Carbon nanotube grafted silica fibres:

Characterising the interface at the single fibre level

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Abstract

Model polymer composites containing carbon nanotube (CNT) grafted fibres provide a means to investigate the influence of nanostructures on interfacial properties. Well-aligned nanotubes, with controllable length, were grown on silica fibres by using the injection chemical vapour deposition method, leading to a significant increase of the fibre surface area. In single fibre tensile tests, this CNT growth reaction reduced the fibre strength, apparently due to catalyst etching; however, the fibre modulus increased significantly. Contact angle measurements, using the drop-on-fibre method, indicated an excellent wettability of the CNT-grafted fibres by poly(methyl methacrylate) (PMMA). PMMA model composites were fabricated and studied using the single fibre fragmentation tests. A dramatic improvement (up to 150%) of the apparent interfacial shear strength (IFSS) was obtained for the composites containing CNT-grafted fibres. The improvement of IFSS was also influenced by the length and morphology of the grafted CNTs.

Keywords: A. Carbon nanotubes; A. Hybrid composites; B. Fragmentation;

B. Interfacial strength; E. Chemical vapour deposition (CVD)

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1. Introduction

The idea of incorporating CNTs into conventional fibre-reinforced polymer composites has attracted significant interest from the composite industry [1], particularly in the field of high performance, continuous fibre structures. Such materials, based on aligned fibre tows or weaves, possess outstanding in-plane properties but relatively weak out-of-plane (or through thickness) properties, which control compression and delamination performance [2]. CNTs, in themselves, are promising components for composite materials due to their nanoscale dimensions, low density, intrinsically superior mechanical properties, and remarkable electrical and thermal properties [3, 4]. However, their introduction into conventional continuous fibre composite structures, may provide a means to mitigate matrix-dominated failures. One particularly attractive strategy is to graft CNTs onto the primary reinforcing fibre surfaces, forming a hierarchical structure. This approach has the potential to provide high loadings of CNTs in the composites, while alleviating the critical problems that usually encountered in the composite fabrication process, such as extremely high viscosity, agglomeration and self-filtration [5]. In addition, the CNTs can be grown perpendicularly to the fibres, expected to be the ideal orientation to enhance the transverse performance of conventional fibre reinforced composites. Similarly, the radial array of CNTs extending into the surrounding matrix may inhibit microbuckling, a critical failure mode especially associated with uniaxial fibres under compression [6]. As well as enhancing matrix properties, locating the CNTs at the fibre surface may be a particularly effective method to improve fibre-matrix interface, as discussed in detail within this paper. Lastly, as for pure nanocomposites [3, 4, 7], the introduction of CNTs may improve other important properties including, for example, wear resistance, flame retardance, or self-sensing

abilities; by exploiting the excellent thermal and electrical performance of CNTs, a new generation of multi-functional structural composite materials may be produced [1, 8].

The interface between fibres and matrices is known to be a critical parameter in controlling the overall performance of conventional polymer composites. Good adhesion between fibres and matrices is a precondition for stress transfer [9-11]. Reinforcing fibres are often modified to increase chemical or mechanical interactions [12], for example by oxidation [13, 14] or whiskerization [15]. Grafting of CNTs is expected to increase the surface area, also create mechanical interlocking, and/or local stiffening at the fibre/matrix interface, all of which may improve stress transfer. Downs and Baker [16] first reported an increase of around 4.75 times (in the best case) of the IFSS of the composites with carbon nanofibre-grafted carbon fibres. An improvement of interfacial load transfer was subsequently reported by grafting CNTs on carbon fibres [17]. More recently, a 60% improvement of IFSS was observed for the CNT-grafted carbon fibres/epoxy composites [18]. Although some promising results have been obtained, a better understanding is required of the critical factors that determine the composite interfacial properties, such as the surface area, fibre wettability, and CNT dimensions.

Chemical vapour deposition (CVD) techniques are the most promising route for large scale production of CNTs, capable of meeting the criteria for composite applications, specifically, low cost, bulk production, high purity, and acceptable quality. CVD is also the most common method for grafting CNTs onto fibre surfaces [17-22]. In the present study, a simple injection chemical vapour deposition (ICVD) method was used to grow CNTs on silica fibres; CNT-grafting with different lengths was produced by varying the growth time. The effects of the grafting process on the tensile mechanical properties of silica fibres were evaluated because these properties dominate the in-plane performance

of continuous fibre composites. Direct contact angle measurements, using the drop-on-fibre method, were used to study the wettability of CNT-grafted fibres by the polymer matrix. In addition, single fibre fragmentation tests were conducted on model composites to determine the IFSS.

2. Experimental

2.1. Materials

Commercially-available, sized silica fibres (Silfa, Albert Hellhake GmbH) were thermally desized at 600 °C for 1h. Poly(methyl methacrylate) (PMMA) (PLEXIGLAS® zk6BR, Evonik Röhm GmbH) was selected as the matrix for single fibre fragmentation tests, which requires a relatively high strain at break. All chemicals were used as-received.

2.2. Grafting CNTs on fibres

CNTs were grafted onto silica fibres using the ICVD method, which involves the pyrolysis of solutions containing both a catalyst precursor and a hydrocarbon source [23, 24]. 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 wt.% of ferrocene (98%, Aldrich) in toluene (BDH AnalaR grade, VWR International Ltd) 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 °C, immediately volatilised and swept into the furnace by a flow of carrier gas, argon (Ar). The reaction temperature was 760 °C and the growth time was set to be either 12 or 15 min.

The modified silica fibres were characterised using a field emission gun scanning electron microscope (Gemini LEO 1525 FEG-SEM, Carl Zeiss NTS GmbH). The

specific BET surface area of fibres was determined according to ISO 9277 using a Micromeritics TriStar 3000 analyser with pure N₂.

2.3. Single fibre tensile tests

Single fibre tensile tests were performed at a crosshead speed of 15 µm/s at room temperature, according to the British industrial standard ISO 11566:1996 using a TST 350 tensile testing rig (Linkam Scientific Instrument Ltd.) equipped with a 20 N force sensor. A single fibre was fixed at either end to a small piece of cardboard for better handling. The gauge lengths were 15, 25 and 35 mm. A minimum of twenty measurements were conducted for each fibre specimen at each gauge length. The system compliance C was estimated to be 0.9 mm/N under the relevant experimental conditions. The apparent elastic modulus was therefore corrected using the following equation (BS ISO 11566:1996 Method B):

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

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. Contact angle measurements

The wettability of CNT-grafted fibres by PMMA was quantified directly using the drop-on-fibre method [25, 26]. Single fibres were glued to a metal washer using an epoxy adhesive (Adhesive weld, J-B Weld, Slough) and dipped into PMMA powder. The specimen was then transferred into a hot stage (THM600, Linkam Scientific Instrument Ltd.) and heated to 270 °C, at which temperature the PMMA was liquid-like. Stable polymer droplets were formed on fibres and images were captured using an Olympus DP70 camera system under an Olympus BH-2 optical microscope. The droplet profiles

were extracted and contact angles were determined (specific derivations are detailed in [25]) from at least 50 droplets on at least three fibres for each type of silica fibre, in order to obtain statistically significant averages.

2.5. Single fibre fragmentation tests

Single fibres were attached at both ends to a glass slide using double-sided tape with a defined thickness of approximately 100 μm . This method kept the fibres away from the slide surface and positioned in the centre of the eventual polymer specimens. A solution of 10 wt.% of PMMA in 1,4-dioxane (Aldrich) was prepared and cast onto the glass slides, covering the fibres completely. The films were first dried for 48 h in a fume hood and for a further 24 h in a vacuum oven to remove any traces of solvent. Dogbone shaped specimens were then cut using the Zwick D-7900 cutting device (Zwick Roell Group) and tested on the TST 350 tensile stress testing system (Linkam Scientific Instrument Ltd.). The dimensions of the specimens tested were about 0.2 mm thick, 4 mm wide (at gauge region) and 30 mm long. During the tests, the specimens were strained up to 25% to ensure crack saturation at a crosshead speed of 15 $\mu\text{m/s}$ and the entire single fibre fragmentation process was monitored using a polarized light microscope (Wild Heerbrugg). At least six specimens were tested for each case. The fibre fragment lengths were measured under an Olympus BX51M reflected light optical microscope using an Olympus DP70 camera system, which was calibrated using a glass scale (10mm stage micrometre scale, 0.1mm divisions, Graticules Ltd.). The apparent shear strength at the interface was estimated from the Kelly-Tyson model [27]:

$$\tau_{IFSS} = \frac{\sigma_f d_f}{2l_c} \quad (2)$$

$$l_c = \frac{4}{3} l \quad (3)$$

where σ_f is the fibre strength at the critical fragment 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 [28].

3. Results and discussion

3.1. CNT grafting on fibres

Surface morphologies of the silica fibres after different CNT growth times are shown in Fig. 1. Aligned CNTs were successfully grafted onto the silica fibre surfaces, resulting in a brush-like structure. It is believed that the CNTs sterically interact and are gradually forced to grow perpendicularly to the surface, due to the dense number of nucleation sites formed during the initial deposition of iron [23]. As expected, following a significant incubation period, the length of the CNT-grafting varied from a few micrometres to a few tens of micrometres when the growth time was increased from 12 mins (Fig. 1b) to 15 mins (Fig. 1c). As the CNTs became longer, the CNT layer ‘parted’ (Fig. 1c), breaking the cylindrical symmetry. The average diameter of CNTs also increased slightly with growth time, from around 40 to 50 nm, due to catalyst ripening during this base growth process [24]. As shown in Fig. 2, the BET surface area of fibres increased dramatically from 0.12 ± 0.01 initially to 1.10 ± 0.03 and 4.21 ± 0.38 m²/g, after 12 and 15 min reactions respectively, due to the high surface area of CNTs.

After deliberately removing the grafted CNTs, many particles and pits, with the same diameter as the CNTs, were observed on the fibre surfaces (Fig. 1d). This observation suggests that the base growth mechanism [23, 24, 29] is active, i.e. the carbon is extruded from the catalyst particles which remained attached to the fibre base. The pitting also indicates that the CNTs were attached to the fibre surface via etching or some other chemical reaction [24, 30] between the catalyst and the substrate.

3.2. Single fibre tensile tests

The strength of the silica fibres (Fig. 3) slightly decreased after thermal desizing, and much more significantly by around 30% following CNT-growth, an effect that presumably relates to the surface damage shown in Fig. 1d. The fibre strength decreased further on increasing the CVD reaction time from 12 mins to 15 mins, likely due to increasing catalyst coverage; however, the effect is very weak, suggesting that the formation of the catalyst particles during the incubation period is the dominant effect, not the carbon extrusion process. It is well known that the flaw-induced nature of fibre failure results in a length dependence for its tensile strength [31]. Indeed, the averaged tensile strength of all the fibres decreased as the gauge length increased. The Weibull distribution [32] was fitted to the experimental data (lines in Fig. 3a), showing similar trends for different types of fibres. This phenomenon indicated that the surface damage was relatively homogeneous, which was consistent with a uniform distribution of nanoscale pitting over the whole fibre surfaces (Fig. 1d). More surprisingly, a significant increase of the fibre modulus was detected after the grafting process (Fig. 3b), from around 60 to 80 GPa. This phenomenon may be attributed to the polycondensation of silica, i.e. increasing number of bonds in the amorphous network of silica [33], during the high temperature grafting reactions; no devitrification was detected by X-ray diffraction studies. Similar increases in fibre modulus were observed after an equivalent thermal treatment of fibres, in the absence of the catalyst precursor or hydrocarbon source; however, the magnitude of the effect was smaller (from around 60 to 70 GPa).

3.3. Contact angle measurements

The drop-on-fibre method provides an indication of the interfacial properties of composites [26, 34]. For fibres that are well wetted by the polymer, axially symmetric polymer droplets are expected to form due to the geometrical constraints of a Laplace

ellipsoid on a cylindrical fibre [35]. The contact angles, determined from the shape profiles of PMMA droplets (Fig. 4a, b), showed a decrease from $26.0 \pm 1.0^\circ$ to $20.2 \pm 1.2^\circ$ after thermal desizing, indicating better wettability (the sizing was designed for use with epoxy). As shown in Fig. 4a and 4b, the bare fibre surfaces adjacent to the wetting droplets can be clearly seen for both the as-received and desized fibres. In contrast, after introducing the CNTs, the fibres were completely covered by polymer (Fig. 4c, d), preventing the determination of contact angles. The small droplets observed on the fibres grafted with relatively short CNTs (Fig. 4c) are simply the most efficient arrangement of excess polymer following full wetting of the CNT layer. As the CNT-grafting became longer, the polymer was accommodated within the CNT layer, forming a uniform wetting (Fig. 4d).

The kinetics of the PMMA infiltration into the CNT layer was recorded by taking pictures every 0.5 s (Fig. 5). As the temperature increased, the PMMA particles rapidly transformed into liquid-like state [36], forming polymer droplets around the polymer fibre. Due to the high viscosity of the polymer melt and the narrow channels within the densely-packed CNT layer, a relatively slow infiltration process of polymer was observed (the rate-controlling step). Nevertheless, in the end, driven by the capillary action, the polymer completely infiltrated into the CNT layer, demonstrating a good wettability of the grafted CNTs by PMMA.

3.4. Single fibre fragmentation tests

Single fibre fragmentation tests were carried out to determine the bonding strength between CNT-grafted fibres and PMMA. Typical optical micrographs of the composite specimens after reaching crack saturation are shown in Fig. 6. The shape of the fibre breaks gives a qualitative indication of the interface between the fibre and the matrix [37]. For the composite specimens with as-received silica fibres, shown in Fig. 6a, the

fibre fractures did not damage the surrounding matrix and there was apparent debonding of the interface, typical of a relatively weak interface. In contrast, a strong interface can lead to damage of the matrix around the fibre fractures and limit debonding [37]; this situation was observed in the CNT-grafted samples (Fig. 6c and 6d).

The histogram of fragment length (Fig. 7a) shows that the desizing treatment resulted in a reduced fragment length. All of the specimens with CNT-grafted fibres, regardless of CNT length, displayed shorter fibre fragment than the desized control, leading to a shift to lower fragment length in the cumulative distributions (Fig. 7b). A shorter fragment length can result from an enhanced fibre/matrix adhesion and/or a lower tensile strength of the fibre; both factors may be related to the CNT-grafting process. Thus, a further quantitative study of the IFSS was performed, using the Kelly-Tyson model (Table 1), and fitting a Weibull distribution (refer to Fig. 3a) to predict the fibre tensile strength at the critical length. Clearly, there is a potential error in extrapolating the strength data to short fragments; however, the approach is widely used and underlying data is relatively robust, having been collected from at least 60 individual fibres. In addition, the similarity of the Weibull curves provides further confidence, and suggests that the relative assessment of performance is likely to be reliable, even if there is some absolute offset. Using this approach, the IFSS was found to increase dramatically from 9.5 to 24.3 MPa (150%), on grafting the silica fibres with CNTs of a few micrometres in length; the improvement can be attributed to the increased surface area, excellent wettability and mechanical interlocking of CNTs with the matrix. The IFSS obtained is very close to the bulk shear strength of the matrix, defined as half of their tensile strength (specified as 45 MPa by the manufacturer). This result suggests that the matrix properties are fully utilised in the composites, in this case. Interestingly, the shorter CNTs were more effective at improving the IFSS, with the longer CNTs providing only

an 80% increase. This unexpected result can be attributed to the changed morphology of the grafted CNTs. As mentioned earlier, in the case of longer CNTs, the cylindrical symmetry is broken (see Fig. 1c and 8c), which is likely to cause uneven stress transfer; on the other hand, the shorter CNTs, symmetrically accommodated around the fibres, performed more efficiently. Further investigations of the optimal length and arrangement of grafted CNTs for reinforcement are warranted.

To explore the nature of the failed interface, the single fibre fragmentation specimens were fully fractured in flexure, perpendicular to the fibres, and the cross-sections were characterised using SEM (Fig. 8). Similar fracture mechanisms were observed for both composites without and with CNTs, i.e. the fracture plane was at the silica fibre/matrix interface. The CNTs were completely embedded into the polymer matrix, again demonstrating its excellent wettability by PMMA. Since the failure is at or near the root of the CNTs, the adhesion (or shear strength) between the CNTs and the fibres must be good, greater than that between the matrix and the fibres. The complex root structure is likely to be a benefit in this context, despite the disadvantage of reduced fibre strength.

4. Conclusions

CNTs can be grafted to silica fibres with controllable length using a simple injection CVD method, offering a dramatic increase in surface area. The grafting process resulted in a decrease in the tensile strength, which can be attributed to the catalyst etching. However, the tensile modulus of fibres was significantly increased, probably due to the polycondensation of silica materials at high temperature. Complete wetting of the CNT-grafted fibres by PMMA was observed, indicating an excellent wettability of the CNTs themselves. Single fibre fragmentation tests showed that IFSS can be improved by between 80 to 150%, after grafting silica fibres with CNTs of different lengths. Ideally, these data would be supported by other measurements based, for example, on single

fibre pull-out or push-out; both these approaches were attempted but neither yielded usable information due to premature failure of the silica fibre. The strategy of forming hierarchical composites using CNT-grafted fibres can not only improve IFSS, but also provides a controlled means of introducing high loadings of oriented CNTs into the matrix surrounding the fibres, which should improve critical engineering properties of conventional continuous fibre reinforced composites, such as transverse stiffness, longitudinal compression strength, and interlaminar shear strength. Although not the focus of this paper, similar grafting strategies may be usefully employed in short fibre composites, in which an improvement in strength transfer may be particularly helpful, along with the other benefits of a nanocomposite matrix mentioned in the introduction.

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Table 1

Weibull distribution parameters and single fibre fragmentation test results for the silica fibres. The fibre tensile strengths at the critical length are predicted from the Weibull distributions. The standard errors are shown in parentheses.

fibres	m	σ_0 (MPa)	σ_f (MPa)	d_f (μm)	l_c (μm)	τ_{IFSS} (MPa)
as-received	6.32	1700	1630	9	820 (10)	9.5 (0.1)
desized	5.17	1590	1620	9	590 (10)	13.6 (0.2)
with CNTs (12 min)	5.12	1350	1540	9	340 (10)	24.3 (0.3)
with CNTs (15 min)	5.86	1110	1220	9	370 (10)	17.0 (0.3)

Fig. 1. SEM images of silica fibres (a) before and after (b) 12 min, (c) 15 min growth reaction using the ICVD method and (d) after the deliberate removal of the grafted CNTs.

Fig. 2. BET surface areas of the silica fibres.

Fig. 3. Single fibre tensile data: (a) strength and (b) modulus plotted as a function of gauge length for the silica fibres. The Weibull distribution (shown as lines) in (a) was used to account for the gauge length dependence of the tensile strength.

Fig. 4. Optical micrographs of typical PMMA droplets formed on (a) as-received, (b) desized, (c) CNT-grafted (12 min) and (d) CNT-grafted (15 min) silica fibres.

Fig. 5. Time lapse optical micrographs showing the wetting process of CNT-grafted silica fibres by PMMA.

Fig. 6. Typical dark field optical micrographs of the matrix cracks around (a) as-received, (b) desized, (c) CNT-grafted (12 min) and (d) CNT-grafted (15 min) silica fibres in the PMMA matrix after the fragmentation test. The white areas represent the cracks and the arrows indicate the fragment length.

Fig. 7. (a) Histogram and (b) cumulative distributions of fragment lengths for the silica fibres.

Fig. 8. SEM images of the fracture surfaces of silica fibres/PMMA composites (a), (b) without and (c), (d) with CNTs grafted on fibres (produced in the 15 min reaction). (b), (d) are enlarged views from (a) and (c), respectively.