MECHANICAL AND INTERFACIAL PROPERTIES OF CARBON NANOFIBERS FOR POLYMER NANOCOMPOSITES

BY

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THESIS

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ABSTRACT

The mechanical and failure response of vapor grown carbon nanofibers (VGCNFs) has been unexplored despite the large volume of carbon nanofiber composites fabricated today. Three grades of VGCNFs, namely as-fabricated, high temperature heat treated, and graphitized/surface oxidized, with average diameters of 150 nm were tested individually for their tensile strength by a MEMS mechanical testing platform. Their nominal tensile strengths followed Weibull distributions with characteristic strength values between 2.74 - 3.34 GPa, which correlated well with the expected effects of heat treatment and oxidative post-processing. These values are the first measurements reported for VGCNFs and are more than 50% smaller than the generally accepted values for the tensile strength of this class of nanofibers. The as-fabricated nanofibers had the smallest Weibull modulus indicating a wide flaw population that was reduced significantly upon heat treatment. The nanofiber fracture surface was that of a stacked truncated cup structure with oblique graphene layers comprising the backbone of VGCNFs. Under uniaxial tension, cleavage of the outer turbostratic layer occurred first, followed by relative slip of the internal oblique graphene layers. The change in the mechanical strength (Weibull strength), and its scatter (Weibull moduli), with heat treatment correlated well with the fiber structure evidence in Transmission Electron Microscopy (TEM) images, which showed graphitization of the outer turbostratic layer and the formation of a new interface with the inner, originally graphitic, layer that was characterized by structural discontinuities that reduced the total load bearing capacity of the nanofibers. In this work, the strength of the carbon nanofiber-polymer matrix interfaces was also quantified for the first time by means of novel nanoscale fiber pull-out experiments. The interfacial shear strength averaged 55 MPa revealing that the adhesion and bonding of the heat-treated, non-functionalized carbon nanofibers is quite better than that of non-functionalized carbon fibers (15-28 MPa) and as good as that of functionalized carbon fibers (40-65 MPa), which underscores that extrapolations of macroscale interfacial measurements to the nanoscale are not appropriate.
ACKNOWLEDGMENTS

The whole scientific progress can be interpreted as the dialectic outcome of the interaction between the two kinds of research processes: The positivist experimentation and categorization of natural phenomena, which gradually expands the boundaries of existing knowledge and the leap of rationalized human thought which redefines and transcends those boundaries through critical questioning. This thesis has been a productive fusion of these two distinct research processes and there are many people who have supported me in many ways to reach this point. I would like to express my most sincere gratitude to my research advisor Prof. Ioannis Chasiotis, whose scientific guidance during the entire course of this study and vast technical background in analyzing nanoscale mechanical phenomena have been of fundamental importance in setting and accomplishing the objectives of this dissertation. I am also greatly indebted to my co-advisor Prof. Andreas A. Polycarpou, for his strong academic support and help with the formalities I encountered in the last 2 years.

I would also like to thank Mr. M. Naraghi for his useful discussions and tutoring about the practicalities of employed experimental techniques. The most systematic and meticulous experimentalist I have seen in my life, Ms. Qi Chen deserves my acknowledgement for her productive suggestions and collaboration during the data generation process. I have also greatly enjoyed working with my colleagues Mr. S. N. Arshad, Mr. N. Karanjgaokar, Mr. S. Yagnamurthy, Mr. P. Kolluru, Mr. M. Tusz, Mr. D. Groysman and Mr. E. Nadal in the Chasiotis Research Group, and I would like to thank them all for their help in scheduling my experiments and shared use of technical equipment. I acknowledge the support by the Air Force Office of Scientific Research (AFOSR) through Grant FA9550-06-1-0140 with Dr. B. L. Lee as the program manager for making this project into reality. I also would like thank Dr. H. Kahn at CASE for the fabrication of the MEMS loadcells, and Drs. M. Marshall and W. Swiech at the Frederick Seitz Materials Research Laboratory of UIUC for their help with SEM and TEM imaging. Finally, I want to express my gratitude to my family, for their unconditional love and support.

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CHAPTER 1

INTRODUCTION

Since their advent, more than two decades ago [1], significant effort has been devoted to exploring the potential of vapor grown carbon nanofibers (VGCNFs) to provide multi-functionality in advanced nanostructured composites by improving on the matrix thermal and electrical conductivities and at the same time maintaining the low composite density and compatibility with common polymer forming manufacturing methods [2-4]. With the introduction of all-carbon fiber composite fuselage aircraft to the commercial aerospace industry [5], carbon based nanostructures in general and vapor grown carbon nanofibers in particular have gained significance as nanoscale matrix reinforcement materials in traditional carbon fiber composites due to their multifunctional characteristics, such as increased electrical conductivity, reduced high frequency spectra electromagnetic signal attenuation, improved thermal mismatch mitigation and thus reduced residual stress buildup between the constituents of structural composites [6,7]. In addition to these primary benefits of VGCNF in the polymeric matrix of a composite, significant improvements in the overall mechanical response and microscale damage tolerance have been observed experimentally in terms of enhanced modulus, ultimate tensile strength, fracture toughness and interlaminar shear strength [8-10].

Considering the higher yield and cost effectiveness of VGCNF synthesis in comparison with single- or multi-wall carbon nanotube (SWCNT, MWCNT) fabrication methods [11,12], the former emerge as a strong candidate material in short term technologies. Together with their inherent multifunctionality benefits, which are in essence comparable to those obtained through carbon nanotube (CNTs) reinforcements in polymer matrix composites (PMCs) and the ease of post-fabrication treatments (such as pyrolytically stripping, chemical surface functionalization etc.), VGCNFs are being explored in high performance applications ranging from aerospace to microelectronics [13]. However, challenging scientific and technical issues concerning the development
and utilization of unequivocal mechanical characterization methods applicable at the scale of these nanostructures that will support our understanding of the ensuing nanoscale load-transfer and damage mechanisms remain to be resolved [14,15]. Direct measurement of interfacial interactions between different grades of VGCNFs and their surrounding polymeric matrix and the description of these interactions in terms of commonly used damage and failure quantities such as interfacial shear strength (IFSS) are of fundamental importance, not only for the validation of simulations in this field but also for the development of reliable performance assessment and optimization tools for emerging nanostructured engineering materials [16,17].

1.1. Nanostructure of VGCNFs as a Function of Post-Fabrication Processing

VGCNFs are produced by catalytic (nanoscale iron, nickel, or cobalt alloys) exposure of carbon compounds such as gaseous hydrocarbons, carbon dioxide or carbon monoxide, to high temperatures [18,19]. In this synthesis process, carbon is separated from hydrocarbons by chemical and mechanical scission and is transported on the surface of the catalyst nanoparticle by lateral diffusion to lengthen a fiber-like structure in the longitudinal direction [2,20] as shown schematically in Figures 1.1(a,b). Depending on the size, shape and physical state of the catalyst particle, the stacking conformation of highly graphitic carbon (non-perfect graphene) layers can vary between the two limiting conformations (horizontal or vertical stacking of individual graphene layers) specified by Figures 1.2(a,b) [2]. Often the resulting nanofiber structure is the assembly of at least two different substructures of the same material bearing different morphology and/or conformation but nested inseparably as one physical entity. The overall structure is composed of oblique graphene layers arranged as stacked truncated cups surrounded by turbostratic deposited carbon [6,21]. During synthesis of the graphitic carbon nanofiber backbone, chemical vapor deposition (CVD) annular thickening occurs, so that the chemically and electronically active edges of densely stacked oblique graphene planes remain on the exterior fiber surface. Such active sites are oriented towards the interface imparting enhanced transport properties that are desirable in composite applications [22].
Catalyst nanoparticle, Individual layers of oblique graphene

Figure 1.1 Structure of VGCNFs as defined by catalytic synthesis when atomic carbon is transported on the surface of the catalyst nanoparticle via lateral diffusion. The shape of the polyhedral catalyst particle defines the conformation of the graphitic carbon layers in the nanofiber backbone, resembling a stacked truncated cone, also called stacked "Dixie-cups". In figure (a) the front and rear faces of the VGCNF are not shown for visual clarity. Figures were reproduced from reference [2].

This catalytic CVD tubular nanofiber growth inevitably results in structural inhomogeneities and defects with potentially adverse effects on the mechanical and transport properties of the nanofibers [21,23-27]. For instance, the vapor deposited turbostratic carbon layers surrounding the catalytically grown graphitic backbone of as-grown VGCNFs are structurally discontinuous both along the fiber axis and in the transverse plane, mostly due to orientation differences between neighboring concentric planes and the formation of localized transitional amorphous carbon on the fiber's outermost annulus during the CVD process, as shown in Figures 1.3(a) and 1.3(b), respectively. Large impurities in VGCNFs can originate by the inclusion of metallic catalyst compounds as shown in Figure 1.4(a). In addition, infiltration of hydrocarbon
feedstock compounds into the hollow core of VGCNFs during the catalytic lengthening of the truncated cone or bamboo-shaped fiber backbone might lead to the formation of amorphous carbon residues in the fiber interior as seen in Figure 1.4(b). Finally, internal separation walls between chambers of the hollow fiber core, Figure 1.4(c), are among common morphological irregularities handicapping the structural uniformity and thus the mechanical integrity of VGCNFs.

**Figure 1.2** Limiting conformations for CNF growth on the catalyst particle (a) vertical stacking of neighboring graphene layers (b) horizontal stacking of concentric graphene layers similar to the CVD based formation of multi-walled carbon nanotubes (MWCNTs). The front and rear faces of the VGCNF are not shown for visual clarity. Figures were reproduced from reference [2].

As in the case of their microscale counterparts, the turbostratic annular regions of as-grown VGCNFs are structurally less ordered and, therefore, presumably more defect prone compared to the catalytically grown graphitic inner core which contains highly ordered graphene-like planes of carbon atoms oriented in a truncated cone like geometry [6]. The implications of such a gradient of defect density on the mechanical performance...
of different CNF grades with varying post-fabrication treatment and hence different turbostratic layer thickness are a central objective of this thesis and will be elaborated extensively in the subsequent Chapters. Defects observed in microscale carbon fibers are stacking disorders, disclinations, intraplanar vacancies, and line defects, such as screw and edge dislocations, with harmful effects on the fiber structural integrity [28]. Similar classifications can also be applied to nanoscale carbon fibers for the analysis of defect related failure but the close spatial arrangement of such defects within the fiber structure makes unequivocal explanations very difficult.

Figure 1.3 (a) Orientation differences between neighboring layers of vapor deposited turbostratic carbon layers give rise to the formation of structural discontinuities along the fiber, which can also coincide with severe morphological irregularities, (b) aggregation of amorphous carbon at terminal sites and in-between the oblique layers of turbostratic carbon regions.
Figure 1.4 Fabrication-induced impurities and morphological irregularities: (a) Inclusion of metallic catalyst compounds in the fiber, (b) formation of amorphous carbon residues in the fiber interior due to the infiltration of hydrocarbon feedstock compounds into the hollow VGCNF core, (c) internal separation walls arising from the bifurcations of the graphitic innermost annulus during the catalytic lengthening of the carbon nanofiber.

Earlier attempts to quantify the severity of such defects as a function of their size, shape, orientation and distribution, have been restricted to theoretical and computational studies [29-33], although experimental validation has been sought through atomic force microscopy (AFM) based experiments with single or multi-walled carbon nanotubes [34-37]. The inadequate cantilever stiffness to provide the high forces required for fiber rupture and problems arising from the lack of uniaxial loading reduced the applicability of previously employed experimental methods. Thus, it is the objective of this
dissertation research to generate the necessary experimental methods and employ them to quantify the failure mechanics of carbon nanofibers at the individual fiber level as well as the interfacial failure between a single nanofiber and a surrounding polymeric matrix.

1.2. Objectives and Methods of this Dissertation Research

This thesis addresses major experimental challenges pertaining to the mechanics of carbon nanofibers by providing direct nanoscale measurements of the mechanical failure and adhesion strength of VGCNFs in connection with post-fabrication treatment. The Microelectromechanical (MEMS) System based experimental methods specifically developed to achieve these tasks are also applicable to other fiber-like nanostructures, such as electrospun polymer nanofibers or metallic nanowires, thus establishing an experimental protocol in the fields of nanoscale mechanics and nanofabrication [38]. In this context, the failure modes of three VGCNF grades under uniaxial tension were analyzed by means of high resolution scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Post fabrication treatment induced nanostructural changes in VGCNFs were investigated in order to elucidate the process of failure initiation leading to brittle fiber fracture [39]. Finally, the results of nanoscale pull-out model experiments with a common material system composed of a high temperature heat treated grade carbon nanofiber without an oxidative surface treatment (PR-24 HHT-LD) and an aerospace grade epoxy (EPON 828) were evaluated to quantify interface adhesion and failure properties such as interfacial shear strength and its dependence on the embedded fiber length. The results can be the basis for fracture toughness modeling and can be used to evaluate interfacial interactions leading during microcracking, crack growth and coalescence resulting in composite failure [40].
CHAPTER 2

TENSILE STRENGTH AND ELASTIC MODULUS OF VGCNFs

The effect of the heat treatment and surface functionalization processes on the mechanical strength of three different grades of VGCNFs was investigated by nanoscale tensile experiments on individual nanofibers with the aid of Microelectromechanical (MEM) tools. These are the first measurements with single nanofibers with diameters of 150-200 nm and lengths 30-60 μm and are compared to previous experiments carried out with submicron and micron sized fibers [41-43]. Three types of carbon nanofibers, pyrolytically stripped (PR-24-XT-PS), high temperature heat treated (PR-24-XT-HHT-LD) and high temperature heat and oxidatively surface treated (PR-24-XT-HHT-LD-OX), were tested in this research. The Weibull strength and modulus were quantified [44] and are discussed here in the context of nanofiber structure and modes of failure as observed in SEM and TEM images.

2.1. Materials and Experimental Methods

The three grades of highly graphitic, Pyrograf-III, VGCNFs were obtained from Applied Sciences Inc. (Dayton, OH). The first grade, PR-24-XT-PS, is the closest derivative of the as-grown VGCNFs produced as described in the previous section. Post-fabrication pyrolytic stripping (designated as PS) removes the polyaromatic hydrocarbon residues of the synthesis process from the nanofiber surface. This surface stripping takes place at around 600°C without altering the existing carbon nanofiber microstructure. The second fiber grade, designated as PR-24-XT-HHT-LD, is the high-temperature heat treated (above 2100°C, typically around 2800°C) form of low density VGCNFs, with significantly different microstructure than the PR-24-XT-PS fibers. The high temperature
heat treated VGCNFs have improved electrical and thermal conductivities, by reducing the structural disorder of the turbostratic layer and by increasing the graphitic content of localized amorphous carbon regions on the fiber surface [45]. The last grade considered, with the designation PR-24-XT-HHT-LD-OX, is the surface functionalized derivative of PR-24-XT-HHT and it is produced by subjecting the PR-24-XT-HHT-LD fibers to oxidative surface treatment in oxygen plasma to improve its bonded interactions with organic materials. Although, some analogies may be established with microscale carbon fibers to predict the effect of thermal and oxidative treatments on the mechanical properties of carbon nanofibers, limited experimental evidence on the mechanical and failure behavior of individual nanofibers is available in the literature [41], mostly due to the difficulty of experimental studies at the scale of individual carbon nanofibers.

The VGCNFs tested in this work were received in a highly entangled form which required the isolation of individual nanofibers that were sufficiently long for experimentation. The as-received VGCNFs were treated with distilled water to remove agglomerates which also facilitated the isolation of individual nanofibers. High frequency ultrasonication reduced the length of individual fibers significantly, and, therefore, a surfactant solution was applied to further disperse individual nanofibers, which were then picked up by a flexible metallic probe, attached outside the fiber test section so that no additional defects were introduced during fiber manipulation.

The experiments with individual nanofibers were conducted via a MEMS-based experimental setup according to the work by Naraghi et al. [46,47]. The polysilicon microdevices incorporated a 4.5-μm or a 6-μm thick, folded beam loadcell as shown in Figure 2.1. A 3-D precision stage was employed to position the nanofibers onto the loadcells under an optical microscope which was equipped with a CCD camera. A small amount of UV-curable epoxy adhesive was deployed on the crosshead of the polysilicon loadcell to mount one end of the carbon nanofiber. The loose nanofiber end was fixed to a movable platform, as seen on the left of Figure 2.2. During each experiment, the nanofiber was stretched to failure by actuating a picomotor-spring assembly, which pulled the moving platform away from the loadcell, hence performing a displacement controlled (fixed grip) type uniaxial tension experiment. The evolution of loadcell
Deflection during each experiment was recorded by the CCD camera and a Digital Image Correlation (DIC) calculation of the loadcell deflection was performed in a similar manner to references [46,47]. The texture of the utilized surface micromachined loadcells facilitated the application of DIC to calculate the loadcell deflection with subpixel resolution and thus to improve the precision in associated force measurements. The application of DIC provided measurements with a displacement resolution of approximately 23 nm as explained in [46]. Therefore, the use of optical microscopy in combination with DIC calculations provided high resolution in force measurements, without necessitating the carrying out of intended tests within an electron microscope as usually preferred for the mechanical experimentation of objects at similar scales [48].

Figure 2.1 SEM image of a 4.5-μm thick loadcell used in the VGCNF strength experiments.

Figure 2.2. Optical snapshot during a fiber strength experiment showing the fiber mounting and the loadcell.

In order to calculate the axial force in the fiber from the measured loadcell deflection, the spring constants of the folded beam, double column, loadcells were acquired experimentally. To obtain a traceable calibration, microscale glass beads of known volumes and density were attached to the loadcell end, Figure 2.3(a), and their cumulative weight was plotted with respect to the measured loadcell deflection. The latter was acquired by means of DIC applied to the detail of Figure 2.3(a) seen in Figure 2.3(b).
The natural pattern on the surface of the loadcell was due to the inherent surface roughness of polysilicon. The force-loadcell response was linear even for large loadcell deflections, which provided confidence in the reported strength values. The stiffness of the 6-μm thick folded beam loadcells, extracted from the calibration curves, was 1.58 N/m. If the loadcell dimensions, as measured with an SEM, were employed instead of original design parameters, the loadcell stiffness was calculated as 2.10 N/m, i.e. a 25% difference from the experimentally determined stiffness, which can be attributed to the filleted folded-beam edges and the tapered film cross-section, not considered while using the linear elasticity formulation for stiffness calculations.

Figure 2.3 (a) Calibration of a folded beam loadcell with glass beads. (b) Detail of the loadcell during calibration used in the calculation of its deflection by DIC, (c) force-loadcell deflection curve for a 6-μm thick loadcell.
After each experiment, both ends of the ruptured carbon nanofibers were imaged by an SEM at ×200k magnification to measure the outer fiber diameter as well as to identify the mode of failure. Although the fiber outer radius was determined accurately, the inner radius was not always possible to measure due to difficulties in positioning the fiber cross-section normal to the SEM electron detector. The Weibull analysis in this work employed the nominal nanofiber strength based on the fiber outer diameter that was measured with an SEM. Furthermore, only those experiments with a clear gage section rupture occurring at least 3 μm (approximately 20 times the average fiber diameter) away from the specimen fixture were considered as successful experiments and were included in the statistical failure analysis presented in this Chapter.

Within the general framework of the probability theory and reliability analysis, the distribution of a random variable \([49]\) can be apprehended by the Weibull distribution \([44, 50]\) if it can be described by the Weibull cumulative density function for uniformly stressed specimens under uniaxial tensile loading is described by

\[
P_f(\sigma) = 1 - \exp\left(-\left(\frac{\sigma - \sigma_u}{\sigma_0}\right)^m\right) \tag{2.1}
\]

The parameters \(m\), \(\sigma_u\) and \(\sigma_0\), when derived from a uniform tension experiment are considered material specific constants and the uniaxial tensile stress, \(\sigma\), is the applied stress which results in the assigned probability of failure, \(P_f(\sigma)\). The shape parameter (or the so-called Weibull modulus), \(m\), provides a quantitative measure of the scatter in the strength data. The location parameter, \(\sigma_u\), which is also called the failure initiation threshold, is the stress below which failure will not occur. The scale parameter, \(\sigma_0\), combined with the location parameter gives the tensile stress value at which the probability of failure becomes 63.2%, i.e.

\[
P_f(\sigma_{63.2\%}) = P_f(\sigma_0 + \sigma_u) = 0.632 \tag{2.2}
\]

The stress value at which the probability of failure becomes 63.2%, is also called the characteristic strength (material stress parameter) and it is useful for conclusive
comparison purposes of different derivatives or grades of a defect prone brittle structure and thus assess the influence of different synthesis, fabrication and post-fabrication treatment processes on the ultimate mechanical performance and durability of the considered material system instead of using the average strength value of Gaussian statistical analysis. The Weibull modulus on the other hand, is a handy tool for comparing the scatter of each particular strength data set with those of different grades and thus depicts the degree of uniformity of the mechanical strength achieved by various synthesis, fabrication or post-fabrication treatment processes performed on the tested material. The greater the scatter of the obtained data is, the lower the value of Weibull modulus becomes.

The location parameter is often assumed to be zero so that a conservative description of strength is introduced to the analysis, implicitly implying that no failure will occur at zero stress level. The plausibility of such an assumption is clear, although in general for many material systems zero stress level represents an underestimate for the failure initiation threshold [51]. This assumption renders the determination of the Weibull modulus and associated scale parameter from the above given formulation straightforward. In this case, Equation (2.1) takes the so-called two parameter form

$$P_f(\sigma) = 1 - \exp \left( - \left( \frac{\sigma}{\sigma_0} \right)^m \right) \tag{2.3}$$

and the characteristic strength becomes equal to the scale parameter, $\sigma_0$. Extracting the Weibull parameters of a statistical distribution from a given data set necessitates the use of an ordinal probability estimator for sequencing single data points with respect to each other such that a linear regression analysis can be conducted accordingly. In nanoscale experiments, the number of tests is usually small due to the associated experimental difficulties such as the limited availability of suitable experimental tools, the geometric and morphologic nonconformity of the isolated specimens with established experimental requirements and high specimen failure rates in the sample preparation stages before the actual experiment. For the relatively small sample sizes produced in this work (12 successful experiments for each fiber grade, i.e. 36 valid experiments out of 258 tests in
total), Bernard's method for probability estimation is assessed to be statistically
descriptive [52] such that

\[ P_{f1}(\sigma) = \frac{i - 0.3}{n + 0.4} \]  \hspace{1cm} (2.4)

where \( n \) is the total number of collected data points and \( i \) is the ordinal rank of the single
datum within each set.

In order to carry out the subsequent linear regression analysis, equation (2.1) can
be manipulated in such a way that by taking the natural logarithm of both sides twice
following line equation is obtained:

\[ \ln \left( \ln \left( \frac{1}{1 - P_{f1}} \right) \right) = m \ln(\sigma - \sigma_u) - m \ln \sigma_0 \]  \hspace{1cm} (2.5)

As can be clearly seen from equation (2.8), for the simplified two-parameter
Weibull failure probability function, in which case failure initiation threshold \( \sigma_u \) is set to
0, the slope of the linear fit would be equal to the Weibull modulus, \( m \). The scale
parameter \( \sigma_0 \) can be easily determined using the intercept of the resulting fit with the
abscissa once the Weibull modulus has been determined from the previous analysis. This
method represents a convenient way of conducting a quantitative probabilistic strength
analysis because the only requirement to determine the probability of failure for a
particular strength measurement datum is the rank of the measurement relative to the
other data. Also, the characteristic strength can be determined accurately by maximizing
the correlation coefficient (\( R^2 \) value) through least squares approximation, thus yielding
the best-fit line.

The maximum likelihood method might be used as an alternative approach to the
above given statistical analysis scheme [53]. The most probable statistical parameters of a
distribution are identified through the maximum likelihood method so that the best
possible description of the whole population can be achieved from the analysis of a
random sample [54]. The likelihood function is defined as the product of the probability
density function evaluated at each of the available data points:

\[ L(\theta) = \prod_{i=1}^{n} P(\sigma_i, \theta) \quad (2.6) \]

where \( P(\sigma_i, \theta) \), stands for the probability density function, \( \sigma_i \) designates the result of the \( i^{th} \) test and \( \theta \) represents the parameters whose most likely values are to be
determined through statistical analysis. For the case of the simplified Weibull probability
function, where the 2 parameters \( m \) and \( \sigma_0 \) are taken to be descriptive enough for the
whole data set, equation (2.6) takes the following form:

\[ L(\theta) = \prod_{i=1}^{n} \left( \frac{m \sigma_i^{m-1}}{\sigma_0^m} \right) \exp \left[ -\left( \frac{\sigma_i}{\sigma_0} \right)^m \right] \quad (2.7) \]

In order to attain these two Weibull parameters, which provide the best
probabilistic fit (notice that the statistical representation quality of this fit does not suffer
from any nonlinearity associated with the acquired data, which is a net benefit compared
to the linear regression based method explained before) for the data set at hand, a system
of equations needs to be generated by setting the partial derivatives of the above given
likelihood function expression with respect to the parameters \( m \) and \( \sigma_0 \) equal to zero.
Hence, the following system of equations is obtained, where equations (2.8) and (2.9) are
coupled together and might be solved through numerical iteration to determine \( \hat{m} \) and
\( \hat{\sigma}_0 \), which are defined as the maximum likelihood estimates of the Weibull modulus and
the characteristic strength respectively:

\[ \hat{\sigma}_0 = \left[ \left( \frac{1}{n} \sum_{i=1}^{n} \sigma_i^m \right)^{\frac{1}{m}} \right] \quad (2.8) \]

\[ \hat{m} = \frac{n}{\left( \frac{1}{\hat{\sigma}_0} \right)^m \sum_{i=1}^{n} \sigma_i^m \ln \sigma_i - \sum_{i=1}^{n} \ln \sigma_i} \quad (2.9) \]
2.2. Effect of Fabrication Treatments on the Mechanical Strength of VGCNFs

Table 1 lists the Weibull cumulative probability density function parameters computed for the three data sets in Figures 2.4(a-c). For two of the three fiber grades, the calculated Weibull moduli were relatively small indicating the presence of a broad spectrum of flaws. The Weibull modulus and strength were calculated by the maximum likelihood function and by linear regression and both approaches provided similar values. This agreement provides a strong indication that the experimental data sets, although not large in number, were very descriptive of the failure strength distributions of all nanofiber grades. In general, the maximum likelihood analysis provided marginally better fitting, due to the relatively small number of data points that could not be described as precisely as the likelihood function by the probability estimator of the linear regression analysis [54].

The characteristic strength of pyrolytically stripped (PS) nanofibers based on outer fiber diameter was 3.34 GPa compared to the characteristic strength of 2.84 GPa for the high temperature heat-treated carbon nanofibers (HHT) without an oxidative surface treatment (OX), see Table 2.1. On the other hand, the effect of oxidative surface treatment on the average fiber strength was less significant than that of the high-temperature heat treatment, as the characteristic strength decreased slightly to 2.74 GPa after surface oxidation (HHT-OX). The positive effect of post-fabrication heat treatment on the spread of the tensile strength data was reflected in the higher Weibull moduli of HHT and HHT-OX grades compared to that of the PS grade, as seen in Figure 2.4 and the characteristic strength and standard deviation values in Figure 2.5. A comparison between the HHT and the HHT-OX fibers implies a slight increase in size and in randomness of catastrophic flaws.
Table 2.1. Weibull parameters for the three VGCNF grades.

<table>
<thead>
<tr>
<th>Weibull parameter</th>
<th>Maximum likelihood function</th>
<th>Linear regression analysis</th>
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<tbody>
<tr>
<td></td>
<td>PR-24-XT PS</td>
<td>PR-24-XT HHT-LD</td>
</tr>
<tr>
<td>Weibull modulus, m</td>
<td>2.36</td>
<td>7.29</td>
</tr>
<tr>
<td>Characteristic strength, $\sigma_c$ (GPa)</td>
<td>3.34</td>
<td>2.84</td>
</tr>
</tbody>
</table>

The present strength analysis considers only the nanofiber outer diameter for the calculation of nominal cross-sectional area of the carbon nanofiber. Although such an analysis does not provide the true strength of the fiber, it results in a distribution of nominal fiber strengths which can be directly used in nanocomposite materials property predictions in agreement with the objectives of this study. Moreover, since polymer infiltration into the nanofiber inner hollow core is not observed, any physical interaction of the hollow fiber interior with the surrounding matrix is immaterial. Therefore, for all practical purposes, the effective fiber diameter is of primary interest. An assessment of the true strength of the nanofibers would require a model of the stresses in the turbostratic layer and the graphitic core, and detailed measurements of their individual thicknesses (also the tilt angle of the inner graphene layer) in each experiment in addition to the fiber outer diameter, which was outside the scope of this study. For a few carbon nanofibers we obtained this information via post-mortem imaging by TEM or SEM as seen in Figure 2.6(c) and Figures 2.7(a-c). In general, the diameter of the hollow core is about $\frac{1}{2}$ that of the outer fiber diameter [6]. Consequently, the true fiber strength is $\sim$33% higher than that reported here. In this regard, the high values of true fiber strength are similar to that of high strength microscale carbon fibers [28,55].
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<tr>
<td>Weibull modulus, m</td>
<td>2.36</td>
<td>7.29</td>
</tr>
<tr>
<td>Characteristic strength, $\sigma_c$ (GPa)</td>
<td>3.34</td>
<td>2.84</td>
</tr>
</tbody>
</table>

The present strength analysis considers only the nanofiber outer diameter for the calculation of nominal cross-sectional area of the carbon nanofiber. Although such an analysis does not provide the true strength of the fiber, it results in a distribution of nominal fiber strengths which can be directly used in nanocomposite materials property predictions in agreement with the objectives of this study. Moreover, since polymer infiltration into the nanofiber inner hollow core is not observed, any physical interaction of the hollow fiber interior with the surrounding matrix is immaterial. Therefore, for all practical purposes, the effective fiber diameter is of primary interest. An assessment of the true strength of the nanofibers would require a model of the stresses in the turbostratic layer and the graphitic core, and detailed measurements of their individual thicknesses (also the tilt angle of the inner graphene layer) in each experiment in addition to the fiber outer diameter, which was outside the scope of this study. For a few carbon nanofibers we obtained this information via post-mortem imaging by TEM or SEM as seen in Figure 2.6(c) and Figures 2.7(a-c). In general, the diameter of the hollow core is about $\frac{1}{2}$ that of the outer fiber diameter [6]. Consequently, the true fiber strength is $\sim$33% higher than that reported here. In this regard, the high values of true fiber strength are similar to that of high strength microscale carbon fibers [28,55].
Figure 2.4 Probability of failure vs. tensile strength for (a) pyrolytically stripped, (b) high temperature heat treated, and (c) oxidatively processed high temperature heat treated carbon nanofibers.
Figure 2.5 Characteristic strength for three VGCNF grades. The error bars correspond to one standard deviation.

In an analogy to conventional carbon fibers, for instance see Lake et al. [45], the decrease in the scatter of the tensile strength values from PS to the HHT grade can be explained by the transformation of the turbostratic layer to a graphitic layer that is coaxial to the fiber, as opposed to the inner graphitic shell that pre-existed the heat treatment. Figure 2.8(c) later in this section clearly shows the different orientations of the two graphitic layers. According to Endo et al. [21], high-temperature heat treatment increases the nanofiber structural organization and, therefore, the associated strength uniformity by reducing both the size and number of micro- and nanoscale defects residing in the catalytically grown graphene layers of the carbon nanofiber inner layer. This improvement is achieved through several thermally induced, microstructural transformations, such as graphitization, decreased interlayer spacing and loop formations between adjacent active edge sites of the oblique graphene cones at the interior and the exterior ends of the nanofiber backbone [21]. Our results for VGCNFs are in agreement with existing literature, where an increase in the graphitization temperature decreases the fiber strength. According to [45], this is due to the reduction of the load bearing turbostratic layer and the increase of the order of the graphene planes.
Figure 2.5 Characteristic strength for three VGCNF grades. The error bars correspond to one standard deviation.

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Figure 2.6 TEM images of (a) pyrolytically stripped, and (b,c) high temperature heat treated VGCNFs. The turbostratic carbon layer is shown with the double sided arrow in (a) followed by a (dark) graphitic layer and the (gray) hollow fiber core. The turbostratic carbon layer is reduced after heat treatment as shown in (b) where the dark band is the hollow fiber core. Heat treatment is responsible for the interior and exterior edge loops (shown with single sided arrows) in (b). (c) Nanofiber failure section with a protruding inner cone due to graphene layer sliding.

These structural transformations occur at the expense of the vapor deposited turbostratic carbon layer, as shown in the TEM pictures in Figures 2.6(a,b). Similarly to microscale carbon fibers, the turbostratic outermost carbon layer in pyrolytically stripped carbon nanofibers tends to inhibit crack propagation due to misorientation of neighboring graphitic planes which limits transverse crack propagation during fracture and hence
increases the fracture resistance of the overall fiber structure [55]. The mechanical benefit of the turbostratic carbon layer is owed to its coaxial orientation with respect to the nanofiber, although the catalytically grown inner graphene layers are oriented obliquely with respect to the nanofiber axis as shown in Figure 2.6(a).

![Figure 2.7](image)

**Figure 2.7** Rupture surfaces of (a) PS, (b) HHT-OX, and (c) HHT-LD VGCNFs. The fiber fracture profile includes evidence of sliding of the inner graphene planes which is owed to the stacked truncated cone structure of the nanofibers.

From the mechanics point of view, it is clear that the ultimate load-bearing capacity of this hybrid structural arrangement would reach its maximum for a monomorphic structure that is solely comprised of parallel-oriented graphene layers, as can be inferred from continuum elasticity models and molecular dynamics (MD) simulations [56,57]. Thus, the experimentally recorded reduction in the strength of the graphitized (heat treated) nanofibers can be explained on the basis of load transfer from the outer layer to the inside graphitic layer. SEM and TEM fractography revealed mutual sliding of graphene planes following the cleavage failure of the outer fiber shell, Figures 2.6(c) and 2.7(a,c). In the as-fabricated fibers, failure initiated in the outer fiber layer with subsequent sliding of the inner graphitic layer. The outer layer is aligned in the fiber direction and, therefore, it is subjected to higher stresses compared to the oblique inner graphitic layer since both layers experience the same strain. Since the outer layer is more defect prone than the inner layer, fracture is expected to begin in the former where carbon is also more disorganized and crack paths can easily form.
Figure 2.8 TEM images of nanofibers showing (a) turbostratic layer, graphic layer, and hollow core of a pyrolytically stripped nanofiber, (b) the converted to graphitic turbostratic layer in high temperature heat treated nanofibers, (c) connectivity loops between the graphitized turbostratic layer and the oblique graphene planes of the inner layer, and wedge discontinuities at the interface of the two layers. The arrows point to the graphene planes that are extended from the graphitized turbostratic to the original graphitic layer at the wedge discontinuities. (d) Loops at the end of the stacked graphene inner layers that form during heat treatment. In all figures, the inner graphitic layer appears darker than the outer graphitized, formerly turbostratic, layer.
On the other hand, in HHT and HHT-OX fibers the outer turbostratic layers have been converted into graphitic but the re-organization of the oblique inner graphitic layer resulted in the serrated (truncated cone) structure in the nanofiber core, see arrows in 2.6(b). These steps may also serve as stress concentrations and sites of failure initiation which proceeds with sliding of the graphene planes. However, since the outer graphitic layer determines the fiber strain (it is stiffer than the inner layer and therefore it experiences higher stresses than the inner layer) it is expected that failure initiation still occurs in that the outer layer due to its surface flaws. This mode of failure was observed in the majority of the failed fiber cross-sections, as shown in Figure 2.7.

It is of interest to further explore the origin of failure in the pyrolytically stripped and the high temperature heat-treated nanofibers. High temperature heat treatment does decrease the carbon fiber strength and increases its modulus [28,55]. The increase in the modulus is due to the graphitization of the turbostratic layer. However, the trends in the fiber tensile strength must be put in perspective of the structural lay up of the two-layer VGCNFs. In doing so, one should account for the structural changes occurring to the outer turbostratic layer and its interface with the inner graphitic layer upon heat treatment. The majority of these morphological changes have also been reported before in [21] and other references, but in this study they are discussed in terms of failure initiation in the fibers. Figure 2.8(a) shows the relative orientation of the two layers before heat treatment. Upon heat treatment, the majority of the turbostratic layer is converted into graphitic that is coaxial with the fiber, Figure 2.8(b). The graphitization of the amorphous carbon at the interface of the two layers results in discontinuities at the interface upon heat treatment. The incompatibility in the orientations of the two graphene layers is accommodated by the slender wedge discontinuities seen in Figure 2.8(c). These discontinuities at the interface are quite large, allowing for a limited number of graphene sheets to bridge the two graphene layers in a limited and "loose" fashion. This discrete and limited connectivity does not allow for significant and uniform transmission of forces (stresses) from the outer to the inner layer. Therefore, the heat treated nanofibers carry the applied load with their outer, and stiffer, graphitic layer, while the inner, more compliant along the direction of the fiber, layer can undergo rotations at the connectivity points, see arrows in Figure 2.8(c), before it carries significant load. In other words, the
inner layer carries smaller fraction of the fiber force than it did before its heat treatment. Thus, the fibers appear less strong after heat treatment, mainly due to their reduced cross-section which carries the majority of the applied load. The load transfer at the interface of the turbostratic and the graphitic layers in the original pyrolytically stripped fibers was more effective due to the presence of disorganized turbostratic carbon, missing in Figure 2.8(c).

Given the SEM and TEM images of the fiber fracture in Figures 2.6(c) and 2.7(c) failure was initiated due to defects on the fiber outer surface. It is less likely that fracture initiates at the wedge discontinuities in Figure 2.8(c) as that surface is well graphitized and almost all defects were annihilated during heat treatment. On the other hand, the outer fiber surface is always exposed to environmental conditions and still contains a thin layer of turbostratic carbon, see for example Figures 2.8(b,c), with defects. Upon fracture of the graphitized turbostratic layer, failure proceeds through the very weak interface between the two layers, Figure 2.8(c), to generate the conical protrusions at the fiber fracture surface seen in Figures 2.6(c) and 2.7(c). Finally, the marginal additional reduction in the fiber strength (characteristic strength 2.74 GPa) due to surface oxidation (functionalization) can be attributed to an increase in the size of the defects on the outside fiber surface that are also responsible for the fracture of the graphitized nanofibers.

There are additional changes in the nanofiber structure occurring upon heat treatment which play a less important role in the reduction of the force carrying capacity of the nanofibers, such as the serrated, step-like, structure of the inner graphitic layer, and the diameter shrinkage of the turbostratic layer upon its graphitization. With regards to the first point, the inner graphene layer termination loops form to accommodate the graphitization of disorganized carbon that existed at the inner hollow fiber surface, and this way they generate steps that may act as stress concentrations and initiate failure. However, according to the aforementioned discussion, the inner layer is subject to smaller stresses during axial fiber loading and, therefore, these steps are not the likely loci of fracture initiation. This is also corroborated by Figures 2.6(c) and 2.7(c) where the inner graphene layer slides upon fiber fracture, rather than cleaving. This, again, implies that the graphitized outer layer is stronger than the original turbostratic layer but it also
carries the majority of the force in the heat treated nanofibers. As a consequence, the latter appear to be less strong (characteristic strength 2.84 GPa) than the original pyrolytically stripped nanofibers (characteristic strength 3.34 GPa). On the other hand, the diameter shrinkage of the turbostratic layer upon graphitization is rather small to explain the smaller force carrying capability of the heat-treated nanofibers. According to reference [21] the change in carbon layer spacing between as-grown and heat-treated nanofibers at 2800 °C is about 1%. Given that the thickness of the inner graphitic fiber layer does not change significantly with heat treatment, the net reduction in the fiber cross-section is 1-2% which is not enough to justify the 15-20% reduction in the average fiber strength with heat treatment.

In comparison with the few literature data on VGCNF strength, the nanofiber strengths measured in this study were obtained from the thinnest fibers tested individually to date; they were on average 50% thinner than the smallest fibers tested in [41]. The strength of the thinnest fibers in the last reference was at most 2 GPa, while the majority of fiber strength values reported in [41] were in the 500-1000 MPa range for nanofiber diameters between 300-1000 nm. The authors showed a significant diameter size effect on the mechanical strength of their nanofibers and a rapidly increasing strength for diameters ~300 nm. Their reported trends in fiber strength could actually predict the considerably higher nanofiber strengths presented here. On the other hand, the only other literature report on VGCNF strength [42] provided a nanofiber strength value of 2.92 GPa, which is very similar to the average fiber strengths measured in this paper. The latter fibers were grown to micron scale diameters by the same commercial process that furnished the fibers tested in this work. However, the fact that the strength of VGCNFs from the same fabrication process does not appear to change with fiber diameter potentially points out to surface defects in the fibers that are not scalable with fiber size. Nevertheless, this disagreement between the strengths reported in references [41] and [42] points out to the need for experiments every time a new fabrication method is developed, or modifications to an existing fabrication process are introduced, especially if nanostructured materials are concerned.
2.3. Elastic Modulus of Nanoscale Carbon Fibers

The analysis of individual nanofiber pull-out experiments that follows in Chapter 3 requires the value for the elastic modulus of high-temperature-heat-treated PR-24-HHT-LD grade carbon nanofibers. In order to obtain a reliable estimate of their modulus, a new MEMS device was developed particularly for this task. It was manufactured from polycrystalline silicon using the Sandia National Laboratories’ SUMMIT™ process. It incorporates a double column loadcell with a nominal stiffness of 248 N/m. The ideal loadcell stiffness for the intended modulus experiments was determined considering a report on “indirect” experimental modulus measurements with the same type of fibers [58] and the values reported by the manufacturer. The strain resolution depends on the length of the nanofibers, therefore, it was attempted to select long and straight fibers for these experiments. To expedite this process multiple gripping positions were fabricated as shown in Figures 2.9 (a,b). These fixtures allowed the placement of nanofibers with gage sections 30, 65 and 80 microns long.

![Figure 2.9](image)

**Figure 2.9 (a)** Optical image a MEMS device for modulus measurements of carbon nanofibers, **(b)** dark field image of the device section showing the possible fiber grips and the field of view monitored during the experiments.

Similarly to the tensile strength experiments described earlier, a 3-D precision motion stage was employed to position the nanofibers onto the MEMS loadcell. A small amount of fast curing epoxy adhesive was deployed onto the crosshead of the polysilicon
load cell and the surface of the appropriate fixture seen in Figure 2.9(b), to mount a carbon nanofiber. In order to prevent sliding at the grips or compliant fixtures due to the epoxy adhesive, the fibers were further fixed with a 2-μm thick platinum layer deposited with the aid of a Focused Ion Beam (FIB) as shown in Figure 2.10. The nanofiber was stretched until rupture by actuating a picomotor-spring assembly, which pulled the moving platform away from the loadcell, hence performing a uniaxial test. The loadcell deflection and the fiber extension during each experiment were resolved from optical images recorded at 2 Hz frame rate and 500x magnification via a CCD camera by the application of DIC, in a similar manner to the strength experiments so that stress-strain curves can be generated for the extraction of Young’s modulus. Illumination with mercury light significantly improved the visualization of the natural speckle pattern on the polysilicon surface micromachined loadcells so that the loadcell deflection could be calculated with subpixel resolution by means of DIC, resulting in improved precision in stress-strain measurements.

![Deposited platinum bonding block](image)

Figure 2.10 Pt-deposition to ensure proper mounting of a nanofiber onto the grips. Although a layer of the cured epoxy covers the nanofiber surface before deposition of Pt, it will be removed during the deposition process.

A representative optical microscopy image of a carbon nanofiber during an experiment and the stress-strain curve calculated by considering only the outer fiber
diameter are given in Figure 2.11(a). The mechanical response of the carbon nanofiber in Figure 2.11(b) has an initial exponential profile followed by a linear behavior for the points in the enclosed circles. The best fit line of the latter is the fiber stiffness which is acquired once the fiber is completely stretched. The initial non-linear behavior of reduced compliance is due to the small bending stiffness that the nanofiber has, since it is not perfectly straight as mounted on the device grips.

![Optical microscopy image of a fully stretched carbon nanofiber](image)

**Figure 2.11 (a)** Optical microscopy image of a fully stretched carbon nanofiber taken during an experiment. **(b)** Stress-strain curve recorded starting at a loose fiber configuration. The slope of the linear fit of the last portion of the data points (shown in filled circles) corresponds to the elastic modulus.

In total, four modulus experiments were conducted with the PR-24-HHT-LD grade carbon nanofibers, the results of which are presented in Table 2.3. The standard deviation reflects the experimental accuracy and not the statistical distribution of measured values. The resulting values of the nominal Young's moduli are spanning a very broad range due to several reasons: (a) the outer nanofiber diameters used in the modulus calculation varied between 230-420 nm without proportional change in the diameter of the hollow fiber core, (b) the nanofibers have a composite structure of an outer turbostratic layer and an inner graphitic layer whose relative thicknesses do not change proportionally with the outer fiber diameter, (c) the angle of the obliquely oriented inner graphitic layer is not the same for all nanofibers which affects significantly
the effective fiber modulus. Therefore, one can hardly speak about a unique value of the elastic modulus of VGCNFs and as a result a range of values, with a statistically significant number of experiments, is needed. These experimental values for the effective modulus are significantly higher than those reported in reference [58] from bending experiments with an AFM. This difference can be explained by the initial, exponentially increasing, segment of the stress-strain curve in Figure 2.11(b). Until the fiber is completely stretched, which requires several tens of μN of force, the effective stiffness is significantly smaller than its elastic modulus. The experiments reported in [58] were conducted via bending of VGCNFs with AFM probes that provide limited force capacity which is not enough to perfectly straighten the nanofibers. Therefore, the modulus measurements presented here are more reliable than the bending experiments reported in literature before.

Table 2.3. Elastic moduli measured for four VGCNFs.

<table>
<thead>
<tr>
<th>Experiment #</th>
<th>Nanofiber outer diameter (nm)</th>
<th>Elastic modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>310</td>
<td>226±12</td>
</tr>
<tr>
<td>2</td>
<td>420</td>
<td>302±15</td>
</tr>
<tr>
<td>3</td>
<td>230</td>
<td>325±16</td>
</tr>
<tr>
<td>4</td>
<td>360</td>
<td>239±12</td>
</tr>
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</table>
CHAPTER 3

MECHANICAL STRENGTH OF VGCNF – POLYMER INTERFACES

In the previous chapter, the strength of individual VGCNFs strength was shown to depend greatly on their hybrid microstructure and the flaw populations in different grades associated with post-fabrication treatment processes. Structural parameters, such as the orientation angle of the oblique graphene layers with respect to the fiber axis, the relative thicknesses of annular coaxial turbostratic layer (in as-grown carbon nanofiber grades) and the highly graphitized carbon layer (in high temperature heat-treated carbon nanofiber grades) with respect to the internal oblique graphene core, the lack of a well-developed structurally connective interface between graphitized (previously turbostratic) annular regions and internal oblique graphene layers in high temperature heat-treated carbon nanofibers, and the formation and extent of circular loop structures around the neighboring ends of the oblique graphene basal planes, are all important factors affecting the overall nanofiber strength. Moreover, intrinsic and synthesis process specific material parameters such as the flaw density of the vapor deposited turbostratic carbon and its change with increased graphitization content, or the interlayer spacing between oblique graphene layers (i.e. stacking density) and the dependence of their orientation angle on post-fabrication heat treatment should be taken into account in optimizing VGCNFs for their mechanical strength.

However, increased individual carbon nanofiber strength is not the exclusive metric in synthesizing strong and tough composites as the ultimate material environment and local stresses define the mechanical role of the reinforcement. Polymer nanocomposites for aerospace applications incorporate nanoscale reinforcements of varying morphologies (particulates, whiskers, platelets and nanofibers, etc.) as fabricated or treated with functionalization agents before embedded in a polymeric matrix [59].
Polymer nanocomposites emerge as an economically feasible [59,60] and technologically superior alternative to conventional polymers, especially in terms of their multifunctionality [59,61,62]. From structural integrity viewpoint continuous fiber reinforced laminated composites remain the golden standard in terms of key mechanical properties, such as specific strength, stiffness, fracture toughness, impact strength, environmental resistance and durability compared to the neat matrix [63]. Polymer nanocomposites on the other hand, have an immense potential in terms of thermal, electrical, magnetic and/or other transport properties competing with conventional structural composites where the later naturally fall short [59,61,64-67]. From pure mechanical point of view, it is a well known fact that, although the degree of reinforcement depends partially on the intrinsic properties of the matrix and the reinforcement agent, the interface between the constituents of a nanocomposite emerges as a key parameter [59,68-70].

In the case of carbon nanofibers (CNFs) their enormous specific surface area, which is on the order of 50 m²/g, is expected to result in substantial interaction with the surrounding polymeric matrix [4,42]. Taking advantage of this interfacial interaction still requires advancements in composite processing and chemical surface functionalization techniques, such that currently existing problems such as fiber agglomeration, Figure 3.1, and lack of alignment favorably to the applied load can be eliminated [61,71-73].

In mechanical terms, a strong and perfectly bonded interface is a prerequisite for effective stress transfer so that the mechanical properties of the nanoscale reinforcement material can be harnessed. The interfacial shear strength (IFSS) and resilience are two quantitative measures indicating the mechanical quality of the interface as they define the capability of the matrix to transfer stresses and deformations onto the carbon nanofiber. Similar arguments can also be applied to mechanical properties such as the elastic modulus and the fracture toughness based on the quality of the interface attesting its governing character in nanocomposites performance [42,72-75].
Figure 3.1 (a) SEM image of a 5 wt. % PR-24-XT-HHT-LD - Epon 828 composite manufactured by Resin Transfer Molding (RTM) at the Composites Manufacturing Laboratory of UIUC by the author. Non-uniform dispersion and agglomeration resulted in composite subdomains with different conductivities as expressed by the presence of strong contrast in the image. (b) Although fiber alignment has been achieved to some extent, relatively long sections of pulled-out VGCNFs suggest inadequate wetting and interfacial bonding between the reinforcement and polymeric matrix.

3.1. Background on Mechanics of CNF-Polymer Interfaces

To date, experimental characterization of the mechanical behavior of interfaces in polymer composites was limited to microscale reinforcements due to experimental limitations in force and strain metrology at the submicron scale. Additional practical issues stem from difficulties in isolation, manipulation, mounting and gripping of individual nanoscale fibers. Lack of precise control of key experimental parameters, such as the embedded fiber length and its precise definition could also be listed among the factors preventing the direct interfacial experimentation at the nanoscale. The experimental foundation in microscale mechanical characterization of matrix-reinforcement interfaces has been laid by a series of investigations in references [76-83],
and by later improved experimental tools, sample preparation and manipulation methods, and more accurate measurement techniques [84-87]. The use of measurement devices, such as wetting force scanners [88], strain-resistivity coupling based sensitive fiber extensometers [89] and acoustic emitters [90] provided invaluable information about different aspects of interfacial characterization of carbon fiber composites, such as the extent of cohesive failure, the relative contribution of different fracture mechanisms operating at the interface, the influence of matrix cracking on the interface failure and load transfer efficiency, etc.

Additional advances have been made with the application of scanning probe microscopy (SPM) [91]. The adhesion of individual nanotubes SWCNTs and MWCNTs to an epoxy matrix was investigated by performing non-standardized pull-out experiments, in which SWCNTs and MWCNTs were pulled laterally from the midpoint of their span length inside tiny holes in a thin film of a polymer composite specimen by means of an SPM, until the nanotube was completely retracted from the matrix. The force extracted from SPM cantilever deflection and the length of the detached portion of the nanotube were used to estimate the value of the interfacial shear strength (IFSS) along with other quantities such as the nanotube diameter and orientation angle of the pulled-out section within the thin film composite specimen. This first attempt to measure the interfacial shear strength (IFSS) of SWCNTs and MWCNTs in a nanocomposite has been a widely acknowledged experimental undertaking, but the particular experimental technique had some intrinsic deficiencies. As acknowledged by the authors in [91], the applied loading was not uniaxial in nature as required for a traceable pull-out test [86] due to the lateral application of force to the test specimen. The bending load induced to a nanotube by this mode of loading resulted in a complex fracture process under mixed mode-II (shearing) and mode-III (tearing) loading. The lack of control over the embedded nanotube length and its alignment were additional drawbacks.

This technique was improved [92] and applied to pull-out experiments of individual MWCNTs from polyethylene-butene. The fracture energy for the nanotube-polymer interface was estimated by measuring the pull-out force and the embedded nanotube length. A major difference from the previous technique was that individual
MWCNTs were isolated by approaching randomly distributed MWCNT bundles dispersed on a carbon tape with the pyramidal tip of an Atomic Force Microscope (AFM) cantilever until a MWCNT was attached by van der Waals forces. Further fixation of the single MWCNTs onto the AFM tip to guarantee bonding was achieved by amorphous carbon deposition on the MWCNT-AFM tip attachment similarly to previously established practices [93]. The MWCNT was subsequently inserted into a molten thermoplastic polymer film that was then resolidified, while the nanotube position within the polymer was maintained through the AFM cantilever position feedback. Finally, nanotube pull-out experiments were performed by retracting the AFM tip from the solid polymer and cantilever deflection was monitored to compute the resulting force [92]. Similar experiments were conducted with a thermosetting epoxy matrix within an SEM chamber to reveal the effect of MWCNT chemical surface functionalization (carboxyl side group addition) on the pull-out force and the average IFSS [94]. Resorting to the shear lag theory [95], the authors calculated the shear lag constant for both unmodified and chemically functionalized nanotubes and compared these with those of microscale fiber reinforced composites to predicate about the enhanced stress transfer efficiency in polymer nanocomposites [94,96].

In these experiments [92,94], the force required to pull individual nanotubes out of the surrounding polymeric matrix was proportional to the embedded length. For sufficiently large embedded lengths, nanotube rupture and telescopic nanotube pull-out was observed. Compared to non-functionalized, neat carbon nanotubes, the chemically functionalized (carboxyl side group grafted) nanotubes demonstrated fracture and subsequent partial pull-out at smaller embedded lengths, due to improved interfacial adhesion. These result agreed with the numerical calculations of the IFSS which were in the 20-40 MPa range for the non-functionalized nanotubes whereas values as high as 140 MPa were attained with the functionalized nanotubes. Although, both functionalized and non-functionalized nanotubes exhibited an inversely proportional correlation between the average IFSS and embedded length, this trend was more pronounced in the case of functionalized nanotubes, indicating the loss of atomically smooth character of the nanotube surface through the addition of side groups. The larger IFSS of non-functionalized carbon nanotubes compared to carbon fibers was postulated to originate in
covalent bonding between the nanotubes and the polymer matrix at the sites of intrinsic defects in the tube structure and the favorable coiling of polymer chains around the nanotubes. The decrease in the IFSS with increasing nanotube embedded length was consistent with the predictions of the shear lag theory, which was used to determine the shear lag constant, $\beta$, in each case. For both functionalized and non-functionalized nanotubes, the shear lag constant was orders of magnitude greater than that calculated for carbon fibers, pointing out to improved stress transfer in polymer composites with nanoscale reinforcements.

Although being a significant experimental milestone, the aforementioned technique bears some problems that limit its applicability as a versatile experimentation method for nanoscale interfacial mechanics. The process of amorphous carbon deposition is accomplished inside an SEM at electron beam acceleration voltages of several tens of kilovolts, which might introduce superficial or even internal defects to the nanoscale specimens depending on the beam penetration depth, as was also admitted by the authors [92]. Furthermore, this approach is not directly applicable to thermosetting matrices which are the most commonly employed aerospace materials. The degree of nanofiber bonding as a function of curing cycle and the associated matrix shrinkage and thermal stresses which cannot be investigated by employing such a technique are also of great interest. Therefore, in the method developed in this work, the exclusive use of AFM and SEM tools was limited significantly and new tools adopted from MEMS technology were employed.

3.2. IFSS Experiments for Nanofiber-Matrix Interfaces

The development of a MEMS-based experimental method was instrumental in overcoming the limitations and deficiencies of earlier techniques for nanoscale pull-out experiments that were explained in the previous section. In order to determine the design specifications such as the ideal stiffness of the required loadcell for precise pull-out force measurement and the embedded fiber length that allow for a successful pull-out experiment without nanofiber rupture, of the embedment section to ensure a successful
pull-out process rather than fiber rupture, a parametric design analysis was performed by considering the experimentally obtained individual carbon nanofiber strength values in Chapter 2, the range of fiber diameters, and literature values for the interfacial shear strength (IFSS) of microscale carbon fiber-epoxy systems [97,98].

Figure 3.2 Maximum embedded VGCNF lengths as a function of tensile strength, diameter and IFSS. Assuming a fiber diameter of 200 nm, the fiber embedded length/diameter (L/D) ratios can be converted into the embedded fiber lengths shown in parentheses. The shaded rectangle indicates the region of experimental feasibility initially determined for the purposes of the present work using the lowest and the highest experimental strength values obtained in the previous Chapter and the anticipated lower and upper bounds, 50 and 100 MPa, respectively, for the IFSS. The dash-dot line indicates the tensile stress in the fiber corresponding to a 50% probability of failure.
Figure 3.2 shows the range of possible embedded fiber lengths as a function of nanofiber strength, diameter and IFSS that could be used in pull-out experiments. For instance, the maximum embedded fiber length is ~2 μm for an IFSS of 65 MPa and a nanofiber diameter of 200 nm. For embedded lengths larger than 2 μm, the 50% fiber rupture probability line in Figure 3.2 will be crossed at IFSS values less than 65 MPa, indicating that fiber rupture will be more likely than fiber pull-out.

A prototype MEMS-based pull-out device was designed at UIUC considering the outcomes of the parametric analysis for 'proof of concept' experiments. Fabrication of this device was carried out by Sandia National Laboratories using the SUMMIT™ ultra-planar, multi-level MEMS manufacturing technologies. Controlling the embedded VGCNF length emerged as an important factor in conducting proper pull-out experiments due to the potentially high interfacial shear strength due to the optimized adhesion properties of the specific nanofibers. To regulate the epoxy profile and the embedded fiber length, a segmented pull-out channel was implemented with 4 matrix compartments in the side of the embedded fiber, each of them being 3 μm long, thus allowing for a maximum embedded length of 12 μm, as shown in Figures 3.3(a) and 3.3(b). In order to prevent the uncured epoxy polymer from flowing to adjacent compartments, each compartment was filled with a dedicated epoxy well high that was large enough to supply the required amount of epoxy.

A common aerospace grade composite matrix, the Epon™ 828 difunctional bisphenol A/epichlorohydrin derived liquid epoxy resin compounded with EPIKURE™ 3140 polyamide curing agent. This epoxy, acquired from Hexion Specialty Chemicals Inc. was used as the matrix to conduct interfacial adhesion experiments with Pyrograf®-III nanofibers. A 1.5 hr curing cycle with 1 hr curing at 80°C was applied according to recommendations by the manufacturer. In each experiment, an individual VGCNF was appropriately positioned so that it was surrounded by epoxy matrix with enough thickness in every direction in the plane transverse to pull-out direction to reduce the effect of boundaries and free surfaces to the interfacial shear stresses [86]. The thickness of the fully-cured epoxy was checked before the experiment with an SEM at low electron acceleration voltages to maintain small electron penetration.
Figure 3.3 Prototype nanofiber pull-out device: (a) Pull-out channel with epoxy wells and CNF grip, (b) mounted CNF in the pull-out channel before is covered by epoxy.

The procedure for nanofiber loading and measurement of the applied force and cross-head displacement was conducted according to the methodology described in Chapter 2 on the mechanical strength experiments with VGCNFs. On-chip mechanical actuation of the pull-out device was achieved by an external probe attached to a picomotor with 23 nm step size. The instantaneous deflection of the loadcell was recorded at a sampling frequency of 2 Hz by imaging the experimental pull-out device under an optical microscope equipped with a high resolution CCD camera. Precise measurement of the loadcell deflection was performed by means of DIC that provided the opening of the loadcell arms with an accuracy better than 50 nm [46,47]. Since the surface of the fabricated polysilicon loadcell inherently possessed a pattern clearly visible under dark-field optical imaging, owed to the grain associated surface roughness, no additional surface patterning was generated, although methods appropriate for MEMS scale experimentation have been developed in our laboratory in the recent years [99]. Using the instantaneous loadcell deflection extracted by DIC calculations and its stiffness (6.42 μN/μm) the pull-out force vs. cross-head displacement curves were generated showing different interfacial processes occurring during an experiment from the onset of the interfacial debonding to the frictional pull-out.
In order to compute a first estimate for the IFSS of the VGCNF-epoxy, the following simple equation was used assuming perfect bonding at the interface and uniform shear stress along the embedded fiber portion (i.e. no shear lag) so that

$$\tau_{\text{max}} = \frac{F_{\text{max}}}{\pi \cdot d \cdot l_{\text{emb}}}$$

(3.1)

where $\tau_{\text{max}}$ is the interfacial shear strength, $F_{\text{max}}$ is the maximum force value extracted from the experimental pull-out curve, $l_{\text{emb}}$ is the embedded fiber length and $d$ is the nanofiber diameter.

Preliminary analysis of this pull-out experiment with an embedded PR-24-XT-HHT-LD grade carbon nanofiber revealed a typical pull-out force vs. cross-head displacement curve very similar to the ones obtained with microscale fibers extracted from polymer matrices [86], as shown in Figure 3.4. Specifically, the initial stress buildup was followed by a sudden failure of the matrix-fiber interface (no slope change associated with stable partial debonding was observed) and subsequent drastic drop in the loadcell force. The reduction in the recorded force during debonding contains the effect of the loadcell recoil because of the finite loadcell stiffness and the instantaneous release of part of the strain energy stored in the loadcell. Further imposed displacement to the free end of the carbon fiber produces a local maximum (the pull-out shoulder) due to static friction, followed by frictional sliding of the nanofiber through the matrix. The frictional component of this measurement is possible because the fiber extended beyond its embedded length.

The small amplitude fluctuations observed in the force during the friction governed pull-out phase indicated the significant presence of stick-slip (caused by temporal adhesion of the two sliding surfaces), which can be due to a clamping stress on the nanofiber because of matrix contraction during the curing phase, and the van der Waals interaction between the matrix and the non-functionalized carbon nanofiber. Interestingly, this frictional force is reduced over time, possible because of shearing polymer matrix from the interface. The IFSS calculated from this experiment in Figure 3.4 was approximately 45 MPa, implying relatively good bonding of the epoxy matrix to
this non-functionalized nanofiber compared to typical IFSS values reported in the literature for non-surface-treated microscale carbon fiber-epoxy systems, which range from 14.9 MPa (IM6-U carbon fiber-Epon 828 mPDA tested using the microbond method) to 28 MPa (HS carbon fiber-epoxy matrix tested using a pull-out method) [98,100].

![Force-cross head displacement curve](image)

**Figure 3.4** Force-cross head displacement curve obtained from a pull-out experiment of a PR-24-XT-HHT-LD grade carbon nanofiber with an embedded length of 1.5 μm in the Epon 828 epoxy and the device shown in Figure 3.3(a). The pull-out curve shows the processes of nanofiber debonding (failure of covalent bonds) and frictional sliding.

### 3.2.a. Improved MEMS-based Method for Nanoscale Pull-out Experiments

As discussed in the previous section, the development of the prototype experimental pull-out device served to the purpose of conducting "proof of concept" experiments to obtain the relative importance of the energy dissipation processes taking place during a nanofiber IFSS experiment. Although these experiments were successful in capturing the pull-out process and provide good estimates of the IFSS of the nanofiber-epoxy system, some key issues concerning specimen preparation and the precise definition of the embedded nanofiber length were identified, which needed to be
addressed in order to obtain a refined and accurate nanoscale pull-out experimental method with high success rate and repeatability.

The first aspect of the prototype nanofiber IFSS measurement device that needed to be addressed was associated with the specimen preparation and mounting. As seen in Figure 3.2(b), the CNF grip and the channel were to be used simultaneously during the mounting process of the fiber which would necessitate the isolation of long fibers with straight ends on both sides. Although carbon nanofibers matching with this morphological description can be found in the VGCNF “wool” purchased from the manufacturer, their frequency is rare. Hence, to increase the number of qualifying specimens and expedite the process of specimen isolation, the on-chip stationary grip concept was replaced by a more versatile approach. Secondly, the long, segmented pull-out channel with high sidewalls and large polymer wells to control epoxy profile formation, although a convenient tool, its use was limited by strong wetting of the polysilicon well walls by the epoxy resulting in large menisci. The segmented channel did not provide the necessary resolution in controlling the embedded nanofiber length, as the high bonding strength and the specific tensile strength of the nanofibers limited this value to about 2 μm. Another concern was the meniscus forming in the front free end of the nanofiber. Epoxies are designed for good wetting of carbon nanofibers, which, however, limited our precision in defining the nanofiber embedded length.

To address the aforementioned issues and maintain the overall simplicity of the experimental process, a new experimental methodology was developed. This process aimed at facilitating embedded fiber lengths between 500-2000 nm and controlling the profile of the epoxy. Key in this development was the use of microfabricated auxiliary polysilicon bridges on a silicon chip using Sandia National Laboratories’ SUMMIT™ technology. These nanofiber mounts were 5 μm wide 30 μm long, as shown in Figure 3.5(a). Considering the relatively high IFSS obtained in the previous section, and the tensile strength values for different carbon nanofiber grades discussed in Chapter 2, it can be shown that embedded fiber lengths of up to 2-3 μm could be used in our pull-out experiments to quantify the IFSS. For this purpose, several 5-μm long and 0.8-μm deep trenches were ion-milled by a Focused Ion Beam (FIB), as shown in Figure 3.5(b), to
facilitate the initial deposition of epoxy. The trenches were filled simultaneous with epoxy which was cured in an oven for 30 min and at 80°C.

Figure 3.5 (a) A 5 µm wide and 9 µm high auxiliary bridge fabricated to facilitate mounting of the carbon nanofibers, (b) top view of 0.8 µm deep trenches fabricated by ion-milling that served as wells of initial deposition of Epon epoxy (c) trench ion-milled inside the trenches in figure (b), also removing the polysilicon walls of the epoxy wells shown in figure (b), (d) precise control of the embedded fiber length by ion milling the carbon nanofiber fiber inside the epoxy.
After this initial curing process, the embedded fiber region was further defined as a secondary ion-milled trench, which was 2.5 μm wide, and 0.3 μm deep generated in the middle of the initial filled trench as shown in Figure 3.5(c). This cut served several purposes. Firstly, it allowed for sufficient epoxy surrounding the nanofiber that is subsequently positioned in the trench, as it is common for nanofibers to attach themselves to the walls of the trenches rather than stay in their center. For accurate interfacial measurements and proper definition of the compliance of the surrounding matrix, it is important that a micron or more of epoxy exists around the fiber in its embedded section. This process also guaranteed that the depth of the epoxy underneath was at least 0.5 μm. Secondly, it provided a flat edge of front side of the final epoxy well, see Figure 3.5(c), which limited the meniscus size that forms in the edge of the epoxy where the fiber exits. Traces of a large initial meniscus can be seen in the rear side of the trench in the same figure. The secondary trench in Figure 3.5(c) was also filled with epoxy, a VDCNF was mounted in the trench and the epoxy was cured for 30 minutes at 80°C. Finally, mounted nanofiber was taken to the FIB to define its embedded length as seen in Figure 3.5(d). This process was carried out at low amperage (50 mA) to reduce the effect of gallium ion bombardment on the chemical composition and the adhesion of the carbon nanofiber to the epoxy.

The nanofiber pull-out experiments were executed with a double-column folded beam loadcell, whose true stiffness was determined by the calibration process discussed in Chapter 2. The loadcell was attached to a tungsten grip and then was brought to the close proximity of the pull-out trench with the mounted fiber. After alignment of the loadcell axis with the embedded fiber, the free end of the fiber was raised onto the loadcell with an ultra-sharp tungsten probe. Finally, a small amount of rapidly curing two part epoxy was applied with to the fiber portion on the loadcell.

The actuation of the nanofiber IFSS apparatus and the data acquisition were performed similarly to the methodology described in the previous section. The ultimate loadcell deflection required to determine the IFSS was measured by DIC in the region of interest as shown in Figures 3.6(c) and 3.6(d). Post-mortem images of the remaining pull-out channel and the debonded fiber were taken with an SEM to measure the embedded
fiber length, the fiber diameter, and to determine the type of interfacial failure, i.e. adhesive, cohesive or mixed, that occurred during the experiments.

Figure 3.6 (a) Loadcell deflection recorded to determine the IFSS measured by performing DIC analysis in the indicated region, (b) loadcell returns to its unloaded state after interfacial failure and nanofiber pull-out. In the DIC analysis this particular frame showing the unloaded configuration is used as the reference for the extraction of force-deflection curve.

3.2.b. Theoretical Considerations of Carbon Nanofiber Debonding

The nanofiber IFSS experiments were performed following the refined MEMS-based method described in detail in the previous section. For all nanofiber debonding experiments, the high temperature heat treated, but non-functionalized, carbon nanofiber grade PR-24-XT-HHT-LD was used. The IFSS of this grade is expected to be at the lower bound of IFSSs of VGCNFs, due to smallest content of turbostratic carbon among all VGCNF grades, the smoothest surface with the least number of defects, and the lack of any binding side groups. The IFSS values obtained for the present system of EPON 828 with PR-24-XT-HHT-LD carbon nanofibers can serve as reference for molecular dynamics simulations. The exact chemical and compositional details of the interface can
be determined through physical-chemical characterization tools, such as ion scattering spectroscopy (ISS), Fourier transform infrared spectroscopy (FTIR), secondary ion mass spectroscopy (SIMS) etc. [86,101]. The shear strength of the carbon nanofiber-epoxy matrix interface can be calculated to a first order approximation from the force equilibrium established between the tensile stress, $\sigma_f$, acting on the fiber cross-section and the shear stress, $\tau$, acting on the nanofiber-epoxy matrix interface. Assuming that the interfacial shear stress is uniform on the fiber perimeter and it decays linearly along the embedded fiber length starting at a maximum, $\tau_{\text{max}}$, at the point where the nanofiber enters the epoxy matrix and becoming zero at the free end that is generated by ion-milling, see Figure 3.5(d), results in

$$\tau(x) = \tau_{\text{max}} \left(1 - \frac{x}{L_{\text{emb}}} \right) = \tau_{\text{max}} - \frac{x}{L_{\text{emb}}} \tau_{\text{max}}$$

(3.2)

Then, the force equilibrium gives:

$$\sigma_f \cdot \pi \cdot \frac{d^2}{4} = \pi \cdot d \cdot \int_0^{L_{\text{emb}}} \left( \tau_{\text{max}} - \frac{x}{L_{\text{emb}}} \tau_{\text{max}} \right) dx \Rightarrow$$

$$\sigma_f \cdot d = \left[ \tau_{\text{max}} \cdot x - \frac{x^2}{2 \cdot L_{\text{emb}}} \tau_{\text{max}} \right]_0^{L_{\text{emb}}} \Rightarrow \sigma_f \cdot d \cdot 4 = \frac{1}{2} \cdot \tau_{\text{max}} \cdot L_{\text{emb}} \Rightarrow$$

(3.3)

$$\tau_{\text{max}} = \frac{\sigma_f \cdot d}{2 \cdot L_{\text{emb}}}$$

where $d$ is the nanofiber diameter and $L_{\text{emb}}$ is embedded length. The physical rationale of this analysis is based on the experimental observation regarding the failure of the interface that initiates at the fiber-matrix junction and develops into an interfacial crack that propagates along the embedded fiber [98]. One can find more thorough analytical models for the interfacial failure using fracture mechanics principles and energy methods [102,103].

As an alternative to this analysis, the micromechanics approach developed by Chua and Piggott considered the entire pull-out process from the initiation of the interfacial crack to the frictional terminal pull-out phase, which is controlled by five
variables: the interfacial pressure, \( p_0 \), the coefficient of friction, \( \mu \), along the debonded fiber, the work of fracture of the interface, \( G_i \), the remaining embedded fiber length within the pull-out channel, \( L \), and the free fiber length, \( l_f \) [104-106]. By assuming elastic mechanical behavior for both the fiber and the matrix and stress transfer at the interface without localized yielding or sliding (i.e. perfect bonding) until the initiation of the interface failure, the authors formulated an expression for the tensile stress along the embedded fiber length [98,104]:

\[
\sigma_f = \sigma_f' \cdot \frac{\sinh \frac{2n(L-x)}{d}}{\sinh(ns)}
\]

where \( s \) is the aspect ratio of the embedment channel defined as \( s = \frac{2L}{d} \), \( \sigma_f' \) is the average tensile stress in the free section of the fiber before the embedded section, and \( n \) incorporates material specific constants and the effect of the traction free boundary into the resulting expression for \( \sigma_f \) and it is defined as:

\[
n^2 = \frac{E_f}{E_m} \cdot \frac{E_f}{E_m} \cdot \frac{(1 + \nu_m) \ln \left( \frac{2R}{d} \right)}{1 + \nu_m}
\]

where \( E_f \) and \( E_m \) are the Young's moduli of the fiber and matrix, respectively, \( \nu_m \) is the Poisson's ratio of the matrix and \( R \) is the distance from the axis of the fiber to the topmost point of the surrounding polymeric matrix [98, 104].

In order to obtain a better approximation of the variation of shear stress along the fiber embedded length than the first order expression given by Equation (3.2), Equation (3.4) can be applied to the force equilibrium of a differential fiber element of length \( dx \) as shown in Figure 3.7:

\[
\sigma_f \cdot \pi \cdot \frac{d^2}{4} + \pi \cdot d \cdot \tau_i \cdot dx = (\sigma_f + d\sigma_f) \cdot \pi \cdot \frac{d^2}{4}
\]

Hence, assuming no bonding across the end of the fiber, which is the case for the present experiments since the nanofiber ended at the sidewall of the ion-milled trench, the
The following expression is obtained for the shear stress at the interface \( \tau_i \), which correlates the interfacial shear stress to the spatial derivative of the axial tensile stress in the fiber along the embedded length:

\[
\tau_i = \frac{d\sigma_f}{4} \frac{d\sigma_f}{dx} \tag{3.7}
\]

**Figure 3.7** Differential fiber element under force equilibrium according to Equation (3.6). Figure was reproduced with appropriate changes from reference [98].

Substituting Equation (3.4) into Equation (3.7), we obtain the expression of the shear stress at the interface in terms of the tensile stress at a point \( x \) along the embedded fiber:

\[
\tau_i = n\sigma_f \frac{\cosh \left( \frac{2n(L-x)}{d} \right)}{2 \sinh(ns)} \tag{3.8}
\]

Assuming that interface failure occurs when the maximum shear stress \( \tau_{\text{max}} \), which has a maximum at \( x=0 \), reaches the IFSS, the uniaxial pull-out (debonding) force, \( F_d \), can be estimated as:

\[
F_d = \pi \cdot d^2 \cdot \sigma_f \cdot \frac{\tau_{\text{max}} \cdot \tanh(ns)}{2 \cdot n} \tag{3.9}
\]

such that the IFSS becomes [98]:

47
\[ \tau_{\text{max}} = \frac{2 \cdot n \cdot F_d}{\pi \cdot d^2 \cdot \tanh(ns)} \]  

(3.10)

As the third and final approach adopted in this study to quantify the value of the interfacial shear strength; uniform yielding situation all over the interface will be assumed, such that the maximum shear stress \( \tau_{\text{max}} \) value resulting in yielding is attained and sustained in every point at the interface in agreement with the elastic-perfectly plastic type mechanical behavior. Such an assumption automatically implies a constant shear stress distribution along the embedded fiber length and presumes negligible work hardening effects during the loading phase of the executed pull-out experiment [98, 104]. Hence, the pull-out force (or debonding force) can be expressed as:

\[ F_d = \pi \cdot d \cdot I_{\text{emb}} \cdot \tau_{\text{max}} \]  

(3.11)

such that the interfacial shear strength \( \tau_{\text{max}} \) will be determined via

\[ \tau_{\text{max}} = \frac{F_d}{\pi \cdot d \cdot L_{\text{emb}}} \]  

(3.12)

3.2.c. Determination of IFSS of Individual VGCNFs Embedded in Epoxy

The experimental results obtained by the method presented in section 3.2(a) were analyzed according to the three approaches discussed in the previous section, namely the maximum shear stress criterion with linearly decaying shear stress (LDSSC), the Chua-Piggott criterion (CPC), and the uniform interfacial yielding based criterion (abbreviated as UIYC). The results are listed in Table 3.1. For the calculation of the IFSS according to the Chua-Piggott criterion, following material properties are used: \( E_m = 2.89 \) GPa [107], \( E_f = 250 \) GPa and \( \nu_m = 0.35 \) [98]. As seen in Table 3.1, the LDSSC and CPC criteria gave very similar results because both criteria were developed with the assumption that the maximum shear stress initiated failure of the interface. The UIYC criterion resulted in IFSS values which were 50% of those calculated by LDSCC.
The measured pull-out force was normalized with respect to the nanofiber diameter and plotted in Figure 3.8(a) versus the embedded fiber length to reveal its effect on the IFSS. The slope of the best fit line is the least squares approximation of the IFSS multiplied by $\pi$. The plot shows a distinct trend of IFSS with the embedded length which points, which, according to the models described in the previous section, was described by a straight line. Dividing its slope by $\pi$, we obtained the average IFSS as 54.7 MPa which is approximately 17% lower than the arithmetic average of the value for uniform interfacial yielding in Table 3.1. Some experimental results in the 0.6-0.9 $\mu$m embedded length range reduced the overall linearity of the data set, indicating an increased influence of the meniscus formation for shorter embedded lengths. On the other hand, the variation of the IFSS with increasing fiber diameter is plotted in Figure 3.8(b), generally showing a decreasing trend with increasing fiber diameter. In addition to experimental artifacts, this distribution of IFSS values can be explained by variations in the fiber thickness and the graphitic/defect content of the high temperature heat treated outermost layer, since covalent bonding with the epoxy polymer is affected by surface defects.

In order to obtain further understanding of the process of interface failure which also affects the precision of the aforementioned models, post-mortem images of the debonded fiber channels and the fibers themselves were recorded with an SEM. As shown in Figures 3.9(a) and 3.9(b), the pull-out channels had approximately round entry holes without substantial matrix plasticity at the hole circumference. Furthermore, no significant traces of matrix could be detected in the section of the nanofiber that was embedded in the matrix, as shown in Figures 3.10(b) and 3.11(b). In almost all cases, the pulled-out section of the nanofiber was clean and smooth, pointing to the adhesive (i.e. non-cohesive) interface failure, with crack initiation and progression happening on the same plane of the interface. Considering the numerical values for the IFSS in Table 3.1 that were obtained with the three different criteria, it is highly unlikely that the IFSS could attain values as high as the ones suggested by LDSSC and CPC, matrix yielding would have occurred near the interface before interfacial debonding could occur. Therefore, the matrix yield surface would have been imaged in Figures 3.10(b) and 3.11(b). This argument, of course, is based on macroscale tensile strength measurements for this class of epoxies that do not exceed 80-100 MPa [108]. Therefore, the IFSS values
computed based on the simpler UIYC criterion represent a good approximation for the IFSS of PR-24-HHT-LD - Epon 828/Epikure 3140 epoxy.

**Table 3.1** IFSS values, calculated by three different models, from nanoscale pull-out experiments with PR-24-HHT-LD nanofibers embedded in Epon 828/Epikure 3140 epoxy matrix.

<table>
<thead>
<tr>
<th>Experiment #</th>
<th>Embedded fiber length (μm)</th>
<th>Fiber diameter (μm)</th>
<th>LDSSC (MPa)</th>
<th>CPC (MPa)</th>
<th>UIYC (MPa)</th>
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<td><strong>65.6</strong></td>
</tr>
<tr>
<td><strong>± SD</strong></td>
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<td></td>
<td>±19.0</td>
<td>±19.6</td>
<td>±9.5</td>
</tr>
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</table>
Figure 3.8 (a) Interfacial strength force normalized by the nanofiber diameter vs. the embedded fiber length. The slope of the best fit line is the IFSS multiplied by \( \pi \). (b) Variation in IFSS with fiber diameter. Despite the data scatter, a decrease in the IFSS with increasing fiber diameter can be established.
Figure 3.9 Post-mortem images of pull-out channels. (a) Remnants of the pull-out channels revealed round exit holes. (b) No circumferential cracking was observed in the vicinity of the exit holes.

Figure 3.10 Post-mortem images of pulled-out nanofiber ends: (a) Fiber mounted at the MEMS device grip, (b) detail of the originally embedded nanofiber section showing clear matrix debonding and matrix failure at the meniscus entrance into the matrix.
Figure 3.11 (a) Pulled-out nanofiber and (b) detail showing no significant trace of matrix residue on the embedded fiber. Notice that there is failure of the meniscus formed at the fiber entrance to the epoxy.

Figure 3.12 (a) Force vs. cross head displacement curve for the pulled-out fiber shown in Figure 3.10. There is no "softening" before fiber debonding which indicates that the meniscus at the fiber entrance into the matrix in Figure 3.10(b) did not contribute to the measured value of the IFSS. (b) Force vs. cross head displacement curve for the pulled-out fiber shown in Figure 3.11. No effect of the polymer meniscus can be detected in this curve either.
In comparison with the very limited literature data on the IFSS between MWCNTs and epoxy matrices, varying in the wide range between 20-376 MPa [91,92,109], the experimentally determined IFSS in this study of 55 MPa for the VGCNF-epoxy system appears to be a reasonable value. Yet, we believe that the present method is considerably more reliable than prior attempts to quantify the interfacial mechanics of individual nanostructures in epoxies. The decrease in the IFSS with increasing nanofiber diameter in our data is much less pronounced than the case of carbon nanotubes [75,91], which, as mentioned before, could be attributed to local variations in the density of reactive binding sites at the ends of graphitic basal planes on the high-temperature-heat-treated CNF surface. The calculated IFSS values are also in good agreement with carbon fiber experimental pull-out values, which can be as low as 28 MPa for carbon fibers without being subjected to a surface treatment and can attain values as high as 64.6 MPa following chemical functionalization or surface treatment [86,98,100]. The average IFSS of ~55 MPa for the VGCNF-epoxy system of this study indicates that the adhesion of the heat-treated, non-functionalized carbon nanofiber grade PR-24-HHT-LD is almost as good as its chemical side group functionalized and oxidized microscale counterparts. Whether such improved adhesion arises from nanoscale details, such as preferable molecular orientation of polymeric chains along the nanoscale fiber-matrix interaction surface or the presence of covalent CNF-polymer bonding due to intrinsic defects in nanofiber structure [91,92,110], remains to be further explored.
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The experimental work and the results presented in Chapters 2 and 3 of this dissertation provided a definitive step in meeting the objectives set in the Introduction for establishing a robust experimental method for the determination of the interfacial mechanics of nanoscale reinforcements in soft matrices. A series of repeatable experiments were conducted to measure for the first time the tensile and interfacial shear strengths of VGCNFs in epoxy, while their mechanical behavior was corroborated with SEM and TEM images of the nanofiber structure and the surface of VGCNFs after debonding experiments.

In terms of tensile strength experiments, the nominal tensile strengths of the nanofibers followed Weibull distributions with characteristic strength values in the range of 2.74 - 3.34 GPa, which quantitatively delineated the effect of post-fabrication treatments and associated microstructural transformations on their strength. As-grown nanofibers had small Weibull modulus indicating the presence of a wide flaw population, which was significantly reduced upon heat treatment as evidenced by the 230% increase in the value of the Weibull modulus. These strength values are the first obtained in literature [39,111] and are 50% or smaller than the previously estimated values commonly reported for VGCNFs. Fractography of the nanofiber rupture region revealed that the stacked truncated cup structure of the oblique graphene layers comprising the backbone of VGCNFs is retained during the rupture process. Cleavage of the outer turbostratic layer occurs first, followed by relative slip of the internal oblique graphene layers, indicating the limited participation of the stronger sp²-bonds in the (discontinuous) graphene basal planes during fiber fracture. A 16% decrease in the mechanical strength (Weibull strength) has been noticed with high-temperature-heat-treated nanofibers, which correlated well with TEM images, showing the graphitization of the outer turbostratic layer and the evolution of its interface with the inner, originally graphitic, layer with
attendant structural discontinuities that reduced the total load bearing capacity of the nanofibers.

The IFSS of individual VGCNFs-epoxy polymers interface was addressed by novel nanoscale pull-out experiments. An IFSS value of 55 MPa revealed that the adhesion and bonding of the heat-treated, non-functionalized and non-oxidized carbon nanofiber grade (PR-24-HHT-LD) to the Epon 828/Epikure 3140 epoxy matrix can be as good as functionalized micron size carbon fibers with IFSS values between 40-65 MPa. Compared to the few literature data on the IFSS between MWCNTs and epoxy matrices [92], the experimentally determined IFSS of 55 MPa for the VGCNF-epoxy system is significantly lower than the maximum value of 140 MPa that has been reported for chemically functionalized MWCNTs, but it is quite higher than the IFSS value of 30 MPa reported for non-functionalized, pristine multi-walled nanotubes. Although the literature measurements with MWCNTs do not meet macroscale standards for accurate and reliable experimental mechanics, these differences in the IFSS values could be due to defects residing on carbon nanofiber that promote increased interfacial interactions and therefore larger IFSS compared to MWCNTs that allow only for periodic surface interactions due the perfect atomic organization of their surface. On the other hand, the decrease in the IFSS with increasing nanofiber diameter has been reported to be significantly more pronounced in the case of MWCNTs [91].

Thus, all the objectives outlined in Chapter 1 of this dissertation were accomplished with the development of novel MEMS-based experimental methods that allowed us to obtain unequivocal experimental measurements at the nanoscale. These experimental methods are also applicable to other fiber-like nanostructures, such as electrospun polymer nanofibers or metallic nanowires and can serve to extend our current understanding of nanoscale mechanical phenomena. Combined with the results of parallel experimental studies at our laboratory on the effect of chemical functionalizations on the interfacial mechanics of similar nanostructures, the findings of this dissertation can serve as validation data for existing molecular interaction potentials so that nanoscale interfacial phenomena and composite materials damage can be accurately predicted. The experimental results of this research also provide the input data and the fundamental basis
for continuum mechanics fracture modeling of nanostructured composites supporting a quantitative assessment of the competing interfacial interactions leading to energy dissipation during microcracking, crack growth and coalescence in nanocomposites failure.


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