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Carbon nanotube enhanced carbon Fibre-Poly(ether ether ketone) interfaces in model hierarchical composites

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ABSTRACT

Poly (ether ether ketone) (PEEK) has a high continuous service temperature, excellent mechanical properties, and good solvent and abrasion resistance, which can be further improved through the addition of carbon nanotubes (CNTs). CNT-PEEK nanocomposites are promising matrices for continuous carbon fibre composites; powder processing can mitigate the high melt viscosities in these systems. In this study, model single fibre (hierarchical) composites were produced by embedding sized and desized carbon fibres in nanocomposite CNT-PEEK powders followed by single fibre pull-out tests to assess interfacial characteristics. Carbon fibre-PEEK interfacial shear strength is typically 40–45 MPa. Increasing CNT loadings increased fibre-matrix interfacial shear strength linearly up to ~70 MPa at 5.0 wt%, which was attributed to the CNT-based mechanical modification of the PEEK matrix. Apparent interfacial shear strength was inversely correlated with the embedded fibre length irrespective of carbon fibre sizing or CNT loading, indicating brittle fracture of the fibre-matrix interface. Pulled out carbon fibres were still coated with the matrix, which indicated strong adhesion at the interface in all samples, likely related to a transcrystalline region. Adhesion was, however, negatively affected by the presence of epoxy sizings. Frictional shear strength was independent of embedded fibre length and CNT content for all samples.

1. Introduction

Hierarchical composites combine multiple reinforcements at different characteristic length scales. Typically, nanoscale carbon nanotubes (CNTs), or other nanomaterials, are used to reinforce the polymer matrix surrounding microscale carbon or glass fibres. This approach provides the opportunity to improve the matrix dominated properties of current state-of-the-art structural materials, based on conventional continuous fibre reinforced polymer composites [1,2]. CNTs are common reinforcing agents due to their low density and theoretically exceptional mechanical properties, including tensile strengths of up to 50–100 GPa [3,4]; even small quantities of less perfect CNTs can improve matrix tensile strength and modulus usefully (~10% increase in tensile modulus with a 1 wt% unmodified CNT loading in poly ether ether ketone, PEEK) [5–7]. In hierarchical composites, CNTs also have the potential to act as intra- and interlaminar reinforcement, alleviating existing limitations in matrix dominated properties and improving delamination resistance without compromising in-plane properties [1]. These benefits contrast with traditional through-plane performance improvement methods, such as z-pinning, stitching and braiding, which disturb fibre alignment and damage primary fibres [8].

While hierarchical composites have been successfully produced using CNT-reinforced epoxy resins reinforced by both glass [9–11] and carbon fibres [12–15], high-performance thermoplastic polymer matrices have received considerably less attention. In general, thermoplastic matrix composites offer better toughness and recyclability, but

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they can be challenging to prepare and often suffer from weak fibre-matrix interfaces [16]. It was shown that CNT grafting and CNT or graphene oxide (GO) sizing of carbon fibres improve the fibre-matrix (thermoplastics [17] including PEEK [18–20] and thermoset [21,22]) [2,23] adhesion, however, using a CNT-enhanced matrix system would also provide additional benefits not possible with the addition of a CNT or GO enhanced sizing, such as improved toughness and through thickness electrical conductivity. PEEK is an important high performance matrix, generally used in demanding applications in the aerospace and biomedical sector, but currently experiencing increased use in the automotive and chemical processing industries due to its high continuous service temperature $T_s > 250$ °C, excellent mechanical properties, and good solvent and abrasion resistance [24,25]. The high melting temperature of PEEK and the increased melt viscosity associated with CNT inclusion does [26], however, make the processing of PEEK hierarchical composites particularly challenging. One good approach, developed for pure carbon fibre reinforced PEEK, relies on powder prepregging to reduce flow path length and heating time [27]. Powder prepregging refers to the process of impregnating carbon fibre tows with polymer powder from a water-based slurry containing dispersed polymer particles with particle sized ranging from 5 to 30 μm. However, achieving nanocomposite particle sizes ranging from 10 to 20 μm to facilitate powder impregnation of fibres is difficult [1,27].

This study explores the powder-based manufacturing and interfacial characteristics of single fibre (hierarchical) composites, comprising carbon fibres embedded in a CNT-PEEK matrix, as a model system examining the feasibility of bulk PEEK hierarchical composites with the aim to improve matrix dominate properties, such as compression strength and through thickness electrical conductivity. Composite samples were produced using sized and desized carbon fibres and varying weight fractions of CNTs, which were melt blended with PEEK during extrusion and powdered using a temperature induced phase separation method. Single fibre pull-out tests were used to determine the apparent interfacial and frictional shear strength as a measure of practical adhesion and debonding of fibre-matrix interfaces. This investigation was supported by scanning electron microscopy (SEM) imaging of matrix fracture surfaces and the extracted fibres following pull-out.

2. Experimental section

2.1. Materials

Sized and desized (by Soxhet extraction in acetone) Torayca® T700SC carbon fibres were kindly supplied by Torayca® (Toray Industries, Tokyo, Japan). Industrial grade multi-walled CNTs (NC7000, ~10 nm in diameter, 1.5 μm long and with a CNT density of 1.9 g/cm^3 corrected for the remaining catalyst content [28], see also Fig. S1) were kindly provided by Nanocyl (Sambreville, Belgium). Low melt viscosity PEEK (grade 150) was provided as a powder by Victrex (Lancashire, UK). Diphenyl sulfone, acetone, ethanol (VWR, UK), dry ice (BOC, UK) and a polypropylene membrane support (Novaltex 3471, UK) were purchased for use in this study. All materials were used as received, except if otherwise stated.

2.2. Melt blending and extrusion of CNT-reinforced PEEK nanocomposite pellets

All materials were dried in an air circulated oven overnight at a temperature of 50 °C prior to processing. CNTs were initially distributed in the PEEK powder using a 1 L laboratory blender (Waring Laboratory Blender, UK) to break up any large CNT agglomerates and obtain a pre-mix of CNTs and PEEK. The PEEK powder was added in 50 g aliquots at 30 s intervals and blended for 1 min. This pre-mix was then transferred into a dry powder-rotating mixer (tumble blender) and mixed at 50 rpm for 1 h to further homogenise the blend.

PEEK (500 g) and the desired amount of CNTs were melt blended using a continuous twin-screw co-rotating extruder (PRISM TSE-16 TC laboratory extruder, Thermo Scientific Haake, UK) with a length to diameter ratio of 15 and a screw diameter of 16 mm. Nanocomposite pre-blends were force fed into the extruder running at 80 rpm at a rate of 1 kg/h and 360 °C to ensure a constant supply of polymer (or nanocomposite pellets) to the screws. Nitrogen gas was used during processing to reduce polymer degradation. Residence time of the blend within the extruder was ~40 s. Continuous strands of extruded CNT and PEEK nanocomposites were pelletised using a PRISM pelletiser unit before being re-extruded twice under the same conditions to ensure consistency of CNT dispersion within the nanocomposite pellets.

Melt shear viscosity and stress were measured using a capillary rheometer (RH2000, Bohlin, Cirencester, UK) with a simple shear rate sweep from 100 to 1000/s at a temperature of 380 °C using 25 g of material.

2.3. Manufacturing of CNT-reinforced PEEK nanocomposite powder

CNT-reinforced PEEK nanocomposite pellets were converted to powder, targeting mean particle sizes ranging from 10 to 20 μm, to facilitate the manufacture of hierarchical composites utilising powder impregnation [27]. Initial trials utilised cryogenic mills, however, due to the toughness of the PEEK nanocomposite pellets, particle sizes <200 μm could not be achieved, even at low temperatures. Solution precipitation methods, whereby PEEK is dissolved in a solvent, offer an alternative method to produce powders. A temperature induced phase separation process utilising diphenyl sulfone (DPS) as a high boiling point solvent [29] was adapted to produce PEEK (nanocomposite) powders (Fig. 1) [30]. DPS itself is a solid at room temperature with a melting temperature of 140 °C. PEEK completely dissolves in DPS at 300 °C.

Two consecutive 100 g batches of PEEK nanocomposite pellets were dissolved in 900 g of DPS inside a 1 L heated cylindrical glass reaction vessel, yielding 2 kg of PEEK nanocomposite dissolved in DPS in total. The vessel was covered with a stainless-steel lid and stirred at 200 rpm using a stainless-steel double anchor stirrer to facilitate uniform mixing and heat distribution. The vessel temperature was maintained at 300 °C using a heating mantle (Glas-Col 100 B TM573, Wilmad Lab Glass, USA) equipped with a digital temperature controller, since lower temperatures in the top of the reactor would result in the formation of a solid surface layer and inhibit homogenous temperature induced precipitation of the PEEK (nanocomposite) powder. Once all PEEK nanocomposite pellets were completely dissolved, the temperature was reduced to 240 °C at a rate of 10 °C/h to ensure that the PEEK would recrystallise as solid particles, with the DPS remaining liquid. PEEK started to crystallise at 265 °C. The precipitated PEEK nanocomposite in DPS was then further cooled to 200 °C, the highly viscous solution poured into a ceramic dish and hand mixed for ~5 min using a spatula to prevent particle agglomeration during DPS crystallisation. The resulting toffee-like solid was allowed to cool to room temperature. A hammer was used to fracture it into smaller pieces. The resulting particles were then sieved (2 mm), to reduce the particle size distribution, and ground to a finer powder. This process was completed by blending 75 g of the powder with an ethanol solution, maintained at −70 °C using dry ice, for 5 min in a 1 L laboratory blender (Waring Laboratory Blender, UK). Additional dry ice was added directly into the mixture of powder and ethanol at intervals to keep the temperature low and ensure that the powder was as brittle as possible during blending. After mixing, the mixture of powder and ethanol was transferred to a 5 L beaker and further ground using a high-speed homogeniser (SL2T, Silverson, Chesham Bucks, UK) at 7000 rpm with the temperature maintained at −70 °C using dry ice. Once returned to room temperature, the DPS dissolves in excess ethanol, and was removed by filtration through a polypropylene membrane. This membrane was selected over a standard filter paper due to its open mesh structure, which promotes transmission of DPS and is especially important since filters can be easily clogged

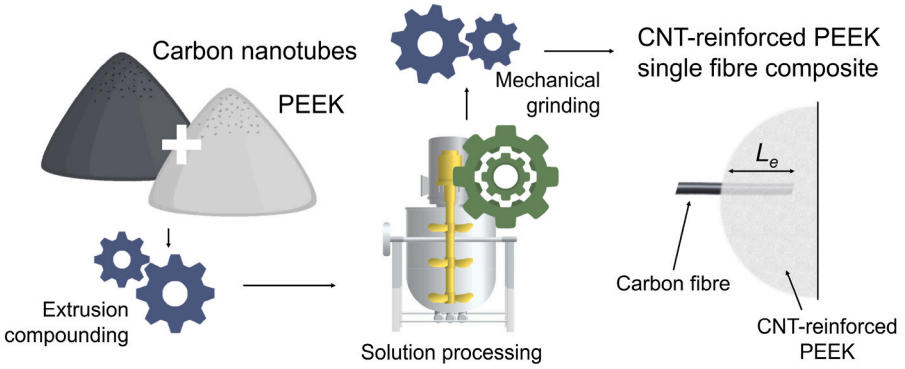


Fig. 1. Schematic illustrating the process used to prepare carbon nanotube (CNT) reinforced polyether ether ketone (PEEK) single fibre (model) composites. Initially, carbon nanotubes and PEEK are extrusion compounded and solution processed to form a nanocomposite powder. This nanocomposite powder is then mechanically ground, and a carbon fibre is inserted to form the single fibre composite.

when DPS crystallises. The filtered powder was then redispersed in 5 L of acetone at 80 °C, with stirring, to dissolve remaining DPS before again being filtered off using the polypropylene membrane. Re-dispersion in acetone and filtration was performed three times to ensure as little DPS as possible remained in the final CNT-reinforced PEEK nanocomposite powder. Unfortunately, it is impossible to verify the actual CNT loading of nanocomposite powders after processing, due to the similar thermal degradation profiles of PEEK and CNTs (Fig. S1).

2.4. Injection moulding and processing of mechanical test specimens

Mechanical test specimens were prepared using injection moulding (Thermo Scientific Haake Minijet, UK). All materials were dried in an air circulated oven overnight at a temperature of 50 °C. Pellets were then fed into the heated barrel at a temperature of 400 °C and allowed to melt for 10 min before being injected into the mould (type V, ASTM D638) at a temperature of 250 °C using a pressure of 800 bar. Pressure was maintained at 800 bar for 10 s before being reduced to 400 bar for 30 s. Specimens were then removed from the mould. An identical thermal history was maintained for all the specimens. Samples were annealed at 240 °C for 4 h and cooled to 140 °C at a rate of 10 °C/h prior to mechanical testing to ensure a similar crystallinity.

2.5. Manufacturing of single fibre (hierarchical) composites

Single fibre composites, comprising sized or desized T700 carbon fibres and a PEEK matrix, and single fibre hierarchical composites, comprising desized T700 carbon fibres and a PEEK matrix loaded with 1.0, 2.5 and 5.0 wt% CNTs (which corresponded to CNT volume fractions V_f of 0.69%, 1.72% and 3.48%, respectively) were produced by embedding a single fibre to a length varying between 50 and 150 μm into a polymer melt droplet, which was produced by melting the PEEK (nanocomposite) powder in the hot stage of an aluminium sample carrier heated to 390 °C. The melt impregnated fibre was than cooled to 250 °C using a compressed air jet followed by further slow cooling to room temperature. Fibre diameters were determined using the laser diffraction method proposed by Meretz, Linke, Schulz, Hampe and Hentschel [31].

2.6. Characterisation of sample morphology and crystallinity

SEM was performed on samples using an electron microscope (Philips SEM 515, Eindhoven, The Netherlands) with an electron beam voltage of 15 kV.

Differential scanning calorimetry (DSC) (Q2000, TA Instruments, UK) was used to evaluate sample crystallinity in a nitrogen environment. Annealed PEEK samples, ~10 mg in mass, were heated/cooled/reheated at a rate of 10 °C/min. The degree of crystallinity was calculated from the area under the melting peak, with each DSC curve fitted with a baseline using the in-built analytical software. An enthalpy of fusion of 130 J/g was assumed for fully crystalline PEEK [32]. Cold crystallisation was not observed.

2.7. Mechanical characterisation of PEEK nanocomposites

Nanocomposite specimens (type V) with a gauge length of 25 mm were tested at loading rates of 1 mm/min using a tensile screw-driven test frame (Model 4466, Instron, High Wycombe, UK) equipped with a 10 kN load cell. Six replicate specimens were tested for all configurations and the loading conditions with data presented in the form of averages and standard error. Machine compliance was accounted for in all the tests.

2.8. Characterisation of fibre/matrix interface properties using single fibre pull-out tests

Single fibre pull-out tests were conducted to determine the apparent interfacial shear strength between carbon fibres and the PEEK (nanocomposite) matrix. Fibres were drawn from the matrix at a rate of 0.2 μm/s using a piezoelectric actuator (PI model 216) fixed to a stiff frame. In order to avoid energy storage in the free fibre length between the matrix surface and the clamping device, the gauge length was set to 30 μm. Force was recorded by a stiff load cell (Kistler Typ 9207) over the course of the fibre pull-out, with the maximum load corresponding to complete debonding of the interface between the fibre and matrix along its embedded length. Apparent shear strength τ_{IFSS} was calculated from the maximum pull-out force F_{max} required to trigger debonding of the embedded carbon fibre from the matrix, the diameter of the fibre d_f and its embedded length L (Equation (1)):

$$\tau_{IFSS} = \frac{F_{max}}{\pi d_f L} \quad (1)$$

3. Results and discussion

3.1. CNT-reinforced PEEK nanocomposite powder characteristics

The nanocomposite preparation protocol successfully produced fine, free-flowing, black CNT-reinforced PEEK powders. The particle size distribution (PSD) of the nanocomposite powders decreased with increasing CNT loading, with the mean dropping from 75 μm to 41 μm and then 38 μm for CNT weight fractions of 1.0, 2.5 and 5.0 wt%, respectively (Fig. 2). Neat PEEK powder processed using the same method had an average particle size of 56 μm. It appears that the distributions are bimodal but shift to the smaller particle size at higher CNT content, perhaps due to a lower ductility, as often observed in

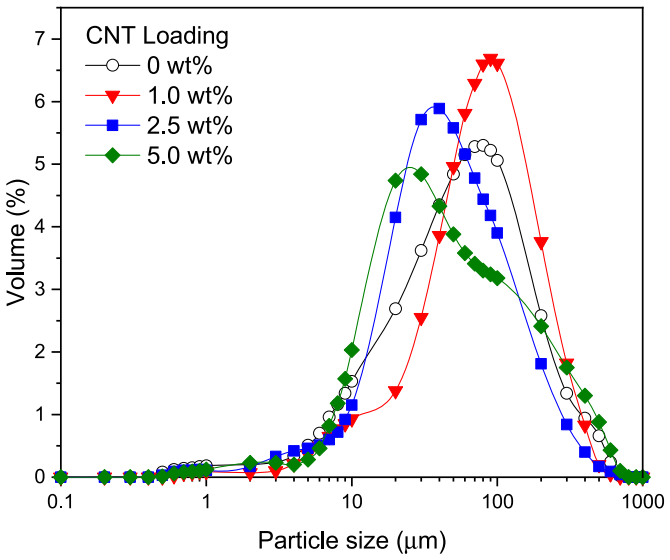


Fig. 2. Particle size distribution (particle size [μm] with respect to volume [%]) of neat PEEK (hollow black circles) and PEEK nanocomposite powders reinforced with 1.0 (red inverted triangles), 2.5 (blue squares) and 5.0 wt% (green diamonds) CNTs. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

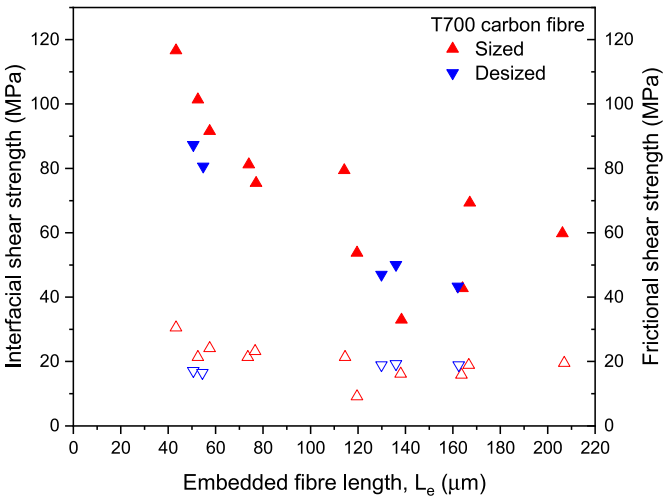


Fig. 4. Apparent interfacial shear strength τ_{IFSS} (solid markers) and frictional shear strength (hollow markers) as a function of embedded fibre length L_e for single fibre composites comprising PEEK and sized (red triangles) or desized T700 (inverted blue triangles) carbon fibres. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

nanocomposites [33], and seen here as a lower strain to failure (see below). The particles are larger than that of commercially available PEEK powder (~10 μm) produced using cryogenic grinding, which could not be replicated at laboratory scale. The particle size distribution will be important during hierarchical composite manufacturing. The temperature induced phase separation process described here could be refined to produce smaller particles by increasing the cooling rate.

SEM identified particles consistent with the size distributions. The CNT-reinforced nanocomposite powder was free of any obvious CNT agglomerates and, at higher resolution, individual CNTs were observed protruding from the surface of the powder, evidencing an even distribution throughout the bulk of the matrix rather than condensed on its surface (Fig. 3).

3.2. Interfacial properties of single fibre composites

The apparent interfacial shear strength of single fibres embedded in pure powder-processed PEEK is inversely correlated with the embedded fibre length (1/L), for both industrially oxidised sized and desized T700 fibres (Fig. 4). Shorter embedded fibre lengths, of ~50 μm, were associated with apparent interfacial shear strengths of 80–85 MPa, which halved to ~40 MPa as the embedded fibre length increased to 160 μm. This trend again indicates predominantly brittle fracture behaviour governed by a (semi-)crystalline interface layer [34] or transcrystalline layer [35] as observed in model AS4 PEEK composites [36]. Conversely, the frictional shear strength of the single fibre composites was virtually independent of the embedded fibre length for both sized and desized carbon fibres.

SEM imaging of the PEEK matrix and extracted carbon fibres, following fibre pull-out, showed that a wetting cone formed around the fibre (Fig. 5). This meniscus resulted from the partial wetting of the carbon fibres by the PEEK melt during sample preparation. The size and shape of the wetting cone is governed by the contact angle between fibre and matrix, which is in turn correlated with the surface tension of the PEEK melt, carbon fibre substrate, and the interfacial tension between them, in addition to the frictional force resisting the immersion of the fibre into the liquid matrix. Failure usually occurred in the contact region between fibre and matrix, which attracted the highest stresses in the single fibre composites, initiating with the fracture of the wetting cone or at the interface between the fibre and matrix. Carbon fibres were pulled from the matrix, with the energy required to fracture the matrix and separate the wetting cone from the fibre lower than that necessary to completely debond the interface between the fibre and the matrix.

In order to determine the average interfacial shear strength, in case of a brittle interface, the maximum pull-out force is plotted as a function of the embedded fibre area, which should result in a linear relationship [37]. The tendency for matrix fracture during wetting cone separation (Fig. 6) causes a translation of maximum pull-out force as a function of embedded fibre area away from the origin (zero) (Fig. 6). The formation of PEEK microfibrils on the fracture surfaces, caused by plastic deformation and drawing of the matrix present in the wetting cone, and the

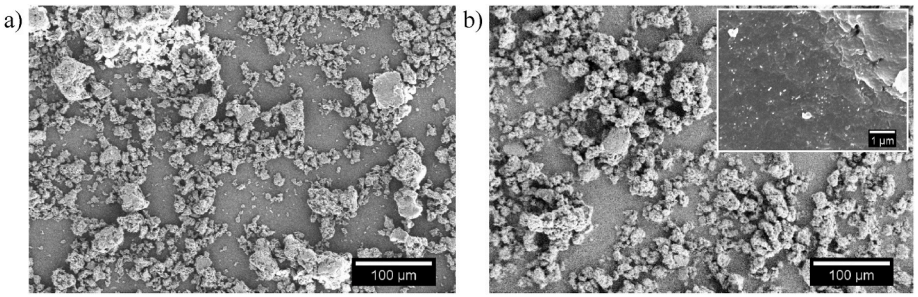


Fig. 3. SEM micrographs detailing (a) neat PEEK powder and (b) PEEK nanocomposite powder reinforced with 5.0 wt% CNTs. CNT agglomerates were not observed in the CNT-reinforced nanocomposite powder. Inset: higher magnification micrograph indicating a uniform CNT distribution throughout the bulk of the matrix.

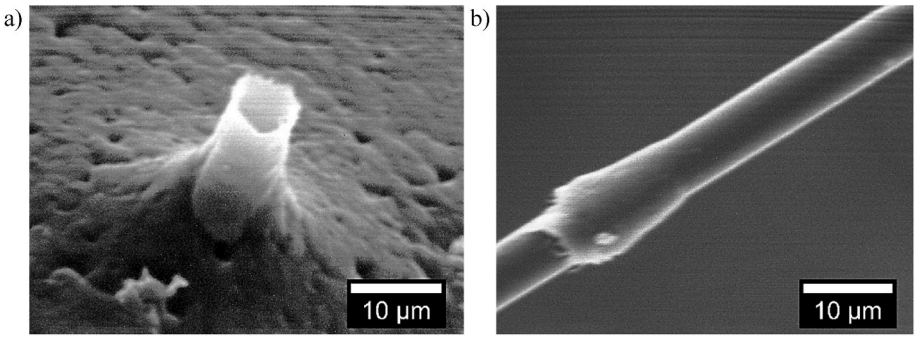


Fig. 5. Representative SEM micrographs detailing the PEEK matrix following fibre pull-out (a) and an extracted desized T700 fibre (b). A PEEK wetting cone can be seen (a) due to partial wetting of the carbon fibres by the PEEK melt. Fibres were pulled from the matrix but still had parts of the wetting cone attached also showing the formation of PEEK microfibrils caused by plastic deformation of the pure PEEK matrix (b).

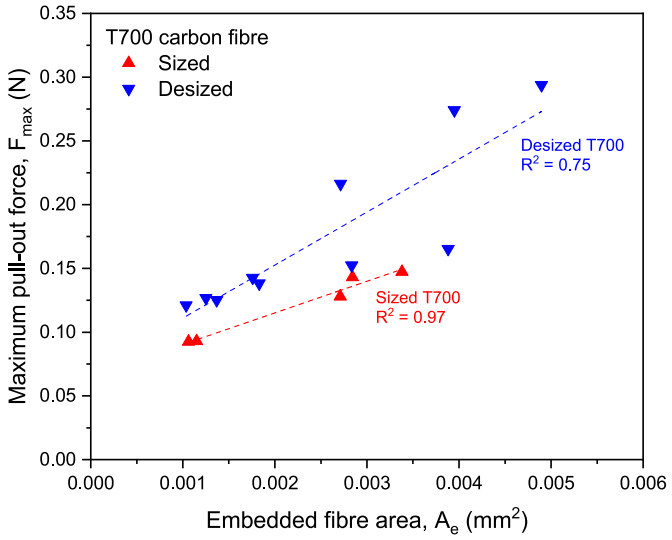


Fig. 6. Maximum pull-out force F_{max} as a function of embedded fibre area for single fibre model composites comprising PEEK and sized (red triangles) or desized T700 (inverted blue triangles) fibres. Linear fits are marked for each carbon fibre type using dashed lines and labelled with their respective R^2 values. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

presence of pure PEEK matrix still attached to the separated fibre (Fig. 5b) evidence sufficiently strong fibre/matrix adhesion. A linear relationship can be observed between maximum pull-out force and embedded fibre area for sized ($R^2 = 0.97$) and desized T700 ($R^2 = 0.75$) fibres. The slope of $F_{max} = f(A_e)$ provides the average apparent interfacial shear strength τ_{IFSS} for sized and desized T700 fibres in unreinforced PEEK matrix, which were 24.8 ± 2.5 MPa and 41.6 ± 8.4 MPa, respectively. These values are in line with literature values (desized T700: 43 MPa [38] and AS4: 45–50 MPa [39–41]). These results confirmed that epoxy sizes are detrimental to developing strong interfaces between fibres and thermoplastics [40,42]. The epoxy sizes are neither miscible with nor dissolve into the PEEK melt (and might actually decompose at the high processing temperatures used), resulting in a weak boundary between the solidified matrix and the fibre [43]. Thus, the interfacial shear strength between fibres and thermoplastic matrices (in this case PEEK) can be significantly improved by removing the sizing, for instance by acetone extraction (or, better, by using unsized fibres).

3.3. Tensile and interfacial properties of CNT loaded model hierarchical composites

Increasing the CNT loading (0, 1.0, 2.5 and 5.0 wt% multi-walled carbon nanotubes, MWCNTs) (Table 1) resulted in increased elastic moduli from 4.3 GPa for annealed neat PEEK to 4.7 GPa for nanocomposites containing 5.0 wt% CNTs, which is in line with published data for PEEK nanocomposites for CNT loadings up to 5 wt% [26,33]. Using the measured increments in elastic modulus (E) and the rule of mixtures with length (η_l) and orientation (η_o) factors (Equation (2)) based on the Krenchel equation [44] for short carbon fibre composites:

$$E = \eta_o \bullet \eta_l \bullet V_f \bullet E_f + (1 - V_f) \bullet E_m \quad (2)$$

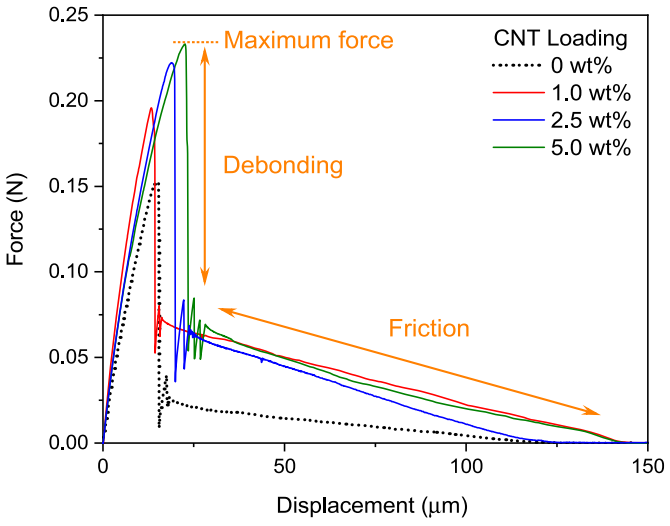
where V_f is the CNT volume fraction, E_m the measured matrix modulus and E_f the CNT modulus and values for $\eta_l = 0.186$ reported by Herceg et al. [28] and $\eta_o = 0.375$ for an anisotropic CNT network we estimated E_f to be 64.3 ± 1.4 MPa. This value is in line with those determined by Herceg et al. and references cited therein. No such improvement was observed in the tensile strength of injection moulded but annealed PEEK nanocomposites, which exhibited tensile strengths in the range 113–115 MPa regardless of CNT loading. Sandler et al. [33] reported increases in tensile strength of annealed PEEK from 80 MPa to around 105 MPa upon incorporation of 5.0 wt% carbon nanofibres (CNF). Conversely, unannealed samples did exhibit improved tensile strengths with increased CNT loading (ESI Table S1). Incorporation of CNTs into annealed PEEK was associated with a small decrease in strain to failure and loss of matrix ductility as CNT loading increased, even at loadings as low as 1.0 wt%. All PEEK samples loaded with CNTs underwent brittle fracture, compared to neat injection moulded PEEK specimens, which exhibited plastic deformation including necking and drawing of the polymer prior to failure.

The apparent interfacial shear strength of single fibre hierarchical composites comprising desized T700 fibres and a PEEK matrix loaded with varying weight fractions of CNTs (0, 1.0, 2.5, 5.0 wt%) was again inversely correlated with the embedded fibre length in all cases (Fig. 7a). The frictional shear strength, determined from pull-out curves after debonding (Fig. 7b) was virtually independent of embedded fibre length at all CNT loadings, with no dependence on CNT loading.

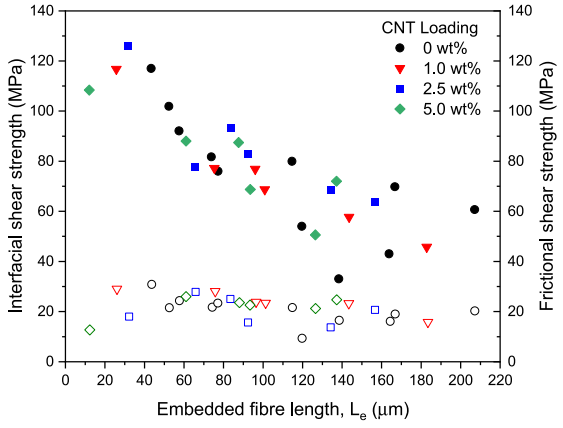
However, the average interfacial shear strength of single fibre hierarchical composites, based on the gradient of the maximum pull-out

Table 1
Crystallinity, tensile strength at break σ_{break}, elastic modulus E and strain to failure ε_f of PEEK nanocomposites with varying weight fractions (0, 2.5, 5.0 wt %) of multi-walled CNTs.

CNT loading	Crystallinity	Tensile properties (±SE)		
(wt%)	(%)	σ_{break} (MPa)	E (GPa)	ε_f (%)
0	34	115.2 ± 0.3	4.26 ± 0.02	5.4 ± 0.1
1.0	35	113.4 ± 0.9	4.49 ± 0.02	4.3 ± 0.3
2.5	31.5	115.4 ± 0.8	4.63 ± 0.07	3.7 ± 0.2
5.0	34	113.7 ± 1.7	4.73 ± 0.09	4.1 ± 0.9



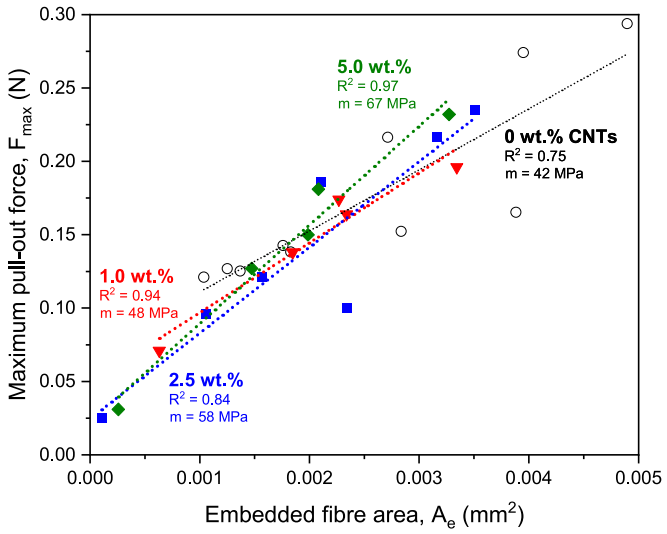
(a)



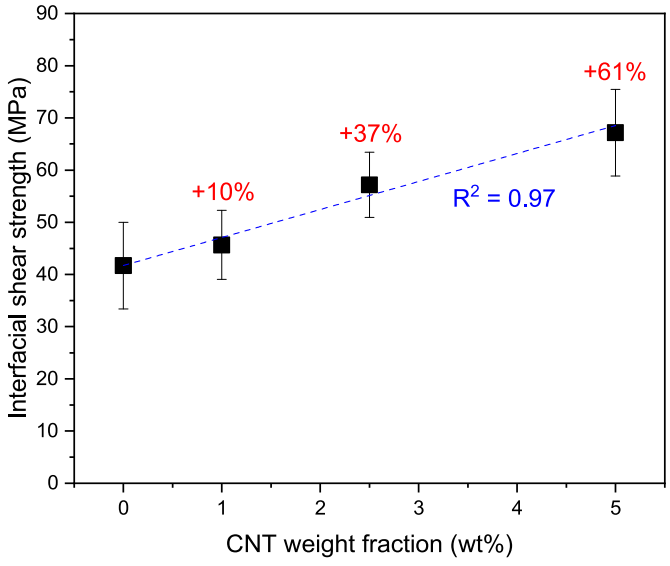
(b)

Fig. 7. (a) Representative fibre pull-out curves and (b) apparent interfacial shear strength (solid markers) and frictional shear strength (hollow markers) as a function of embedded fibre length L_e for single fibre hierarchical composites comprising desized T700 carbon fibres and a PEEK matrix loaded with 0 (black), 1.0 (red), 2.5 (blue) and 5.0 wt% (green) CNTs. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

force as a function of embedded fibre area (Fig. 8a), increased linearly (R^2 = 0.97) with increasing CNT loading, with a 61% improvement achieved at a CNT weight fraction of 5.0 wt% (Fig. 8b). Since the crystallinity of the PEEK matrix remained unaffected (~32–35%) by the presence of CNTs (Table 1, Fig. S2), the increase in interfacial shear strength likely resulted from the CNT-based mechanical modification of PEEK, i.e., the increased modulus (Table 1), which must also be reflected in shear, and improves stress transfer from the fibre to the matrix during pull-out. The increased modulus could result in a zone of higher stiffness and strength near the rough carbon fibre surface and thus more resistance must be overcome in order to deform the CNT enhanced matrix prior to interfacial failure and pull out. Another contribution to the enhanced interfacial shear strength could stem from the possibility that CNTs were oriented in a thin zone along the fibre axis when it is partially embedded in a viscous droplet. This orientation in the contact zone could further enhance the mechanical properties, and may also affect



(a)



(b)

Fig. 8. (a) Maximum pull-out force F_{max} and embedded fibre area A_e and (b) interfacial shear strength, determined from the gradient of $F_{max} = f(A_e)$ for single fibre hierarchical model composites comprising desized T700 fibres and a PEEK matrix loaded with 0, 1.0, 2.5 and 5.0 wt% of CNTs. A linearly increasing trend in interfacial shear strength with increasing CNT weight fraction is marked with a blue dotted line (R^2 = 0.97). Percentage improvement in interfacial shear strength is marked in red for each CNT weight fraction. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

the transcrystalline layer, as observed for aligned CNF reinforced PEEK fibres [45], even if the bulk crystallinity is apparently unchanged.

SEM imaging of the CNT-reinforced PEEK matrix, and extracted carbon fibres following fibre pull-out, revealed a depression, which formed as the fibres were embedded into the matrix during the manufacturing process (Fig. 9a, c). This finding contrasts with the single fibre pure PEEK composites, which exhibited a wetting cone around the fibre, and can be attributed to the significantly increased viscosity of the

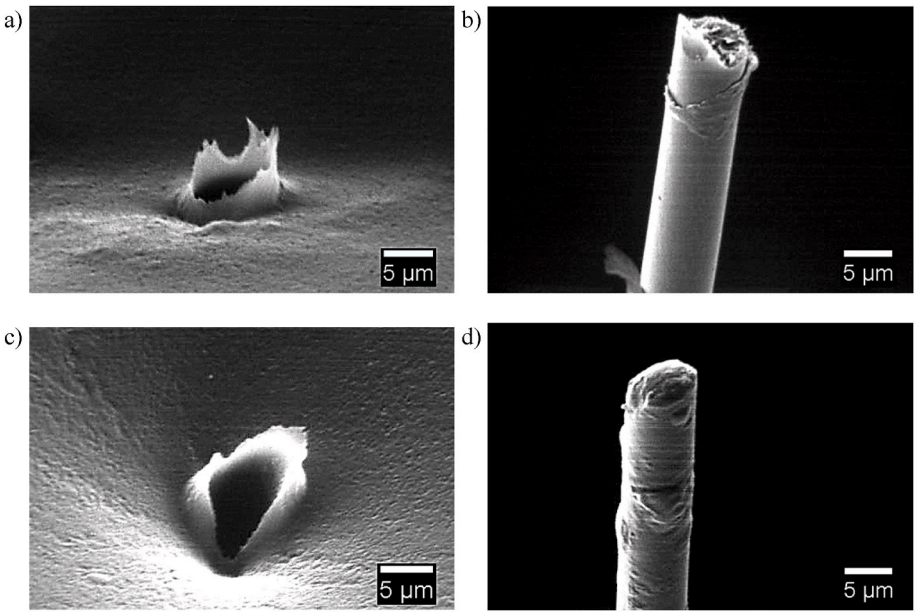


Fig. 9. SEM micrographs detailing the CNT-reinforced PEEK matrix and separated desized T700 fibres following fibre pull-out for (a, b) 2.5 wt% and (c, d) 5.0 wt% PEEK matrix CNT loadings. A depression was present in the CNT-reinforced PEEK matrix (a, c) due to the high viscosity of CNT-reinforced PEEK melts.

PEEK melts incorporating CNTs (542 Pa s compared with 246 Pa s) (Fig. S3). The strength of adhesion between the fibres and the CNT-reinforced matrix was evidenced by the presence of matrix coating the fibres following pull-out. This indicted the influence of the transcrystalline layer adhering to the fibres (Fig. 9b, d) and causing a cohesive shear failure in the PEEK nanocomposite matrix (shear strength of annealed pure PEEK 150 is 63.4 MPa) [46] that resulted in a higher interfacial shear strength (Fig. 8) [47].

Addition of CNTs resulted in interfacial shear strength improvements of up to 32% in single glass fibre-epoxy resin composites [48]. Slight improvements in the interfacial shear strength of single fibre composites comprising carbon fibres and silica nanoparticle reinforced epoxy have also been reported [49], while reductions in interfacial adhesion, manifested as an increase in fibre aspect ratio during single fibre fragmentation tests, have been found in E-glass fibre/nano-sized exfoliated synthetic layered silicate reinforced polyamide-6 matrices [50]. Graphene oxide sizing has been reported to result in improvements similar to those detailed in this study for desized T700SC fibres in PEEK; τ_{IFSS} increased from 43.4 MPa to 62.5 MPa [38] but required a loading of 10.0 wt% graphene oxide to achieve a similar effect to model hierarchical composites containing 5.0 wt% CNTs (67 MPa). Yang et al. [51] describe an elaborate PEEK carbon fibre sizing process to form a crystalline PEEK interface layer around an undisclosed desized fibre using a soluble PEEK precursor (PEEK-1,3-dioxolane). They report improvements in τ_{IFSS} from 43.4 MPa to 81.1 MPa, which are only slightly better than those achievable by the simpler process of dispersing CNTs throughout the matrix, which will also simultaneously improve other matrix-dominated properties, such as interlaminar shear strength and transverse electrical conductivity, when translated into real hierarchical composites. The results, here, for PEEK are considerably better, perhaps in part due to the low baseline strengths expected for thermoplastics, and enhanced interface crystallinity.

4. Conclusion

CNT-PEEK nanocomposite powders were successfully prepared using a temperature induced phase separation method; this approach may be widely applicable to other nanocomposite matrices where cryogenic milling is challenging or undesirable. The resulting nanocomposites were investigated as potential matrices for carbon fibres using single fibre pull-out tests. Apparent interfacial shear strength was inversely correlated with the embedded fibre length irrespective of sizing on the carbon fibre or CNT loading, indicating primarily brittle fracture of the fibre-matrix interface. Pulled out fibres were still coated with matrix, indicating the formation of a transcrystalline layer bordering the fibres and affecting the interfacial shear strength. Adhesion was negatively affected by the presence of an epoxy sizing. Interfacial shear strength increased linearly with increasing CNT weight fraction due to mechanical modification of the PEEK matrix and the formation of a transcrystalline layer. This caused the failure plane to shift into the matrix resulting in cohesive shear failure in the PEEK. Interfacial shear strengths up to ~70 MPa were achieved at a CNT loading of 5.0 wt%, a 61% improvement on neat PEEK matrices. However, frictional shear strength was independent of embedded fibre length or the presence of CNTs in all model composites; indicating that the CNTs did not affect strength after debonding. Since thermoplastic-carbon fibre interfaces are challenging to improve, the results are promising, and suggest that overall improvements in full hierarchical CNT-PEEK carbon fibre composites might be achievable.

Author statement

S.L.: experimental design, visualisation, data collection and analysis, drafting the manuscript; MPJ: visualisation, data analysis, drafting the manuscript; K.H.: experimental design, visualisation, data collection and analysis, manuscript draft revision; G.K.: conceptualisation, supervision, data analysis, revision of draft: M.S.P.S.: conceptualisation, experimental design, visualisation, supervision, revision of draft, funding acquisition; A.B.: conceptualisation, methodology, supervision, manuscript draft revision, editing and proofing, funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.compscitech.2022.109327.

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