HIERARCHICAL COMPOSITES WITH CARBON NANOTUBE GRAFTED FIBRES

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ABSTRACT

The study of reinforcing conventional fibre/matrix composites by grafting carbon nanotubes (CNTs) onto fibre surfaces is reported. Carbon nanotubes were grown on silica and carbon fibres using the chemical vapor deposition (CVD) method; however, two different methods were used for introducing the iron catalyst. The morphology of the products was characterized using scanning electron microscopy (SEM), which showed a higher density of CNT grafting on silica fibres compared to that on carbon fibres. Single fibre tensile tests on individual fibres, before and after the CNT growth, indicated a degradation in fibre strength that has been attributed either to the catalyst etching or dissolution of the fibre surface. Model composites based on CNT-grafted fibres/PMMA were fabricated in order to examine apparent interfacial shear strength (IFSS). A dramatic improvement in IFSS over silica fibre-based composites was observed, but relatively less improvement was shown in the case of carbon fibres. The different IFSS results were provisionally attributed to the different morphology and density of CNT grafting on fibres.

1. INTRODUCTION

Carbon nanotubes have generated huge activity in composites science due to their low density, high aspect ratio, intrinsically superior mechanical properties and remarkable electrical and thermal properties. Many studies have reported the production and characterisation of CNT-based polymer composites [1, 2]. Although promising results have been obtained, progress has been limited by several factors, including nanotube synthesis, dispersion, alignment and interfacial bonding. On the other hand, traditional fibre-reinforced composites are currently used in a wide range of fields; although they have excellent in-plane properties, the relatively weak compression and transverse performance remain a major issue [3]. Thus, one of the desirable approaches to introduce CNTs into conventional composites is to graft carbon nanotubes onto the fibre surfaces, forming a hierarchical structure [4, 5]. The approach is to exploit the CNT performance to enhance the longitudinal compression and interlaminar performance of fibre/matrix composites. The presence of the CNTs at the fibre surface is likely to enhance the fibre/matrix interfacial strength, thus improving the delamination resistance. Such reinforcement radial to the fibres, extending into the surrounding matrix, will inhibit fibre microbuckling, which is the critical failure mode under compressive loading [6].

The single fibre fragmentation test, which has developed from the early work of Kelly and Tyson [7], is commonly used to evaluate the interface properties of fibre/matrix composites. The test is performed under a light microscope so that the fragmentation process can be observed in-situ. A single fibre is axially aligned in a specimen of matrix material, and loaded in tension. The tensile stress is transferred to the fibre through interfacial shear strength. As the shear strength reaches the fibre tensile strength, the fibre breaks. Since the fractured fibre segments continue to carry load, further increases in strain leads to additional fibre breaks. The process continues until a

saturation point is reached. At this point, the fibre is too short to transfer enough shear stress for further breaks. The fragment length can be measured. Given a constant fibre diameter and strength, shorter fragment lengths imply a stronger interface.

The present study investigates the feasibility of reinforcing conventional fibre/matrix composites by grafting CNTs onto fibre surfaces. A variety of methods were applied on silica and carbon fibres for the CNT growth. Mechanical properties of individual fibres were tested before and after the grafting process. Model composites with CNT-grafted fibres were fabricated to examine the interfacial shear strength (IFSS) using single fibre fragmentation tests. Different degrees of improvements in IFSS were observed for the composite specimens containing CNT-grafted fibres, which could be related to the morphology and density of the CNT grafting.

2. EXPERIMENTS

2.1 Materials

Commercially available Silfa silica fibres (Albert Hellhake GmbH, Germany) and polyacrylonitrile(PAN)-based IM7 carbon fibres (Hexcel Composites) were used for this work. To improve the surface chemical reactivity, the carbon fibres were modified using a wet chemical method [8, 9], including an acid oxidation (65% HNO3, Fluka), followed by a base wash (0.05 M NaOH, Fluka).

2.2 Growth of CNTs on fibres

CNTs were synthesised on silica fibres using the injection chemical vapour deposition (CVD) method, which involves the pyrolysis of solutions containing both the catalyst precursor and the carbon source [10]. The reactions were carried out in a tubular quartz reactor (50 mm in diameter) equipped with an electrical furnace (PTF 12/50/610, Lenton). The fibres were held by an alumina frame holder and placed in the middle of the furnace to expose them to the hydrocarbon source. A feed solution of 3% weight fraction of ferrocene in toluene was injected continuously into the reaction tube at a rate of 5 ml/h using a syringe pump (KDS100, Linton). The liquid feed was preheated to 200 ºC, immediately volatilised and swept into the furnace by a flow of carrier gas, argon (Ar). The reaction temperature was 760 ºC.

However, the as-received surface of the carbon fibres was not conducive to this method, and therefore an incipient wetness techniques [11] were employed to load the catalyst on the fibre surface prior to the CVD synthesis. The iron catalyst was introduced onto the oxidised carbon fibres using a 100 mM ethanol solution of $Fe(NO_3)_3 \cdot 9H_2O$ (A.C.S reagent, Aldrich); a final iron loading of 0.1 wt% was achieved. The growth of CNTs on the catalyst pre-deposited carbon fibres was achieved by using acetylene (C_2H_2) as the hydrocarbon source by the CVD method in a tubular quartz furnace (~50 mm in diameter). A 10% H_2/Ar mixture was used as the carrier gas. The reactions were performed at 750 °C for 1 h using a 1:300 flow ratio of C_2H_2 to carrier gas. The modified carbon fibres were characterised using a field emission gun scanning electron microscope (Gemini LEO 1525 FEG-SEM, Carl Zeiss NTS GmbH).

2.3 Single fibre tensile tests

Single fibre tensile tests were carried out at room temperature, according to the British industrial standard ISO 11566:1996 using a TST 350 tensile stress testing system (Linkam Scientific Instrument Ltd.) equipped with a 20 N force sensor. A single fibre was glued at either end onto a small piece of cardboard for better handling. The gauge

lengths were 15, 25 and 35 mm. A typical crosshead speed of 15 μm/s was applied for the tests. A minimum of twenty measurements were recorded for each fibre specimen at each gauge length. The system compliance C was not insignificant and was estimated under the relevant experimental conditions. The apparent elastic modulus was therefore corrected using the following equation (BS ISO 11566:1996 Method B):

$$E = E^* \Big/ \left(1 - C\frac{E^* A}{L}\right) \tag{1}$$

where C is the system compliance E^* is the apparent modulus, derived from the gradient of the stress-strain curve A is the cross-sectional area of the fibre, and L is the gauge length.

2.4 Single fibre fragmentation tests

Single fibres were glued at either end onto glass slides by using double sided tapes with a defined thickness of approximately 100 μm. A solution of 10% weight fraction of poly(methyl methacrylate) (PMMA) (PLEXIGLAS® zk6BR, Degussa) in 1,4-dioxane (Sigma-Aldrich) was prepared and cast onto the glass slides, covering the fibres completely. The films were dried for 48h in the fume hood and afterwards 24h in a vacuum oven to remove any trace of solvent. The dumbbell shaped specimens were then cut and tested on a TST 350 tensile stress testing system (Linkam Scientific Instrument Ltd.). The dimensions of the specimens tested were around 0.2 mm thick, 4 mm wide and 30 mm long. During the tests, the specimens were strained up to 25% to ensure saturation at a crosshead speed of 15 μm/s and the entire single fibre fragmentation process was monitored via polarized light microscopy (Wild, Heerbrugg, Switzerland). Approximately 20 specimens were tested for each case. The fibre fragment lengths were measured after testing, under an Olympus BX51M reflected light optical microscope using an Olympus DP70 camera system. The apparent shear strength at the interface can be estimated from the simple Kelly-Tyson model [7]:

$$\tau_{IFSS} = \frac{\sigma_f d_f}{2l_c} \tag{2}$$

$$l_c = \frac{4}{3} l \tag{3}$$

where σ_f is the fibre strength at the critical length, d_f is the fibre diameter, l_c is the critical fragment length of the fibre, which can be obtained from the mean fibre fragment length l at saturation [12].

3. RESULTS AND DISCUSSION

3.1 Growth of CNTs on fibres

Surface morphologies of the silica fibres after different CVD growth time are shown in Figure 1. Well-aligned CNTs were successfully grown onto the silica fibre surfaces, resulting in a brush-like structure. It is believed that in the early stage of the growth, the CNTs sterically interacted and were gradually forced to grow perpendicularly to the surface, due to the dense number of nucleation sites formed by the initial deposition of ferrocene [10]. As expected, the length of CNT-grafting was increased from a few microns to a few tens of microns when the growth time was varied from 12 minutes (Figure 1b) to 15 minutes (Figure 1c). The average diameter of the grafted CNTs is around 50 nm. By deliberately removing the grafted CNTs with a razor blade, many

particles and holes were observed on the silica fibre surfaces (Figure 1d). This observation suggests that the expected, base growth mechanism [10] is active, i.e., the new carbon is extruded from the catalyst particle at the fibre base. The pitting also shows that the CNTs were attached to the fibre surface via an etching or some other chemical reaction between the catalyst and the substrate. Similar surface damage has been reported in the CNT growth reactions [13], which involved the high-temperature pyrolysis of iron phthalocyanine (FePc).

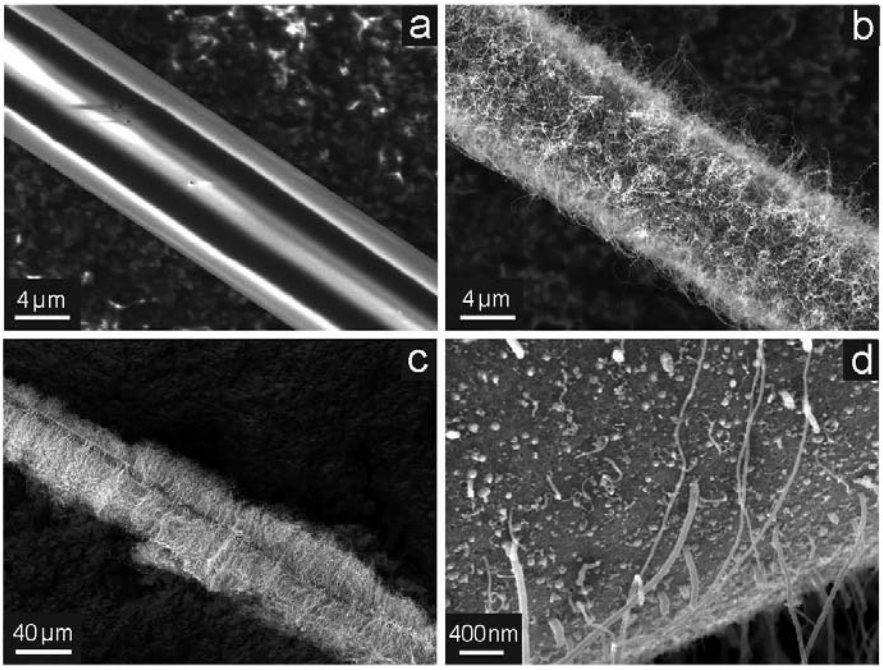

Figure 1: SEM images of Silfa silica fibres (a) before and after (b) 12 min, (c) 15 min growth reaction using the injection CVD method and (d) after deliberate removal of the CNT-grafting.

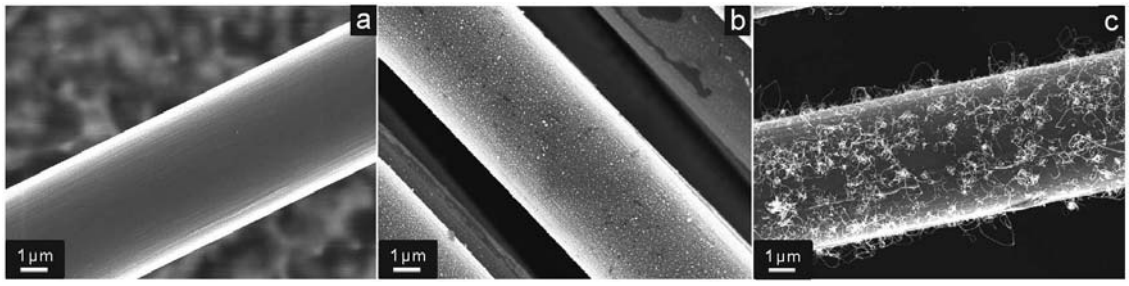

Figure 2: SEM images of IM7 carbon fibres (a) before and after (b) deposition of iron catalyst particles and (c) CNT growth using the CVD method.

Carbon fibres were characterised using scanning electron microscopy after different treatments (Figure 2). After performing the incipient wetness technique, iron particles with diameters of between 20 and 45 nm were uniformly coated onto the fibre surface (Figure 2b). These particles acted as the catalyst for CNT growth, giving rise to a relatively homogeneous CNT-grafting (Figure 2c). The diameter of the CNTs grown on the surface was in the range of 20 to 50 nm, which was consistent with the diameter of iron particles, indicating that the diameter of CNTs synthesised via CVD was strongly

dependent on the size of the catalyst nanoparticles employed for their growth [14]. It was reported in earlier work [9] that the initial oxidation of the carbon fibres before catalyst deposition is crucial. Presumably, the oxygen-containing groups present after acid treatment, particularly carboxylate groups, encouraged wetting and helped to stabilise small iron particles on the surface, during the initial metal deposition.

3.2 Single fibre tensile tests

Single fibre tensile tests on both types of fibres before and after CNT growth were carried out at three different gauge lengths and the results are given in Figure 3 (silica fibres) and Figure 4 (carbon fibres). The strength of silica fibres fell by around 30% after the grafting process, an effect that presumably relates to the surface damage shown in Figure 1d. Moreover, the fibre strength decreased slightly as the CVD reaction time increased from 12 minutes to 15 minutes, which may be due to the increasing density of the catalyst during the early stages of CNT growth. It is well known that the flaw-induced nature of fibre failure results in a length dependence for its tensile strength [15]. Indeed, the averaged tensile strength of all the fibres decreased as the gauge length increased. The Weibull distribution [16] was fitted to the data in order to account for the length dependency of the strength (Figure 3a). The good correlation between the Weibull predictions and the experimental data with increasing gauge length indicates that the surface damage was relatively homogeneous and consistent with a uniform distribution of nanoscale pitting over the whole fibre surface. In addition, a significant increase of the fibre modulus after the grafting process was detected, which may be attributed to crystallization of silica fibres during the high temperature reaction.

In the case of the carbon fibres (Figure 4), the tensile test results again showed a decrease in the fibre strength after the CNT grafting process, of around 17%. The degradation was attributed to the dissolution of iron into the carbon fibres at the reaction temperature, as reported in the earlier work [9]. The Weibull distribution was again used to account for the length dependency and demonstrated good correlation. However, the tensile modulus of the fibres was unaffected, suggesting an undamaged fibre core.

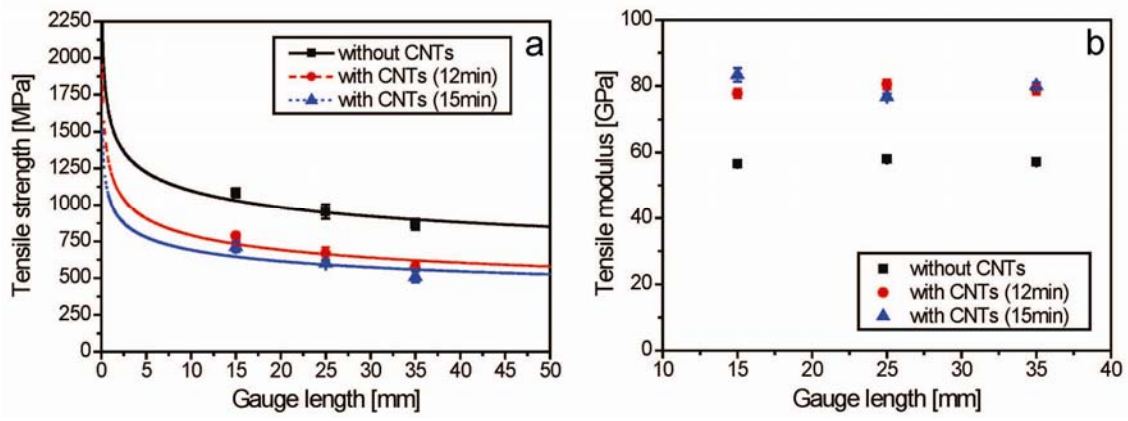

Figure 3: (a) Tensile strength and (b) tensile modulus plotted as a function of gauge length for the silica fibres. The Weibull distribution (shown as lines) in (a) accounts for the gauge length dependency of the tensile strength.

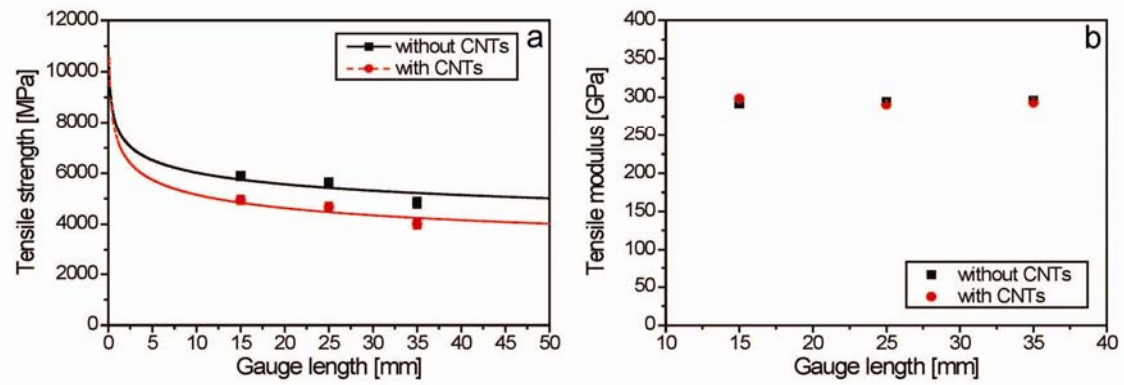

Figure 4: (a) Tensile strength and (b) tensile modulus plotted as a function of gauge length for the carbon fibres. The Weibull distribution (shown as lines) in (a) accounts for the gauge length dependency of the tensile strength.

3.3 Single fibre fragmentation tests

The composite specimens after the fragmentation tests were examined and typical micrographs are shown in Figure 5 (silica fibres) and Figure 6 (carbon fibres). The shape of the fibre breaks can give a meaningful indication of the interface strength [17]. For the composite specimen with as-received silica fibres, shown in Figure 5a, the fibre cracks did not damage the matrix and exhibited significant debonding of the interface, which typically indicates a relatively weak interfacial system. In contrast, a strong interface can often introduce damage to the matrix around the fibre breaks; this effect was observed in the composite specimens with CNT-grafted silica fibres (Figure 5b, c). The carbon fibre samples showed similar results. The crack shapes of the composite specimens without CNTs showed no damage of the matrix around the fibre breaks and apparent debonding of the interface (Figure 6a), implying a relatively weak interface. After grafting CNTs, the failure of the composite specimen indicated a moderately strong interface bond, with a mixture of break widening and deformation of the matrix (Figure 6b) apparent.

After fragmentation, fragment lengths distributions were obtained. The statistical analyses are summarized in Figure 7 (silica fibres) and Figure 8 (carbon fibres). It is clear in the histogram plot (Figure 7a, 8a) that the composite specimens with CNT-grafted fibres, regardless of the fibre types, displayed shorter fragment lengths than the composite specimens without CNTs, resulting in a shift to lower fragment length in the cumulative distributions (Figure 7b, 8b). It is generally accepted that the change of the curve shape in the cumulative distributions can be attributed to differences in fibre strength variability. A shorter fragment length may be caused by better fibre/matrix adhesion or by a lower strain to failure of the fibre; both may have been affected by the CNT-grafting process. Thus, a further quantitative study of the interfacial shear strength (IFSS) was performed by using the Kelly-Tyson model, the results of which are shown in Table 1. As discussed previously, the Weibull distribution was used to account for the length dependency of fibre strength, so the fibre tensile strength at the critical length can be predicted from the distribution and used in the calculation. It is clear that the IFSS increased dramatically, up to 150%, by grafting the silica fibres with CNTs; the improvement can be attributed to the increased surface area, and the interaction between CNTs and the matrix. The improvement in IFSS was dependent on the length of the CNT grafting, with the shorter CNTs appearing more effective; further investigations of the optimal grafting length for reinforcement are warranted. For

carbon fibres, the IFSS again increased after CNT grafting; however, the increase was relatively lower (around 26%), possibly due to the relatively low density of CNT-grafting. Presumably, with further development of the grafting process, higher loadings of CNTs could be obtained on carbon fibres, leading to further increases in the IFSS.

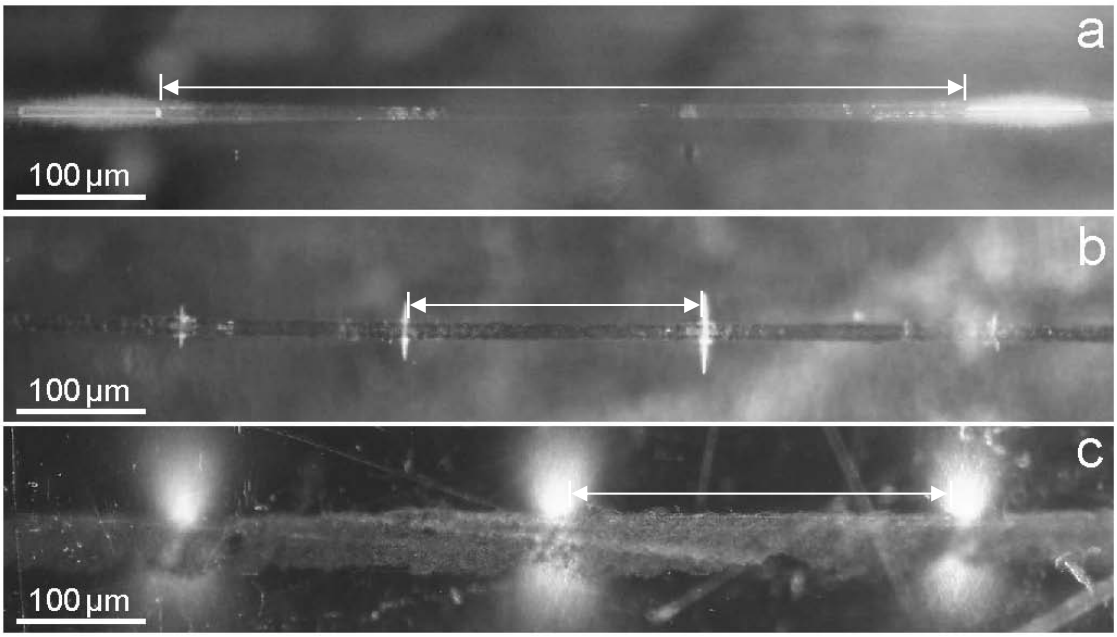

Figure 5: Dark field micrographs of the silica fibre breaks in the PMMA matrix after the fragmentation test. The white areas represent the cracks and the arrows indicate the fragment length. (a) Before CVD reaction, (b) after 12 min and (c) after 15 min CVD reaction.

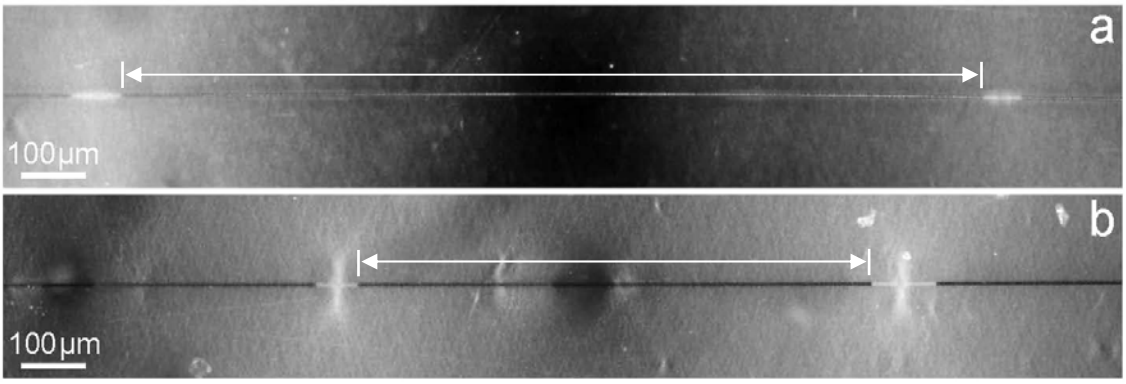

Figure 6: Dark field micrographs of (a) as received and (b) CNT-grafted carbon fibre breaks in PMMA matrix after the fragmentation test. The white areas represent the cracks and the arrows indicate the fragment length.

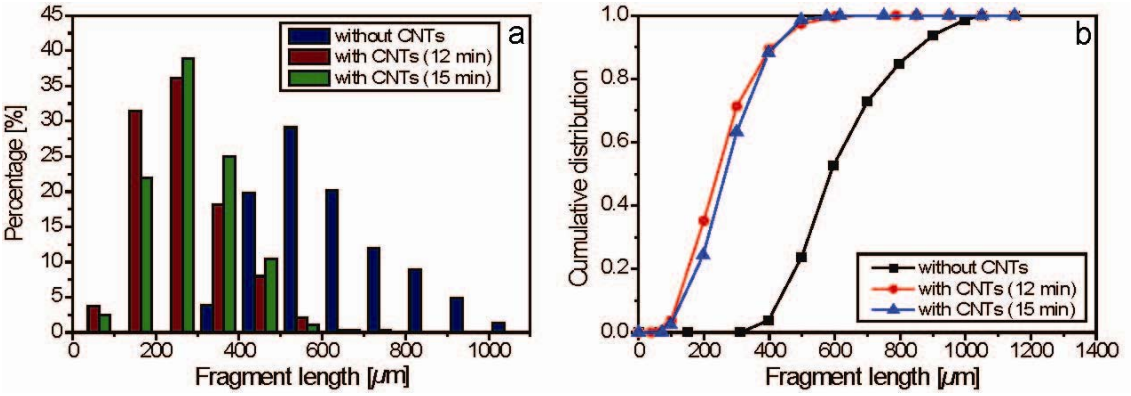

Figure 7: (a) Histogram and (b) cumulative distributions of fragment lengths for as-received and CNT-grafted silica fibres.

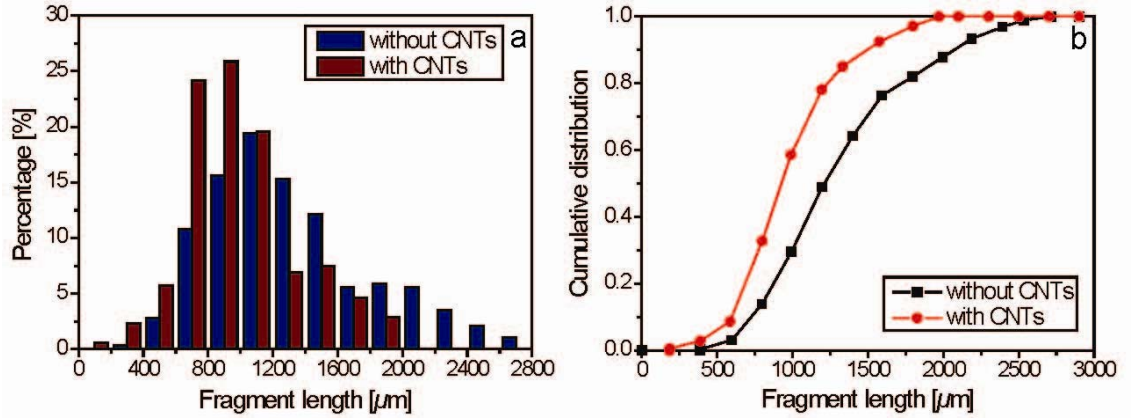

Figure 8: (a) Histogram and (b) cumulative distributions of fragment lengths for as-received and CNT-grafted carbon fibres.

Table 1. Single fibre fragmentation test results for the investigated silica and carbon fibres. The fibre tensile strengths at critical length are predicted from the Weibull distribution. The standard errors are shown in the parentheses.

fibre	CNT-grafting	σ_f (MPa)	d_f (μm)	l_c (μm)	τ_{IFSS} (MPa)
silica fibre	without CNTs	1630	9	820 (10)	9.5 (0.1)
	with CNTs (12 min)	1540	9	340 (10)	24.3 (0.3)
	with CNTs (15 min)	1220	9	370 (10)	17.0 (0.3)
carbon fibre	without CNTs	7360	5.2	1750 (40)	12.5 (0.2)
	with CNTs	7070	5.2	1310 (40)	15.8 (0.4)

4. CONCLUSIONS

CNTs can be grafted to silica and carbon fibres using the CVD method, using appropriate methods to incorporate catalyst. The single fibre tensile tests revealed that the grafting process resulted in a decrease in the tensile strength of pristine fibres, which can be attributed to the catalyst etching or dissolution into fibres. The tensile

modulus was unaffected for carbon fibres, but increased in the case of silica fibres, probably due to a limited degree of devitrification. Single fibre fragmentation tests indicated that the IFSS can be improved by 150% after grafting silica fibres with CNTs; the increase in IFSS was lower (around 26%) in the case of carbon fibres, which may be attributed to the relatively low density of CNT-grafting. Thus, the length and density of the CNT-grafting significantly influence the interfacial properties of fibre/matrix composites. The approach of grafting CNTs onto fibre surfaces has wider implications than simply increasing IFSS; it provides a controlled means of introducing high loadings of oriented nanotubes into the matrix of conventional fibres composites. In principle, with development, the methodology should yield CNT-grafted fibres suitable for improving critical engineering properties of conventional fibre reinforced composites, such as inhibiting microbuckling during compressive loading. The ideal density, diameter, and length of the grafted CNTs remain to be determined.

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