

# PROTECTIVE EFFECT OF THIN ALUMINA LAYER ON CARBON FIBRE TO PRESERVE TENSILE STRENGTH DURING CNT GROWTH BY CVD

S. Vogel<sup>a, b, c\*</sup>, C. Dransfeld<sup>a</sup>, B. Fiedler<sup>d</sup>, J. Gobrecht<sup>c</sup>

<sup>a</sup> University of Applied Sciences and Arts Northwestern Switzerland, Institute of Polymer Engineering, Klosterzelgstrasse 2, CH-5210 Windisch, SWITZERLAND.

<sup>b</sup> University of Basel, Institute of Physics, Nanoelectronics Group, Klingelbergstrasse 82, CH-4056 Basel, SWITZERLAND.

<sup>c</sup> Paul Scherrer Institute, Laboratory for Micro- and Nanotechnology, ODRA/102, CH-5232 Villigen PSI, SWITZERLAND

<sup>d</sup> Technical University Hamburg Harburg, Polymer Composites, Denickestrasse 15, D-21073 Hamburg, GERMANY

\*Samuel.vogel@fhnw.ch

**Keywords:** Hierarchical composites, fibre tensile strength, chemical vapour deposition, multi scale composites

## Abstract

*As received AS4 carbon fibres were covered with a thin alumina layer by atomic layer deposition prior to the growth of radially aligned carbon nano tubes onto the fibre surface. The deposition of alumina was found to preserve the initial fibre tensile strength in the harsh conditions during carbon nanotube growth by chemical vapour deposition. The fibre tensile strength was measured by single fibre tensile test for fibres treated with different processing parameters. The interphase properties between carbon fibre, alumina layer and matrix material were characterized by carrying out single fibre fragmentation tests. The length of the ongrown carbon nano tubes can exceed 7  $\mu\text{m}$ , i.e. the carbon fibre diameter. Experiments prove that the deposited alumina layer with a thickness of as little as 12.8 nm preserves the fibres initial tensile strength.*

## 1 Introduction

Carbon fibre reinforced polymer (CFRP) composites have gained great importance as lightweight materials in many applications in the space, aerospace, automotive, renewable energies and the oil and gas industry. Their high strength- and stiffness-to-weight ratio makes them ideal for highly tailored engineering applications, and conventional metallic materials are outperformed. Such CFRPs are supremely effective when exploiting their tensile properties in the unidirectional fibre direction. Real engineering applications are, however, governed by complex stress states in intricate structural geometries. This has led to engineering methods, such as classical laminate theory. In order to better fulfil design requirements for such conditions, layers of unidirectional fibres are arranged at various angles, also referred to as lay-up. The failure of a state of the art CFRP laminate is often governed by compressive failure in fibre direction or transverse strength. The former is driven by the comparatively low matrix stiffness, resulting in buckling of single fibres at the

microscopic level, whereas the latter is driven by the matrix strength at the fibre to matrix interface, described in [1]. Therefore, there has always been a high interest to enhance the properties of the fibre to matrix interface. This interface is influenced by i) the number of reactive groups on the fibre surface, controlled by its manufacturing process, and by ii) the application of silane, epoxy or polyvinyl alcohol based coatings (or proprietary mixtures thereof), often referred to as “sizing”. Careful control of the manufacturing process and sizing has yielded acceptable transverse properties in the composite [2-4].

A novel and promising approach to address the challenge of the fibre-matrix disparity of properties is the development of multi scale composites (MSC), also referred to as hierarchical composites. MSCs contain reinforcing fibres at typically two length scales; the nano- and micro-scale. The reinforcing fibres on the nano scale are typically carbon nanotubes (CNT) with their extraordinary intrinsic mechanical properties [5], which complement the micron sized ( $\varnothing 7 \mu\text{m}$ ) carbon fibres.

One approach has been to disperse CNTs or nanoparticles as additives homogeneously in the matrix polymer. In these experiments, single wall or multiwall CNTs were used, but they have had limited success [6] and marginal commercial impact. The reinforcement of matrix systems with spherical silica particles, however, has proven beneficial as they have a synergistic effect in increasing the matrix modulus, which increases the compression strength in fibre direction and the matrix fracture toughness [7, 8].

Another approach with the potential to increase the fracture toughness is based on the growth or attachment of CNTs to standard carbon fibres [6]. Among the options to grow or attach CNTs onto carbon fibres (CF), electrophoretic deposition does not provide aligned and perpendicular CNT coverage on the substrate fibre [9, 10]. On the other hand, chemical functionalization of CNTs has been reported to be rather difficult, and is usually chemically intensive [11], and the density of the attached CNTs is low. The method with the highest potential seems to be the direct growth of CNTs on CF by a metal catalysed CVD route. However, thus far, most reported results seem to severely degrade the tensile strength of the used CF [12, 13]. Hence the focus of this study is to apply a metal oxide layer to preserve the fibre tensile strength during the processing steps of growing CNTs on the CF.

The deposition of an alumina layer prior to CNT growth protects the CF from being oxidised and etched in the harsh conditions during the CVD process. Atomic layer deposition (ALD) is ideal to deposit metal oxides on complex three dimensional shapes and at the same time enables a good control of the layer thickness. In an alternating process, the metal containing precursor and the oxygen containing precursor, usually deionised water, are evaporated and pulsed into the reaction chamber. The sample surface is uniformly covered by each reactant, building up a uniform layer of metal oxide.

As carbon fibres are linear elastic brittle materials, their strength distribution can be approximated by the two-parameter Weibull distribution [14]:

$$P(\sigma) = 1 - \exp\left(-\frac{l}{l_0} \left[\frac{\sigma}{\beta}\right]^\alpha\right) \quad (1)$$

The Weibull shape parameter is denoted by  $\alpha$ , and the scale parameter by  $\beta$ ,  $l$  stands for fibre specimen length and  $l_0$  for a chosen reference length. The focus of this work is not the dependence of the fibre specimen length on the tensile strength. Therefore all samples are

tested at the same length of 20 mm which is chosen as reference length  $l_0$ . Thus, the average fibre strength  $\langle\sigma\rangle$  is not length dependent, and can be described as:

$$\langle\sigma\rangle = \beta \cdot \Gamma\left(1 + \frac{1}{\alpha}\right) \quad (2)$$

How thick an effective protection layer must be, can be analysed by comparing the average fibre strength calculated by Eq. (2) for samples with varying alumina thicknesses, i.e. ALD cycles.

The adhesion between CF, alumina layer and matrix material are characterised by single fibre fragmentation test (SFFT). For this method a single CF is embedded in the centre of a matrix material tensile test sample. After preparation, the sample is loaded with uniaxial tensile force (along the fibre direction) at a constant displacement rate, typically 0.5  $\mu\text{m/s}$ . The applied strain is transferred to the embedded CF via shear stress through the interface surface. At a certain level, the transferred shear stress reaches the failure stress  $\sigma_f$  of the CF causing the first fibre break. The steadily increased strain drives the fragmentation process until the fragments become too short to reach  $\sigma_f$  within the fragments. At this point the fragmentation saturation is reached. The occurring fibre breaks can be made visible under cross polarised light due to strain induced birefringence patterns and the fragment length is measured under a cross polarized light optical microscope.

The interfacial shear strength,  $\tau$ , is calculated by the Kelly-Tyson model [15], using the fibre diameter  $d$  and the critical fragment length  $l_c$ :

$$\tau = \frac{\sigma_f d}{2 l_c} \quad , \text{with } l_c = \frac{4}{3} l_{\text{fragment}} \quad (3)$$

This model does not allow an accurate calculation of the interfacial shear strength, as identified by [16]. However this method permits a qualitative comparison between differently treated samples within this work, to characterise the adhesion of the alumina layer on the CF after ALD processing and eventual heat treatment at different temperatures. Understanding and improving the adhesion between the CF and applied alumina layer is a prerequisite to use the presented method for growing CNTs on CF and thereby produce hierarchical composites.

## **2 Experimental**

The carbon fibre used in the experiments was an oxidative treated but unsized type of AS4 produced by HexTow, USA. The manufacturer provided the following fibre characteristics: Tensile modulus 231 GPa, tensile strength 4,432 MPa, elongation at break 1.8 %, filament diameter 7.1  $\mu\text{m}$ .

In a first step, a 1.5 m long single carbon fibre filament was extracted from the roving. The attachment of 3.7 g weight at one fibre end pre-strained the carbon fibre to approximately 0.2 %. Two parallel quartz rods with a diameter of 6 mm separated by 70 mm were used to hold the fibre. By carefully rolling the fibre around the sample holder, it is assured both that the fibre pre-strain was maintained during all following processes and the single fibre has neither contact with neighbouring fibres nor other surfaces of process equipment at all times. Both fibre ends were secured with high temperature compatible adhesive tape or ceramic adhesive if processing temperatures exceeded 250 °C.

After cleaning the prepared sample in an ultra violet (UV) /Ozone cleaner for 10 minutes, alumina was deposited in an ALD machine (Savannah 100, Cambridge NanoTech, UK) at different cycle numbers. The aluminium precursor used was trimethylaluminium (TMA). The oxygen source was deionised water. The ALD chamber temperature was set to 225 °C. The resulting alumina layer thickness was determined by ellipsometry measurements of a co-processed silicon wafer with 410 nm SiO<sub>2</sub> layer and was found to be 12.8 nm after 100 ALD cycles.

The catalyst solution was prepared from 1.875 mMol iron nitrate solution sonicated for 10 minutes. Samples were dipped four times during 10 minutes and let dry 10 minutes in an oven at 50 °C between each dipping.

Finally, the CNTs were grown on the samples with CVD processing parameters kept constant in a 136 mm diameter quartz tube oven during 10 minutes at 750 °C with 1 l/min H<sub>2</sub> and 0.8 l/min ethylene flows respectively. Thermally treated samples, used for the investigation of the alumina adhesion, were produced in the same oven at the same temperature and duration, under Argon atmosphere without being dip-coated with iron nitrate. Verification of CNT growth was confirmed by subsequent scanning electron microscopy (SEM).

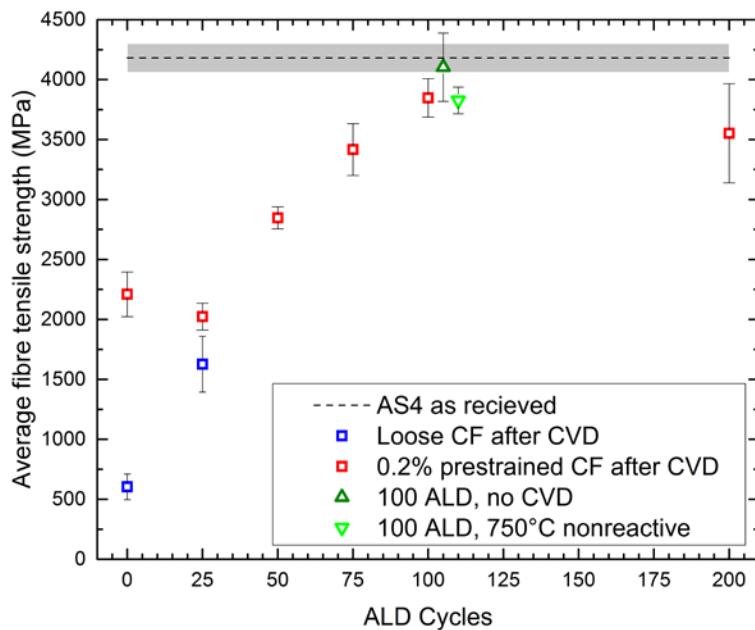
The single carbon fibres with grown CNTs or thermally treated carbon fibres were bonded to paper (160 g/m<sup>2</sup>) frames for tensile testing according ASTM C1557-03 [17] at a gauge length of 20 mm with cyanoacrylate adhesive. Protected by the paper frame, the samples were mounted in a small tensile testing machine (Linkam TST 350, UK). The jaws were closed by 10 µm prior to removal of the sides of the paper frame. The tensile test was performed with a testing speed of 15 µm/s. The load was recorded by the Linkam built in 20 N load cell with micro-Newton resolution. Time until fibre fracture was measured and samples with more than 30 seconds testing time were discarded (according [17]). For all samples the tensile strength  $\sigma_{ts}$  was determined by measuring the maximum force  $F_{max}$  before break and calculated by  $\sigma_{ts} = F_{max}/A$ , with  $A$  denoting the cross section area of the fibre.

Single fibre fragmentation test (SFFT) samples were produced by embedding a single treated CF in a resin sample with a gauge length of 12 mm and square section of 2 mm<sup>2</sup>. The treated CF was pre-strained by attaching 3.75 g on each side of the fibre, enabling alignment of the fibre in the mould. Furthermore pre-straining the CF increases the strain to failure difference between the matrix material and the embedded CF, which was required for reaching the fragmentation saturation during testing in non-plasticised matrix materials. For the experiments commercially available epoxy resin Araldite LY 564 with hardener Aradur 22962 (Huntsman, USA) were used. After curing at 130 °C during two hours, the samples were de-moulded from the silicone mould; the excess resin was grinded away and the surface is polished down to polishing paper of grade P 4000 (FEPA). The samples were tested with a constant tensile displacement rate of 0.5 µm/s in a small tensile testing machine (Linkam TST 350) with a 200 N load cell mounted. The fragments were observed under cross polarised light with a Leica optical microscope. The fragmentation process was recorded on video for further analysis and fragment length measurement.

### 3 Results and discussion

#### 3.1 Fibre tensile strength preservation

The effect of the gauge length on the fibre tensile strength was neglected within this work, allowing direct comparison of the influence of the different growth conditions on the fibre strength. The Weibull parameters were estimated by the maximum likelihood method for each sample set. The average fibre strength of the sample sets were calculated by Eq. (2) and are compared in Figure 1. The average fibre strength standard deviation was estimated by  $s_\sigma/\sqrt{n}$ , with  $s_\sigma$  denoting the standard deviation from the fibre strengths and  $n$  is the number of samples tested within each sample set.



**Figure 1:** Tensile strength preservation of different alumina layer thickness after CVD processing. Losses in tensile strength due to CF etching below the red dashed line and losses due to mechanochemical reorganisation below the blue dashed line.

ALD cycles, that were in contrast to the preparation routine (described in Chapter 2) not pre-strengthened, was heavily degraded (see the blue data points). Samples with the same ALD cycle number and pre-strengthening of 0.2 % however preserved half of their initial average fibre strength. The heavy degradation of tensile strength for untensioned CF thermally treated above 550 °C has recently been referred to as mechanochemical reorganisation of the CF structure by [18]. Increased alumina thickness preserves the fibre tensile strength more. The optimal alumina layer thickness for fibre strength preservation, within the range studied, is found to be 12.8 nm (i.e. 100 ALD cycles). Increasing the alumina layer further did not prove to be beneficial (see data point at 200 ALD cycles in Figure 1).

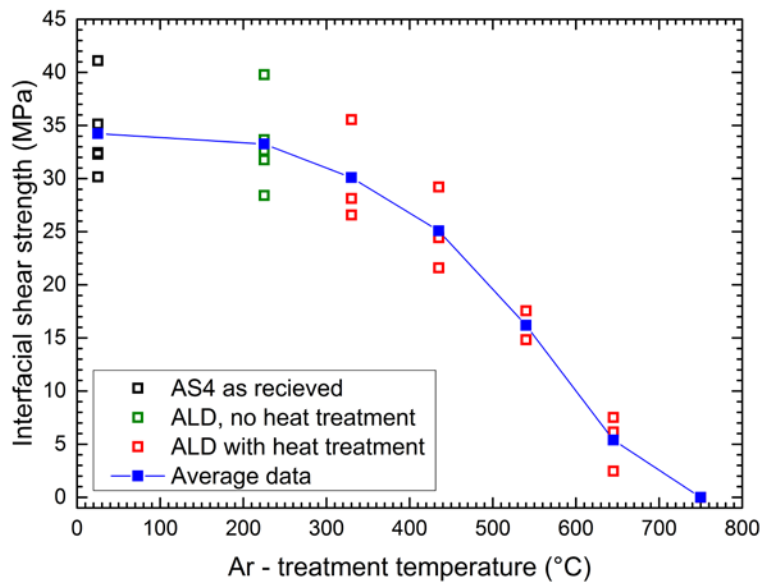
The ALD process itself did not change the fibre tensile strength (see dark green data point). If heated to 750 °C under inert atmosphere, the sample with 100 ALD cycles had the same tensile strength as samples treated with reactive gas, proving the alumina layer of 12.8 nm protects the CF from any etching and oxidation processes during CVD growth of CNTs on its surface.

Samples were prepared within a range between 0 and 200 ALD cycles, as described above. For comparison, the fibre tensile strength was measured also for i) samples directly after 100 ALD cycles, i.e. without any further treatment and ii) with a thermal treatment at 750 °C, i.e. the CVD growth temperature under inert gas (Argon) after alumina deposition of 100 ALD cycles.

The as received unsized fibre had an average tensile strength of 4,180 MPa and is shown as black dashed reference line with the standard deviation in grey in Figure 1.

The average fibre strength of samples treated with 0 and 25

### 3.2 Alumina layer adhesion



**Figure 2:** Alumina layer adhesion after thermal treatment at different temperatures characterised by measuring the interfacial shear strength according Kelly-Tyson.

The adhesion between the CF, the alumina layer and the surrounding matrix material was characterised by the interfacial shear strength (ISS), measured by SFFT. As received CF exhibited an ISS of 34 MPa, according the Kelly-Tyson model (see Eq. (3)). After ALD processing the ISS was preserved, proving that the adhesion between the matrix resin, the deposited alumina layer and the CF was as good as between matrix resin and as received fibres. However, thermal treatment at increased temperatures under inert gas decreased the ISS. By SEM imaging, the debonding was found to occur between the CF

and the alumina layer. This phenomena was attributed to i) the opposite coefficient of thermal expansion between CF and alumina layer in fibre direction, and ii) the phase transitions occurring in the alumina layer at higher temperatures [19].

## 4 Conclusion

An alumina layer has been deposited on CF before CNT growth by the CVD process. It has been demonstrated that this alumina layer can effectively inhibit degradation of the tensile strength of the CF.

The adhesion of the alumina layer on the CF at elevated temperatures is challenging, but could be circumnavigated by depositing alumina at higher temperatures and using CVD processing routes at lower temperatures, thus reducing the temperature difference between the ALD and the CVD processes.

A layer thickness of 12.8 nm (i.e. 100 ALD cycles) was found to be optimal, within the range studied, to provide good protection during CVD processing, and the fibre strength was degraded by 8-13% only. Thicker layers did not provide better protection within the context of this study.

## 5 References

1. Schürmann, H., *Konstruieren mit Faser-Kunststoff-Verbunden*. 2 ed. 2007, Berlin Heidelberg: Springer.
2. Hughes, J.D.H., *The carbon fibre/epoxy interface--A review*. Composites Science and Technology, 1991. **41**(1): p. 13-45.
3. Manocha, L.M., et al., *Effect of carbon fiber surface-treatment on mechanical properties of C/C composites*. Carbon, 1988. **26**(3): p. 333-337.
4. Fiedler, B., *Hochleistungs- Faserverbundwerkstoffe mit Duroplastmatrix*. 2009, Hamburg: TuTech Innovation GmbH. 260.
5. Fischer, J., *Carbon Nanotubes*, in *Carbon Nanomaterials*. 2006, CRC Press. p. 41-75.
6. Qian, H., et al., *Carbon nanotube-based hierarchical composites: a review*. Journal of Materials Chemistry, 2010. **20**(23): p. 4751-4762.
7. Hsieh, T.H., et al., *The effect of silica nanoparticles and carbon nanotubes on the toughness of a thermosetting epoxy polymer*. Journal of Applied Polymer Science, 2011. **119**(4): p. 2135-2142.
8. Kinloch, A.J., et al., *The fracture of glass-fibre-reinforced epoxy composites using nanoparticle-modified matrices*. Journal of Materials Science, 2008. **43**(3): p. 1151-1154.
9. Bekyarova, E., et al., *Multiscale carbon nanotube-carbon fiber reinforcement for advanced epoxy composites*. Langmuir, 2007. **23**(7): p. 3970-3974.
10. Rodriguez, A.J., et al., *Mechanical properties of carbon nanofiber/fiber-reinforced hierarchical polymer composites manufactured with multiscale-reinforcement fabrics*. Carbon, 2011. **49**(3): p. 937-948.
11. Zhang, F.-H., et al., *Interfacial shearing strength and reinforcing mechanisms of an epoxy composite reinforced using a carbon nanotube/carbon fiber hybrid*. Journal of Materials Science, 2009. **44**(13): p. 3574-3577.
12. Qian, H., et al., *Carbon nanotube grafted carbon fibres: A study of wetting and fibre fragmentation*. Composites Part A: Applied Science and Manufacturing, 2010. **41**(9): p. 1107-1114.
13. Qian, H., et al., *Hierarchical Composites Reinforced with Carbon Nanotube Grafted Fibers: The Potential Assessed at the Single Fiber Level*. Chemistry of Materials, 2008. **20**(5): p. 1862-1869.
14. Andersons, J., et al., *Glass fibre strength distribution determined by common experimental methods*. Composites Science and Technology, 2002. **62**(1): p. 131-145.
15. Kelly, A. and W.R. Tyson, *Tensile properties of fibre-reinforced metals: Copper/tungsten and copper/molybdenum*. Journal of the Mechanics and Physics of Solids, 1965. **13**(6): p. 329-350.
16. van den Heuvel, P.W.J., B. Hogeweg, and T. Peijs, *An experimental and numerical investigation into the single-fibre fragmentation test: stress transfer by a locally yielding matrix*. Composites Part A: Applied Science and Manufacturing, 1997. **28**(3): p. 237-249.
17. *Standard test method for tensile strength and young's modulus of fibers*. ASTM C 1557 - 03.
18. Steiner, S.A., R. Li, and B.L. Wardle, *Circumventing the Mechanochemical Origins of Strength Loss in the Synthesis of Hierarchical Carbon Fibers*. ACS Applied Materials & Interfaces, 2013. **5**(11): p. 4892-4903.
19. Andersson, J.M., *Ph. D. Thesis: Controlling the Formation and Stability of Alumina Phases*, in *Department of Physics, Chemistry and Biology*. 2005, Linköpings Universitet: Linköping, Sweden.