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NANOENGINEERING OF FIBRE SURFACE FOR CARBON FIBRE-CARBON NANOTUBE HIERARCHICAL COMPOSITES

Wojciech Szmyt[1], Michel Calame[2], Celestino Padeste[3], Clemens Dransfeld[4]

[1] Institute of Polymer Engineering, Fachhochschule Nordwestschweiz, Klosterzelgstrasse 2, 5210 Windisch, Switzerland, Wojciech.Szmyt@fhnw.ch, https://www.fhnw.ch/ikt
[2] Transport at Nanoscale Interfaces, Empa, Überlandstrasse 129, 8600 Dübendorf, Switzerland, Michel.Calame@empa.ch, https://www.empa.ch/web/s405
[3] Laboratory for Micro and Nanotechnology, Paul Scherrer Institute, 5232 Villigen PSI, Switzerland, Celestino.Padeste@psi.ch, https://www.psi.ch/en/lmn
[4] Aerospace Manufacturing Technologies, Delft University of Technology, Kluyverweg 1, 2629 HS Delft, The Netherlands, C.A.Dransfeld@tudelft.nl, https://www.tudelft.nl/ae/AMT

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ABSTRACT

We aim to enhance the carbon fibre (CF)-matrix interface by synthesizing carbon nanotubes (CNTs) on the surface of the CF, creating a hierarchical composite. A 12 nm thick aluminium oxide film applied by atomic layer deposition (ALD) provides protection of the CF from deterioration during CNT growth in a chemical vapour deposition (CVD) process. However, the adhesion of alumina to CF, grown in classical water/trimethylaluminium ALD is severely diminishing during CNT growth, as detected by interface shear strength (IFSS) measurements. In our approach to improve the CF-alumina adhesion, we employed a pre-treatment of the CF with ozone and entirely replaced water with ozone in the ALD process, to promote the covalent bonding of the alumina to the CF surface. The current results show a new perspective in achieving the CNT synthesis on the CF while successfully mitigating its detrimental effects on the fibre mechanical properties.

1 INTRODUCTION

Modern high-performance structural parts are often made of carbon fibre (CF)-reinforced plastics due to their excellent mechanical properties and low weight. Their mechanical advantages are well-pronounced mainly in the fibre direction, dominated by the CF properties. However, in the direction perpendicular to the fibre or upon shear loading, the mechanical performance is significantly weaker, governed by the properties of the polymer matrix and fibre-matrix interface in particular.

We aim to significantly enhance the fibre-matrix interface by synthesizing carbon nanotubes (CNTs) directly on the surface of the CF, thus creating a hierarchical composite (see: Fig. 1). The CNTs exhibit outstanding mechanical properties, which makes them a great choice for the nanoscale reinforcement. We are synthesizing CNTs directly on the CF in an aligned and dense manner. This approach results in the higher load and alignment of CNTs in the matrix between the fibres as compared to other approaches, e.g. CNT dispersion in the matrix or grafting of CNTs onto CF using electrophoresis [1]. Moreover, owing to the outstanding heat- and electrical conductivity of the CNTs, the incorporation of CNTs in the matrix results in a significant increase in the conductivities of the composite [1] desirable in many applications.

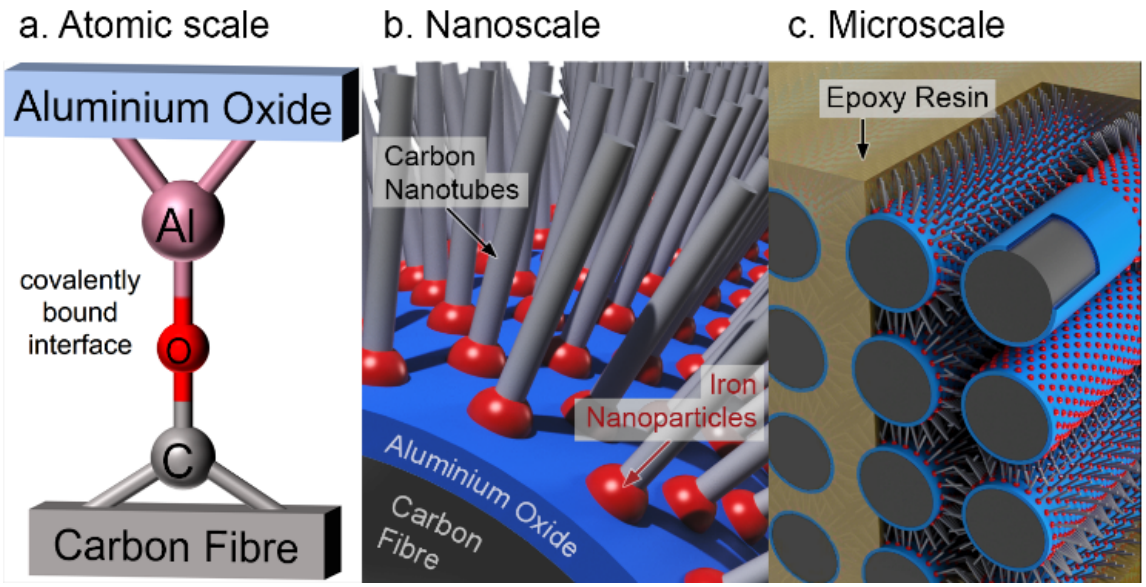

Figure 1. Schematic illustration of the scales of the hierarchical composite.

There are many challenges in the development of the hierarchical composite. It has been shown, that in the chemical vapour deposition (CVD) process of CNT synthesis, the CF mechanical properties are severely deteriorated [2]. We have identified that the migration of the iron catalyst nanoparticles into CF in is a phenomenon significantly contributing to this process. We have also established that a 12 nm thick aluminium oxide film provides a sufficient diffusion barrier, ensuring the protection of the CF in the harsh CVD conditions [3, 4]. We have however found that the adhesion of the alumina to the CF, measured as interfacial shear strength (IFSS), diminishes substantially at the high-temperature CNT synthesis conditions [3]. This issue is addressed in this study.

To ensure a good adhesion of the protective alumina film to the CF, we are developing a process that results in covalent bonding between the film and the fibre. For this purpose, we are modifying the atomic layer deposition (ALD) process used to coat the CF with alumina. In the classical alumina film synthesis, one alternately exposes the substrates to vapours of water and trimethylaluminium (TMA), forming an extremely uniform layer of aluminium oxide with atomic precision control of thickness. This process is referred to as "TMA+H_2O" in this work. In the new approach, we are employing a pre-treatment of CF with ozone and we entirely replace water with ozone in the ALD process in order to promote the covalent bonding not only at defect sites of the graphitic CF surface, but also uniformly over its entire surface. In this work, we are referring to this ALD configuration as "TMA+O_3".

So far, we have been testing the IFSS between alumina and CFs by means of single fibre fragmentation tests as described in [3]. In this study, we are employing a different micromechanical testing approach - the single fibre pull-out test. We have found it to be vastly more efficient with large sample sets when an automated embedding and testing system is employed (FIMATEST by Textechno Herbert Stein GmbH & Co. KG, Germany [5]). In order to elucidate the particular mechanisms of failure, the pulled-out fibre tips were analysed by scanning electron microscopy (SEM).

2 EXPERIMENTAL

2.1 Sample preparation and processing

Single PAN-based unsized CFs (HexTow® 12k AS4by Hexcel®) of 110 cm length and of 7.1 µm diameter were carefully separated from the continuous tow and wound around 65 mm × 65 mm quartz frames for further processing (see: Fig. 2a). During the winding, the fibres were kept under tension of 0.9 GPa (20% of the ultimate fibre tensile strength) provided by 3.6 g weight attached to the free fibre end while winding. The CFs were stabilised on the quartz frames with a ceramic adhesive that sustains temperatures up to 1400 °C.

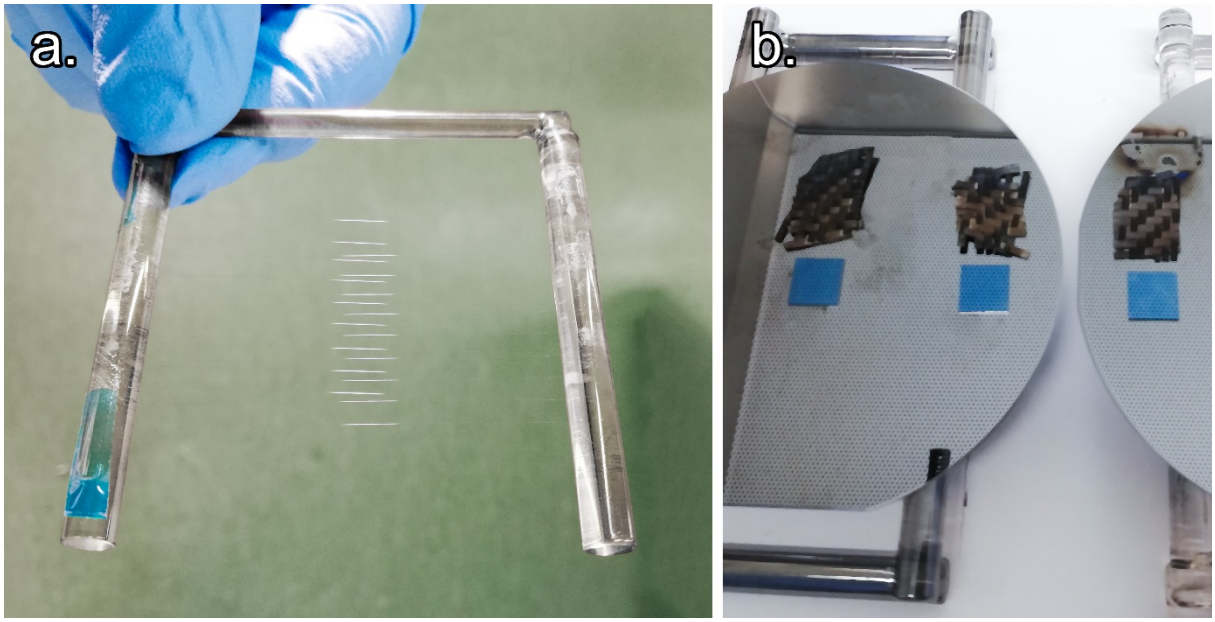

Figure 2: The types of samples analyzed in this study: a) continuous CF wound around a quartz frame under tension, stabilised by adhesive tape. The fibre is barely visible with naked due to its small diameter of 7.1 µm, however a bright reflection of light from its surface allows to distinguish its position; b) silicon pieces and CF woven pieces coated with CNT growth catalyst put on a silicon wafer support ready for CVD.

The fibres were afterwards heat-treated in air for 2 h at 400 °C in order to burn off any possible residues of sizing or other impurities and underwent 10 min room-temperature UV-ozone cleaning in air. Subsequently, ALD coating with alumina was done at two different configurations (TMA+H_2O and TMA+O_3). Alumina-coated CFs were afterwards heat-treated at various temperatures in a CVD furnace under inert atmosphere of argon to mimic the high temperature conditions of CNT growth, omitting the exposure to reactive gases. Such prepared single CFs were then subjected to pull-out testing in order to mechanically examine the CF-alumina interface. The failure CF interfaces were ultimately examined by SEM. An analogous treatment has been applied to the substrates for the subsequent CNT growth, 15 mm × 20 mm pieces of PAN-based 0°-90° CF woven and to 10 mm × 10 mm silicon wafer pieces with 100 nm thermal oxide, see: Fig. 2b. The Table 1 summarises the sample processing.

Purpose	Examination of CF-alumina interface	Demonstration of CNT growth on alumina-coated silicon wafer and on alumina-coated CF fabric	
Sample type	PAN-based single continuous CF wound on a quartz frame	Si wafer with ~100 nm thermal oxide	PAN-based 0°-90° CF woven fabric
Processing steps	2 h at 400 °C in air	Isopropanol rinsing in ultrasound	2 h at 400 °C in air
	10 min UV-plasma cleaning	10 min UV-plasma cleaning	
	Alumina ALD, 2 variants: TMA+H_2O, TMA+O_3	Alumina ALD, 1 variant: TMA+O_3	
	15 min at temperatures in range 400 °C-750 °C in Ar	CNT growth catalyst coating, CNT CVD at 725 °C	
Examination	Pull-out test, SEM, EDX	SEM	

Table 1: Summary of the sample processing.

2.2 Atomic layer deposition

The alumina ALD has been carried out in a commercial Cambridge NanoTech Inc. Savannah 100 reactor. All gases used in the system were of purity class 6.0, all liquid precursors were ALD-grade (Sigma Aldrich). The aluminium precursor was TMA. The oxidants were either ultrapure water or ozone delivered by an ozone generator OL80F (OzoneLab^{TM} Instruments) that used a feed of oxygen. Nitrogen was used as a carrier gas, which was constantly fed at 20 sccm throughout the synthesis. The reactor temperature was 225 °C, at base pressure of 48 Pa. In each deposition, the ALD consisted of 100 coating cycles resulting in a 12 nm thick alumina film [3]. In the TMA+O_3 ALD process, the ozone exposure was carried out as a first processing step in the ALD reactor. The TMA+H_2O and TMA+O_3 ALD programs are summarised in the Table 2.

ALD variant	TMA+H_2O	TMA+O_3
Ozone exposure	-	(0.1 s O_3 pulse, 1 s wait)×30
Nitrogen purging	-	40 s wait
Alumina synthesis	(0.15 s TMA pulse, 40 s wait, 0.1 s H_2O pulse, 40 s wait)×100	(0.15 s TMA pulse, 40 s wait, 0.1 s O_3 pulse, 40 s wait)×100

Table 2: Summary of ALD programs for alumina synthesis.

2.3 Heat treatment under inert atmosphere

The heat treatment process has been performed in a CVD reactor custom-made for the purpose of CNT synthesis. The reactor chamber is a quartz tube of 13.6 cm inner diameter. Argon (Ar, purity class 6.0) is delivered at one end of the quartz tube.

The continuous single fibre samples wound on quartz frames (Fig. 2a) are put on quartz stands and inserted into the reactor chamber. The system is then purged with 3 L/min of Ar for 10 min. Afterwards the heating from the room temperature to the set temperature begins, which takes ~10 min. When the temperature is reached, we wait 20 min. The oven cooldown to 200 °C takes about 2h, followed by sample extraction.

2.4 Single fibre pull-out test

The micromechanical testing method that we used to examine the fibre-matrix IFSS on the single fibre level is the singlefibre pull-out test facilitated by The semi-automatic FIMATEST system by Textechno H. Stein GmbH & Co. KG, Germany. The system is comprised of the FIMABOND embedding station and the FAVIMAT testing station equipped with the specialised fibre pull-out device. More detailed information on the system itself can be found in the literature [5, 6], while here we focus on describing our specific procedure parameters.

For embedding, the fibre is inserted into a nozzle under air suction, which stabilises the fibre in the nozzle and keeps it straight, see Fig. 3a. The fibre is trimmed to stick out by few milimeters. A crucible is placed on a heater in the embedding chamber and a droplet of epoxy matrix (low viscosity, hot-curing epoxy system Araldite® LY 564 / Aradur® 2954, Huntsman, US) is delivered into the crucible (Fig. 3b). The crucible is heated up to 70 °C in 1 min to decrease the viscosity of the resin mix. The fibre is then positioned over the middle of the droplet lowered to contact the matrix (Fig. 3d). The positioning process takes ~2 min. The embedding proceeds at 200 µm/min down to the set depth of 60 µm. Afterwards, the temperature is increased to 120 °C in 1 min and held constant for 10 min, which is enough to reach the gelation point of the matrix. Afterwards, the system is cooled down to 30 °C, the sample is extracted, put on a hot plate at 130 °C for 2 h for post-curing and cooled down to room temperature. According to a kinetic model established for this particular epoxy system [7], degree of cure of the epoxy is over 95% after this treatment. Such prepared samples are ready for the pull-out test. We prepared 6-10 samples for each IFSS datapoint, which provided enough statistics for conclusive results.

The pullout testing has been carried out at the following configuration: the load cell of maximum force of 210 cN was installed, the pull-out speed was set to 100 µm/min. The software provided by Textechno evaluates the following quantities describing the mechanical performance of the interface:

critical interfacial energy release rate, apparent IFSS, local IFSS, interfacial frictional stress, debonding work and pull-out work, based on the theoretical framework described and discussed in [8-10]. While we are focusing on the stress-controlled debonding, the comparison of the mechanical performance of our samples is based on the value of the local IFSS. This way, we avoid the influence of the friction and scale effects on the measured IFSS value (no averaging or apparent behaviour) [8]. Therefore, in this work the IFSS refers to the local IFSS.

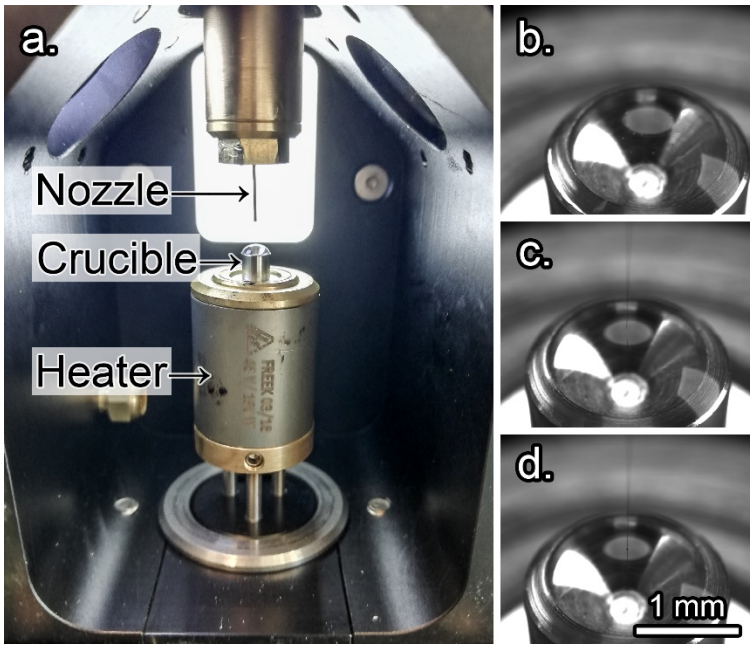

Figure 3: Single fibre pull-out test sample preparation in FIMABOND system – embedding phase; a – picture of the embedding chamber, b – epoxy droplet in a crucible heating up, c – fibre approaching the middle of the droplet, d – fibre-matrix contact, embedding at a desired length.

2.5 Scanning electron microscopy and Energy-Dispersive X-ray spectroscopy

The topographic qualitative imaging of the pull-out failure surfaces has been carried out in a Hitachi S-4800 high-resolution SEM equipped with the cold field emission gun. The working distance was kept at ~5 mm, acceleration voltage was set to 5 kV. The imaging has been carried out using a secondary electron detector.

3 RESULTS AND DISCUSSION

3.1 Interface shear strength

The results of the mechanical testing of the fibre-matrix interface are summarised in Fig. 4. Of note is that the error bars represent the 95% confidence intervals of the mean value obtained by a bootstrap method described in more detail in [11]. This method is advised for an accurate evaluation of distributions of statistical estimators given small number of samples [12], like in the case of this study.

From the available data we can clearly conclude, that there is a declining trend of the IFSS at increasing heat treatment temperatures for the CFs coated with aluminium oxide with the classical TMA + H_2O ALD (blue open squares in Fig. 4). This observation is in agreement with our previous findings from single fibre fragmentation testing [3], which constitutes a confirmation, that the alumina-CF interface degrades upon exposure to thermal treatment equivalent to the CNT growth conditions by CVD. The sample corresponding to the datapoint at 225 °C did not undergo heat treatment other than during the ALD process, which itself is carried out at 225 °C.

Our new approach of pre-treatment of the CF with ozone and replacing water with ozone entirely in the ALD process (TMA + O_3) was hypothesised to i) improve on the thermomechanical stability of the interface as compared to TMA+H_2O and ii) to retain the IFSS at the level of interface between

the matrix and pristine fibre. The experimental data is clearly confirming that the both hypotheses. Hence, we conclude, that with the TMA+O_3 ALD approach, the CF is protected by the alumina film against the harsh CVD conditions, while the mechanical properties of alumina-CF interface are preserved and will not constitute a weak spot of the hierarchical composite ultimately aimed for.

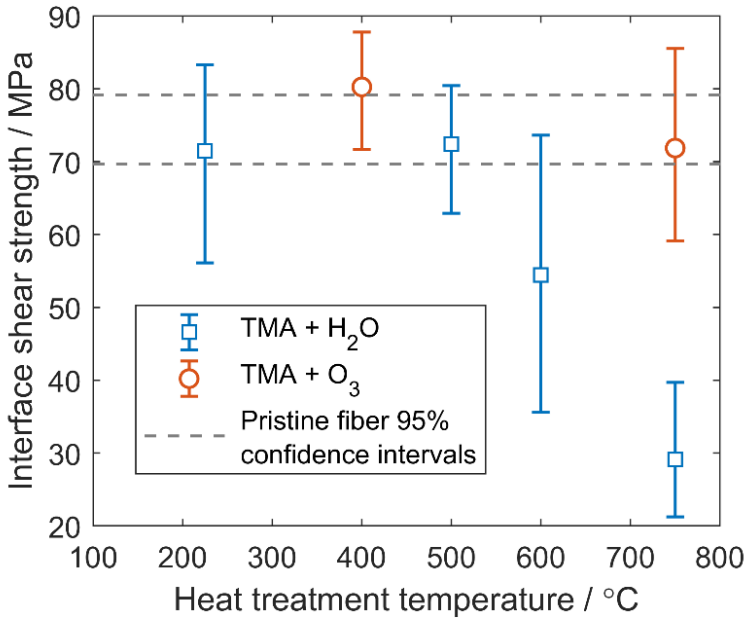

Figure 4: IFSS measured by pull-out tests of alumina-coated CF in two different ALD configurations: classical TMA+H_2O and TMA+O_3, after heat treatment under inert atmosphere of Ar in the CVD furnace. The dashed line represents the 95% confidence interval of the IFSS between pristine fibre and the matrix. Error bars represent 95% confidence intervals obtained by a bootstrap method.

3.2 CF-epoxy interface failure analysis

The CF tips after pull-out tests were examined with SEM, see Fig. 5. The secondary electron contrast in the SEM images is indicating that the sample TMA+H_2O heat treated at 600 °C has two distinct surfaces. Because of the fact, that alumina is an insulator, it tends to give higher secondary electron contrast due to charging effects. Apparently, parts of the alumina film were peeled off in the course of the pull-out test. This means, that the alumina-CF interface failed on a large fraction of the embedded surface. The sample TMA+O_3 heat treated at 750 °C however does not exhibit this kind of feature – the alumina film remained on the CF surface and the failure has occurred at the alumina-resin interface.

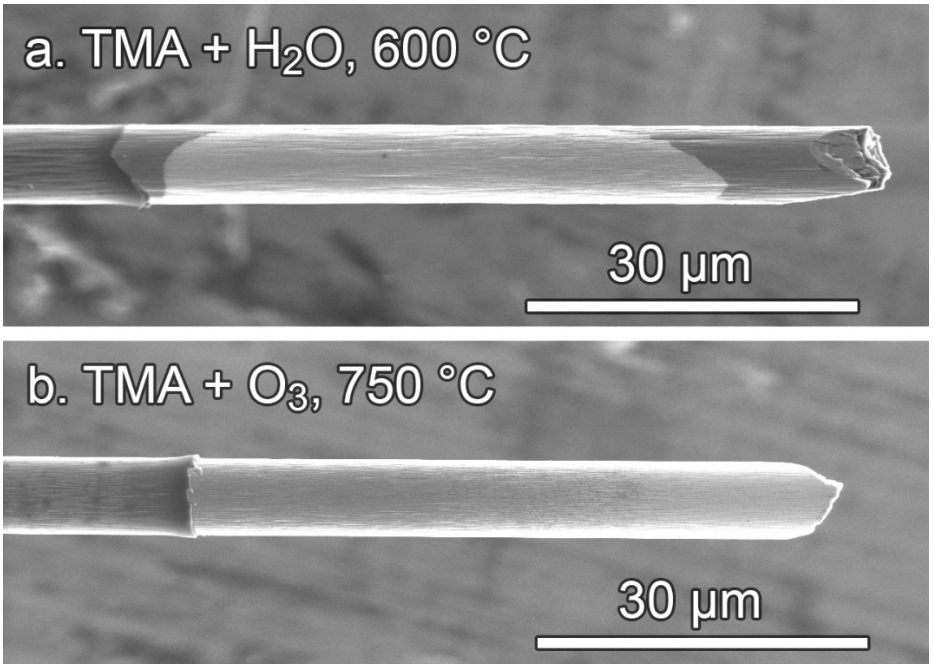

Figure 5: Interface failure analysis by SEM imaging of the typical fibre tips after pull-out test ALD configuration and heat treatment temperatures are noted on the in the figure.

4 OUTLOOK - CNT GROWTH

Having established a thermomechanically stable alumina interface we are now aiming for a CF-CNT-epoxy based hierarchical composite. Here, we are showing preliminary results of CNT syntheses that we found to be reproducible and applicable to alumina-coated surfaces. The substrates may be flat, like Si wafers, or complex, like CF woven fabrics. For a homogeneous CNT growth, it is critical to coat the surface uniformly with a thin film of catalyst. Prior to the catalyst coating, the samples were coated with Al_2O_3 using the TMA+O_3 process. We developed a method of catalyst coating that relies on surface functionalization with amine groups, which subsequently facilitates the uniform precipitation of catalyst precursor from an iron salt solution. The CVD of CNTs was performed at 725 °C in a similar way as described in our previous work [4]. The SEM images of the preliminary growth results are given in Fig. 6. Fig. 6a shows an overview image of the CNT carpet, part of which was scratched off with a razor blade in order to expose the cross section. The growth is remarkably homogeneous. The higher magnification images (Fig. 6b,c) qualitatively indicate a high apparent degree of CNT alignment and high areal density of the CNT forests on the Si substrate. The images in Fig. 6d-f demonstrate the homogeneous CNT growth obtained on the CF woven. A high areal density and alignment of CNTs is preserved when the technique is applied to as complex substrates as CF at growth length extending over several microns.

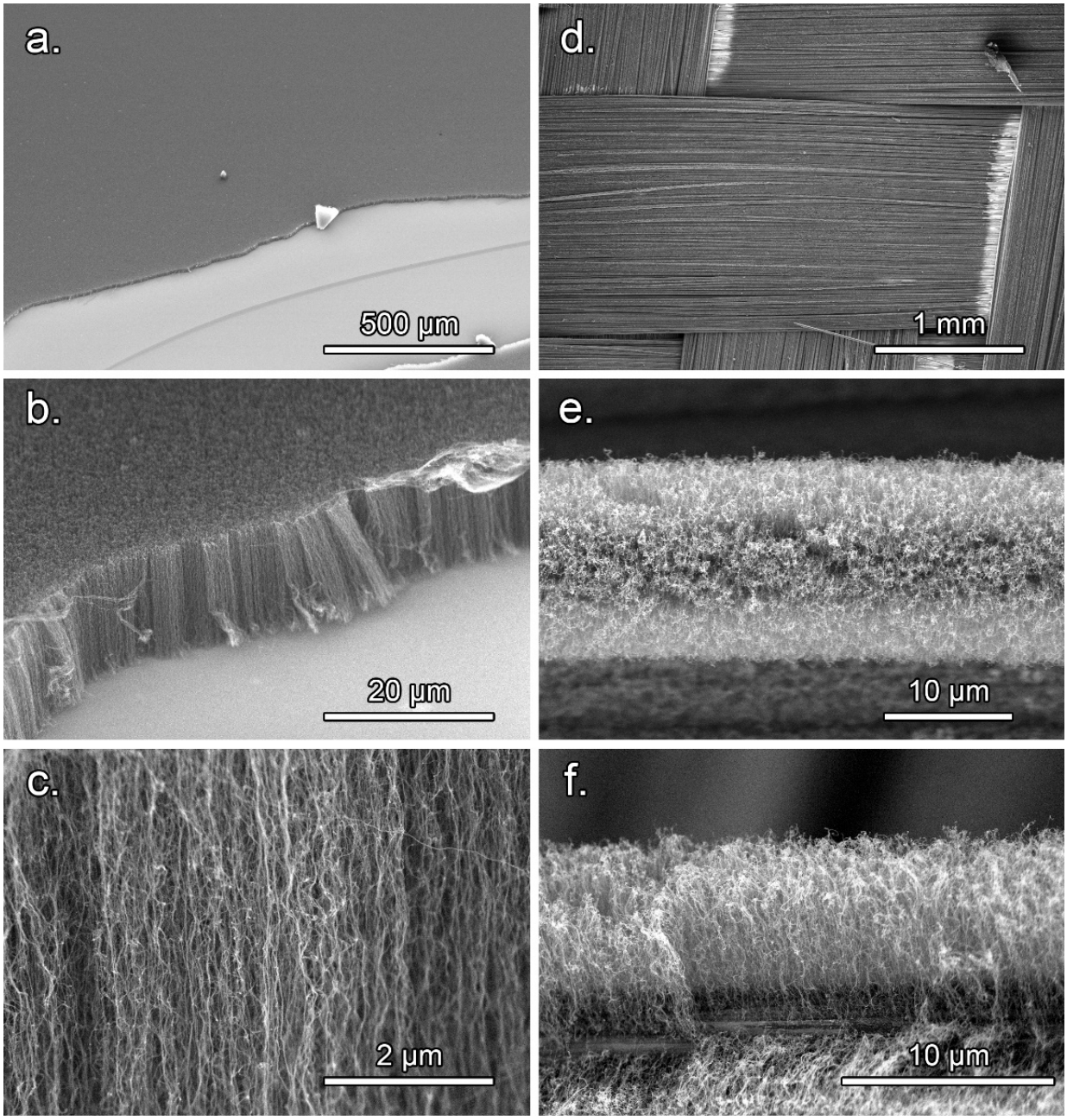

Figure 6: SEM imaging of preliminary CNT growth results on a flat substrate of Si wafer (images a-c) and on complex surface of CF (images d-f) at increasing magnifications (top to bottom).

5 CONCLUSIONS AND OUTLOOK

The current results show a new perspective on achieving the CNT synthesis on CFs while successfully mitigating the detrimental effects on the fibre mechanical properties in the process. The 12 nm thick alumina film protects the fibre under the CVD conditions and we have developed a method that allows to preserve the CF-alumina IFSS. As a consequence, the CF-alumina interface shear strength will not constitute a weak spot of the composite after the CNT growth is performed. Moreover, we have presented the CNT growth of high degree of apparent alignment and density. The CVD parameters still need to be optimised for the desired length of the CNTs and the influence of CNTs on the fibre-matrix IFSS remains yet to be tested. The findings of this study constitute a significant step in the close investigation and development of hierarchical fibre architectures in polymer matrices.

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