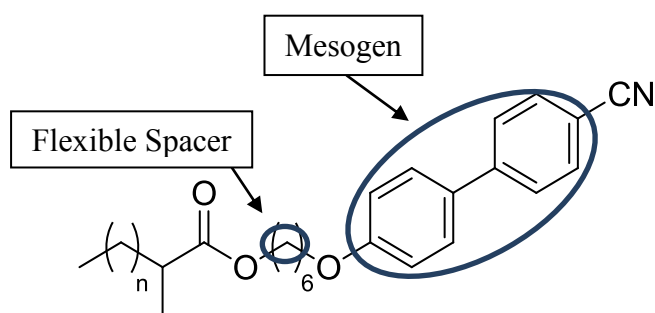


Figure 69: Cyano-biphenyl containing side chain LCP

Liquid crystalline elastomers and combined main chain and side chain LCP also exist [137]. Liquid crystalline elastomers are either main chain or side chain LCPs that are crosslinked.

This characteristic will potentially allow greater control of the composite stiffness at different temperatures. It is also possible to change the crystallinity of the LCP by applying a magnetic field to the polymer in its liquid crystalline phase [74]. This could be achieved by passing a current through the carbon fibres [119]. By changing the crystallinity of the LCP, the adhesion (contact angle) between the fibre and the

matrix could be altered. This would provide further control over the stiffness of the composite at different temperatures.

➤ Coating liquid crystalline polymers onto carbon fibres

Bismarck et al. [118] grafted a side chain LCP onto coated fibres. This was achieved by polymerising a liquid crystalline methacrylic monomer [4-methoxy-phenyl-4'-(6-methacryloyl-oxyhexyloxy)-benzoate] onto oxygen plasma modified carbon fibres via free radical bulk polymerisation. An image of the LCP grafted carbon fibre is shown in Figure 70. The polymer had a  $T_g$  at 46°C, a smectic-A-nematic transition temperature at 74°C and a nematic-isotropic transition temperature at 112°C. A current was passed through the carbon fibres and the LCP was heated to its isotropic phase. This process was reversible as the polymer could be cooled back to its birefringent range.

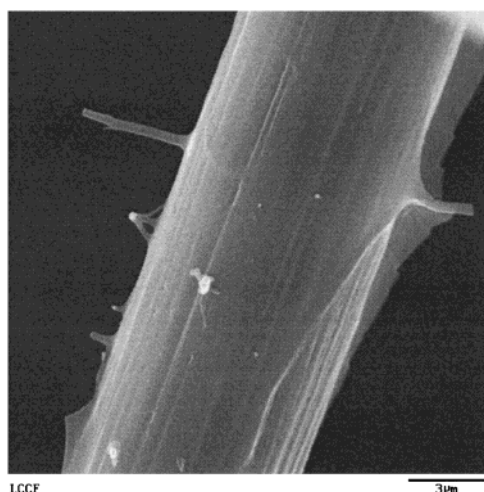


Figure 70: Side chain LCP grafted onto an oxygen plasma treated carbon fibre [118]

Semilovic et al. [119] grafted side chain liquid crystalline polymers onto carbon fibres and then applied a current to the fibres to heat the LCPs through their different phase transitions. They studied the orientation behaviour of the mesogens and found

it was dependent on the temperature of the carbon fibres. The mesogens aligned when the LCP carbon fibre coatings were heated to their liquid crystalline phases and then became isotropic when the LCPs were heated above their clearing (isotropisation) temperatures. It was not clear whether the magnetic field from the electrically conducting fibres also had an effect on the orientation of the liquid crystals. Sastri et al. [140] polymerised main chain liquid crystalline polymers onto approximately 0.1g carbon fibres via an in situ polycondensation reaction. The polymers were high molecular weight polyesters. A liquid crystalline epoxy resin was produced by Carfagna et al. [141]. A liquid crystalline monomer was synthesised, then combined with a hardener and cured in the presence of carbon fibres. Lebonheur et al. [142, 143] reinforced an epoxy matrix with a single LCP coated carbon fibre. The side chain LCP was grafted onto carbon fibres via an esterification reaction. Composites were manufactured by placing an LCP coated fibre into a silicone mould and then injecting an epoxy resin. Single-fibre fragmentation tests were used to determine the interfacial adhesion between the uncoated/LCP coated carbon fibres and the epoxy matrix. The LCP improved the interfacial adhesion as it could form covalent bonds with both the epoxy matrix and the carbon fibre.

### **A.1.2 Experimental details**

#### **A.1.2.1 Materials**

Unsize carbon fibres (AS4 12k HexTow™) were kindly supplied by Hexcel Corporation (Duxford, Cambridge, UK). The resin system Araldite® LY556 and hardener XB3473 was purchased from Huntsman Advanced Materials Ltd. (Cambridge, UK). The epoxy was prepared using a resin to hardener mixing ratio of

100:23 by mass. 37 % HCl was purchased from VWR (Lutterworth, UK). Oxygen and nitrogen gas were bought from BOC (UK). 6-hydroxy-2-naphthoic acid (98 %), suberic acid (99 %), sebacic acid (98 %) and sulphuric acid (98 %) were purchased from Fisher Scientific (Loughborough, UK). Hydroquinone ( $\geq 99$  %), acetic anhydride ( $\geq 99$  %), sodium acetate ( $\geq 99$  %), 4-acetoxybenzoic acid (96 %), NaOH ( $\geq 98$  %) and benzene ( $\geq 99$  %) were purchased from Sigma Aldrich (Dorset, UK).

#### A.1.2.2 Oxygen plasma modification of carbon fibres

Continuous, unsized PAN-based carbon fibres (AS4, Hexcel) were modified with Atmospheric Plasma Oxidation (APO) using a single rotating FLUME Jet RD1004, Plasmatrete (Steinhagen, Germany). The plasma jet was formed by ionisation of oxygen gas at a flow rate of 35 l/min, at 2.5 bar of pressure and using 2.1 kW of power. Oxygen Plasma (OP) modification was performed at three fibre processing speeds: 0.1, 0.58 and 1 m/min, through a glass T-piece (20 cm in length) below the plasma nozzle. These correspond to a residence time (RT) within the T-piece of 360, 60 and 36 seconds respectively. As shown in Figure 71, the fibres were looped three times below the plasma nozzle to ensure both sides of the carbon fibres could be oxidised. A heavily oxidised sample was prepared by suspending an 80 mm long carbon fibre tow between two aluminium clamps and exposing it to oxygen plasma (4 mins each side) at a distance of 15 mm from the tip of the plasma nozzle. Although it was not oxidised in the same way as the other fibres it shall be considered to have a residence time of 480 seconds.

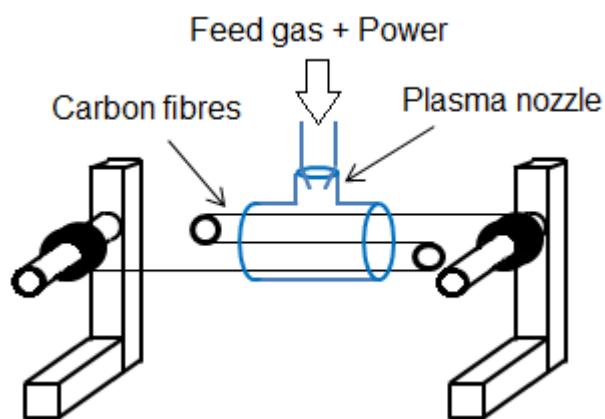


Figure 71: Setup for oxygen plasma modification of carbon fibres

#### A.1.2.3 Synthesis of liquid crystalline polymer

The monomers containing aromatic hydroxyl groups i.e. hydroquinone, 4-hydroxybenzoic acid and 6-hydroxybenzoic acid had to be acetylated separately and then polymerised with suberic and sebacic acid for 3 hours at 250 °C. 4-acetoxybenzoic acid was commercially available, however hydroquinone diacetate and 6-acetoxy-2-naphthoic acid had to be synthesised.

##### Synthesis of hydroquinone diacetate (HQDA)

Hydroquinone diacetate was synthesised according to Prichard [144]. 1 drop of 0.19 M sulphuric acid was added to 1.1 g (0.01 mol) hydroquinone and 1.9 ml (0.02 mol) acetic anhydride. The solution was then stirred gently by hand. After 5 minutes 8 ml crushed ice was added to the reaction mixture and the product that precipitated was collected on a Büchner funnel and washed thoroughly with water.

##### Synthesis of 6-acetoxy-2-naphthoic acid (ANA)

2.73 g (0.01 mol) 6-acetoxy-2-naphthoic acid was combined with 5.8 ml of 6.25 N NaOH and 10.9 g crushed ice. 2.5 ml (0.01 mol) acetic anhydride was added in a

single portion to the reaction mixture and after 10 minutes of stirring 7 ml 6.25 N HCl was added in one portion. The product was collected on a Buchner funnel via suction filtration. The white powder was washed thoroughly with water and then recrystallised from benzene.

### Synthesis of polymer

0.5 g ( $2.17 \times 10^{-3}$  mol) 6-acetoxy-2-naphthoic acid, 0.39 g ( $2.17 \times 10^{-3}$  mol) 4-acetoxybenzoic acid, 0.36 g ( $1.86 \times 10^{-3}$  mol) hydroquinone diacetate, 0.16 g ( $9.3 \times 10^{-3}$  mol) suberic acid and 0.19 g ( $9.1 \times 10^{-3}$  mol) sebacic acid were heated to 250 °C over 3 hours under nitrogen (Figure 72).

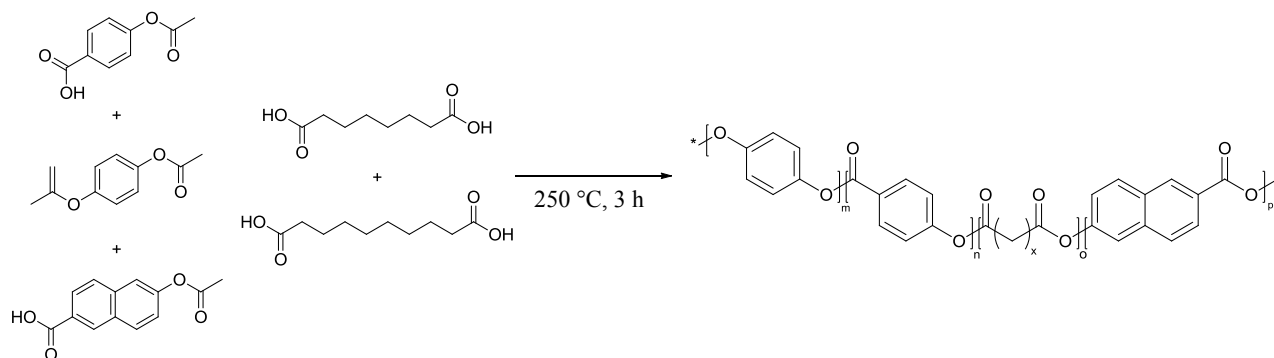


Figure 72: Reaction scheme for synthesis of LCP 1

#### A.1.2.4 Coating liquid crystalline polymer continuously onto carbon fibres

A spool of AS4 unsized carbon fibres were placed onto a tension control machine (CTS setting panel, Izumi international, Osaka, Japan) and the fibre tow wound over a force detector (DTH 6120, Izumi international, Osaka, Japan). 120 g tension was applied. The setup is shown in Figure 73.

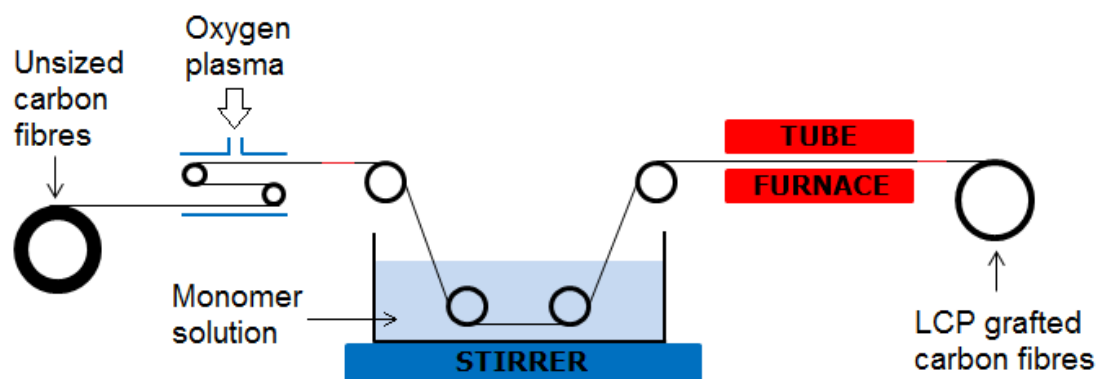


Figure 73: Setup for attempted continuous grafting of LCP 1 onto carbon fibres

Atmospheric Plasma Oxidation modification was performed at a fibre processing speed of 1 m/min through a glass T-piece (20 cm in length) below the plasma nozzle. This corresponded to a residence time (RT) of 36 seconds within the T-piece. The fibres were looped three times below the plasma nozzle to ensure both sides of the carbon fibres were oxidised. The method for oxidising the fibres is described in detail in section A.1.2.2.

The fibres were then passed through a 150 ml beaker (VWR, Lutterworth, UK) containing 1.64 g 6-acetoxynaphthoic acid, 1.28 g p-acetoxybenzoic acid, 0.52 g suberic acid, 0.62 g sebacic acid and 1.18 g hydroquinone dissolved in 48 ml acetone. The spreading was controlled using a custom made pin set. The fibres were then passed through a tube furnace (STF 16/75, Carbolite Furnaces, Sheffield, UK) at 100 °C in order to remove any residual acetone. Approximately 30 m coated carbon fibres were collected onto a custom built fibre winding unit with a brushless DC Motor (FBLM5120W-GFB/ GFB5G200, VEXTA, Oriental Motor Co., Hampshire, UK). The fibres were then wound onto a hollow glass tube (15 mm diameter) and placed back into the furnace at 250 °C under nitrogen for 3 hours in

order to polymerise the monomers. The fibres were finally wound onto a cardboard drum (83 mm diameter, 3 mm wall thickness).

#### A.1.2.5 Manufacturing carbon fibre reinforced epoxy composites

The methods used to filament wind the carbon fibres and manufacture composites are described in Chapter 3. The cured composites were cut into 40 mm × 5 mm test specimens for DMTA using a water cooled diamond bladed cutter (Diadisc 4200, Mutronic, Rieden, Germany).

#### A.1.2.6 Analysis of LCP, polymer coated fibres and composites

The techniques used to analyse the LCP, polymer coated carbon fibres and composite are also described in Chapter 3.

#### ➤ Characterisation of liquid crystalline phases

Optical Polarisation Microscopy was used to observe the liquid crystalline phase of LCP 1. An Olympus BH-2 microscope was used in conjunction with an Olympus DP70 camera (Tokyo, Japan) at 20 × magnification. The polymer samples were heated from room temperature to 300 °C at a heating rate of 40 °C/ min on a heating stage (THMS600, Linkam Scientific Instruments, Surrey, UK).

### **A.1.3 Results and discussion**

#### A.1.3.1 Thermal analysis of liquid crystalline polymer

The thermal properties of LCP 1 are summarised in Table 17. The  $T_g$  of LCP 1 was recorded at 62 °C from the DSC heating and cooling traces. The low  $T_g$  of this polymer makes it unsuitable for use in aerostructures where the maximum service

temperature is 90 °C [94]. However, the  $T_g$  can be tailored by controlling the amount of flexible spacer in the polymer.

Table 17: Thermal properties of liquid crystalline polymer

| <b>Polymer</b> | <b><math>T_g</math>/ °C<br/>(DSC)</b> | <b><math>T_g</math>/ °C<br/>(DMTA)</b> | <b>Liquid<br/>Crystalline<br/>(Nematic)<br/>Range/ °C</b> | <b>Onset<br/>degradation<br/>temperature<br/>in air/ °C</b> |
|----------------|---------------------------------------|----------------------------------------|-----------------------------------------------------------|-------------------------------------------------------------|
| LCP 1          | 62                                    | 69                                     | 150-350                                                   | 350                                                         |

Endothermic LC transition peaks were not present as the polymer exhibited a quenched nematic phase at room temperature which became fluid above the glass transition temperature. This is consistent with the literature [145]. The temperature at which the polymers began to degrade in air was recorded at approximately 350 °C by TGA. A nematic liquid crystalline range for LCP 1 was observed between 150 °C and 350 °C using optical polarisation microscopy. A quenched nematic range was seen at room temperature that became fluid above the  $T_g$  of the polymer.

#### A.1.3.2 Viscoelastic properties of liquid crystalline polymer

The viscoelastic properties of LCP 1 were measured using DMTA. The glass transition temperature of LCP 1 was calculated from the maximum value of the loss modulus and was measured at 69 °C (Figure 74). This value is slightly higher than that recorded by DSC.

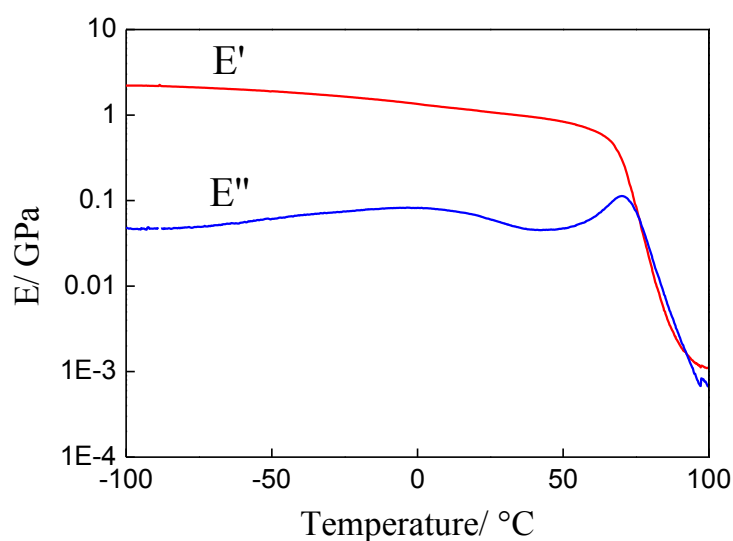


Figure 74: DMTA curves showing the storage modulus ( $E'$ ) and loss modulus ( $E''$ ) of LCP 1 as a function of temperature

There is a slight  $\beta$  transition at approximately 0 °C that can be associated with localised movement in the main chain [127]. At 30 °C the storage modulus of LCP 1 was 1.5 GPa. The storage modulus fell dramatically at the  $T_g$ .

#### A.1.3.3 Surface composition of carbon fibres

The oxygen content on the fibre surface increased with exposure to plasma. The percentage of oxygen on the unsized AS4 carbon fibres was measured at 13 %, which increased to 17 % for fibres modified for 36 seconds with APO. After a 10 fold exposure to the plasma (RT: 360 s) the oxygen content increased to 21 %. The stationary/batch sample (equivalent RT: 480 s) contained 29 % oxygen on the surface (Figure 75).

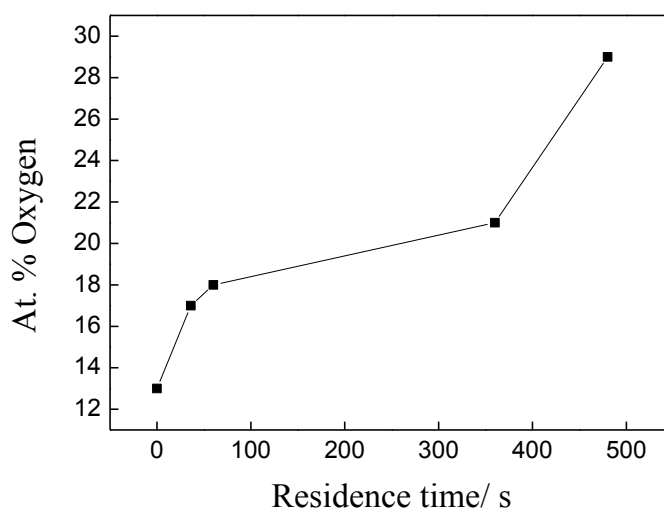


Figure 75: % oxygen content of AS4 carbon fibres run at different residence times in the plasma chamber

The peak fitted high resolution C 1s XP spectra of the unsized, oxygen plasma modified (RT: 36 s) and LCP 1 coated carbon fibres can be seen in Figure 76. Although it is not shown, there was very little difference in the surface composition of the APO fibres (RT: 36, 60 and 360 s) despite the varying exposure time to oxygen plasma. The % of carboxylic acid groups was important as it should have allowed the liquid crystalline polymer to covalently bond to the fibre surface. The percentage of carboxylic acid groups on the unsized carbon fibres was measured at 2.2 %. The carbon fibres modified with oxygen plasma for 36 seconds (RT: 36 s) contained the highest percentage of carboxylic acid groups (4.7 %). Therefore, it was this residence time used in the continuous coating of LCP 1 onto carbon fibres.

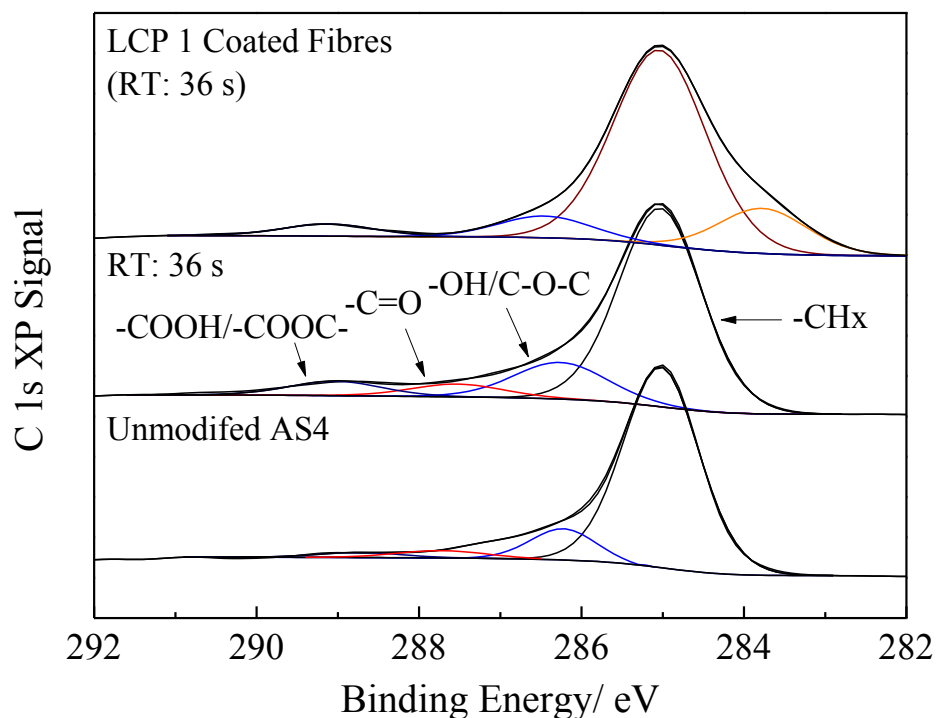


Figure 76: High resolution C 1s XP spectra of the unsized, OP modified (RT: 36 s) and LCP 1 coated carbon fibres

From the C 1s XP spectra of the LCP 1 coated fibres there are peaks at 285 eV ( $\text{CH}_x$ ), 286.5 eV (C-O) and 289.1 eV (COOH/COOC). There is also a peak at 283.77 eV that can be attributed to silicon carbide, an impurity on the fibre surface that more than likely originated from the tube furnace during the coating process. The atomic composition of the unsized fibres, from the wide scan spectrum, was 85 % carbon, 13 % oxygen and 2 % nitrogen (Table 18). The O:C ratio was 0.15. The atomic composition of the LCP 1 coated fibres was 82 % carbon and 18 % oxygen (O:C ratio of 0.22).

Table 18: Surface atomic composition of the unsized, oxygen plasma (OP) modified and polymer coated carbon fibres

| Sample                        | Surface composition, atomic % |    |   |      |
|-------------------------------|-------------------------------|----|---|------|
|                               | C                             | O  | N | O:C  |
| Unsize AS4 fibres             | 85                            | 13 | 2 | 0.15 |
| OP modified fibres (RT: 36 s) | 80                            | 17 | 3 | 0.21 |
| LCP 1 coated fibres           | 82                            | 18 | - | 0.22 |
| LCP 1 (pure polymer)*         | 71                            | 29 | - | 0.41 |

\* Theoretical values for pure LCP 1 assuming there are no impurities

The theoretical composition of pure LCP 1 was 71 % carbon and 29 % oxygen (O:C ratio of 0.41). The difference between the atomic composition of pure LCP 1 and the LCP 1 coated fibres implies that the fibres were not successfully coated with the liquid crystalline polymer. The atomic composition of the LCP 1 coated fibres was similar to that of the OP modified fibres (RT: 36 s). This was expected as the LCP 1 coated fibres were modified with oxygen plasma (residence time: 36 seconds) prior to coating. A likely explanation for the lack of coating is that the quantity of monomers in the coating bath was too low. A difficulty with this study was that there were limited quantities of monomers available for coating due to their cost. Another problem was that the coating bath contained 5 different monomers that may not have been distributed evenly over the length of the fibres during the coating process.

#### A.1.3.4 Thermal analysis of coated carbon fibres

No transitions could be seen for either the unsized or the LCP 1 coated carbon fibres. This showed that LCP 1 was not polymerised onto the fibres. Thermal gravimetric analysis (TGA) revealed the unsized carbon fibres remained thermally stable up to 500 °C, after which point they start to degrade. Both the unsized and LCP 1 coated

fibres showed little degradation up to 500 °C, suggesting that there was very little grafting on the fibres.

#### A.1.3.5 Fibre diameter and interfacial shear strength measurements

The fibre diameters of the carbon fibres, measured using the modified Wilhelmy-technique, can be seen in Table 19. The fibre diameter of the OP modified fibres ( $7.13 \pm 0.01 \mu\text{m}$ ) was approximately that of the unsized AS4 fibres ( $7.10 \pm 0.01 \text{ mm}$ ). This confirms that plasma modification did not etch the fibres. The fibre diameter for the LCP 1 coated fibres was  $7.32 \pm 0.23 \mu\text{m}$ . The large error for the LCP 1 coated fibres is most likely due to the presence of impurities. The interfacial shear strength of the unsized, OP modified and LCP 1 coated fibres to an epoxy matrix was calculated using single fibre pull-out tests. The IFSS for each fibre was very similar (Table 19). This is surprising as oxygen plasma modification was expected to increase the IFSS, which suggests that the plasma modification was not uniform.

Table 19: Fibre diameters and interfacial shear strengths of LCP coated carbon fibres to an epoxy resin

| <b>Sample</b>                 | <b>Fibre Diameter/ <math>\mu\text{m}</math></b> | <b>Interfacial Shear Strength/ MPa</b> |
|-------------------------------|-------------------------------------------------|----------------------------------------|
| Unsize AS4 fibres             | $7.10 \pm 0.01$                                 | $101.2 \pm 2.6^b$                      |
| OP modified fibres (RT: 36 s) | $7.13 \pm 0.01$                                 | $106.1 \pm 14.3$                       |
| LCP 1 coated fibres           | $7.32 \pm 0.23$                                 | $98.7 \pm 3.4$                         |

<sup>b</sup> [2]

#### A.1.3.6 Fibre morphology and cross sectional images of carbon fibre reinforced composites

The LCP 1 coated fibres were analysed using SEM and there appeared to be very little coating (Figure 77).

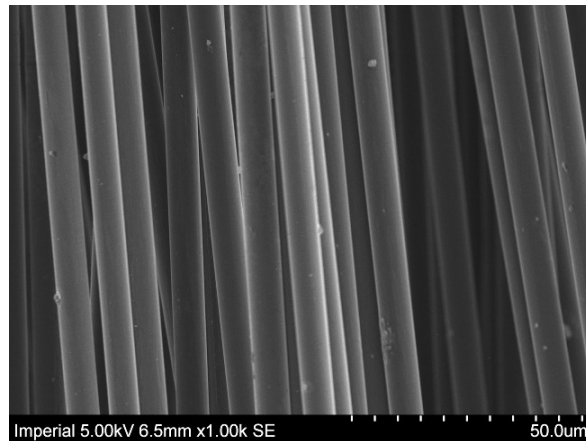


Figure 77: SEM image of LCP 1 coated carbon fibres

From microsection images the number of voids in the LCP coated fibre reinforced composite appear to be high (Figure 78). From acid digestion tests the fibre volume percentage was calculated as  $46 \pm 2 \%$  and the void content as  $2.8 \pm 1.4 \%$ .

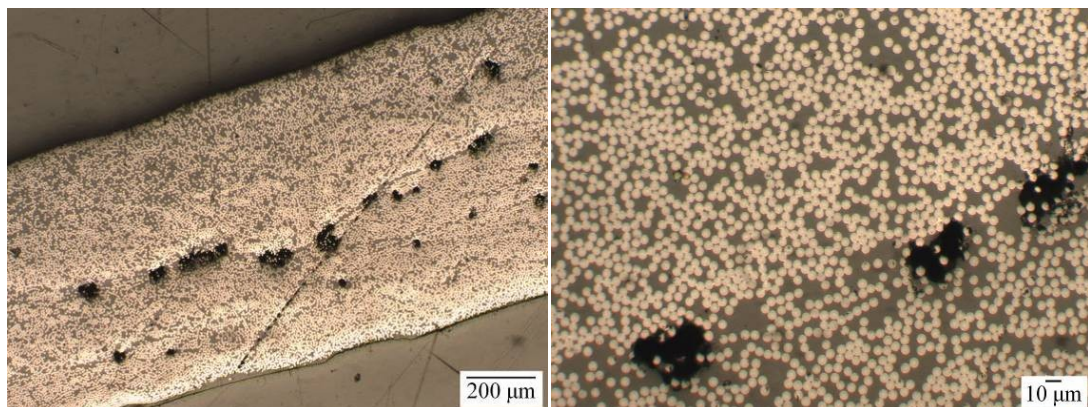


Figure 78: Cross sections of LCP 1 coated carbon fibre reinforced composite at 5× magnification (left) and 20× magnification (right)

#### A.1.3.7 Viscoelastic properties of composites

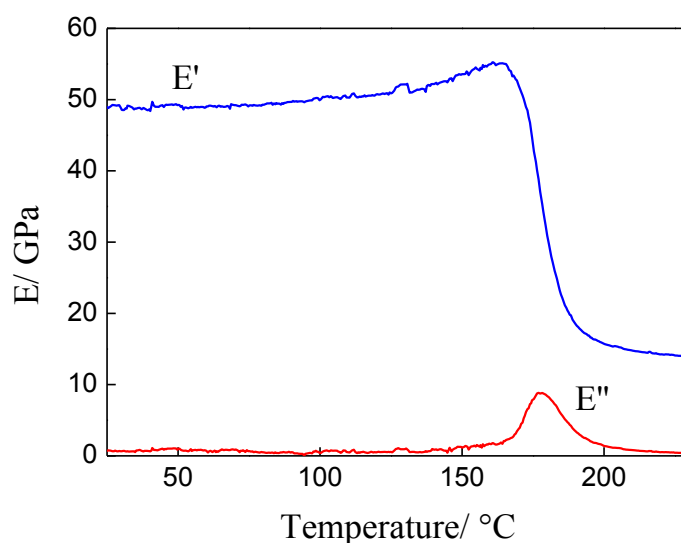


Figure 79: DMTA curves for the LCP 1 coated carbon fibre reinforced epoxy composite as a function of temperature

The LCP coated fibre reinforced composite was analysed using DMTA (Figure 79). There was no loss in storage modulus around the  $T_g$  of the fibre coating confirming that LCP 1 was not coated onto the carbon fibres. There was only a single transition at 176 °C corresponding the  $T_g$  of the epoxy.

#### A.1.4 Conclusions

A liquid crystalline polymer was synthesised for use as a potential carbon fibre coating. The thermal properties of the polymer were analysed using DSC, TGA and DMTA. An attempt was made to graft the polymer onto oxygen plasma modified carbon fibres. Analysis of the coated fibres showed this was unsuccessful. In conclusion, due to the difficulty and cost in coating this LCP onto carbon fibres a

much simpler and effective coating experiment should be conducted in any future studies.

## **A.2 Kynar coated metal wire reinforced epoxy composite**

### **A.2.1 Experimental: Preparation of metal wire reinforced epoxy composite**

Approximately 20 m Kynar insulated copper wire (209-4849, RS, Northants, UK) was wound by hand onto a release fabric (FF03PM, Aerovac, West Yorkshire, UK) covered aluminium plate (75 mm width, 200 mm length and 3 mm thickness). The release fabric and the ends of the fibre tows were taped to the metal plate using high temperature resistant tape (Flashtape 1, Aerovac, West Yorkshire, UK).

A low temperature cure resin (Prime 20ULV, SP-High Modulus, Gurit, Isle of Wight, UK) was chosen as the matrix due to the low melting point and crystallisation of the Kynar coating. The mixing ratio was 100:19 by weight. The mixture was degassed thoroughly using a vacuum desiccator (Jencons, Hemel Hempstead, UK) connected to a vacuum pump (E-Lab 2, 230V, Edwards, Crawley, UK). Resin infusion was then carried out according to section 3.2.4.2, except that curing was performed at room temperature for 48 h. Images of the cured specimens were taken using an optical microscope (BX51M, Olympus, Tokyo, Japan).

### **A.2.2 Results and discussion**

In order to illustrate that the fibres do slide in composites with controllable stiffness a coated metal wire reinforced epoxy model composite was manufactured. When the specimen was bent at room temperature the metal wires slid within the wire coating

adhering to the resin matrix because of the weak coating wire interface. Images of the specimen were taken before and after bending (Figure 80).

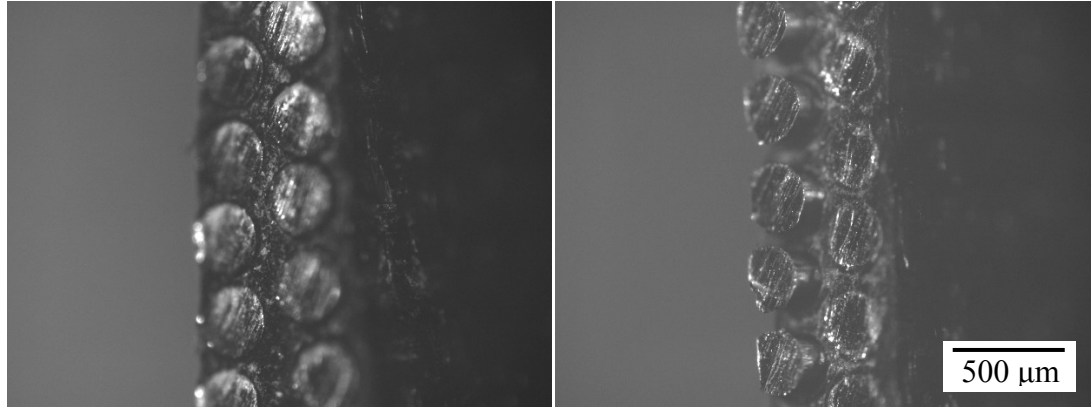


Figure 80: Kynar coated copper wire reinforced epoxy composite before bending (left) and after bending (right)

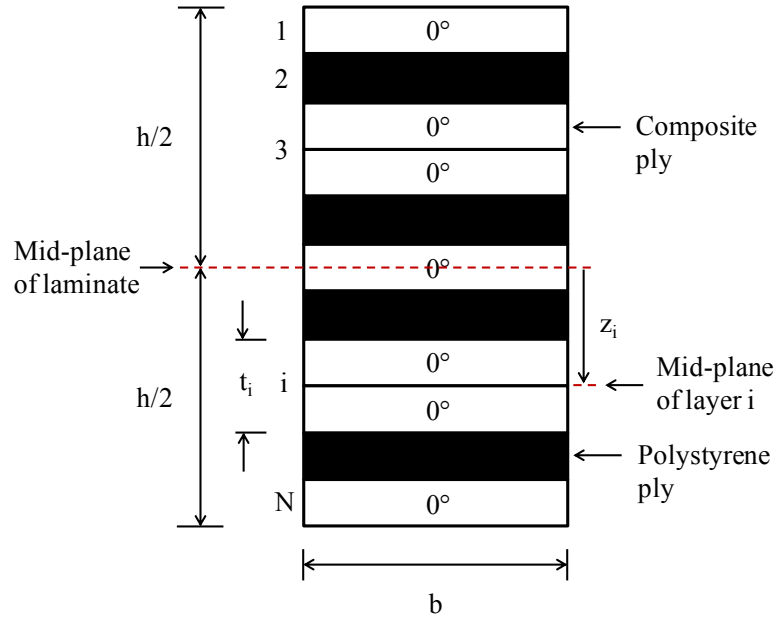
Prior to bending the ends of the wires are in alignment with the epoxy matrix. When composites were bent by hand, the wires on the compression side of the composite can be seen protruding from the specimen. The wires on the tensile side are receding slightly, although this is not as obvious.

### **A.3 Predictions of flexural stiffness and strength**

Simple beam theory can be used to approximate the bending behaviour of the interleaved composites [12]. The polystyrene layer can be treated in two ways depending on the temperature. At room temperature the elastic modulus will be very small when compared to the fibre direction stiffness of the unidirectional CFRP plies but is assumed to be sufficiently large so as to ensure that the composite plies act as an integral structural element and that sections initially plane and normal to the axis of the beam remain plane and normal to the axis of the beam when the beam is flexed. At high temperature the elastic modulus is also insignificant compared with

the CFRP plies but now the stiffness of the polystyrene is so low that the CFRP plies act as independent structural elements able to effectively slide freely relative to each other so that initially plane sections no longer remain plane.

### 3.1 Analysis of room temperature bending behaviour of interleaved composite containing $0^\circ$ plies



Note: A layer of composite may comprise of more than one ply.

Figure 81: Cross section of interleaved composite beam - definition of terms

Assuming symmetry of layup i.e. the centroidal axis is at mid-thickness, then the second moment of area,  $I^*$ , of the cross section about the centroidal axis (neglecting polystyrene layers) is given by equation 10. The definitions of the terms are shown in Figure 81. Note that a composite layer can consist of more than one composite ply; in Figure 81 layers 3 and i consist of two plies each.

$$I^* = \sum_{i=1}^N \left( \frac{bt_i^3}{12} + bt_i z_i^2 \right) \quad (10)$$

Composite layers only

The flexural stiffness of the beam is given by  $E_c I^*$ , where  $E_c$  is the elastic modulus of the composite ply in the  $0^\circ$  direction.

The effective flexural modulus,  $E_f^{RT}$ , of the beam material at room temperature assuming the beam is homogenous, can be calculated using equation 11.

$$E_f^{RT} I = E_c I^* \quad (11)$$

where  $I$  is the second moment of area of the whole section which, for the rectangular section, is given by equation 12.

$$I = \frac{bh^3}{12} \quad (12)$$

Therefore,  $E_f^{RT}$  can be calculated using equation 13.

$$E_f^{RT} = \frac{12E_c}{h^3} \sum_{i=1}^N \left( \frac{t_i^3}{12} + t_i Z_i^2 \right) \quad (13)$$

Composite layers only

An expression for the apparent flexural strength can also be derived. The magnitude of peak bending stress in a homogenous beam subjected to 3-point bending is given by equation 14.

$$\sigma = \frac{PL}{4I} \cdot \frac{h}{2} = \frac{PLh12}{8bh^3}$$

$$\sigma = \frac{3PL}{2bh^2} \quad (14)$$

Using  $P = P^u$ , where  $P^u$  is the applied load at failure, then for the interleaved beam the apparent flexural strength,  $\sigma^*$  is given by equation 15.

$$\sigma^* = \frac{3P^uL}{2bh^2} \quad (15)$$

The magnitude of the actual maximum stress,  $\sigma^u$ , in the outermost CFRP layers (i.e. the strength of the CFRP in flexure) is given by equation 16.

$$\sigma^u = \frac{P^uL}{4 \sum_{i=1}^N \left( \frac{bt_i^3}{12} + bt_i \cdot Z_i^2 \right)} \cdot \frac{h}{2} \quad (16)$$

Composite layers only

Substituting for  $P^u$  from (15) into (16) gives equation 17.

$$\sigma^* = \frac{12\sigma^u \sum_{i=1}^N \left( \frac{t_i^3}{12} + t_i \cdot Z_i^2 \right)}{h^3} \quad (17)$$

Composite layers only

Using  $\sigma^u$  as the flexural strength measured in the pure CFRP specimen gives the predicted apparent flexural strengths for the interleaved composites.

### 3.2 Analysis of high temperature bending behaviour of interleaved composite containing 0° plies

Assuming the layers are free to slide then the second moment of area,  $I^{**}$ , of the beam is the sum of the second moment of area values of each CFRP layer about its own centroidal axis (equation 18).

$$I^{**} = \sum_{i=1}^N \frac{bt_i^3}{12} \quad (18)$$

Composite layers  
only

Following the previous development, the apparent flexural modulus (i.e. above the  $T_g$  of polystyrene) at high temperature of the interleaved composite is given by equation 19.

$$E_f^{HT} = \frac{E_c \sum_i^N t_i^3}{h^3} \quad (19)$$

Composite layers only

Failure will occur when the maximum stress in any of the CFRP layers exceeds the strength. Since all layers are subjected to the same curvature about their own centroidal axis (i.e. no extension or compression at the mid-plane of each CFRP layer) then the highest stress occurs in the thickest CFRP layer of thickness  $t_{i|max}$ .

The maximum stress,  $\sigma^u$ , is given by equation 20.

$$\sigma^u = \frac{P^u L}{4 \sum_{i=1}^N \left( \frac{b t_i^3}{12} \right)} \cdot \frac{t_{i|max}}{2} \quad (20)$$

Composite layers only

The apparent flexural strength,  $\sigma^*$ , at high temperature can be calculated using equation 21.

$$\sigma^* = \frac{\sigma^u \sum_{i=1}^N t_i^3}{h^2 t_{i|max}} \quad (21)$$

Composite layers only