FAILURE OF CARBON NANOTUBE-GRAFTED CARBON FIBRE REINFORCED COMPOSITES BY SINGLE FIBRE PULL-OUT

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ABSTRACT

Continuous production of carbon nanotube-grafted-carbon fibres (CNT-g-CFs) was performed in an open chemical vapour deposition reactor, and the resultant fibres were used in single-fibre pull-out tests to determine their interfacial properties with epoxy, nanoengineered epoxy, and polypropylene matrices. At a single CNT-g-CF level, the presence of uniform carbon nanotube (CNT) coverage, sub-550 nm length, has been shown to increase the interfacial shear strength (IFSS) by 26% (98.4 ± 7.2 MPa) when compared to the baseline unsized carbon fibre (77.9 ± 5.1 MPa) embedded in a commercial epoxy. The IFSS increased when combining CNT-g-CF with a 2 wt.% multiwall carbon nanotube loaded epoxy matrix to 32% (102.8 ± 6.7 MPa) compared to the same baseline. In a polypropylene matrix, the presence of uniform CNT coverage on the carbon fibre surface also led to an increase in IFSS by 39% (11.2 ± 2.1 MPa) when compared to the unsized carbon fibre/polypropylene baseline (8.1 ± 1.5 MPa).

1 INTRODUCTION

A fibre-reinforced composite is a multiphase material composed of a matrix, fibres, and an interface/interphase. The properties of the interphase region, where stress concentrations occur, can strongly influence the mechanical response of fibre-reinforced composite. Grafting carbon nanotubes (CNTs) onto carbon fibre (CF) to produce “fuzzy” CFs creates hierarchical reinforcement in two different length scales (micro- and nanometre) [1]. This approach improves the interaction between fibres and matrix through enhancing the apparent interfacial shear strength (IFSS). Single fibre pull-out tests are performed to determine the IFSS properties and debonding behaviours by applying a force parallel to partly embedded fibre in a thermoplastic or thermoset polymer matrix (Figure 1) [2].

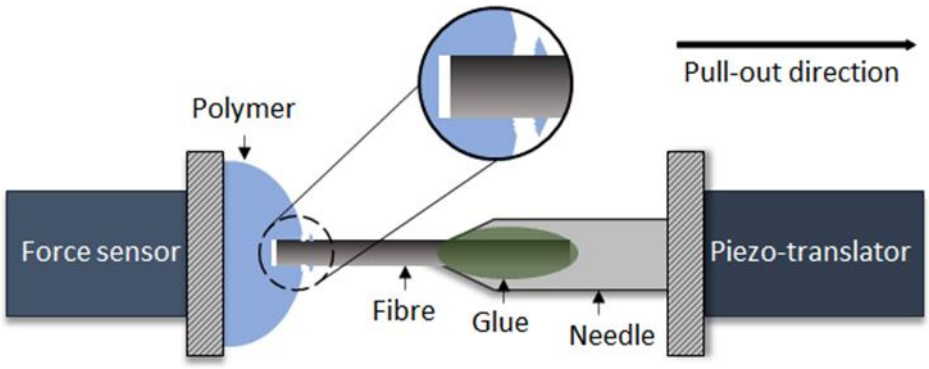

Figure 1: Schematic of single-fibre pull-out test with a close-up view of microscale fibre debonding. Adapted from [3].

Carbon nanotube-grafted-carbon fibres (CNT-g-CFs) increased the IFSS by 8% (96.7 MPa) when embedded in an epoxy compared to the baseline of an unsized CF (89.4 MPa) in single fibre pull-out tests [3]. A further 3.5% (100 MPa) improvement in the IFSS was achieved when combining the CNT-g-CF with single-walled carbon nanotube (SWCNT) reinforced epoxy (up to 1 wt.%) using tri-block (PMACEP-PI-PMACEP) as the SWCNT dispersing agent [3]. Through the synergistic combination of CNT-g-CFs and nanoengineered epoxy, a secondary reinforcement effect occurred, enabling an improvement in stress transfer by displacing the weaker matrix phase from the surrounding CNT/CF interface with the nanoengineered matrix, ultimately delaying the failure [3]. Furthermore, a CNT-g-CF embedded in a non-reactive thermoplastic, such as polypropylene (PP), can show more effective enhancement in the IFSS. A significant improvement in the IFSS was measured with CNT-g-CF compared to as-received unsized CF embedded in PP by 53% [4]. In polyolefins, the IFSS is improved only by mechanical interlocking rather than thermodynamic adhesion; i.e. chemical interactions.

In this work, CNT-g-CFs were continuously manufactured in an open chemical vapour deposition (CVD) reactor while retaining the fibre's original mechanical properties [1, 5] and used to further investigate the IFSS performance with three different matrices. These homogeneously grafted fibres' (Figure 2) fibre-matrix interfacial properties were tested with a commercially supplied unmodified epoxy (baseline), and a commercially nanoengineered 2 wt.% loaded multiwall carbon nanotube (MWCNT) epoxy, and a supplementary study with a commercially supplied PP matrix of the effect of two different CNT lengths on the carbon fibre surface is also presented.

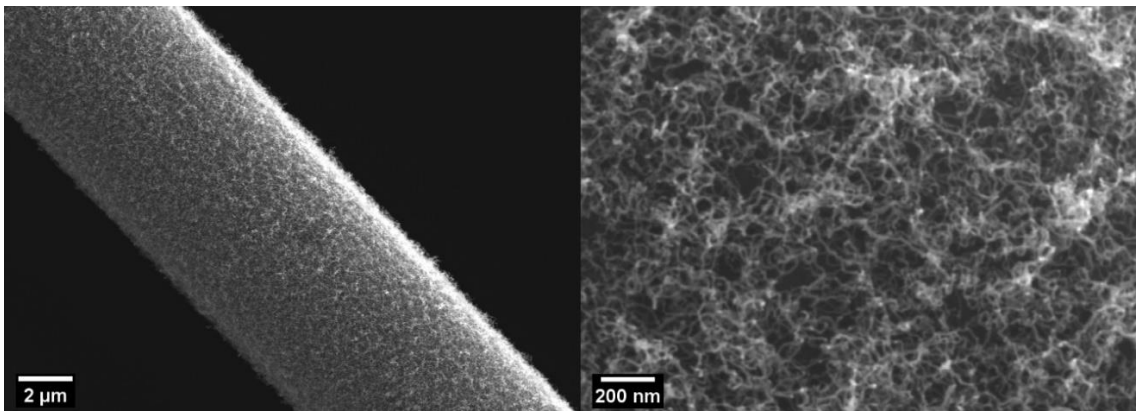

Figure 2: Scanning electron microscopy images of; left, a carbon nanotube-grafted-carbon fibre with 550 ± 150 nm CNTs in length. Right, pane is a magnified view of the fibre surface and the synthesised carbon nanotubes.

2 MATERIALS AND METHODS

Commercially available unsized polyacrylonitrile (PAN)-based CF (AS4-12K, ~7 µm diameter) supplied by Hexcel Composites (Hexcel, GB) was used as a continuous tow as-received. The catalyst precursor was prepared using iron (III) nitrate nonahydrate (≥98% ACS reagent, Merch, DE), nickel (II) acetylacetonate (≥98%, VWR, GB) and ethanol (>99.7% BDH Prolabo, VWR, GB). Continuous CNT synthesis was carried out via CVD using acetylene in nitrogen (N_2 98.7 vol.% and C_2H_2 1.3 vol.%, C certificate, BOC gases, GB), hydrogen in nitrogen (N_2 97.6 vol.% and H_2 2.4 vol.%, C certificate, BOC gases, GB), and nitrogen (99.998 vol.% minimum, BOC gases, GB). For the IFSS tests, Huntsman (Huntsman Advanced Materials, CH) supplied Araldite LY-3585 CH epoxy resin (used without modification, as-received), Araladite GY 40100 (2 wt.% MWCNT loaded epoxy, nanoengineered, used as-received, and Aradur 22962 curing agent were used to fabricate single fibre composites following manufacturer's instructions. SABIC supplied PP595 polypropylene (SABIC, NL), which was used as-received.

2.1 Grafting carbon nanotubes onto carbon fibres

In a continuous in-line process, plasma treatment was performed on the tow of unsized CFs immediately prior to catalyst precursor deposition, in which the CFs passed through a bath containing 1 wt.% of iron (III) nitrate nonahydrate and nickel (II) acetylacetonate (1:0.64 mol.%) in ethanol, the coated fibres passed through drying ovens and were then collected on a spool. After bi-catalyst precursor deposition, the spool fibres, at a speed of 2.4 m/h, were continuously pulled through an open three-zone CVD reactor and subjected to CNT synthesis gas conditions with an *in situ* potential difference of +300 V applied to the CFs in relation to a counter electrode. In short, the CF tow enters the reactor, and is first exposed to an inert nitrogen environment (10000 sccm, 5 bar), then to hydrogen in nitrogen region (3400 sccm, 2 bar) for catalyst reduction at 550 °C. After reduction, the tow was then exposed to acetylene rich region (325 sccm, 2 bar), which acts as the carbon source for CNT synthesis. After passing through another inert nitrogen region, the CNT-g-CF tow exits the reactor. A second configuration for synthesising CNT-g-CF with shorter CNT length (163 ± 32 nm) was produced by using the same conditions except lowering the hydrogen flow to 528 sccm.

2.2 Single fibre pull-out test

The IFSS measurement of adhesion between a single fibre and polymer matrix was assessed by a pull-out test equipment that was commissioned in-house using custom-built apparatus with high stiffness adaptors, piezo translators (P216, Physik Instrumente, DE), modular piezo controller (PI E-500, Physik Instrumente, DE) and low-level force sensor (9207, Kistler, CH) connected to ADwin-light-16 card. The setup was inspired by Hampe *et al.* previously reported work [6]. The test samples were prepared by embedding a single fibre in a polymer filled aluminium screw using a fine vertical translation stage (MT1A, Thorlabs, GB). The curing of epoxy matrix (Araldit 3585: Aradur 22962, 100: 25 by weight) at 120 °C for 15 min, followed by 150 °C for 15 min using a built-in heating stage. For the PP pull-out samples, the matrix was melted at 185 °C before fibre embedding and then cooled to room temperature after fibre insertion without external cooling. The affixed specimens were then mounted on the force sensor (resolution of 0.1 mN). The free fibre end length was stuck by stiff cyanoacrylate adhesive (DA21C, Techni Measure, GB) to a stainless-steel needle (BD 303800, fisher scientific, GB), which in turn was attached to the piezo translator (resolution of 1.8 nm).

In this test, the apparent fibre pull-out shear strength (τ_{app}) was calculated from the peak force (F_{max}) according to equation (1) at a crosshead speed of 0.2 µm/s over a maximum travelling distance of 153 µm. The diameter of the fibre (d_f), includes the contribution of CNTs in grafted fibres (post failure including adhered matrix), and each sample embedded length (l_e) was measured by scanning electron microscopy post-failure. The preliminary IFSS results were calculated based on an average of five samples at least in each sample set.

$$\tau_{app} = F_{max} / \pi \, d_f \, l_e \quad (1)$$

3 RESULTS

A uniform coating of CNTs around 550 nm in length and 10 nm in diameter (Figure 2) was successfully grafted onto CFs. The CNT-g-CF increased the IFSS by 26% (98.4 ± 7.2 MPa) compared to the baseline unsized CF embedded in pure epoxy, with similar trends to those previously reported [1, 3]. The increased IFSS may be attributed to the homogenous CNT network resisting shear loads under pull-out conditions. When the unsized CF is introduced to 2 wt.% MWCNT loaded epoxy, IFSS improved by 8.6% (84.6 ± 3.9 MPa) compared to the baseline with epoxy (Figure 3). The highest IFSS was shown when the CNT-g-CF was combined with 2 wt.% MWCNT loaded epoxy matrix, resulting in 32% enhancement (102.8 ± 6.7 MPa) compared to the baseline (77.9 ± 5.1 MPa). This result indicates a synergistic effect between the nano-engineered epoxy and the CNT-g-CF fibres as failure is observed at the end of the grafted CNT network (CNT/matrix interface).

Single-fibre reinforced PP samples were prepared with unsized CF, and two different length CNT-g-CF configurations: short CNTs (163 ± 32 nm) and long CNTs (550 ± 150 nm). The IFSS of the CNT-g-CF/PP system increased by 39% (11.2 ± 2.1 MPa) and 31% (10.6 ± 3.0 MPa), for the short and long CNTs, respectively, in comparison to the unsized CF (8.1 ± 1.5 MPa). The trend of IFSS shows an improvement for both short and long CNTs in CNT-g-CFs due to the higher roughness. The limited number of samples does not allow for a significant level of confidence in the resulting trend, and thus further examination and samples are required. However, provisionally, the increase of the IFSS indicates that mechanical keying is the dominant mechanism for the IFSS improvement in polyolefin-based matrices which agrees with previous results [4].

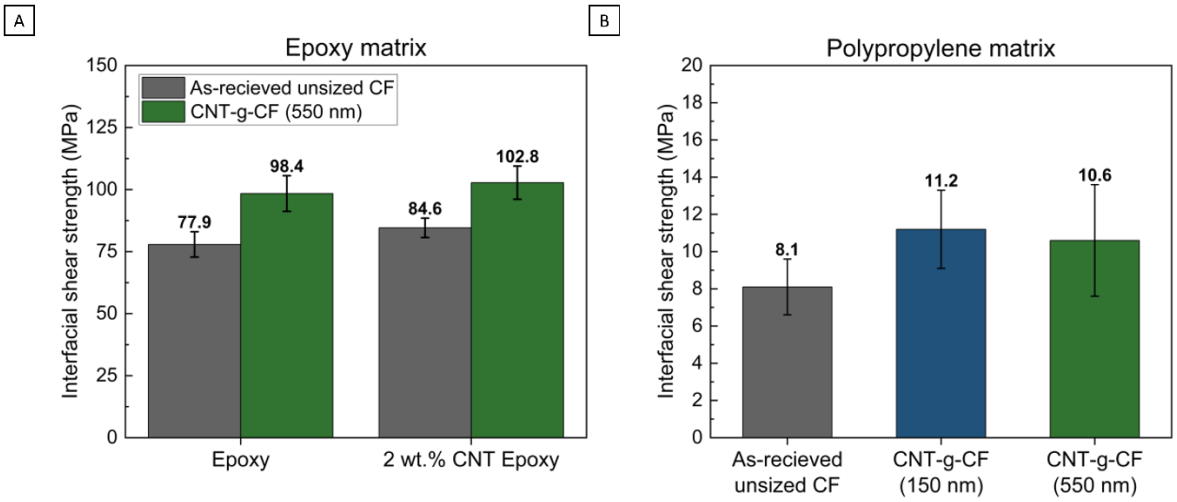

Figure 3: Single fibre pull-out test results for as-received unsized carbon fibres and carbon nanotubes grafted carbon fibres embedded in (A) commercial as-received epoxy and 2 wt.% loaded multi-walled carbon nanotubes epoxy, and (B) polypropylene matrix. Bars represent standard deviation.

4 CONCLUSIONS

A nanostructured coating, in this instance a forest of carbon nanotubes, on carbon fibres (CFs) has shown to enhance the apparent interfacial shear strength (IFSS) with three different matrices. The highest IFSS value obtained was 102.8 ± 6.7 MPa for a carbon nanotube-grafted-carbon fibres (CNT-g-CFs) with 550 ± 150 nm nanotube forest length when embedded in a 2 wt.% multiwalled carbon nanotube reinforced epoxy. This study examined, and demonstrated, the synergistic effect of combining nano-reinforced composites with hierarchical reinforcing fibre elements supporting previous work [1, 3, 4]. The use of CNT-g-CFs to improve IFSS is attractive in unreactive thermoplastic matrices, such as

polypropylene, where wetting and adhesion typically limit composite performance. IFSS is significantly improved, by up to 39%, using CNT-g-CFs in a polypropylene matrix when compared to an as-received unsized CF baseline. This improvement indicates that mechanical interlocking is a more dominant mechanism than thermodynamic adhesion for improving fibre-matrix IFSS in polypropylene, and especially in the case of polyolefins.

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