On the low reinforcing efficiency of carbon nanotubes in high-performance polymer fibres

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ABSTRACT

Driven by the exceptionally high mechanical properties of carbon nanotubes (CNTs), over the years an extensive research effort has been devoted to the reinforcement of high-performance polymer fibres with CNTs. However, to date, improvements in the strength of these fibres have been rather modest even for relatively high CNT contents. After a brief review of CNT reinforced polymer fibres, here, analytical and numerical finite element models will be used to show that these experimental findings are to be expected based on the intrinsic mechanical properties of these polymer fibres and CNTs, their aspect ratio and interfacial characteristics. Results show that for realistic CNT contents and aspect ratios, the extraordinary strength of CNTs cannot be easily fully exploited in high-performance polymer fibres like Dyneema or Kevlar. Even if CNTs are perfectly aligned, bonded and dispersed, the low intrinsic shear strength of these highly anisotropic polymer fibres limits effective stress transfer and nanotube reinforcement.

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1. Introduction

Carbon nanomaterials, in particular carbon nanotubes (CNTs), have been extensively studied as a reinforcement to produce high strength, low density and highly conductive composites, owing to their exceptional mechanical and electrical properties [1–4]. Since their discovery [5], these materials have been considered as ideal reinforcements for a wide range of new multifunctional composites [6]. CNTs have often been considered as the next generation high-performance carbon fibres due to their ultra-high strength [4,7,8]. While the modulus of individual CNTs (~1 TPa) is still rather close to the modulus of some high modulus carbon fibres (600–800 GPa), their tensile strength (~100 GPa), is some order of magnitude greater than that of the strongest carbon fibre (~7 GPa). Despite their promise as the next generation reinforcement for polymer composites, even after several decades of exhaustive research, these high expectations have not been met yet [8,9]. Next to the direct reinforcement of polymer matrices, several groups aimed to develop macroscopic yarns as direct replacement for...
carbon fibre yarns by direct spinning of aligned arrays of nanotubes [10–14]. However, unless tested at ultra-short gauge lengths, these macroscopic yarns possess mostly modest strength values, which are typically well below the strength of commercially available carbon fibre.

Also as nanoreinforcement in polymer matrices the high expectations of CNTs have not always been met. Poor interfacial adhesion to polymer resins, their tendency to agglomerate in bundles, and their entangled nature and random organisation in polymer matrices are some of the reasons for not fully exploiting their intrinsic properties [9,15,16]. As with most nanocomposite studies, initial attempts to optimize properties focussed on improving the dispersion of CNTs in polymer matrices through surface modifications or the use of surfactants [17,18]. Moreover, it was shown that effective mechanical reinforcement is only achieved with single-walled carbon nanotubes (SWCNT) rather than the more commonly used multi-walled carbon nanotubes (MWCNT) [19,20], and only for nanotubes of high aspect ratio (>1000) [4,8]. Even from the early introduction of CNTs it was recognised that a key aspect to the exploitation of the intrinsic properties of CNTs in polymer composites was to orient them in the matrix and to create one dimensional assemblies [21,22]. Nanotubes can be aligned after embedding them in liquid resins by applying an electric or magnetic field [23,24]. Alternatively, they can be oriented by flow during polymer processing [25,26]. Particularly, fibre spinning has proven itself as a methodology that can successfully align nanotubes at relatively low loadings (<5 wt%), and a wide variety of techniques, including melt-, solution-, gel- or electrospinning [4,15,27–32] have all been used.

Classified by their performance, synthetic fibres can be divided into conventional textile fibres, with tensile strengths up to 1 GPa and moduli up to ~15 GPa, and high-performance fibres with tensile strengths of ~3 GPa and moduli of ~100 GPa. To achieve a high modulus and tensile strength, polymer molecules need to exhibit an extended chain conformation. In the case of flexible chain polymers like nylon and polyester this is (partly) achieved by solid-state drawing at elevated temperatures below the melting temperature. However, effective chain alignment requires chain disentanglement, which means that typically properties of melt-spun fibres based on flexible chain polymers are far from optimal, viz. well below their theoretical or crystal modulus [33,34]. Until the late-1960s, nylon and polyester represented the state-of-the-art in manmade fibres, while the development of high-performance polymeric fibres started only in the early 1970s. Since then significant progress has been made in exploiting the intrinsic mechanical properties of macromolecular chains for the development of high-performance fibres and two major routes were developed which differ with respect to the base material, namely, rigid versus flexible polymer chains [35].

A major breakthrough in the production of high modulus and high strength polymer fibres based on flexible chain polymers was achieved by the solution (or gel) spinning process developed at DSM in the Netherlands at the end of the 1970s [36–39]. Smith and Lemstra [36] discovered that as-spun ultra-high molecular weight polyethylene (UHMWPE) filaments from solution could be hot-stretched in the solid-state below the melting temperature to very high draw ratios. In this so-called gel-spinning process, a morphology with a very low entanglement density in the as-spun gel-like fibre is obtained, which renders them ultra-drawable. Dyneema® by DSM (Netherlands) and Spectra® by its licensee Allied Signal (now Honeywell, USA) are two commercially available high-performance UHMWPE fibres. These fibres have Young’s moduli that range from 80 to 150 GPa and tensile strengths of 2.5 to 4 GPa, that is, 100 times that of bulk polyethylene [39]. In combination with their low density (<1 g/cm³), this leads to exceptionally high specific mechanical properties (properties per unit weight), making these UHMWPE fibres of interest for a wide range of applications ranging from maritime ropes to protective gloves, bullet-proof vests, helmets and other advanced composites applications.

The prime example of a rigid chain polymer fibre is aromatic polyamide (aramid) or poly(p-phenylene terephthalamide) (PPTA) [40]. In the late 1960s, DuPont® scientists developed para-aramid fibres that were three times as strong as nylon (~2.5 GPa) and possessed a far higher modulus (60–120 GPa). Here, orientation with an extended chain configuration is achieved through a liquid crystalline phase spinning process. As chain extension in these rigid rods is already built in, it is not essential to highly post-draw the as-spun filaments. Para-aramid fibres are manufactured under the trademark of Kevlar® (Du Pont, USA) and Twaron® (Teijin Aramid, Netherlands). More recent developments in the area of (semi-) rigid rod fibres includes the poly(p-phenylene-2,6-benzobisoxazole) (PBO) fibre from Toyobo (Zylon®), polyimide (PI), and aromatic polyester (Vectran®).

Over the last two decades, significant efforts were made to produce CNT reinforced polymer fibres with superior mechanical and functional properties for a wide range of polymers [27–29]. The majority of these studies involved melt- or solution spun nanotube enhanced fibres with rather modest
mechanical properties based on polymers such as polypropylene (PP) [41–43], poly(ethylene terephthalate) (PET) [44,45], polyamide (PA) [46–48], polycrylonitrile (PAN) [49,50], poly(vinyl alcohol) (PVA) [15,51–53], poly(lactic acid) (PLA) [54], and poly(ether ether keton) (PEEK) [55]. Although many of these studies reported increased fibre properties, only a few actually achieved effective nanotube reinforcement, while none of these nanotube enhanced fibres possessed mechanical properties that are competitive with commercial high-performance fibres. For the majority of these nanocomposite fibres, the effective stress carried by the CNTs, as back-calculated by a rule of mixtures relationship \( \sigma_c = \sigma_f V_f + \sigma_m (1 - V_f) \), was well below 7 GPa [4], that is, the strength of the strongest carbon fibre. In fact, for a number of nanocomposite fibres the stress carried by the CNTs did not even exceed 2–3 GPa, which is the strength of a baseline carbon fibre [4].

Only few nanocomposite fibres attained a reinforcing efficiency in the order of tens of GPa, for example, as mentioned PVA fibres [52,53] with an effective nanotube stress contribution of 19 GPa for PBO [4,27] as compared to 175 and 88 GPa for PVA. Moreover, it should also be noted that the Young’s modulus of the PBO fibres used by Kumar et al. [56] possessed only half the modulus of commercial PBO fibres (270 GPa), meaning that the effective reinforcement effect in such higher modulus fibres would probably be even less. Similar results were reported by Ruan et al. [57,58] for MWCNT reinforced UHMWPE fibres. By adding 5 wt% MWCNTs, the strength of UHMWPE fibres, with a Young’s modulus of around 120 GPa, increased by approximately 20%. Although this study also reported a significant increase in strength (4.2 GPa as compared to 3.5 GPa for neat fibre), the question remains in this, and many other related studies, if this increase in strength is the direct result of reinforcement by the CNTs or merely the result of a more favourable morphology for subsequent ultra-drawing. In other words, did the improvements in fibre properties come directly from the nanofiller or indirectly from a modification of the polymer matrix by the nanofiller, leading to higher draw ratios and improved mechanical properties? For example, while Wang et al. [53], showed that mechanical property improvement in their oriented PVA/SWCNT system was the direct result of effective nanotube reinforcement, property improvement in the oriented PP nanocomposite system of Van Erp et al. [63] was merely the result of improved drawability. Another reason to doubt the effectiveness of nanofillers in fully chain extended polymer systems is related to their effect on the packing density of polymer chains. Since the dimensions of CNTs are comparable to the unit cell of polymers like polyethylene, their efficiency as nanoreinforcement can be questioned since their presence may affect the high degree of chain packing in these systems, and as a result ultimate mechanical properties [64].

Nanotube reinforcement in aramid fibres has also...
been investigated [44,65]. Deng et al. [65] prepared PPTA/SWNT nanocomposite fibres by a dry-jet wet spinning process and different draw ratios. As the presence of nanotubes affected the polymer chain orientation (and thus packing density), in the nanocomposite fibres, particularly at higher draw ratios, mechanical properties were mostly reduced. Although efficient stress transfer was observed through in-situ Raman spectroscopy, a breakdown of the interface above 0.35% strain (≈35 GPa) occurred [65], making these nanotubes basically ineffective at higher strains and stresses.

Hence, given the limited success of CNTs to reinforce high-performance polymer fibres, the question arises if CNTs – even in theory – can effectively reinforce such fibres, for example, significantly improve their tensile strength even further (see Figure 1). To answer this, here, both analytical and finite element models will be employed to study the reinforcing potential of CNTs in high-performance polymer fibres as a function of (anisotropic) fibre properties, CNT content and interface conditions, while assuming that the CNTs are perfectly aligned and homogeneously dispersed within the polymer fibre.

2. Analytical modelling

Among an extensive number of analytical micromechanical composite models available, the models of Hale and Kelly [66] and Sørensen [67] will be used in the present work. The first model is intended to examine the maximum possible reinforcing effect of CNTs in oriented polymer fibres, for example, infinitely long and well aligned CNTs, which are also perfectly bonded to the polymer matrix, that is, the polymer fibre. The second model, which includes interfacial debonding, frictional sliding and residual stresses, will be used to investigate the efficiency of long CNTs of finite length under more realistic conditions. Both analytical models allow us to study the effect of a wide range of material parameters on the strength improvement of high-performance polymer fibres by CNTs. For completeness, the two analytical models are briefly discussed below.

2.1. Infinitely long aligned CNTs in a polymer fibre without debonding

For infinitely long, perfectly aligned CNTs of equal strength, the minimum CNT volume fracture, \( V_{\text{min}} \), which increases the strength of a polymer fibre, \( \sigma_f^i \), depends on the failure strain of the CNTs compared to the failure strain of the polymer fibre [66]. When the CNTs have a low strain-at-break relative to the polymer fibre (\( \epsilon_{\text{CNT}}^u < \epsilon_f^i \)), then \( V_{\text{min}} \) is:

\[
V_{\text{min}} = \frac{\sigma_f^i - \epsilon_f^i}{\sigma_f^i + (\sigma_f^i - \epsilon_f^i)}, \quad \text{for} \quad \epsilon_{\text{CNT}}^u \leq \epsilon_f^i
\]  

(1)

where \( \sigma_f^i \) is the strength of the polymer fibre, \( \sigma_{\text{CNT}}^i \) the CNT strength and \( \epsilon_f^i \) is the stress in the polymer fibre required to induce a strain equal to the failure strain of the CNTs. SWCNTs, with strengths of around 100 GPa, in most cases will have a higher failure strain than a typical high-performance polymer fibre, \( \epsilon_{\text{CNT}}^u > \epsilon_f^i \), [68]. Hence, the minimum CNT volume fracture, \( V_{\text{min}} \), is [66]:

\[
V_{\text{min}} = \frac{\sigma_f^i}{\sigma_{\text{CNT}}^i - \epsilon_f^i}, \quad \text{for} \quad \epsilon_{\text{CNT}}^u > \epsilon_f^i
\]  

(2)

where \( \epsilon_{\text{CNT}}^u \) is equal to \( E_{\text{CNT}} \epsilon_f^u \) and \( E_{\text{CNT}} \) is the effective Young’s modulus of the CNTs. The underlying assumption, that the CNTs and polymer fibre are linear elastic, is reasonable for highly oriented high-performance polymer fibres within the context of the present work.

Equations (1) and (2) should be considered as the lower limit of \( V_{\text{min}} \) since, apart from the conditions mentioned above, it is also assumed that the CNTs are perfectly bonded to the polymer fibre.

2.2. Long aligned CNTs of finite length in a polymer fibre with debonding

A more realistic model, compared to the previous model, should consider debonding of finite length CNTs from the polymer fibre as shown in Figure 2. At a certain applied stress, a CNT of finite length will debond from the polymer fibre at the CNT ends. This stress, denoted as debonding initiation stress, \( \sigma_{\text{CNT}}^i \), is given by [67]:

\[
\sigma_{\text{CNT}}^i = \frac{(1 - V_{\text{CNT}})E_f}{E_c} \Delta \epsilon^T + 2 \sqrt{\frac{(1 - V_{\text{CNT}})E_f}{E_c} \left( \frac{G_{c,i}}{E_{\text{CNT}}r_{\text{CNT}}} \right)}
\]  

(3)

where \( E_c \) and \( E_f \) are the moduli of the reinforced and unreinforced polymer fibre. The CNTs, with radius \( r_{\text{CNT}} \), have a volume fraction \( V_{\text{CNT}} \). The
misfit strain, $\Delta e^T$, is due to the difference in thermal expansion of the CNTs and the polymer fibre. The interface properties expressed by the mode II (shear) fracture energy, $G^i_{c,t}$, affects also the debonding initiation stress.

If there is no friction after the initiation of debonding, then Equation (3) gives the stress level at which the debond crack will propagate along the entire CNT/polymer fibre interface, thus giving a lower bound strength. The difference in strain and surface roughness may induce an interface frictional stress, $T_{fr}$. This frictional stress results in an increase in applied stress, $\sigma_c$, as the debond length, $\ell_d$, increases [67]:

$$\sigma_c = \sigma^i_c + 2\left(\frac{T_{fr}}{E_{CNT}}\right)\left(\frac{\ell_d}{r_{CNT}}\right)$$

(4)

It is clear that the applied stress, $\sigma_c$, is linearly related to the debond length and higher than the debonding initiation stress $\sigma^i_c$. The debond length is:

$$\ell_d = \frac{E_{CNT}}{2T_{fr}}\frac{\sigma_c}{E_c} - \frac{(1-V_{CNT})E_f}{E_c}\frac{\Delta e^T}{G^i_t}$$

(5)

It should be noted that the axisymmetric micromechanical model of Sørensen [67] is originally developed to study debonding initiation and growth from a fibre break location for an infinitely long fibre.

### 2.3. Interface cohesive law

The mode II (shear) interface fracture energy, $G^i_{c,t}$, in Equation (3) can be regarded as a property of the CNT/fibre interface cohesive law, for example, a relation between the normal and shear tractions at the interface and the corresponding opening and tangential displacements [69,70]. The traction in the cohesive zone may originate from Van der Waals forces, chemical bonding or interface friction or a combination of these [1,71,72]. Figure 3 shows such a cohesive law, the mode II (shear) component, which in its simplest form shows a linear softening behaviour. The mode II (shear) traction, or in more general terms interfacial shear strength (IFSS) decreases from its peak value, $T_t$, to zero when the interface tangential crack opening reaches the critical mode II tangential (or sliding) opening $\delta^s_t$. The area under the traction-separation curve equals the mode II interface fracture energy, $G^i_{c,t}$. If friction exists at the interface, then the mode II traction decreases to the frictional stress, $T_{fr}$, and then remains constant as the tangential opening further increases. In Figure 3 it is assumed that the mode II traction becomes equal to $T_{fr}$ when $\delta_t = \delta^s_t$. The area under the traction-separation curves for crack openings larger than $\delta^s_t$ is equal to the dissipated energy due to friction.

It should be noted that the cohesive law of Figure 3 is a phenomenological cohesive law commonly used in solid mechanics for modelling crack initiation and propagation along interfaces or material planes [73,74]. The cohesive law concept (Figure 3) allows in the present work to relate the analytical predictions using the model of Section 2.2 to the numerical predictions using the finite element models introduced in the next section.

### 3. Finite element modelling

The finite element (FE) model used here is based on the CNT distribution shown in Figure 4(a), where it can be seen that the CNTs have a finite length, $2L_{CNT}$, and there is a partial overlap between neighbouring CNTs. The distance between lines passing through the CNT centers is $\ell_c$.

Figure 4(b) shows a cross-section normal to the CNTs (only half of the CNTs are cut), assuming a square array of CNTs of a rectangular cross-section and with length $L_{CNT}$. A more natural way would be to assume circular CNTs with a radius $r_{CNT}$ surrounded by a matrix (read: polymer fibre) of radius $r_c$ (Figure 4(b)). This would allow to approximate the 3D problem of Figure 4 by an axisymmetric model indicated by the hatched region and shown in more detail in Figure 5 [75]. A critical parameter for achieving a high reinforcing efficiency of CNTs is a high interface shear peak traction, $T_t$, defined in the previous section. A drawback of the analytical...
model of Section 2.2 is that (shear) failure of the matrix (read: polymer fibre) itself is not considered. By assuming a rectangular cross-section for the CNTs, the composite damage model [76, 77], available in the Abaqus commercial finite element code for plane stress problems, can now be applied to allow failure of the polymer fibre. Numerical tests, without polymer fibre damage and failure, have shown that the plane stress models yield very similar results to the corresponding axisymmetric models for a wide range of parameters examined. Thus, the assumption of plane stress conditions is considered reasonable and will therefore be used in the present work.

Figure 5 shows the geometry and boundary conditions of the unit cell analysed. Due to symmetry, only a quarter of the geometry is modelled. The radius of the CNTs, rc, is equal to 1.5 nm and the length, lCNT, is equal to 3 mm, giving an aspect ratio (AR) of 2000. The total length of the model is lc and therefore lc/lCNT = (3/8)lCNT (see Figure 4(a)). It should be noted that the overlap length of the CNTs has a negligible effect on the results. The width of the model, rc, is varied depending on the CNT volume fraction. The CNT end is assumed to be fully debonded from the matrix or polymer fibre, an assumption which also has a negligible effect on the results. The CNT/polymer fibre interface is modelled with cohesive elements. The constitutive (cohesive) law is given in Figure 3. The cohesive elements have a length of 0.2 nm and a finite thickness equal to 0.05 nm. With this cohesive element length, the number of cohesive elements within the fracture process zone, df/ct, is in the order of 300, much larger than the minimum required number of cohesive elements which is 4–7 for accurate results [78]. The Abaqus explicit solver is used to solve the problem of Figure 5 under quasi-static conditions using mass-scaling. An explicit solver is preferred to avoid convergence difficulties, which are commonly observed when modelling crack growth with implicit finite element methods [79, 80].

4. Materials properties

The properties of CNTs have been investigated experimentally, numerically and theoretically. Krishnan et al. [81] have experimentally estimated the Young’s modulus of SWCNTs to be about 1.25 TPa. A similar value, 1.28 TPa, was experimentally obtained by Wong et al. [82]. Jin et al. [83], using molecular dynamics, calculated the effective Young’s
Table 1. Elastic properties of CNTs and UHMWPE fibre.

|       | $E_{11}$ (GPa) | $E_{22}$ (GPa) | $E_{33}$ (GPa) | $\nu_{12}$ | $\nu_{13}$ | $\nu_{23}$ | $G_{12}$ (GPa) | $G_{13}$ (GPa) | $G_{23}$ (GPa) |
|-------|----------------|----------------|----------------|------------|------------|------------|----------------|----------------|----------------|
| CNT   | 1000           | 60             | 60             | 0.25       | 0.05       | 0.05       | 500            | 25             | 25             |
| UHMWPE| 100            | 2              | 2              | 0.3        | 0.01       | 0.01       | 0.8            | 0.3            | 0.3            |

$1 \to x, 2 \to y, 3 \to z$. $E_{ii} = E_{CNT}$ for CNTs and $E_{ii} = E_f$ for UHMWPE fibre.

modulus between 1.23 to 1.35 TPa. The Young’s modulus, based on finite element analysis (FEA), was calculated between 1.1 and 1.32 TPa [84] and equal to 0.7 or 1 TPa based on micromechanical analysis [85,86]. In the present work, for the analytical models, the CNTs are assumed isotropic linear elastic with $E_{CNT} = 1$ TPa. An exact value for $E_{CNT}$ is not crucial for the current work. In the FEA, the CNTs are modelled as anisotropic linear elastic solids. The elastic properties are given in Table 1, which are based on theoretical and numerical analyses [83,84,87]. The polymer fibres are modelled as isotropic linear solids in the analytical models. In specific cases where a hypothetical UHMWPE fibre is assumed, the fibre’s Young’s modulus, $E_f$, is set equal to 100 GPa [39,88]. The anisotropic UHMWPE fibre elastic properties as used for the finite element analysis (FEA), are listed in Table 1 and are based on the experimental work of Peijs et al. [88].

Predictions of the intrinsic tensile strength of SWCNTs are in the order of 100 GPa and higher: 117 GPa [89], 110 GPa [90], and 93 GPa [68]. A wide range of experimental strength values were reported: 150 GPa [91], 25–75 GPa [92], and 13–52 GPa [93]. In the present work, the tensile strength of CNTs is taken as equal to 140 GPa, that is, close to the theoretical and numerical predictions. In the FEA, it is assumed that the CNTs do not fail. The strength of the UHMWPE fibre is taken as equal to 3.5 GPa for the analytical models, whereas the experimentally determined anisotropic strength values used are based on the values listed in Table 2 [37,39,88]. In the FEA, the transverse tensile strength, transverse compressive strength and axial compressive strength are equal to 100 MPa to promote failure by shear. The polymer fibre shear strength values are set between 20 and 100 MPa, for example, lower and higher than the peak traction (interfacial shear strength), $T_{f}$, of 25 MPa which is used in the cohesive law. It should be noted that even the lower shear strength value is still higher than reported intrinsic shear strength values of UHMWPE fibres as listed in Table 2. However, the parameter that governs the fracture of the CNT reinforced fibres is the ratio of the mode II (shear) peak traction over the shear strength of the polymer fibre.

The interfacial shear strength ($\text{IFSS}$) of the CNT/polymer interface has been extensively investigated both experimentally and theoretically. Experimental data reported includes shear strength values that vary as widely as 14 and 47 MPa for epoxy resin [94,95], and 160 MPa for functionalized CNTs in PVA [96]. A review on experimentally obtained $\text{IFSS}$ values for different polymers [97] shows that these values typically vary between 20 and 100 MPa. Single nanotube pull-out and microdroplet tests also revealed post-debonding frictional stresses of around 2 to 5 MPa for epoxy [94,95]. On the other hand, only a small number of studies theoretically predicts the CNT/polymer interface cohesive law [71,72]. A (rather unrealistic) peak traction, $T_{f}$, was predicted of approximately 450 MPa with a critical opening, $\delta_c^f$, in the order of 3 nm. In the present work, a large range of $T_{f}$ was examined, whereas in the FEA $T_{f}$ is equal to 25 MPa, which, according to the authors opinion, is of a more realistic order of magnitude. The critical crack opening, $\delta_c$, is varied from 0.1 to 5 nm.

Thermal effects were ignored, for example, $\Delta e^T = 0$. The main effect $\Delta e^T$ is friction along the CNT/polymer interface, which is modelled by prescribing a constant frictional stress in the analytical model of Section 2.2 and by using a mode II (shear) cohesive law with constant traction for shear openings larger than $\delta_c$ (see Figure 3). In other words, friction is directly included in the cohesive law instead of prescribing frictional contact once $\delta_c > \delta_c^f$.

5. Results and discussion

5.1. Aligned CNTs of infinite length in a polymer fibre with perfect bonding

Figure 6 shows an example of the strength of an UHMWPE fibre reinforced with CNTs as a function of the CNT volume fraction. Using Equation (2), it can be seen that the minimum CNT volume fraction, $V_{CNT}$, above which a significant reinforcement effect of the UHMWPE fibre is obtained is approximately 3.6%. Perfect dispersion at this volume fraction is already hard to achieve in practice [98], while in order to have a significant reinforcement effect a much higher SWCNT content would be required. For example, only at $V_{CNT}$ equal to 7.5%, the CNT reinforced UHMWPE fibre would have a strength of...
10 GPa, i.e. three times that of the unreinforced polyethylene fibre, and higher than for example, Toray’s T1000 ultra-high strength carbon fibre. Using Equations (1) and (2), results such as the one presented in Figure 6 can be summarised in the contour plot of Figure 7 where $V_{\text{min}}$ is plotted as a function of neat polymer fibre Young’s modulus, $E_f$, and tensile strength, $\sigma_u$: Figure 7 focuses on highly oriented high modulus polymer fibres as can be seen by the x-axis scale. In this graph, the Young’s modulus and strength of known commercial high-performance polymer fibres like Kevlar, Dyneema, Spectra and Zylon are superimposed. It can be seen that for higher performance fibres, the minimum CNT volume fraction, $V_{\text{min}}$, for effective reinforcement increases to levels that cannot be easily achieved while maintaining perfect dispersion of individual nanotubes for practical reasons. For example, if Zylon fibres were to be reinforced, a CNT volume fraction greater than 5% would be required just to reach $V_{\text{min}}$. Of all commercial high-performance fibres, for the lowest performance Spectra 900 or Dyneema SK60 fibre, $V_{\text{min}}$ is below 2.5%. However, if a non-commercial PVA fibre with a Young’s modulus of only 15 GPa is considered [53] (note that the Young’s modulus of commercial high performance PVA fibre can be as high as 40 or 50 GPa), $V_{\text{min}}$ is approximately equal to 0.35%, that is, a filler content where homogeneous dispersion of individual CNTs is more readily achievable. If the CNT volume fraction is increased to 0.85%, Equation (2) predicts that the strength of the CNT reinforced PVA fibre will increase by a factor of three, a value close to the experimental results of Wang et al. [53] where the corresponding CNT volume fraction for a strength increase by a factor of 3 was 1.0 wt% (~0.8 vol%). Thus, Equation (2) predicts rather accurately at least the reinforcing effect of CNTs in polymer fibres of moderate mechanical performance.

A graph like Figure 6 is well known and well understood for traditional unidirectional composites based on glass or carbon fibres [99]. However, since the minimum reinforcement (fibre) volume fraction, $V_{\text{min}}$, for traditional composites is typically only a few percent, that is, several times lower than practical fibre volume fractions (50–60%), the relevance of $V_{\text{min}}$ is generally not recognised. In case of nanocomposites, however, with filler loadings typically around a few percent, Figure 6 becomes highly relevant.

5.2. Aligned CNTs of finite length in a polymer fibre with debonding

Although the CNTs considered in the model have a high aspect ratio, $AR = 2\epsilon_{\text{CNT}}/2r_{\text{CNT}}$, they are not infinitely long as assumed in Section 5.1. Interfacial debonding can initiate from the CNT ends and propagate along the interface, thus reducing the reinforcing efficiency of the CNTs. Figure 8 shows the debonding initiation stress, using Equation 3, as a function of the polymer fibre Young’s modulus, $E_f$, and the interface peak traction, $T_i$. For $T_i = 0$, $\sigma_i^2 = \sigma_e^2$. Interface: $\delta_{\text{int}} = 5.0$ nm. The CNT volume fraction is 6.0% $> V_{\text{min}}$. A graph like Figure 6 is well known and well understood for traditional unidirectional composites based on glass or carbon fibres [99]. However, since the minimum reinforcement (fibre) volume fraction, $V_{\text{min}}$, for traditional composites is typically only a few percent, that is, several times lower than practical fibre volume fractions (50–60%), the relevance of $V_{\text{min}}$ is generally not recognised. In case of nanocomposites, however, with filler loadings typically around a few percent, Figure 6 becomes highly relevant.
strength (IFSS), for $V_{CNT}$ equal to 6%, which is higher than $V_{min}$ for all cases.

From $T_i$ and assuming a critical tangential opening, $\delta_k$ equal to 5.0 nm, the mode II (shear) fracture energy, $G_{c,t}$, can be calculated (see Figure 3) and used in Equation 3. A value of 5.0 nm is probably rather large [72] and therefore Figure 8 gives a non-conservative debonding initiation stress, $\sigma_i$. The characteristic properties, Young’s modulus and strength, of four commercial high-performance polymer fibres are also plotted. If it is assumed that there are no debonding frictional stresses (see Section 2.2), then the strength of the reinforced polymer fibre, $\sigma_u$, is equal to the debonding initiation stress. If a Spectra 900 fibre is considered, it can be seen that the interfacial shear peak traction (or IFSS) should be higher than 60 MPa in order to have a debonding initiation stress that exceeds the strength of the fibre itself and thus results in a minimum positive reinforcement effect of the polymer fibre. For the Dyneema SK90 fibres, the corresponding required interfacial shear peak traction is close to 100 MPa, for the Zylon AS fibre more than 100 MPa, whereas for Zylon HM it is approximately equal to 165 MPa. Hence, for most high-performance polymer fibres, a very high interface peak traction or IFSS is required to delay initiation of debonding and to achieve a positive reinforcing effect of CNTs on the strength of these high-performance polymer fibres. However, in many cases the calculated required interfacial shear peak tractions exceed the intrinsic shear strength of the polymer fibres, meaning that the shear strength of the fibre itself becomes the limiting factor rather than the interfacial adhesion. In case of highly anisotropic polymer fibres, the favourable characteristics in the fibre (chain) direction in terms of stiffness and strength are not matched in off-axis (shear, transverse) loadings. Fibre anisotropy exists in all high-performance organic fibres. In aramid fibres the PPTA molecules are covalently bonded in one dimension (1D) [40]. In comparison with UHMWPE fibres we could therefore refer to them as (1D+) structures due to the stronger hydrogen bonds between the polymer chains in comparison with the weak Van der Waals interactions in polyethylene. As a result of this, the transverse and shear properties of these fibres can be up to two orders of magnitude lower than their uniaxial tensile properties. Realistic values for the intrinsic shear strength lie somewhere between 10 and 30 MPa for UHMWPE fibres and 60 and 80 MPa for aramid [39,88,100], with PBO somewhere in between. Hence, irrespective of the level of interfacial adhesion the stress transfer in these fibres is often limited by the intrinsic shear strength of the polymer fibre rather than that of the interface. In the next section, FEA results will further examine if such high interfacial peak tractions can lead to CNT reinforced polymer fibres with significantly improved strength properties.

In Figure 9 the combined effect of CNT volume fraction and interface peak traction on the debonding initiation stress is examined. The fibre properties are taken identical to the UHMWPE fibre of Figure 6, for example, $E_f=100$ GPa and $\sigma_i^p=3.5$ GPa. For this fibre, under the assumptions of the model of Section 2.1, $V_{min}=3.6\%$. From Figure 9a, with a large $\delta_k$ and thus large $G_{c,t}$, it can be seen that in case of interfacial debonding the CNT volume fraction has to increase to approximately 10%, together with an interface shear peak traction of around 200 MPa, in order to obtain a minimum positive reinforcement effect. When decreasing the required interfacial peak traction, for example by a factor of two, the CNT volume fraction has to be larger than 30-40% in order to create a CNT reinforced fibre with a higher strength than the unreinforced fibre itself. Figure 9a shows that a high debonding initiation stress, that is greater than the tensile strength of the unreinforced fibre, can
only be achieved by a combined high CNT volume fraction (> 30 vol%) and high interfacial shear peak traction (> 150 MPa), which is difficult if not impossible to achieve. For a more realistic interfacial shear peak traction or IFSS in the order of 25 MPa, the debonding initiation stress is approximately 1.2 GPa for CNT volume fractions as high as 50%. Even for such a high CNT content this value is only one third of the unreinforced fibre strength, hence in this case the CNTs significantly reduce the fibre strength. When the critical interfacial shear crack opening is reduced from 5.0 nm to 0.5 nm (Figure 9b), then even for interface peak tractions up to 200 MPa and CNT volume fractions up to 50%, the strength of the CNT reinforced UHMWPE fibre is well below that of the neat polymer fibre. From this it becomes clear that conditions that can lead to a significant increase in fibre strength are difficult if not impossible to achieve in practical fibre systems.

The predictions of Figures 8 and 9 are more realistic than the predictions of Figure 7. However, they are still conservative as it is assumed that once debonding initiates at the CNT end, it will propagate at a constant stress along the entire nanofibre interface. The presence of interfacial frictional stresses after the initiation of debonding will require a higher applied stress to further increase the debond length, \( \ell_{dh} \), as Equation (4) states, for example, a linear relationship between the applied stress and debonding length, which is given by Equation (5). The effect of interfacial friction is shown in Figure 10 where the strength of a nanocomposite fibre is plotted for different CNT volume fractions. Here, the interface frictional stress is equal to a modest, but in case of polyethylene, still realistic 1 MPa and the polymer fibre properties are the same as in Figures 7 and 9. As discussed above (see Figure 9), debonding initiates at a stress significantly below the fibre strength. In Figure 10 the debonding initiation stress is when the debond length is greater than zero. It can be seen that for all CNT loadings, the applied stress has to be increased in order to propagate the interface crack. If the case of \( V_{CNT} = 10\% \) is considered, then it can be seen that debonding starts when \( \sigma_c \approx 1.45 \) GPa. If the CNTs have an aspect ratio, \( AR \), equal to 1000 and the debond crack initiates and propagates from both CNT ends, then the CNTs will be fully debonded when \( \sigma_c \approx 1.6 \) GPa, which is still nearly half the original UHMWPE fibre strength (3.5 GPa). Even for an \( AR \) of 5000, the CNT “reinforced” fibre has a predicted strength (2.3 GPa) below that of the unreinforced fibre. For an even higher \( AR \), of around 10,000, the nanocomposite fibre has a strength of approximately 3.2 GPa, which is still slightly below the neat fibre at 3.5 GPa. For reference, although ultralong SWNTs have been reported, a commonly used SWCNT grade like Tuball™ graphene nanotubes has an outer diameter of 1.6 nm and length of 5 \( \mu \)m, giving an aspect ratio of \( \sim 3000 \). Only when \( V_{CNT} \) is 15% and an \( AR \) equal to 10,000, the reinforced nanocomposite fibre has a \( \sim 7\% \) higher strength than the neat UHMWPE fibre.

This highlights the importance of aspect ratio and is in agreement with recent analytical studies, based on simple shear-lag models, for graphene reinforced nanocomposites, where properties are also limited by the filler aspect ratio [101]. However, at low \( V_{CNT} (<1\%) \), even for high aspect ratio CNTs (\( AR = 10,000 \)) the strength of the nanocomposite fibre is approximately only half that of a neat UHMWPE fibre. Hence, these model calculations predict that even in the case of 15 vol% CNTs with an \( AR = 10,000 \), no significant reinforcement of the UHMWPE fibre are to be expected in case of a realistic IFSS of 25 MPa and frictional stress of 1 MPa.

As shown in Figure 9, for a constant mode II peak traction, an increase of the critical interfacial crack opening, \( \delta_c^{IF} \), increases the mode II (shear) fracture energy and thus the stress for debonding initiation increases. The same can be seen in Figure 11 where interfacial crack growth is taken into account. The critical crack opening has a significant effect on the tensile strength of the CNT reinforced polymer fibre. For example, for an \( AR \) equal to 10,000, there is a 25% reduction in strength by decreasing \( \delta_c^{IF} \) from 5 to 1 nm.

In Figure 12 the interface frictional stress, \( T_{fr} \), which is active after the initiation of debonding is varied for \( V_{CNT} \) equal to 10%. For this CNT volume fraction and \( T_{fr} = 1 \) MPa, it was shown in Figure 10 that the strength of the CNT reinforced nanocomposite fibre is lower than that of the neat polymer fibre itself even for an \( AR = 10,000 \). By increasing the frictional stress to 2 MPa, the strength of the
CNT reinforced fibre increases by 35%. A further increase of $T_{fr} = 5$ MPa, results in a three times higher strength, whereas for very large values of $T_{fr}$ equal to 15 MPa, the reinforced fibre has a strength of more than 7 times the strength of the unreinforced fibre. However, for low aspect ratio CNTs, $AR = 1000$, even frictional stresses as high as 10 MPa do not improve the fibre strength. Even for $T_{fr} = 15$ MPa, the improvement in strength is only around 15%. The results of Figure 12 can be compared with the results of Figure 9 and from this it can be concluded that only in the case of relatively high interfacial frictional stresses ($\geq 5$ MPa) and CNT aspect ratios ($\geq 5000$), significant improvements in fibre strength can be expected. In fact, only for an AR of 10,000 and a post-debonding frictional stress $\geq 5$ MPa, a strength of the UHMWPE nanocomposite fibre (10 vol% CNT, IFSS = 25 MPa), is predicted that exceeds that of the strongest carbon fibre ($\approx$7 GPa).

Based on the results of this section, it can be concluded that in theory CNTs can reinforce high-performance polymer fibres but only under certain conditions or more precisely a combination of all of the following: (i) high CNT volume fractions ($\geq 10\%$), (ii) high CNT aspect ratios ($\geq 10,000$), (iii) high interfacial shear strength ($\geq 25$ MPa) and (iv) relatively high interfacial frictional stresses ($\geq 5$ MPa).

However, in practice, such high values for $V_{CNT}$ and interfacial shear strength and frictional stresses are not easily achievable. For example, it is well established that nanofiller dispersion becomes more difficult at higher filler loadings, leading to agglomeration and ineffective reinforcement [43]. Even if homogeneous dispersions of individual CNTs at high concentrations and high interfacial adhesion can be achieved, effective stress transfer may still be limited by the intrinsically low shear strength of most high-performance polymer fibres. In fact, shear strengths of oriented UHMWPE have been reported as low as 10 MPa (i.e. significantly below 25 MPa) and may trigger fibre rather than interface dominated failure modes, which again may result in a lower nanocomposite fibre strength. These issues will be examined in more detail in the next section using FEA.

5.3. Finite element results

In Figure 13 the results of Figure 11, solid lines, are plotted together with the results from the finite element (FE) simulations, which include both the debond length and the crack tip position ($T_t - T_i$) for a system based on UHMWPE, 10 vol% CNTs with an AR of 2000 and an IFSS of 25 MPa. In order to reduce computation time we restricted the model simulations to a limited but still realistic AR of 2000. It should be noted that in these simulations no failure is taken into account for the UHMWPE fibre. The simulations run until extensive shear deformation in the polymer fibre close to the CNT end result in a non-convergent solution. It can be seen that the analytical model of Section 2.2,
although a one-dimensional model, predicts quite accurately the stress for debonding initiation and captures the physics of debond growth. The difference in the slope of debond growth is mainly due to the Poisson’s effect which is not included in the one-dimensional (shear-lag) analytical model and secondary to the anisotropic elastic properties used in the FE simulations. The predicted FE strengths for the different critical shear crack openings, are lower than the analytical predictions represented by the solid lines. The debond growth is in the order of 1 μm before excessive shear deformation in the polymer fibre occurs, compared to a debond growth in the order of millimeters for the analytical model. It should be noted that although the FE predicted debond length is significant, it is still approximately only 500 times the CNT radius. Clearly, the low shear properties of the highly anisotropic UHMWPE fibre limits the reinforcing efficiency of the CNTs. The predictions of the analytical model of Section 2.2 gives therefore an upper bound for the strength of CNT reinforced polymer fibres.

If the crack tip position is considered, then it can be seen that interface damage starts at an applied stress of around 0.2 GPa, that is, an order of magnitude below the neat UHMWPE fibre strength and as expected independent of the critical opening, $\delta_i$, which controls the length of the crack tip fracture process zone, for example, the higher the $\delta_i$, the longer the fracture process zone and as a result delayed debonding initiation. The steady-state crack tip fracture process zone can be calculated from the difference of $x_{tip}$ and $\ell_d$.

The effect of the interfacial frictional stress, based on FE simulations, is shown in Figure 14 where again the analytical model predictions of Section 2.2 are included. Similar to Figure 13, failure of the polymer fibre is not included in the FE model. The analytical model predictions represented by the solid lines are in fairly good agreement with the FE predictions, confirming the validity of the analytical model. The differences observed are due to the mode II (shear) fracture energy, $G_{c,t}$, being larger in the FE simulations for the same critical interfacial shear crack opening, $\delta_i$. In the analytical model, $G_{c,t}$ is calculated as the area under the traction-separation curve with $T_i = 0$ for $\delta_i = \delta_f$. In the FE simulations $G_{c,t}$ is the area under the traction-separation curve with $T_i = T_{fr}$ for $\delta_i = \delta_f$ (see Figure 3). However, the main conclusion from Figure 14 is that after debonding initiation, a high interfacial frictional stress results in higher shear deformation in the polymer fibre and the debond length is significantly lower compared to the analytical predictions. Thus, even a relatively high frictional stress of 20 MPa, as indicated in Figure 12, cannot be utilised to improve the nanocomposite fibre strength.

Failure of the polymer matrix or fibre is included in the FE results of Figure 15 where the crack tip position is plotted as a function of the applied stress for different shear failure strengths of the polymer fibre. FE simulations follow the same trend as the analytical model prediction but they do predict earlier failure depending on the shear strength of the fibre. The lowest fibre shear strength value considered, 20 MPa, is lower than $\bar{T}_f$, (25 MPa) while the highest value is four times higher than $\bar{T}_f$. The corresponding FE simulation, from Figure 13, without shear failure of the polymer fibre is also included. As expected, the lower the shear strength of the polymer fibre, the lower the tensile strength of the nanocomposite fibre and in all cases the predicted strength is significantly below that of simulations where failure of these highly anisotropic fibres is not considered. For $\sigma_{f12}^{\infty}$ equal to 20 MPa, that is, below $\bar{T}_f$, the nanocomposite fibre strength is nearly equal to the applied stress necessary to initiate damage near the interface. When $\sigma_{f12}^{\infty}$ increases to 30 and 40 MPa, that is, above $\bar{T}_f$, the interface
fracture process zone develops but is not fully developed before failure of the fibre, for example, the debond length is zero (not shown in Figure 15). For \( \sigma_{ts}^{PBO} = 50 \text{ MPa} \), that is, twice \( T_t \), the debond length is only 0.25 nm when failure occurs. For fibre shear strengths much larger than \( T_t \), shear failure of these anisotropic polymer fibres is delayed and thus debonding initiates and grows prior to failure. For \( \sigma_{ts}^{PBO} = 100 \text{ MPa} \), the debonding length is about 35 nm (\( \sim 24 \ r_{CNT} \)). Thus, increasing the interfacial peak traction, or interfacial shear strength (IFSS), does not lead to a reinforcement of the polymer fibre because the limiting factor is not interfacial adhesion but the shear strength of the anisotropic polymer fibre itself, being typically very low (10–30 MPa) for UHMWPE fibres or fairly low for PBO or PPTA (40–80 MPa) [39,88,100].

Interestingly, from this work it can be concluded that the same property that limits the shear strength of macroscopic UHMWPE/epoxy or aramid/epoxy composites [88,102–104], limits the reinforcing efficiency of CNT reinforced UHMWPE or aramid nanocomposite fibres. For both systems and depending on nanotube aspect ratio, stress transfer and ultimate nanocomposite fibre strength is limited by the relatively low intrinsic shear strength of these anisotropic fibres rather than interfacial adhesion.

Following these arguments it can now also be better understood why the oriented CNT reinforced PVA system of Wang et al. [53] was able to achieve such a high reinforcing efficiency with a near theoretical stress contribution by the 1 wt\% SWCNTs of 88 GPa. Firstly, this system exhibited only a moderate overall fibre strength (\( \sim 1.2 \text{ GPa} \)), reducing the need for a high CNT content and high interfacial shear stress. PVA is also a polar polymer and expected to show good interfacial adhesion. However, more importantly, the polar PVA has also a higher secondary bond strength between the chains than apolar PE, leading to a less anisotropic fibre. For example, the shear modulus of oriented PVA is reported to be about twice that of UHMWPE [39,105]. Both effects, the lower overall strength and less anisotropic character of oriented PVA, lead to a nanocomposite fibre system where the ultimate strength is less dominated by the intrinsic shear strength of the oriented polymer fibre.

Similarly the favourable results of Chae et al. [106] may also be seen in this light. Here the authors reported an up to 60% increase in tensile strength for carbonized PAN fibres with 1 wt\% CNTs, resulting in an effective CNT stress contribution of 67 GPa. Although the authors ascribed the increase in fibre properties to some extend to changes in the carbonization process and graphitic structure as a result of the presence of CNTs, that is, a matrix effect rather than a direct nanotube reinforcement effect, the high reinforcing efficiency was here probably also aided by the higher shear properties of carbon fibre. Carbon fibres have a less anisotropic structure than UHMWPE or PPTA fibres. Graphite possesses strong covalent bonds between hexagonally arranged carbon atoms within the 2D layer-planes, but much weaker bonding between them [107]. Consequently carbon or graphite fibres can be considered as 2D structures as opposed to oriented polymer fibres like UHMWPE and PPTA, which can be considered as 1D structures as here covalent bonding only exists in the chain direction. Because of their less anisotropic character, carbon fibres have significantly higher shear properties. For example, the shear modulus of PAN based carbon fibre is around 14 GPa as compared to 0.8 and 2 GPa for UHMWPE and PPTA [39]. Again this will benefit a nanocomposite fibre system as the ultimate strength is less dominated by the shear properties of the fibre.

6. Conclusions

Analytical micromechanical models and finite element simulations were employed to explain why it is in practice so difficult to significantly reinforce high-performance polymer fibres with CNTs. The main reason for the low reinforcing efficiency of CNTs in high-performance polymer fibres are:

- The minimum CNT content required for effective reinforcement is relatively high \(( \geq 10 \text{ vol\%} \) and increases with polymer fibre modulus. Since it has been proven difficult to homogeneously disperse individual SWCNTs in polymers at such high concentrations this will remain a challenge.
- A relatively high interfacial shear strength (IFSS) or peak traction \(( \geq 25 \text{ MPa} \) is required to prevent debonding of CNTs in the polymer fibre, however, an increase in interfacial bonding does not necessarily result in a higher fibre strength as often the limiting stress transfer factor is the low intrinsic shear strength of the highly anisotropic polymer fibre itself.
- Similarly, a positive contribution from an increase in interface fracture energy or critical crack opening is limited due to the highly anisotropy nature of most high-performance polymer fibres.
- A relatively high interfacial frictional stress is required post-debond initiation in order to increase the strength of the CNT reinforced polymer fibre, however this only concerns polymer fibres with a high shear strength that exceeds the interfacial frictional stress.
- A high aspect ratio \(( \text{AR} \geq 10,000 \) of the CNTs has a significant positive effect on the
nanocomposite fibre strength as long as the polymer fibre does not fail by shear.

- A combination of all of the above (10 vol% CNT, $AR = 10,000$, $IFSS = 25$ MPa, frictional stress $= 5$ MPa) is needed to improve the tensile strength of a baseline UHMWPE fibre to values that exceed those of the world’s strongest synthetic fibres (in GPa).

All factors listed above can in theory lead to CNT reinforced fibres with superior properties if these highly anisotropic polymer fibres were not inherently weak in directions other than the fibre direction. However, highly oriented polymer fibres are intrinsically anisotropic and possess low shear strengths ultimately limiting effective stress transfer. Therefore, it remains doubtful if CNTs can significantly reinforce existing high-performance polymer fibres like Kevlar®, Twaron®, Dyneema®, Spectra® or Zylon® with tensile strengths of around 3–5 GPa. Rather than mechanical reinforcement, here the creation of multifunctional or electrically conductive polymer fibres through nanotube modification [98,108] or coatings [109] may be more promising. On the other hand, nanotube reinforcement might have some merit in textile grade fibres of lower mechanical performance such as nylon, polyester, polyacrylonitrile or poly(vinyl alcohol) or more isotropic carbon fibres.

Disclosure statement

No potential conflict of interest was reported by the authors.

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