

**EFFECT OF SEAWATER AND TEMPERATURE UPON CARBON FIBER/VINYL ESTER
(CF/VE) COMPOSITES AND ITS CONSTITUENTS**

**A Dissertation Presented for the
Doctor of Philosophy
Degree
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DEDICATION

To my parents,
a meal well sacrificed.

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ABSTRACT

An experimental and computational investigation has been carried out to: (1) develop micromechanical characterization techniques for polymeric composites and (2) evaluate the effects of seawater and temperature upon the micro- and macro-response of the carbon fiber vinyl ester composites (CF/VE). Compression properties degradation due to short-term and long-term exposure to seawater is evaluated. A 12-16 % reduction in compression strength is observed due to long-term exposure to seawater, which is attributed to a decrease in interfacial shear strength (IFSS) due to long-term exposure to seawater. The developed Push-out methodology is used to characterize the IFSS. The presented approach consistently yields interfacial failure. However, the failure is found to be thickness dependent. Therefore, a Weibull-based methodology is adopted to quantify the degradation in IFSS for a given interfacial volume.

Subsequently, in Chapter 4, an energy-based parameter, R , is introduced to characterize the local crystal structure of carbon fiber, which is shown to be valid for an extensive range of standard to high-modulus PAN carbon fibers. The presented technique offers spatially resolved qualitative estimation of the crystal parameters. Chapter 5 presents a nanoindentation-based methodology to evaluate the Mode-I fracture toughness using the indentation-based load, the crack length, and the parameter $\gamma_{effective}$ obtained using finite element modeling. It is found that the fracture toughness of carbon fiber decreases as the modulus of the PAN-based carbon fibers increases.

Finally, in Chapter 6, the developed techniques are used for micromechanical characterization of CFVE exposed to extreme long-term sea water (15 years) and extreme

temperature temperatures ($\pm 80^\circ\text{C}$) conditioning. It is found that high temperature (80°C) exposure causes cracking, an increase in glass transition (T_g), and an increase in IFSS. On the other hand, low temperature (-80°C) causes a decrease in IFSS while the T_g remains unaffected. For wet-aged coupons, the crack density tends to increase while the residual stresses tend to decrease. It is concluded that as the consequence of thermal aging and an increase in IFSS, short-term exposure at annealing temperatures can cause an improvement in the matrix-dominated fatigue response of CF/VE.

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CHAPTER 1: INTRODUCTION

Polymer Composites and Hygrothermal Effects

Engineering materials exposed to seawater are subjected to hygrothermal stresses and chemical reactions throughout their lifecycle. Hygrothermal fatigue along with consistent exposure to different chemicals can lead to deterioration in their micromechanical and eventually macro-mechanical properties. The absorption of seawater in composite material has been investigated intensively in the past two decades. The extent of degradation depends on fiber, matrix, and fiber–matrix interface characteristics. The load is transferred between the fiber and matrix via interface. Therefore, a chemical or mechanical degradation of the interface due to seawater or temperature can result in overall deterioration of mechanical properties. More specifically, the presence of water molecules at the fiber–matrix interface, originating from diffusion or from capillary action, can lead to degradation of the chemical bonding that assures fiber–matrix adhesion.

Previous Work

For naval applications, sandwich composite structures made from Carbon Fiber Vinyl Ester (CF/VE) facings and polyvinyl chloride (PVC) foam as the core material are of primary interest. The composite sandwich structure offers the advantages of a high strength-to-weight while excellent corrosion resistance. This work focuses on the effects of seawater and temperature on CF/VE facings. Previous work by Siriruk et al. [1–6] focused on evaluating degradation in the mechanical properties of the core, facing, and sandwich structure. Their work is briefly discussed in this section.

Regarding PVC foam, seawater, whose absorption is essentially confined to the outermost cells of the foam, degrades the shear modulus of the saturation region by up to 70%. However, the average value of that reduction is approximately 50%. In comparison, Young's modulus decreases by up to 60 % in the saturated region, with an average reduction of 33% [6]. The diffusion mechanics of seawater upon PVC foam have been established. Using the double cantilever beam (DCB) configuration, Siriruk et al. showed that exposure to seawater does not considerably affect the critical strain energy release rate, G_c [6].

In their investigation of delamination toughness at the facing/foam interface, results primarily showed scatter arising from variation in laminate thickness. Nevertheless, they demonstrated that sustained exposure to seawater resulted in a 30% reduction in delamination fracture toughness [3]. In addition, the failure mechanism between the dry and wet structures was changed, with the dry structure failing within the core while the wet sandwich structures failed at the interface between the facings and the core [3].

For CF/VE facings, immersion saturation had little effect on the tensile modulus [1]. Siriruk et al. also reported that diffusion is the primary mechanism of moisture uptake for polymeric composites [5]. They also investigated the effect of seawater on the tension–tension fatigue of CF/VE facings. They used four configurations, namely a dry sample tested in air, a wet sample tested in air, a dry sample tested while immersed in water, and a wet sample tested while immersed in water. Their work showed that while the degradation due to long-term immersion was ~30 %, significantly more degradation

was noticed for samples immersed in seawater, testing ~71% for dry samples and ~84% for wet samples (Figure 1). They also tested two additional states of only one-sided immersion in which they found 42% and 47% degradation for dry and wet samples, respectively [2].

Mechanical Testing

Understanding the coupon-scale mechanical performance of composites is essential for their design and subsequent implementation in structures. An appropriate structural design that accounts for the static and fatigue response of the material and the effects of long-term exposure to seawater and extreme temperatures is essential for making the material being investigated in a laboratory environment a reality in real-life applications.

Digital Image Correlation

Digital imaging correlation (DIC) is a technique used to track full-field displacements using changes in a grayscale histogram as a function of time. The zone under consideration is divided into sub-volumes using a grid pattern. Displacement within the sub-volume is then averaged to filter the noise. Therefore, the quality of the dataset obtained from DIC is a direct function of the resolution and grid size of the sub-volume. The displacement obtained can then be used to evaluate the strain tensor as well as rotation and translations that might have occurred during the tests. Although the concept of tracking displacement using a grayscale histogram is not new, recent advances in computing have led to more advanced mapping algorithms.

This work implements the Vic-3D digital image correlation (DIC) system from Correlated Solutions and a GOM ARAMIS DIC system. Both systems use a dual-camera

system to measure variation in displacement and consequently the strains. Firstly, the faces of the sample for which the strain needs to be investigated are speckled with black dots and white background. The dual camera system is then focused on the samples and subsequently a calibration panel is used to evaluate the relative position of the two cameras. Once, the relative positions of the cameras are known, a grayscale based algorithm is used evaluate the displacement corresponding to the movement of sub-volumes.

Micromechanical Characterization

Elastic Contact Mechanics

The problem being considered corresponds to an evaluation of the distribution of stress with an elastic indentation caused by the pressure generated by an axisymmetric punch. This problem was first considered by Boussinesq [7]. Using potential functions, Boussinesq derived a solution to the problem corresponding to the penetration of a solid of revolution. However, his solution did not lend itself to a practical solution, with the results only applicable to a few special cases. In the following years, several authors proposed alternative solutions, as described in a book by Galin [8]. Most of these solutions had their difficulties—for example, of only applying to a few special cases or the necessity to guess the appropriate combinations of solutions that satisfy the prescribed boundary conditions as proposed by Love [9,10]. Most notably, we will revisit the solution proposed by Sneddon et al., which was first developed in 1944 and then generalized over the next two decades to any indenter geometry. Sneddon's solution is the backbone of the theory behind nanoindentation. It uses Hankel transform to convert a

two-dimensional partial differential equation to a single-variable ordinary differential equation. Therefore, we will briefly revisit the original derivation of Sneddon's solution [11,12].

Hankel Transformation

Sneddon's solution uses the theory of Hankel transforms to express the axisymmetric solution of the equations of elastic equilibrium in terms of Hankel transforms of an arbitrary function. Boundary conditions are then used to determine the arbitrary function. Hankel transform is an integral transform equivalent to a two-dimensional Fourier transform with a radially symmetric integral kernel [13]. It is defined as:

$$g(u, v) = \iint_{-\infty}^{\infty} f(r) e^{-2\pi i(ux+vy)} dx dy \quad (1.1)$$

The solution to the equation can be found by converting the equation to polar coordinates and integrating. Let

$$x + iy = r e^{i\vartheta} \quad (1.2)$$

$$u + iv = q e^{i\phi} \quad (1.3)$$

The solution to the equation becomes:

$$g(q) = \int_0^{\infty} f(r) J_0(2\pi q r) q dv \quad (1.4)$$

where J_0 is the zeroth-order Bessel function of the first kind (sometimes referred to as cylinder function or cylindrical harmonics). J_n is the solution to the differential equation given by:

$$x^2 \frac{d^2 y}{dx^2} + x \frac{dy}{dx} + (x^2 - n^2)y = 0 \quad (1.5)$$

$$J_n(z) = \frac{1}{2\pi i} \oint e^{\left(\frac{z}{2}\right)\left(t - \frac{1}{t}\right)} t^{-n-1} dt \quad (1.6)$$

Using Hankel transform, a two-variable system is reduced to a single variable (r) with an addition of a parameter (q).

Sneddon et al.'s Solution

In their first work[11], Sneddon et al. considered the stress distribution in a solid of revolution and a semi-infinite medium, which are deformed symmetrically with respect to the axis of revolution. Considering the problem in polar coordinates, the equilibrium equations, the displacement fields, stress equations, and, consequently, the biharmonic equation are all well-known in the mechanics of materials. These equations are described as follows.

Stress equations in terms of stress function Φ :

$$\sigma_r = \lambda \nabla^2 \Phi_z - 2(\lambda + \mu) \Phi_{rrz} \quad (1.7)$$

$$\sigma_z = (3\lambda + 4\mu) \nabla^2 \Phi_z - \Phi_{zzz} \quad (1.8)$$

$$\sigma_\theta = \lambda \nabla^2 \Phi_z - \frac{2(\lambda + \mu)}{r} \Phi_{rz} \quad (1.9)$$

$$\sigma_\theta = (\lambda + 2\mu) \frac{\partial}{\partial r} \nabla^2 \Phi - 2(\lambda + \mu) \Phi_{zzr} \quad (1.10)$$

Displacement field in terms of stress function:

$$u_r = -\frac{\lambda + \mu}{\mu} \Phi_{rz} \quad (1.11)$$

$$u_z = \frac{\lambda + 2\mu}{\mu} \nabla^2 \Phi - \frac{\lambda + \mu}{\mu} \Phi_{zz} \quad (1.12)$$

The usage of the stress function (often referred to as potential function) results in the biharmonic equation, giving the Laplacian of the Laplacian of stress function equating to zero as the well-known equilibrium equation:

$$\nabla^4 \Phi = 0 \quad (1.13)$$

where $\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{1}{r} \frac{\partial}{\partial r} + \frac{\partial^2}{\partial z^2}$ for an axisymmetric case.

Using Hankel transformation, Sneddon could convert the biharmonic equation to an ordinary differential equation. If we consider the integral,

$$\int_0^\infty r \nabla^2 f J_0(\xi r) dr \quad (1.14)$$

note that J_0 is the zero-order Bessel function. As a result of a series of integration by part, we obtain:

$$\int_0^\infty r \nabla^2 f J_0(\xi r) dr = \xi \int_0^\infty \{J_0'(\xi r) + \xi r J_0''(\xi r)\} f dr + \frac{\partial^2}{\partial z^2} \int_0^\infty r f J_0(\xi r) dr \quad (1.15)$$

Knowing that J_0 is the solution of differential equation 1.5, the above equation reduces to

$$\int_0^\infty r \nabla^2 f J_0(\xi r) dr = \left(\frac{\partial^2}{\partial z^2} - \xi^2 \right) \int_0^\infty r f J_0(\xi r) dr \quad (1.16)$$

Now replacing f by $\nabla^2 \Phi$, we find

$$\begin{aligned}
\int_0^{\infty} r \nabla^4 \Phi J_0(\xi r) dr &= \left(\frac{\partial^2}{\partial z^2} - \xi^2 \right) \int_0^{\infty} r \nabla^2 \Phi J_0(\xi r) dr \\
&= \left(\frac{\partial^2}{\partial z^2} - \xi^2 \right)^2 \int_0^{\infty} r \Phi J_0(\xi r) dr
\end{aligned} \tag{1.17}$$

Note that the left-hand side is the biharmonic equation. Therefore,

$$\left(\frac{d}{dz^2} - \xi^2 \right)^2 G = 0 \tag{1.18}$$

where $G = \int_0^{\infty} r \Phi J_0(\xi r) dr$

Thereby, using Hankel transformation,

$$\Phi = \int_0^{\infty} \xi G J_0(\xi r) dr \tag{1.19}$$

The solution to G is straightforward and given as

$$G = (A + Bz)e^{\xi z} + (C + Dz)e^{-\xi z} \tag{1.20}$$

Note that the solution to G is such that the stress, which can now be represented with G , will tend to zero as one moves to infinity. With stress being proportional to the Laplacian of Φ while Φ is represented by a radial integration of G , it is easy to observe that for the stress to be finite as $z \rightarrow \infty$, the constants A and B must be zero. The rest of the constants are found using the boundary conditions, which are not addressed here. The displacement fields and stress equations can also be expressed in terms of G .

In later work by Sneddon [12], the displacement fields and stress equations were expressed in terms of zero and first-order Hankel transform, which can be derived by substituting Φ in terms of G . The equations for stress and displacement fields are written in terms of Hankel transform. The problem of indentation is shown in Figure 2. Body 1

and Body 2 are in contact with the initial separation given by $f(r)$. The contact area is defined between the region where r varies between 0 and a . Body 2 is considered rigid in the original Sneddon solution. However, the solution can easily be found in case of deformation. The boundary conditions are given as follows:

$$\begin{aligned}
 U_{z1}(r,0) + U_{z2}(r,0) + f(r) &= D, \quad r \leq a \text{ (in case of deformable punch)} \\
 U_{z1}(r,0) &= D - f(r), \quad r \leq a \text{ (in case of rigid punch)} \\
 \sigma_{rz}(r,0) &= 0, \quad r \leq a \\
 \sigma_{zz}(r,0) &= 0, \quad r \geq a
 \end{aligned} \tag{1.21}$$

While the shear stress and normal stress boundary conditions arise due to the axisymmetric problem, the third boundary condition corresponding to the normal displacement represents the elasticity (no permanent deformation). The equations of displacements in terms of the Hankel transform are given as follows:

$$U_r(r, z) = \frac{-a}{2(1-\nu)} H_1[\{(1-2\nu) - \xi z\} \xi^{-1} \psi(\xi a) e^{-\xi z}; \xi \rightarrow r] \tag{1.22}$$

$$U_z(r, z) = \frac{a}{2(1-\nu)} H_0[\{2(1-\nu) + \xi z\} \xi^{-1} \psi(\xi a) e^{-\xi z}; \xi \rightarrow r] \tag{1.23}$$

$$U_\phi(r, z) = 0 \tag{1.24}$$

The stress equations are given as follows:

$$\sigma_{rz}(r, z) = -\frac{uaz}{1-\nu} H_1[\xi \psi(\xi a) e^{-\xi z}; \xi \rightarrow r] \tag{1.25}$$

$$\sigma_{zz}(r, z) = -\frac{ua}{1-\nu} H_0[(1 + \xi z) \psi(\xi a) e^{-\xi z}; \xi \rightarrow r] \tag{1.26}$$

$$\sigma_{\phi z}(r, z) = 0 \tag{1.27}$$

Now parametrizing the equations using $x = r/a$ and expressing the boundary conditions results in terms of Hankel transform as follows:

$$U_z(r, 0) = \frac{a}{2(1-\nu)} H_0[\xi^{-1}\psi(\xi); \xi \rightarrow x] = D - f(x) \quad 0 \leq x \leq 1 \quad (1.28)$$

$$\sigma_{zz}(r, 0) = -\frac{u}{2(1-\nu)} H_0[\psi(\xi); \xi \rightarrow x] = 0 \quad x \geq 1 \quad (1.29)$$

If $\psi(\xi)$ is represented as:

$$\psi(\xi) = \int_0^1 X(t) \cos(\xi t) dt \quad (1.30)$$

this formulation satisfies boundary equation 1.29, while solving for boundary equation 2.28 results in the following:

$$X(t) = \frac{2D}{\pi} - \frac{2}{\pi} \frac{d}{dt} \int_0^t \frac{xf(x)dx}{\sqrt{(t^2 - x^2)}} \quad (1.31)$$

Now using the stress equation, it can be found based on the limit for finite stress at $r \rightarrow a$ that $X(1) = 0$, which results in an expression for D as:

$$D = \int_0^1 \frac{f'(x)dx}{\sqrt{(1 - x^2)}} \quad (1.32)$$

Knowing D and describing the load as the integral of the normal stress within the contact area, one can find the total load, P , on the punch required to produce the above penetration. The resulting equation is obtained as follows:

$$P = 2E_r a \int_0^1 \frac{x^2 f'(x)dx}{\sqrt{1 - x^2}} \quad (1.33)$$

Therefore, the load and displacement equations are determined based on the geometry of the indenter (punch) given by $f(x)$. We can obtain the load-depth relationship based on the

punch geometry. We can first consider a case of a paraboloid on a flat surface. Given the geometry of the tip (Figure 3),

$$f(r) = r^2/2R \quad (1.34)$$

where $\frac{1}{R} = \frac{1}{R_1} + \frac{1}{R_2}$, based on Hertzian contact. Note that for paraboloid on a flat surface,

$$R = R_1$$

Parameterizing with $x = r/a$ results in

$$f(x) = x^2 a^2 / 2R \quad (1.35)$$

$$f'(x) = x a^2 / R \quad (1.36)$$

Substituting 1.34-1.36 in 1.32 gives

$$D = \frac{a^2}{R} \quad (1.37)$$

By definition, D_c represents the case when $x = 1$ or $r = a$. Therefore,

$$D_c = \frac{a^2}{2R} \text{ therefore, } \frac{D_c}{D} = \frac{1}{2} \quad (1.38)$$

$$P = \frac{4}{3} E_r a^3 \text{ or } P = \frac{4}{3} E_r D^{3/2} R^{1/2} \quad (1.39)$$

$$S = \frac{dP}{dD} = 2E_r a, \quad (1.40)$$

$$\text{where } \frac{1}{E_r} = \frac{1 - v_1^2}{E_1} + \frac{1 - v_2^2}{E_2} \text{ based on Hertzian contact}$$

For the case of a conical punch, $f(r)$ is given as (Figure 4):

$$f(r) = r \cot \psi \quad (1.41)$$

$$f(x) = ax \cot \psi \quad (1.42)$$

$$f'(x) = a \cot \psi \quad (1.43)$$

Substituting 1.41-1.43 in 1.32 gives:

$$D = \frac{\pi}{2} a \cot \psi \quad (1.44)$$

By definition,

$$D_c = a \cot \psi, \text{ therefore, } \frac{D_c}{D} = \frac{2}{\pi} \quad (1.45)$$

$$P = \frac{\pi}{2} E_r a^2 \cot \psi \text{ or } P = \frac{2}{\pi} E_r \tan \psi D^2 \quad (1.46)$$

$$S = \frac{dP}{dD} = 2E_r a \quad (1.47)$$

It was shown by Oliver, Pharr, and Brotzen [14] that the equation for S remains invariant irrespective of the geometry of the punch.

Nanoindentation

By the early 1980s, great strides had been made in resolving hardware issues in probing the mechanical properties of materials at the submicron scale [15]. The mechanical properties most often measured using indentation are elastic modulus, E , and hardness, H . Although various models have been proposed to measure elastic modulus and hardness using nanoindentation, the author will visit work by Oliver and Pharr, often referred to as the Oliver-Pharr method. In work published in 1992 [16], Oliver and Pharr described a methodology to measure elastic modulus and hardness. In their follow-up work [17], they improved the technique.

The problem of indentation is described as a conical indenter tip coming in contact with a flat elastic half-space. A schematic of the mechanics of indentation is shown in

Figure 5. Let h be the total displacement of the tip resulting in a deformed configuration where some portion of the deformed half-space is in contact with the tip. Let h_c be the height corresponding to the surface in contact. Therefore, $h_s = h - h_c$, represents the height corresponding to the displacement that is not in contact. P represents the load corresponding to the total displacement of h . The challenge is to evaluate hardness and elastic modulus given that the load (P) and total depth (h) are known. Since h_s is unknown, the contact area (A_c) and contact radius (a) are unknown. Unlike elastic contact mechanics, where D_c and D are derived, the nanoindentation problem involves plasticity.

A typical load-depth curve from indentation is shown in Figure 6a. Indentation is performed to a total depth of h_{max} , with h_f being the permanent deformation. Through a series of experiments for different materials, Oliver and Pharr showed that unloading during indentation is elastic. Figure 6b shows the unloading curves during indentation for different materials translated to the origin corresponding to h_f .

Curve fitting the unloading curve with $P = \alpha h^m$, a form given by Sneddon's solution, results in the results reported in Table 1. Note that as derived earlier, $m = 1.5$ for a paraboloid and $m = 2$ for a cone. Also, $m = 1$ corresponds to the case of the flat cylinder. This is because the unloading portion of the indentation is elastic, and, based on Table 1, the deformed shape corresponds most closely to the shape of a paraboloid indenter ($m =$

1.5). Therefore, the concept of an effective indenter in the shape of a paraboloid is often used to represent the mechanics of indentation.

Based on the deformation geometry:

$$h = h_s + h_c \quad (1.48)$$

Based on Sneddon's solution

$$E_r = \frac{\sqrt{\pi}}{2} \frac{S}{\sqrt{A}}, H = \frac{P}{A} \quad (1.49)$$

where $A = \pi a^2$ (*circular contact*) and $\frac{1}{E_r} = \frac{1-v_1^2}{E_1} + \frac{1-v_2^2}{E_2}$ (*Hertzian contact*)

Sneddon's solution determines the contact depth because the unloading is elastic. Since h_s corresponds to the height not in contact during indentation, the variable $D - D_c$ is used to evaluate h_s .

$$h_s = D - D_c = D_c = \frac{3P}{4S} \text{ (assuming paraboloid)} \quad (1.50)$$

giving

$$h_c = h - \frac{3P}{4S} \quad (1.51)$$

Now, if the area function of the indenter tip is known, one can calculate elastic modulus and hardness given by equation 1.49.

Before addressing the area function, it is necessary to describe the geometry and dynamics of the modern-day indentation actuator, as shown in Figure 7. The modern-day actuator is designed to respond in a simple harmonic motion with well-defined spring and damping constants. The actuator is made up of a coil/magnet assembly—the voltage applied to the assembly results in the force generated by the actuator. The actuator is

supported by leaf springs with very high lateral stiffness. A diamond pyramidal tip (often a Berkovich tip) is attached at the end of the actuator. The dynamics of the problem can be described using a simple spring and dashpot model, as shown in Figure 7. The advantage of the assembly is that the indentation is performed by dynamically loading the flat surface such that the stiffness (S) required to evaluate the modulus and hardness is evaluated as a function of depth, thereby evaluating the mechanical properties as a function of depth. This methodology of dynamically loading the specimen and obtaining the properties as a function of depth is known as continuous stiffness measurement (CSM). Solving the dynamics of the actuator, the contact stiffness can be obtained (note that it is not evaluated using the unloading curve). The evaluated stiffness is a function of frame stiffness and known constants.

Using Figure 7, let K^* be the effective stiffness; then,

$$\frac{1}{K^*} = \frac{1}{K_f} + \frac{1}{S} \quad (1.52)$$

where, $S = f(E_r, \sqrt{A})$ and $\sqrt{A} = \sqrt{P/H}$ based on equation 1.49.

Therefore,

$$\frac{1}{K^*} = f(E_r, H) * \left(\frac{1}{\sqrt{P}}\right) + \frac{1}{K_f} \quad (1.53)$$

For a material with constant modulus and hardness, the intercept of the

equivalent stiffness (K^*) and $\frac{1}{\sqrt{P}}$ curve gives the frame stiffness. Since any error

in evaluated frame stiffness can affect the obtained results, a general rule of

thumb is to test the samples to a maximum depth such that $S \leq 0.2 K_f$. An

amorphous, homogeneous, and isotropic material (often fused silica) with known modulus and hardness is used to evaluate the area function. Indenting an amorphous material while ensuring that the modulus remains invariant and equal to the known value is used to evaluate the exact area function. The polynomial used as per [17] is given as:

$$A_C = C_0 + \sum_{n=1}^6 c_n h c^{\frac{2}{2n-1}} \quad (1.54)$$

Once A_c and K_f are known, any unknown material's elastic modulus and hardness can be determined.

Nanoindentation Limitations

The most significant limitation of nanoindentation corresponds to the indentation of elastoplastic materials—materials that significantly harden or soften with indentation. As the material deforms due to dislocation-based activity, if the material hardens, generally, there tends to be pile-up during indentation. *Pile-up* occurs when the material starts to move up or pile up near the edges of the indenter, thereby underestimating the contact area and overestimating the elastic modulus. Alternatively, suppose the material softens with indentation. In that case, a scenario of sink-in happens, in which case the material starts to sink in, thereby overestimating the contact area and underestimating the elastic modulus. The pile-up and sink-in scenarios are shown in Figure 8. Pile-up and sink-in scenarios in nanoindentation have been studied extensively and remain a topic of investigation [18–20]. A commonly adopted solution is to consider $h_s = 0$ in the Oliver-Pharr formulation for the pile-up scenarios. Viscoelasticity of the material can also affect

the indentation results. The dashpot response from the actuator schematic captures the effect of viscoelasticity. It has been shown that the loading the samples while keeping $\frac{\dot{P}}{P}$ constant minimizes the effect of viscoelasticity [21,22].

Measurement of Fracture Toughness Using Nanoindentation

Various advancements have recently been made in the indentation literature to measure beyond the hardness and elastic modulus of a material at the nano to micro scale. More specifically, calculating the loss and storage modulus as a function of time and temperature for viscoelastic materials [23], the stress-strain response of elastoplastic materials [24], the creep response of viscoelastic materials [25,26], and the fracture toughness of brittle materials have been addressed in recent years [27–35]. Among these, the author focuses only on fracture toughness measurement using nanoindentation.

Generally, the crack during indentation experiments initiates and propagates off the corners of the indenter edges. These cracks that form below the indents can be characterized as lateral, half-penny, Palmquist, median, or cone cracks, as shown in Figure 9 [35]. Researchers have addressed the mechanism for crack nucleation in brittle materials. Lawn and Evans [36] argued that a minimum flaw size is required for median cracking. On the other hand, Hagan [37,38] argued that crack initiation is a consequence of the intersection of dislocation slip lines underneath the indentation impressions. Dal Maschio et al. [39] found a similar crack-initiating mechanism. Zhuang et al.'s work [40] demonstrated the interdependency of the crack systems as a function of indentation depth. In recent years, molecular dynamics and finite element simulations have shown the roles of plasticity and tip geometry in crack nucleation. Based on the crack profile,

different linear elastic fracture mechanics (LEFM)-based theories have been proposed by researchers to obtain fracture toughness.

The techniques proposed by researchers to evaluate fracture toughness depend upon the crack profile, which is inherently dependent on the elastoplastic behavior of the material under indentation. In indentation, the degree of plasticity is often judged by the elastic modulus and hardness ratio (E/H), i.e., the more significant the E/H ratio, the higher the plasticity. Among the proposed techniques, indentation cracking and pillar splitting have recently attracted interest. Pillar splitting is discussed in detail here, while indentation cracking is visited briefly.

Indentation cracking is a technique in which a sharp pyramidal indenter is used to conduct indentation on an elastic half-space. The load till which indentation is carried out must be large enough to visualize the crack, which depends upon the elastic-plastic response of the material. After indentation, the crack lengths are measured, and then, assuming the crack profile and based on LEFM fracture, toughness is calculated. Using finite element modeling, Johannis et al. [41] extensively studied the crack profile as a function of the elastic-plastic response of a material. Most notably, the authors summarized that the model of Lawn, Evans, and Marshall worked well over a small range of E/H ratio, where median crack profiles were obtained after unloading. At the same time, a change in cracking mode is observed as one moves from low E/H ratios toward a high E/H ratio, with high E/H ratio materials showing Palmqvist-type cracking [30].

Residual stresses and the substrate influence the fracture toughness calculated using indentation cracking [33]. Recently, the pillar splitting technique developed by

Sebastiani et al. [27,29,33] overcame some of the limitations of indentation cracking. Pillar splitting is a recently proposed indentation cracking technique in which micropillars are prepared using a focused ion beam and then indentation is carried out at the center of the prepared micropillars. In pillar splitting experiments, the cracks evolve as median cracks, and instability occurs when a crack reaches a sidewall. The K_c is a function of instability load $P_{instability}$, and the geometric radius is evaluated using equation 1.55 and parameter γ , which is determined using cohesive zone finite element modeling (CZFEM).

$$K_c = \frac{\gamma P_{instability}}{R^{3/2}} \quad (1.56)$$

Crack modeling using CZFEM is not trivial. The methodology has been described in detail by Johannis et al. [30]. In the realm of LEFM (small plastic zone), the fracture energy is related to fracture toughness as follows:

$$K_c = \sqrt{\frac{E G_{1c}}{(1 - \nu^2)^2}} \quad (1.57)$$

The estimated size of the process zone (ρ), defined by the size of plastic zone at the crack tip, can be estimated by Dugdale's equation.

$$\rho = \frac{\pi}{8} \left(\frac{K_{Ic}}{\sigma_c} \right)^2 \quad (1.58)$$

It is suggested that the size of the cohesive elements must be at least three times smaller than the size of the process zone [30,31] for the correct results. This is because the localized strain near the contact affects the results. Therefore, the crack must be large enough to ensure the minimal effects from the contact. In addition, for the applicability of

equations 1.55–1.57, the process zone must be negligible compared to crack length.

Therefore, it is advised that the pillar radius be at least ten times greater than the size of the process zone, while to avoid the effects of substrate, the height must be at least equal to the diameter of the pillar [29].

In a CZFEM setup, the one-sixth model is used considering the six-fold symmetry of a pyramidal tip and the circular symmetry of the pillar. Zero-thickness cohesive elements are implemented on the sharper edge of the tip (crack grows along these edges based on experimental observations). On one face of the pillar, the cohesive elements and symmetric boundary conditions are applied. The other face of the cohesive element is tied to a pillar. The CZFEM setup is shown in Figure 10. The corresponding load–depth curve and the crack morphologies obtained showing median cracking are shown in Figure 11. The coefficient γ is evaluated using equation 1.55 based on the instability load obtained from the simulations, input fracture toughness, and pillar radius.

Ghidelli et al. [27] studied the pillar geometry’s effects and the material’s elastic–plastic response to the pillar-splitting technique. Figure 12 presents a summary of the results obtained. As the indenter angle increases, the constant γ decreases. The result is unsurprising, as the more significant the inscribed angle for an indentation tip, the less sharp the tip edges are. Therefore, the load required for crack nucleation and propagation to cause instability is higher, resulting in a smaller value for the coefficient γ . For a constant indenter inscribed angle, the parameter γ is dependent upon the elastic–plastic response of the material with a trend of increasing γ with an increase in E/H , indicating a lower instability load being required to cause the instability. With an increase in E/H

ratio, the material undergoing indentation experiences a larger plastic zone, resulting in the material experiencing the effect of the free boundary at a lower load and thus causing fracture. Therefore, the minimum diameter of a free-standing pillar required to generate efficient crack nucleation and propagation increases with the E/H ratio. The minimum diameter required to calculate fracture toughness effectively has been studied; substrate compliance minimally affects the instability load [32]. Given the morphology of the cracks and the difficulty of generating large pillars, both the indentation-cracking and pillar-splitting techniques have been limited to applications in ceramics, glass, and other brittle materials.

Additional Validation Techniques

X-Ray Tomography

X-ray computed tomography (XCT) is a non-destructive technique used to visualize the three-dimensional structure of a material. XCT is done by securing the specimen onto a rotary stage and acquiring a series of radiographs—cumulative attenuation the x-ray beam at every voxel—while the sample is taken through a 360-degree rotation using specified increments. Obtained data consist of a stack of slices that cumulatively characterizes the three-dimensional morphology of the samples. Since x-ray attenuation is a material dependent, the phases within the sample can be segmented based on the differences in attenuation.

Microstructure

Carbon Fiber

Carbon fiber, the most sought-after material in applications requiring a high strength-to-weight ratio, has come a long way in mechanical properties compared to the first carbon fiber manufactured by Sir Joseph Wilson Swan in 1879. Modern-day carbon fiber can exhibit a tensile strength and modulus of 4 GPa and 400 GPa, respectively [42].

Elemental carbon exhibits cubic and hexagonal crystalline modifications. In graphite, the graphene layers are stacked together. Therefore, the bond strength along the c-axis is very strong and conversely, is very weak transverse to the c-axis.

Carbon fibers are made either from polyacrylonitrile (PAN) or pitch-based precursors. PAN fibers, wet or dry spun, must be stretched before processing, while pitch compositions are melt-spun [43]. Various steps are involved in the manufacturing of PAN-based or pitch-based carbon fibers. Firstly, the PAN precursor is either wet or dry spun in a suitable solution. PAN precursors are stretched along the axis. The stretches are done moderately (~ 2.5 times) in the earlier steps and then excessively (up to 14 times) during the later steps. The stretched fiber is slowly heated under tension in the air between 220 to 280 °C [43]. This step is called the stabilization or oxidation of the fibers. During the stabilization step, dehydrogenation of the C–C bonds occur. The steps result in ladder-like chain aligned along the axis of the fiber. The oxidation step is exothermic and causes the fiber to shrink due to oxidation, resulting in the evolution of gaseous species. Carbonization of the fibers is followed by slowly heating the stabilized fiber in an inert atmosphere to a final temperature ranging from 1000 to 1600 °C. Carbonization is endothermic and results in further shrinkage of the fibers. In the carbonization step,

crosslinking occurs with further dehydrogenation, thereby resulting in the evolution of HCN into nitrogen. [43]. A large quantity of oxygen that was present in the carbon fiber due to oxidation is eliminated in the carbonization steps. On the other hand, a significant amount of nitrogen is still trapped within the carbon fiber, which is released during post-heat treatment at higher temperatures. PAN-based carbon fiber exhibits a non-graphitizable carbon fiber. Therefore, the elastic modulus is relatively low, even when exposed to high temperatures during post-processing [43].

Microstructure of Carbon Fibers

Characterization of carbon fibers is difficult because of the scale of the crystalline parameters. However, carbon fibers do scatter x-rays and electrons and, therefore, an assessment of crystal structure can be done by x-rays and electron diffraction. The diffraction pattern for carbon fiber primarily shows a strong 002 reflection due to the turbostratic character of carbon fibers [43]. These reflections can then be used to evaluate the scattering domains, L_a (meridional width parallel to fiber axis and equatorial width perpendicular to fiber axis), and L_c , the interlayer (d) spacing. Table 2 shows the crystalline properties obtained for high tenacity (HT) and high modulus (HM) PAN- and pitch (MP)-based carbon fibers. Based on Table 2, the values of L_a and L_b are in the same order, with larger sizes for mesophase pitch-based carbon fibers. On the other hand, interlayer spacing is greater for the PAN-based carbon fiber, resulting in a lower density of the fibers.

The author addresses only PAN-based carbon fibers since they are the primary focus of this study. The micro-texture of PAN-based carbon fibers is very complex, often referred

to as having an ‘onion-like’ structure. The basic microstructural units are edge-to-edge in a zigzag form, forming wrinkled sheets. The wrinkled sheets are entangled intricately. An aligned wrinkled sheet forms local crystals, with different misaligned crystals forming pores. Weak van der Waals forces constrain the sheets.

Therefore, within the carbon fibers, depending upon the location, the crystalline parameters differ. In a review by Newcomb [44], these local differences in the crystal structures between the core and sheath of carbon fibers were identified as a function of temperature. Based on high-resolution transmission electron microscopy (HRTEM), it was found that as the temperature increases, the pore size increases. As a result, there is a difference between the domain size and stack height obtained for the core and sheath of carbon fiber heat treated at 1000 °C.

Recently, Meek and Penumadu [45] conducted a thorough macroscopic and microscopic characterization of different-grade carbon fibers made from the same precursor but that underwent different processing temperatures. They were able to show that as the temperature increases, the crystalline parameters (i.e., stack height, crystal size, and pore size) proportionally increase, resulting in an interdependence of crystal parameters as well as macroscopic tension modulus and tensile stiffening (Figure 13).

Carbon Fibers in Tension

Carbon fiber in tension shows a nonlinear elastic stress–strain behavior, whereby the Young’s modulus of carbon fiber increases with an increase in strain. This unusual behavior arises from aligning misaligned graphene layers [46]. Based on empirical observation, the behavior can be described by the following relationship:

$$E(\varepsilon) = E_0[1 + \gamma\varepsilon] \quad (1.58)$$

where E is the tangential modulus, E_0 is the initial tangential modulus, and γ is the parameter relating the strain ε to the tangential modulus. The tensile properties of carbon fibers can be evaluated using a resin-impregnated bundle of fiber (tows) or single-fiber tension test. In evaluating properties by using resin-impregnated tows, different inter-fiber effects can dominate the resulting stress–strain curve [46]. In single-fiber tension tests, the single filament of fiber is mounted on a highly aligned surface and then tested in tension using a very high displacement resolution system. A major challenge with single-fiber tension tests is eliminating the system’s compliance. Various standards have been implemented to account for system compliance. Based on the standards, system compliance is calculated by plotting the total compliance as a function of gage length based on equation 1.59, which is derived using a simple mechanics model:

$$D = D_s + D_f = D_f + \frac{l_0}{EA} \quad (1.59)$$

where D is the total compliance, D_s is the sample compliance, D_f is the frame or system compliance, l_0 is the gage length, E is Young’s modulus, and A is the cross-sectional area. The above equation works well for a sample with a linear stress–strain curve and thus does not negate the effect of system compliance during single carbon fiber tension tests. Like nanoindentation, a CSM technique can be used. The system’s compliance can be evaluated by solving the dynamics of the problem when the fiber is slack (not in tension, thus effectively resulting in zero sample compliance). Kant et al. [46] followed this methodology and accurately determined the storage modulus for different grades of

carbon fiber. Once an accurate stress–strain curve is obtained, the coefficient can easily be found based on equation 1.59. More importantly, Kant et al. showed that the coefficient remains invariant independently of the fiber type and depends only on the initial storage modulus (Figure 14).

Following the work by Kant et al., Meek and Penumadu [45] were able to determine that the stiffening parameter given by γE_0 is a function of crystal parameters (Figure 15).

Fracture Toughness of Carbon Fibers

For brittle materials, LEFM often provide acceptable results. Using a simple yet practical LEFM approach, fracture toughness under Mode I conditions is expressed as in the equation:

$$K_{1c} = \sigma_f Y \sqrt{\pi a_c} \quad (1.60)$$

where K_{1c} is the mode 1 stress intensity factor, σ_f the tensile strength, a_c the root of the flaw size, and Y the geometrical correction factor [47]. Unfortunately, Equation 1.60 requires a priori knowledge of flaw size value, which is difficult to evaluate for small-diameter fibers such as carbon fibers. To overcome this drawback, fracture toughness is often calculated using the mirror–zone size relationship, where the critical flaw size to mirror zone (defined by the smooth region around a flaw of the fractured surface) ratio is assumed to be constant and calculated empirically. Recently, a technique was developed by Morishita et. al. [48] to measure fracture toughness directly using Focused Ion beam (FIB)-milled notches [48–50]. A simple LEFM approach, as described by the equation, is used to evaluate fracture toughness. The coefficient, Y , can be estimated by estimating the

crack geometry. Based on work by Kant et al. [51], the reported fracture toughness value for T700 TORAY carbon fiber is $1.73 \text{ MPa}\sqrt{m}$.

Polymer Matrix

Polymers include elastomers, thermoplastics, and most adhesives. *Polymers* are materials in which atoms are arranged into monomer combined to form chain-like structures. The chain molecules can then form networks via crosslinking. Polymers are poor conductors of heat and electricity [52]. Polymers can be distinguished using various approaches. One is to characterize them as natural (cellulose, DNA, protein, etc.) or synthetic (polypropylene, polyester, etc.). Another way to distinguish polymers is by characterizing them as amorphous (polystyrene, polyvinyl chloride, etc.) or semi-crystalline (polyethylene, polyamide, etc.). Another helpful approach is to distinguish them as thermosets or thermoplastics. A thermoset is a polymer crosslinked through the addition of heat. Crosslinking is permanent in thermosets. Therefore, they cannot be reformed with the application of heat. On the other hand, a thermoplastic is a polymer that is not permanently crosslinked. Therefore, a thermoplastic can generally be reheated multiple times without a significant loss in mechanical properties.

The polymerization mechanism includes forming a long chain-like structure from monomers. Consider an example of styrene monomer ($\text{H}_2\text{C}=\text{CH}_2$), where the double bonds can be opened and rearranged upon introducing a free radical catalyst to a chain structure like $\text{R-O-CH}_2\text{-CH}_2\text{-}\dots\text{-CH}_2^*$. Given the above mechanism, voids are formed between the chains of a crosslinked polymer. The total characteristic volume of the voids is often referred to as the free volume of the polymers. Therefore, the total free volume is

an agglomeration of micro volumes whose specific distribution varies within the polymer. The average pore diameter for epoxy has been estimated to be between 2.7 Å and 5 Å [53]. Therefore, for some of the epoxy-based polymers, the pore diameter is too small for water molecules, with a diameter variation between 1.5 Å and 3 Å [53]. The overall amount of free volume fraction ranges between ~0.025-0.03. From a molecular motion perspective, localized bond movements (bending and stretching of bonds) and side chain motions can occur for a crosslinked polymer even at very low temperatures. At higher temperatures, other localized motions and group movement can occur, and the material develops toughness. Upon further increase in temperature, glass transition temperature (T_g) is achieved, characteristic of large-scale polymer chain motions [53]. It is generally agreed that the water migrates within polymeric resins to fill the available micro volumes [53]. There are various mechanisms possible for water transport, and some of these mechanisms will be discussed here. Diffusion is one of the processes via which water transport can occur. *Diffusion* is the process of transport that happens because of random molecular motions. For a one-dimensional case, let a be the characteristic length and ω be the frequency of molecular jump, then assuming a continuous mass distribution i.e., $m(x, t) = aN$, the equation of flux becomes:

$$J = -D \frac{\partial m}{\partial x} \quad (1.61)$$

From conservation of mass:

$$\frac{\partial m}{\partial t} = - \frac{\partial J}{\partial x} \quad (1.62)$$

Therefore

$$\frac{\partial m}{\partial t} = D \frac{\partial^2 J}{\partial x^2} \quad (1.63)$$

Where, $D = (1/2)wa^2$ is the diffusivity for the one-dimensional version of Fick's law. Solving the above parabolic equation can describe the governing time vs. space equation describing mass transport. For a more realistic case of diffusion within a plate, the governing equation is given by:

$$\frac{M(t)}{M_{\infty}} = 4 \sqrt{t^*} \left[\pi^{-\frac{1}{2}} + \sum_{n=1}^{\infty} -(1)^n \operatorname{erfc} \frac{n}{\sqrt{t^*}} \right] \quad (1.64)$$

Where $t^* = Dt/(2l)^2$, erfc denotes the complementary error function. Therefore, a plot of $\frac{M(t)}{M_{\infty}}$ vs $\sqrt{t}$ is used to evaluate the D. Note that the above equation is a simplistic case and assumes independence from the concentration or any variation arising due to damage. Moreover, it does not consider the trapping of diffusing molecules at sites within the polymeric chain. Therefore, a more elegant treatment can be done in cases where the concentration of diffusing fluid is divided into bound and mobile concentrations. This diffusion treatment is regarded as two-phase diffusion, which also considers the rate at which the mobile concentration becomes bounded and simultaneously the rate at which the bound concentration becomes mobile. A further involved reaction rate-dependent treatment can be done for a case in which the diffusion also depends upon the chemical reaction. Figure 16a [53] shows the schematic of diffusion curves corresponding to different cases. Curves A and B correspond to the diffusion of polymer and composites in which the saturation is never attained, characteristic of two-phase diffusion. Curve C accounts for the rapidly increasing fluid content followed by damage growth that leads to

material breakdown, while curve D is representative of the chemical breakdown of the material. This breakdown is primarily associated with the development of separation between the polymer and the fiber reinforcement due to hydrolysis at the interphase followed by chain scissions (breaking of polymeric chains). Figure 16b [5] shows a typical sorption behavior of CF/VE, with saturation being achieved at around three months.

Other mechanisms in which fluid transport happens in composite materials are associated with the ingress of fluids in the fiber (typically glass fibers and Kevlar fibers ingress water), the capillary motion (through microcracks channeled parallel to fiber reinforcements), and wicking action (fluid transport arising along the fiber-matrix interphase regions).

Water sorption often increases the separation between the molecular chains, thereby inducing expansion strains or swelling of the matrix. This phenomenon is called Plasticization of the matrix, and the behavior is analogous to the effect of rising temperature upon the molecular chains. With Plasticization, the chain mobility is increased, and therefore the temperature required to cause the state of large-scale chain motion (T_g) decreases. This reduction is commonly related by [53]:

$$T_{gw} = \frac{\alpha_p V_p T_{gp} + \alpha_m V_m T_{gm}}{\alpha_p V_p + \alpha_m V_m} \quad (1.65)$$

Where, T_{gw} is T_g of the wet polymer. α , V , T_g are the coefficient of thermal expansion, volume fraction, and glass transition temperature. While the subscripts p and m refer to polymer and fluid. For hydrophilic polymers, a significant portion of present water molecules interact with the polar sites along the polymeric chains, relating sorption to

crosslinking density. Therefore, for these polymers, a bound phase and free phase of water exist (as described in two-phase diffusion), while it has been shown that the bound and free phases are interchangeable in cases of weak water-polymeric bonds. In hydrophobic polymers, the water molecule is present as a gaseous phase [53].

The mechanisms associated with vinyl ester hydrolysis have been reviewed by Euranto et al. [54]. In general, the hydrolysis products of vinyl esters are carboxylic acid (2 in Figure 17a), an aldehyde, or a ketone (3 in Figure 17a), depending upon R^2 being hydrogen or an alkyl group. For vinyl esters, electrophilic addition occurs, as shown in Figure 17b, for a case of vinyl ester resin aged in water at 80 °C [55].

From a mechanics perspective, the macro-molecular chains have some degree of mobility due to free volume, resulting in configurational changes under load application.

Therefore, for polymers, creep response corresponds to increasing strain for a given unit stress. Alternatively, the relaxation response shows a trend of decreasing stress for a unit strain. When the temperature is introduced into the equation, both creep and recovery are faster. Therefore, the effect of temperature can be accounted for by introducing a temperature and material-dependent shift factor.

Interface

Since the mechanical response of a composite is determined by the volume of the fibers within it, the surface area of the interface is significant and, therefore, a source of failure initiation. The role of the interface is to transfer the load from the matrix to the fibers.

Interfacial shear strength (IFSS) is the measurement of the strength of the bonding between the fiber and matrix; IFSS affects the tensile [56,57], compression [58–60], and

impact [61,62] properties of composites. Yet, there is no consensus in the literature on evaluating IFSS. A single-fiber fragmentation test [63] is often used to evaluate the interface. However, it has the significant drawback of not considering the IFSS of a composite that has undergone the stresses induced during manufacturing, as the fiber–matrix system is made independently.

Recently, push-out tests [64–66] and push-in tests [64,67,68] have been proposed to characterize the IFSS of manufactured composite. In push-in tests, fibers within a composite are pushed using a ‘rigid’ flat punch until a nonlinearity in the load–depth curve is observed, and the IFSS is then calculated using a shear lag model. In the push-out technique, a thin film of composite is prepared, and the fibers within it are loaded with a rigid flat punch.

Failure in Compression

Compression strength, which can be as low as thirty percent of the tensile strength, is a vital property for the design and failure modeling of fiber-reinforced polymer composites. As mentioned earlier, the evaluation of compression properties is not trivial [69]. The failure in tension usually occurs due to local fiber rupture. As the load increases, fibers are ruptured until the load is large enough and the number of intact fibers few enough to cause a catastrophic failure [70]. Conversely, the failure in compression depends on the local mechanical properties and the microstructure [58,60]. Compression failure modes reported in literature include: delamination [58,60], kinking [58,60,71], tow microbuckling [58,60][72–74], and, in a few cases, fiber failure [58,60].

Modes of Compression Failures

Longitudinal Cracking

Longitudinal cracking is a failure mode in which cracks develop along the length of the fiber. It is often an indication of poor adhesion between the fiber and the matrix. In a study done by Madhukar et al. [75], a series of samples with ‘low’ to ‘high’ interface strength were tested. Longitudinal cracking was observed as the failure mode for the composite having the lowest interfacial strength. The failure mode of microbuckling and kinking was observed for composite with intermediate interfacial strength. For those with the highest interfacial strength, failure was through fiber compression. As a failure mechanism, longitudinal cracking is primarily seen in glass fiber unidirectional composites [58]. Lee et al. [76] conducted an analytical and experimental study to predict the compression strength of glass fiber polymer composite subjected to compression. The experimental results showed longitudinal cracking as the failure mode. Their model, which included the effect of initial misalignment and was carried out for a range of volume fractions, could accurately predict the results. Delamination resulting in longitudinal cracking in most cases originated at the edges due to the free edges effects—excessive shear stress developing at the edges to satisfy the zero-traction boundary condition for the boundary value problem.

Microbuckling

Microbuckling is a failure mode in which individual fibers or fiber tows that act as a load-bearing column inside the matrix material undergo buckling. Dow and Gruntfest [77] were the first to suggest the microbuckling phenomenon. Rosen [78] and Hayashi [79] were the first to solve the elastic mechanics of the microbuckling phenomenon. In

Rosen's analysis, he considered a two-dimensional model in which an elastic matrix supports fibers. Under compression, two failure modes were envisaged: shear mode and extension mode. In extension mode, adjacent layers deform out of phase with each other as a consequence of normal strains evolving in matrix. On the other hand, in shear mode, adjacent layers deform in phase resulting from the shear strain within the matrix. Rosen used Fourier series to represent the deformation and then used the minimization principle associated with energy of the problem to evaluate the buckling load. After Rosen, researchers proposed various models considering matrix plasticity. Brief descriptions and limitations of these models can be found in a review paper by Waas and Schultheisz [58]. None of the proposed models could effectively calculate compression strength. Rosen's model, to date, provides the lowest compression strength, although it still overestimates it. The primary reason for the overestimation of all models is that most models do not account for the three-dimensional development of microbuckling, as has been observed experimentally.

Kinking

Kinking is a fiber level failure mechanism in which the band of fibers within the fiber bundle (tow) rotates, thereby causing an excessive shear deformation of the surrounding matrix. Most experiments have shown that as a consequence of kinking, the fiber breaks at the band boundaries. Kinking was often considered the final consequence of microbuckling where large microbuckled fibers lead to fiber fracturing [60]. However, in recent years, kinking has been considered a separate failure mechanism for stiffer matrix materials. If kinking were a consequence of microbuckling, the boundaries of the kink

band would correspond with the locations of maximum bending stress for a microbuckled fiber tow. However, the kink failure observations in the literature are not consistent with the above hypothesis. For stiffer matrix materials, kink boundaries lie around 60° .

Another important aspect that differentiates the two failure modes is the fact that kinking often occurs within a fiber tow, while microbuckling occurs everywhere in the composite. Therefore, kinking can be considered a separate mode of failure. Argon [80] argued that kinking is initiated by some defect. Kinking as a separate failure mode remains an open problem. However, various strides were taken by various researchers over the following decades. Most notably, Budiansky [81,82], Fleck and Budiansky [82], and Kozey [83] presented various analytical models to predict kinking compressive strength. Kyriakides et al. [84] studied microbuckling and kinking, analytically and experimentally. They employed a 2D-FEM model to correlate the behavior observed from the compression of unidirectional cylindrical composites. They showed that fiber misalignment and softening of the matrix undergoing shear leads to instability. Kinking was the final consequence of the localization process. Their model accurately predicted compression strength, although the kink bandwidth was predicted to be smaller than the ones obtained experimentally. In recent work by Pimenta et al. [85,86], matrix yielding and matrix cracking played an essential role in kink band formation, while fibers were found to fail on the compressive side first. Their model and the compression strength could also predict the kink bandwidth.

Fiber Failure

Fiber rupture as a compression failure initiation mode is rarely seen except in cases in which fibers under compression have an especially low compression strength, such as Kevlar or other organic fibers [60]. However, carbon fibers are anisotropic. In microbuckling or kinking analysis, fiber compression strength is generally assumed to be equal to the tensile strength of carbon fibers. Therefore, based on micromechanical theories, fiber rupture is rarely seen as the primary cause of failure.

In the testing of multidirectional composites, the various failure modes interact. The problem is further complicated by having different zones of imperfection depending upon the microstructure; thus, predicting compression strength remains an open problem. For example, Waas et al. [71] found that longitudinal splitting and kinking are competitive failure modes that depend on matrix stiffness and interfacial shear strength.

Microstructural Factors Influencing Compression Strength

Fiber Effects

Several investigations have been undertaken to understand the importance of the mechanical properties of fiber reinforcements in influencing composites' compression strength. The larger the diameter, the higher the buckling load and bending stiffness and the better the alignment in processing. However, following Weibull's chain link theory, as the diameter of the chain (fiber) increases, the number and size of the flaws also increases. Therefore, Leventz [87] found an upper limit of the diameter for maximum compression strength. Various studies [60] have also shown that compression strength tends to increase with the volume fraction of the fibers.

Matrix Effects

Several authors have studied the matrix response under compression and the compressive strength of polymer composites. Various authors [60] have reported a direct proportionality between compressive strength and matrix yield strength. Some studies [88] have shown that compression strength tends to reach an asymptotic value. The matrix shear modulus was varied by increasing the temperature in most of these studies, while in some studies, this was accomplished by partially to fully curing the matrix.

Interface Effects

For composite materials, the interface between fiber and matrix is the most crucial parameter in the compression of composites. For example, Drzal et al. [75] found an inverse proportionality between the compressive strength and the strength of the interface for carbon/epoxy specimens. In their work, the weakest interfaces showed delamination as the failure mode; intermediate interface showed microbuckling as the failure mode; and the strongest interfaces showed fiber failure.

Fiber Waviness

Various studies have reported a drastic drop in compression strength due to a slight increase in fiber waviness. Hancox et al. [89] determined that the strength of composites decreases by 45 percent when the loading axis is changed from 0° to 15° . As mentioned previously, the work by Kyriakides et al. [84] addresses the relevance of fiber misalignment associated with the formation of kink bands. Wisnom [90] concluded that when there is fiber waviness, instability due to lack of shear stiffness occurs under flexural loading. His analysis indicated that higher maximum compressive stress could be

achieved in bending because of the stress gradient, i.e., the rotation of the most highly stressed fibers near the surface was restrained by adjacent, less highly stressed fiber.

Stitching

The compression strength of composites made from non-crimped fabric (NCF), such as is the case for the composites under investigation, largely depends on the stitching used to tie the fiber tows. Stitching offers a cost-effective method for joining fabric made from fiber tows and thus for manufacturing composite. Stitching has been reported to improve the delamination resistance of carbon fiber-reinforced polymers (CFRP) [91]. However, stitching introduces sources of various geometric nonlinearities in the material's microstructure. Stitching has been shown to cause distortions of both in-plane fibers and the fibers within stitches, resulting in fiber breakage at the stitch hole. The misalignment has been reported to spread by up to 26°. Cox et al. [92] found that the introduction of stitching in homogeneous through thickness–stitched laminates changed the failure from ductile type for woven composites to a brittle failure in stitched laminates. Mouritz and Herszberg [93] summarized the effect of stitching on in-plane compression properties in their review paper; significant degradation in compression properties is observed due to stitching. Farley et al. [94–96], by machining away laminated surfaces to remove stitch loops, showed that discontinuously stitched composites showed 7%–35% higher compression strength than the unaltered stitching materials. Mouritz and Cox [97], in their review, reported a failure map as a function of stitching density and misalignment angle for stitched laminates (Figure 18). For NCF-based composites, Wisnom [59]

conducted a finite element investigation to show that NCF compression strength is controlled by 0° tow geometrical instability.

The effect of moisture on composites has been studied. However, only a few studies have addressed the effect of compression properties subjected to long-term hygrothermal conditioning. When exposed to seawater for a significant period, moisture diffuses within the matrix through diffusion [5]. The long-term effect of exposure to seawater can cause matrix plasticization, matrix swelling, or hydrolysis. Significant degradation in the interface has also been reported. Moisture uptake is dependent on the interface, which is due to the capillary action in the fiber/matrix interface—a process called wicking [98]. Carlsson et al. reported only a slight decrease in the compression properties of carbon fiber/vinyl ester composites [98]. Friedrich et al. [99] reported a negligible difference for Carbon fiber and Polyetherketone matrix (CF/PEEK) composites exposed to seawater for long durations. Soutis and Turkmen [100] noticed a change in failure mechanism from kinking to microbuckling with a significant reduction in compression strength, which they attributed to degradation in the matrix and interfacial properties. More recently, Zafar et al. [101] also reported degradation in the mechanical properties of polymeric composite, which they attributed to degradation in the matrix caused by matrix swelling. The interface was not commented on, since their study found that the interface for the material under investigation was poor, even for the unaged samples. Recent studies [102,103] have also shown degradation in composite compression strength, primarily attributed to matrix plasticization and interface degradation. Barbosa et al. [104] reported insignificant differences between soaked and dry-aged samples even though significant

degradation in the interface was observed. Most studies have shown significant degradation in the compression strength of carbon fiber-reinforced polymer composites when exposed to seawater for prolonged periods, with matrix and interfacial properties being the critical mechanical properties.

Appendix 1

Table 1: m evaluated from unloading curves for different materials [16]

Material	m
Aluminum	1.38
Quartz	1.43
Soda-lime glass	1.37
Sapphire	1.47
Fused silica	1.25
Tungsten	1.51

Table 2: Carbon fiber microstructure. Table source [43].

Fiber	d ₀₀₂ (nm)	L _c (nm)		L _a (nm)	L _b (nm)		Z(°)	
	XRD	XRD	SAD	XRD	XRD	SAD	XRD	SAD
PAN-based (HT)	0.36	1.7	1.4-2.2	3.9	2.7	2	41	35-40
PAN-based (HM)	0.35	6	3	9.8	8	3.5-4.5	20	30-37
MP-based (HM)	0.342	12.5	NA	5.2	9.8	NA	16	NA
MP-based (UHM)	0.337	27	NA	9.2	11.9	NA	8	NA

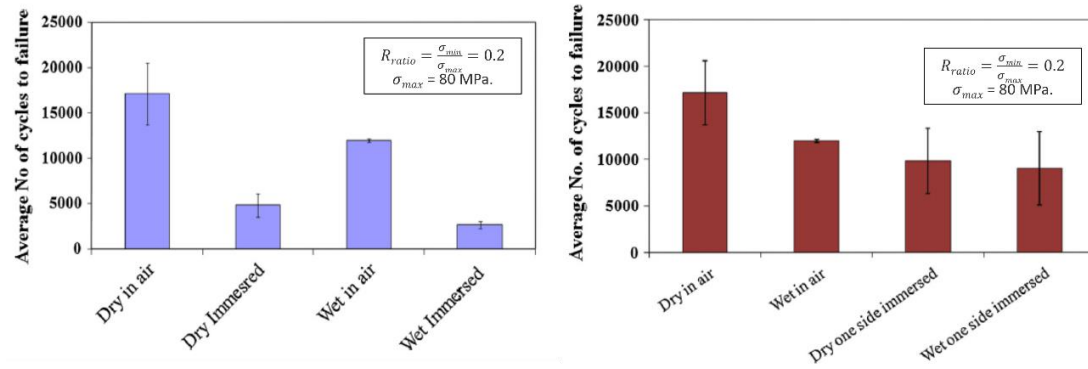


Figure 1: Number of cycles to failure of dry and wet $[\pm 45]_2$ s sample a) in air and under immersed conditions, b) in air and one side exposure conditions. Image source [2]

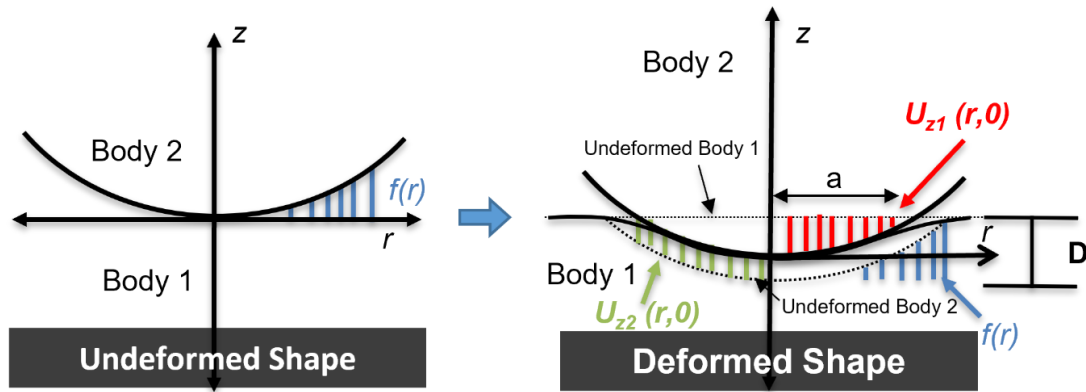


Figure 2: Indentation by an axisymmetric body. Image recreated from [105].

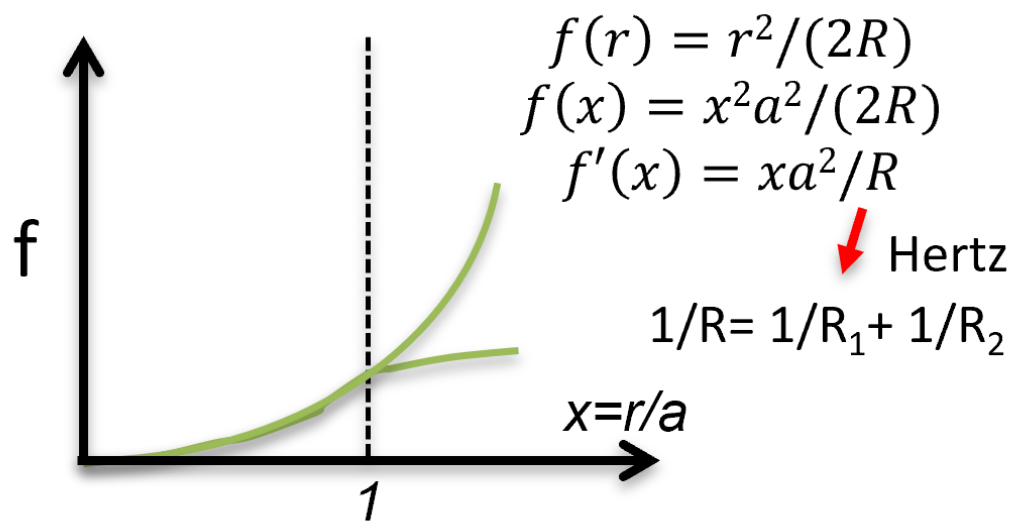


Figure 3: Parameterization of a paraboloid indenter and initial separation. Image recreated from [105]

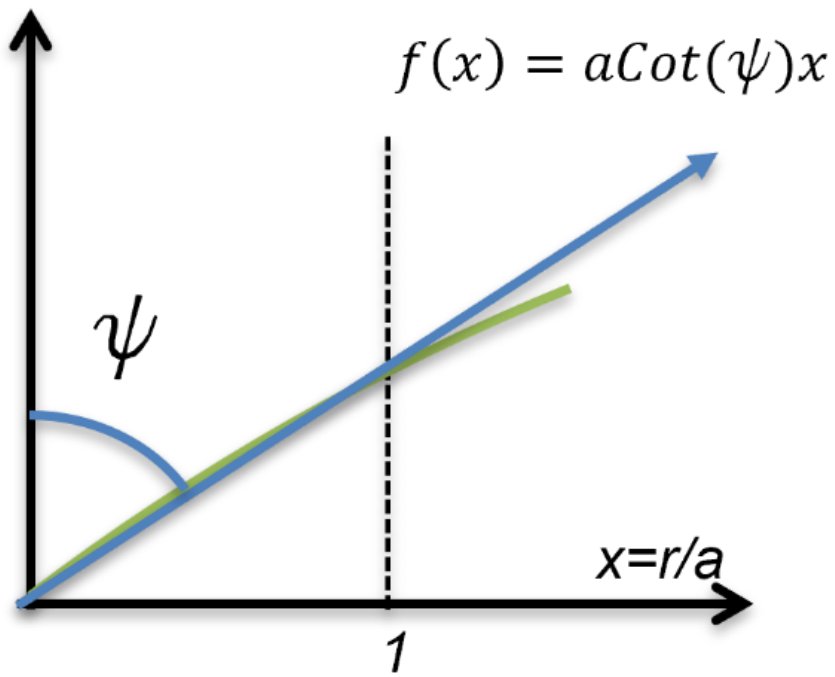


Figure 4: Parameterization of a cone indenter and initial separation. Image recreated from [105]

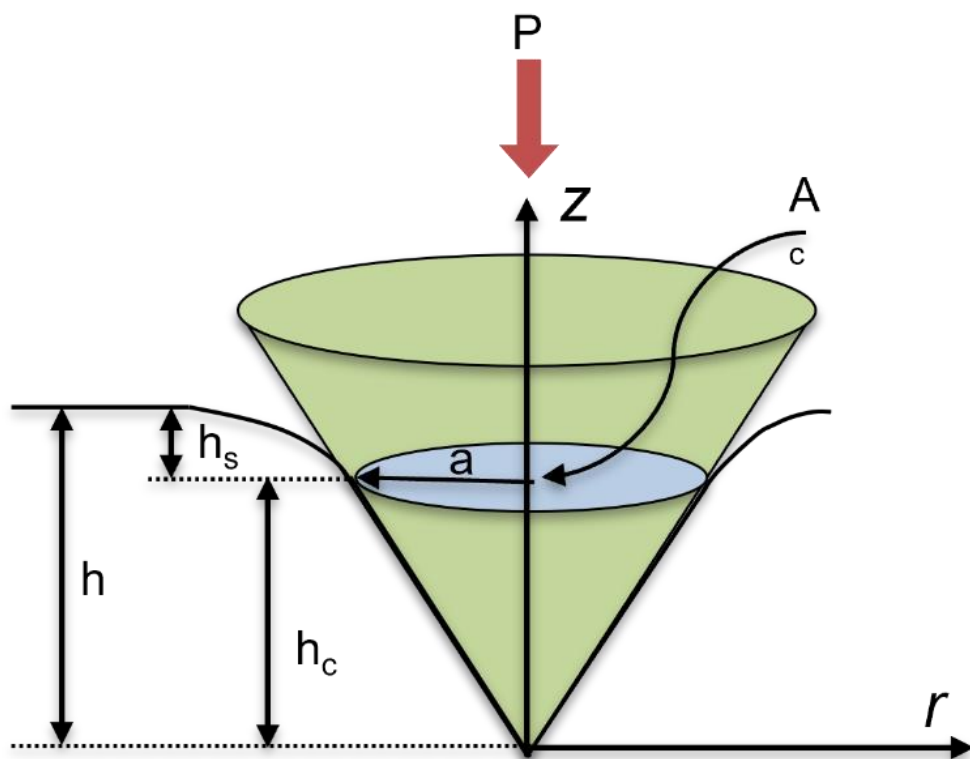


Figure 5: Schematic of deformation in nanoindentation. Image recreated from [105]

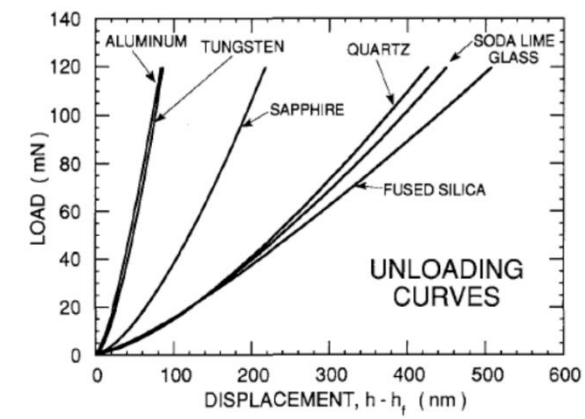
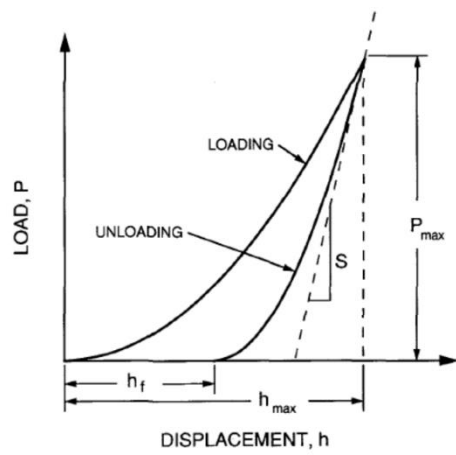


Figure 6: a) Nanoindentation load-depth curve, b) Unloading curves for different materials. Image taken from [16].

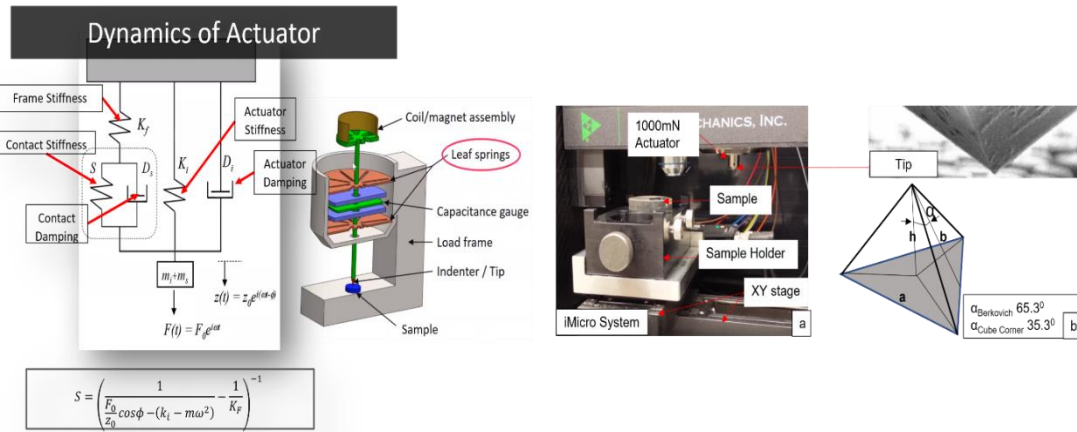


Figure 7: Dynamics and geometry of actuator [105] and indentation tip.

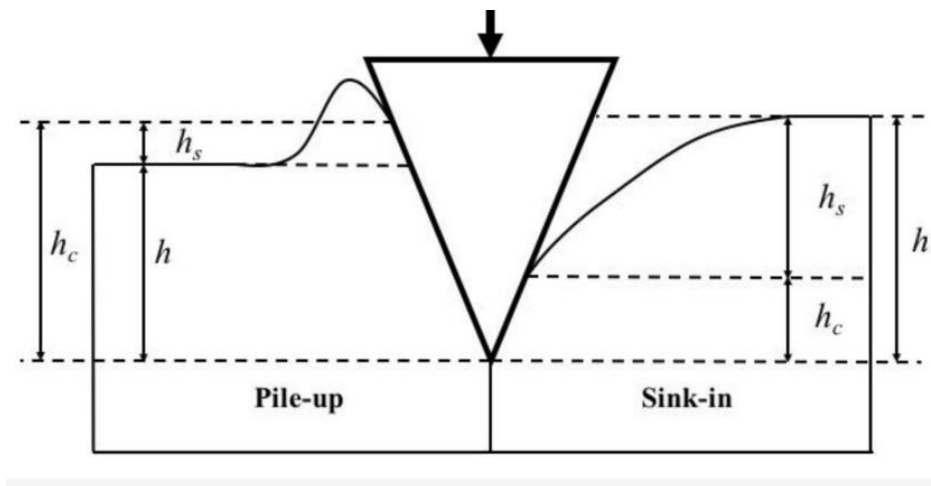


Figure 8: Pile-up and sink-in during indentation. Image source [106].

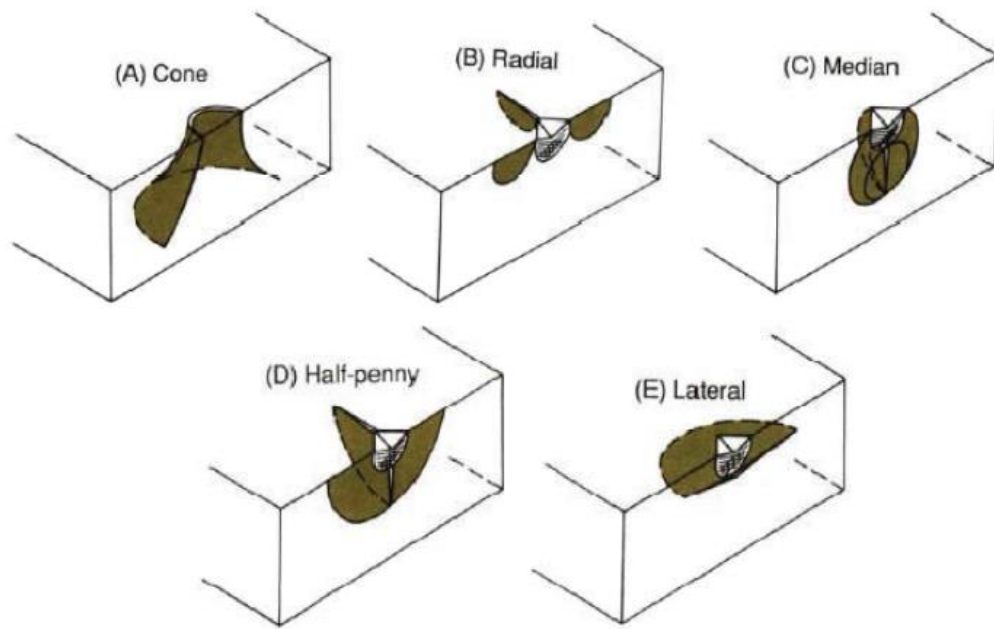


Figure 9: Different crack profiles due to the sharp pyramidal indentation on the surface. Image developed by Cook and Pharr. Image source [35].

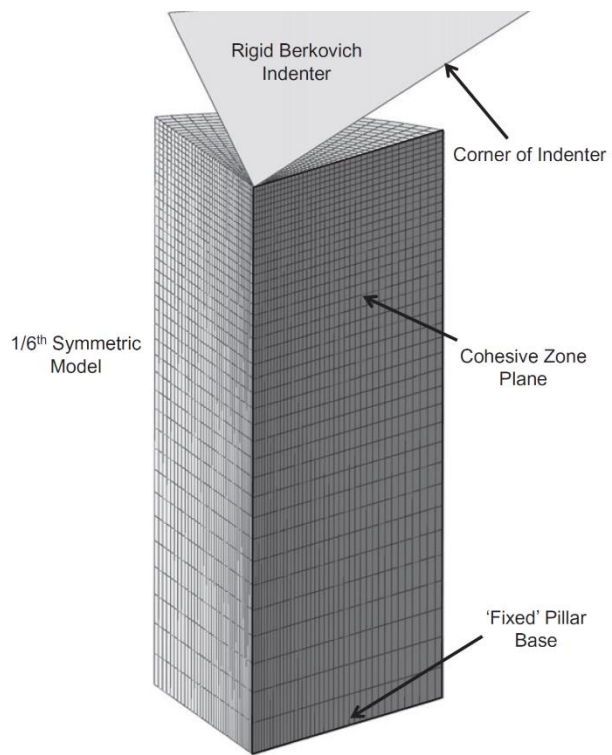


Figure 10: CZFEM setup. Image source[107]

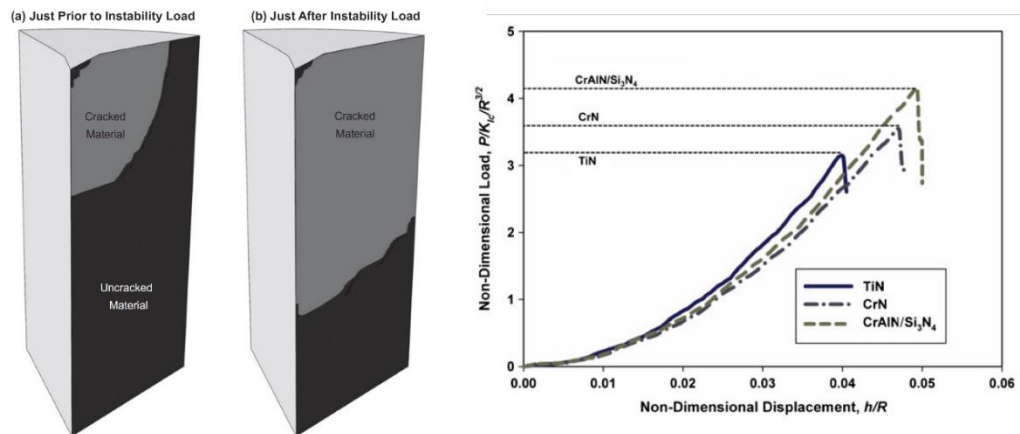


Figure 11: CZFEM-based crack profile, instability, and load–depth curve showing instability. Image source[107]

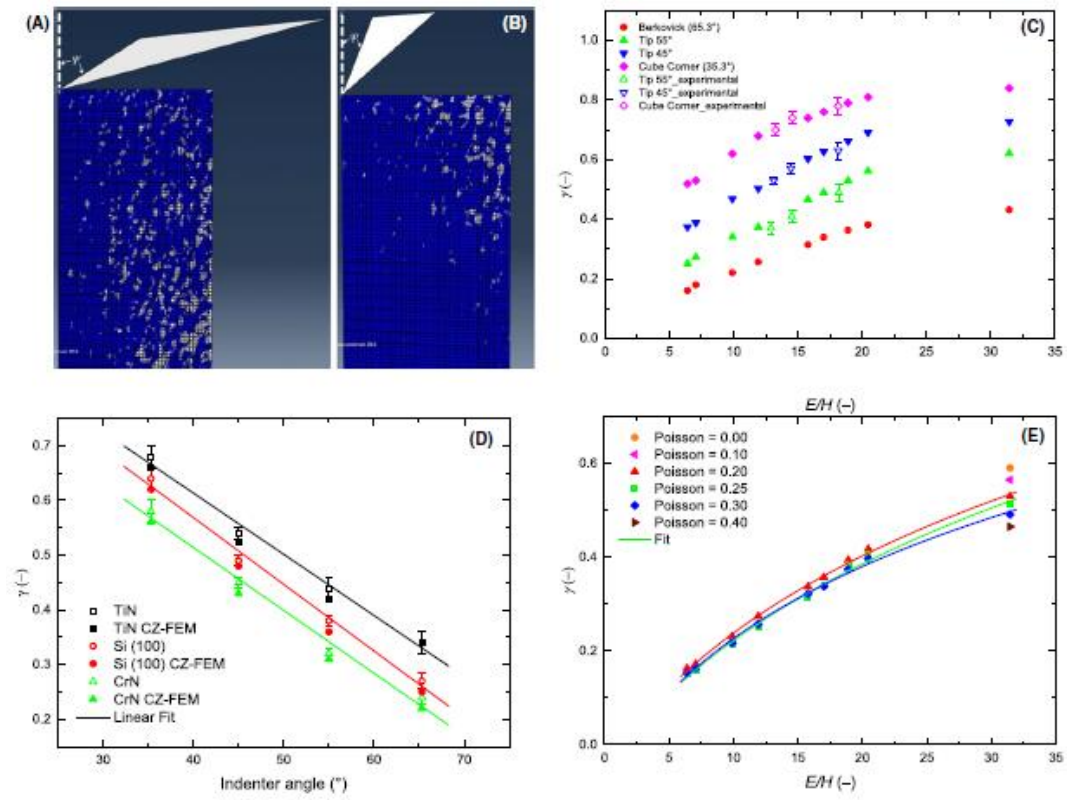


Figure 12: Effect of indenter angle and mechanical constants upon parameter γ . Image source [27]

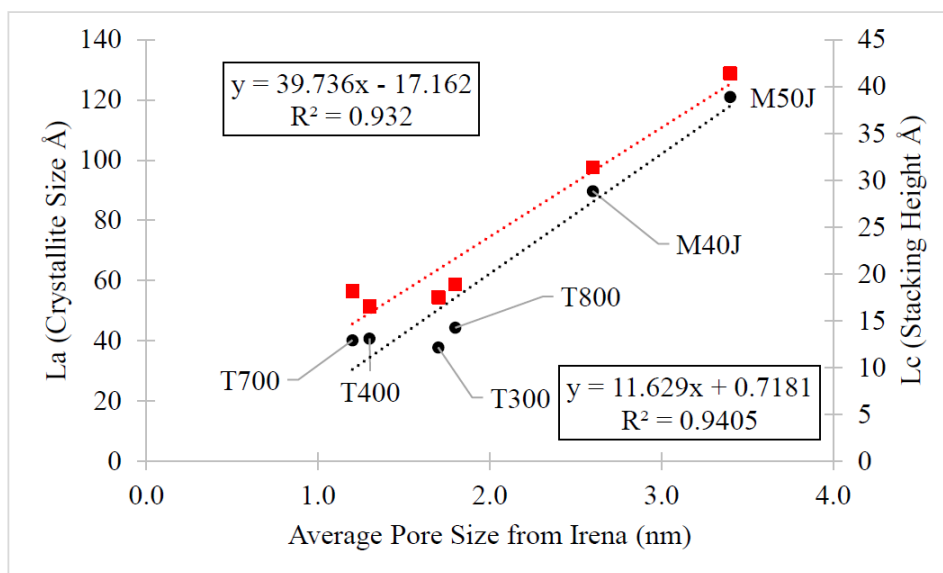


Figure 13: Interdependence of crystal parameters. Image source [45]

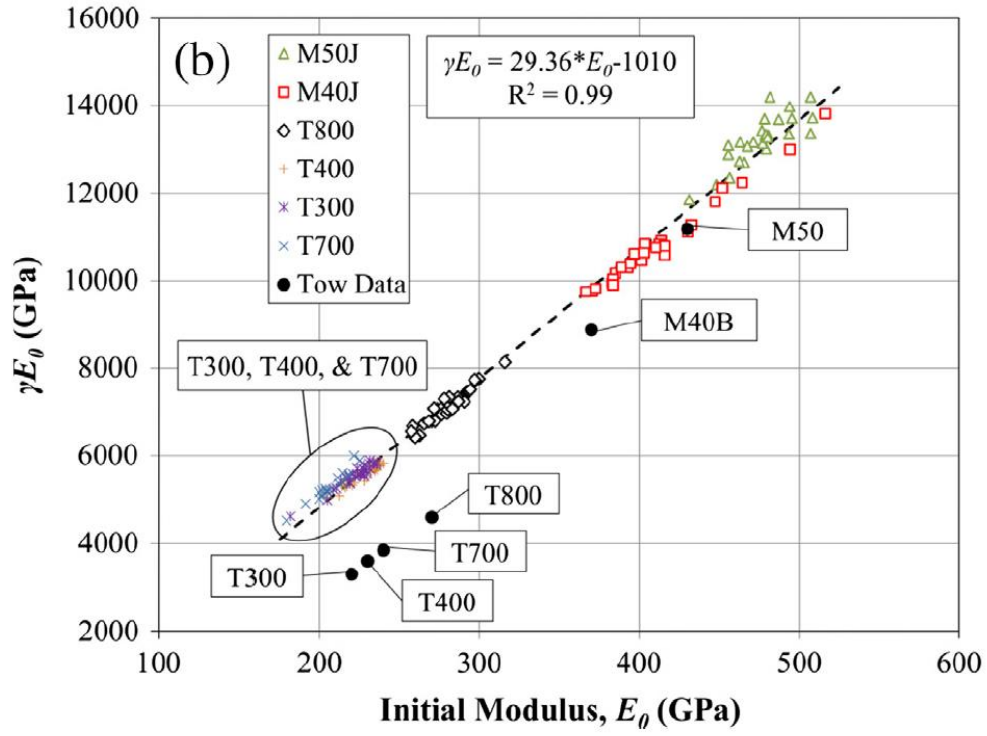


Figure 14: Gamma as a function of initial storage modulus (E_0). Image source [46]

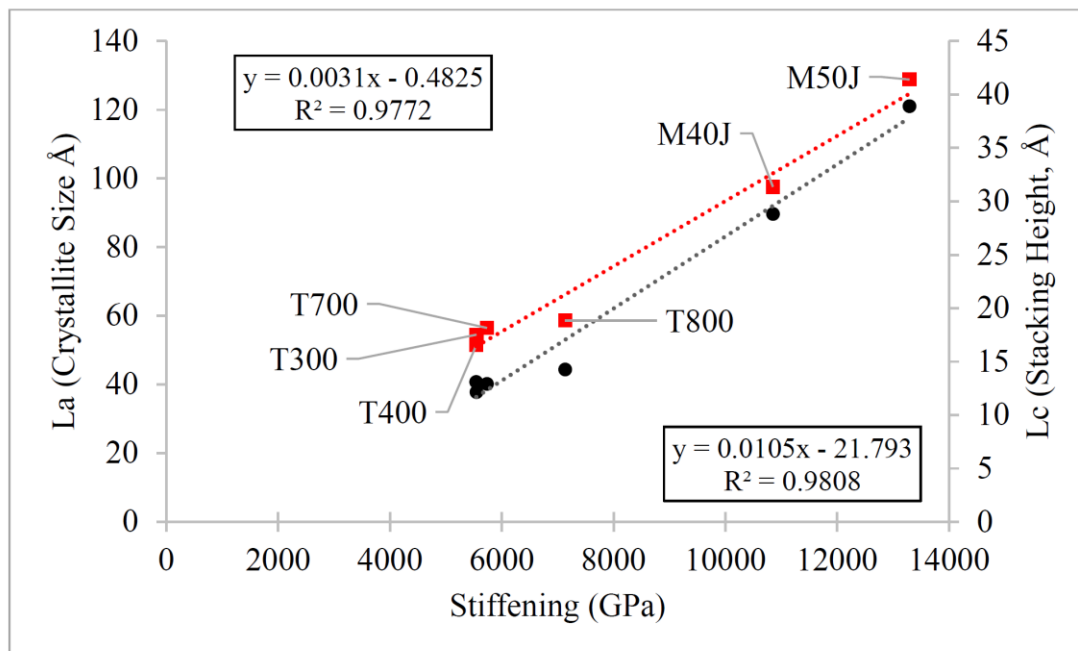


Figure 15: Crystal parameters as a function of stiffening. Image source [45]

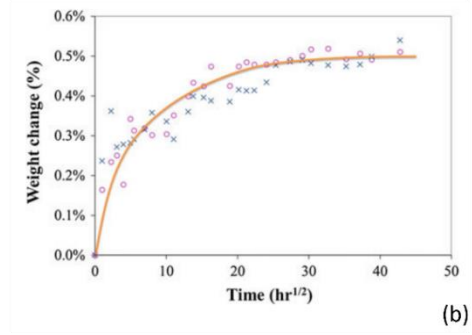
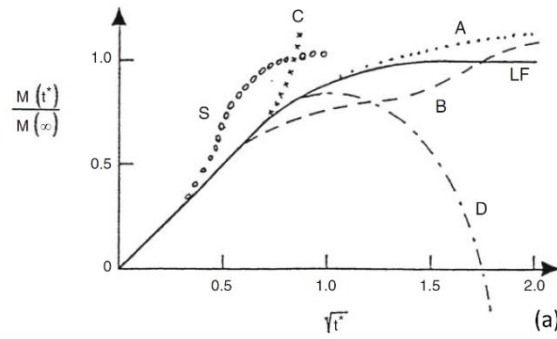


Figure 16: a) diffusion schematic curves of non-Fickian weight-gain sorption (Image source [53]), b) Diffusion curve obtained for CF/VE coupon immersed in seawater at 40 C (Image source [5]),.

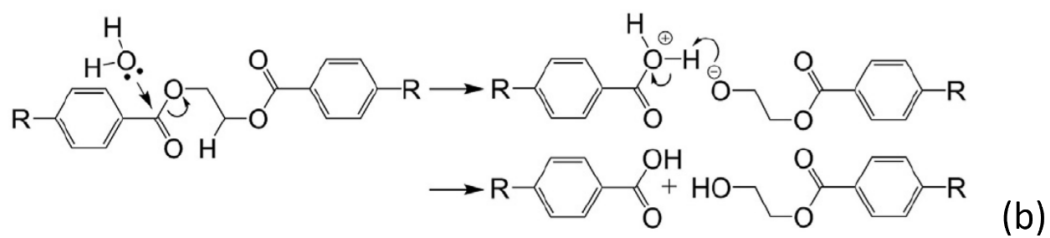
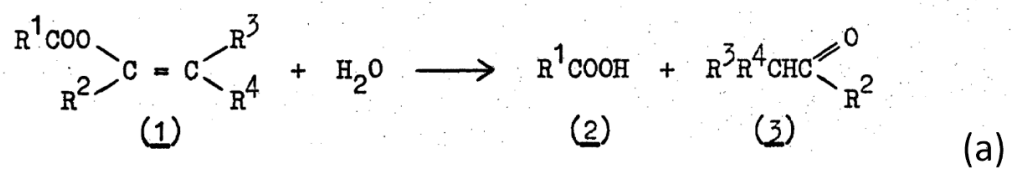


Figure 17: Hydrolysis of Vinyl ester. Image sources [54] & [55].

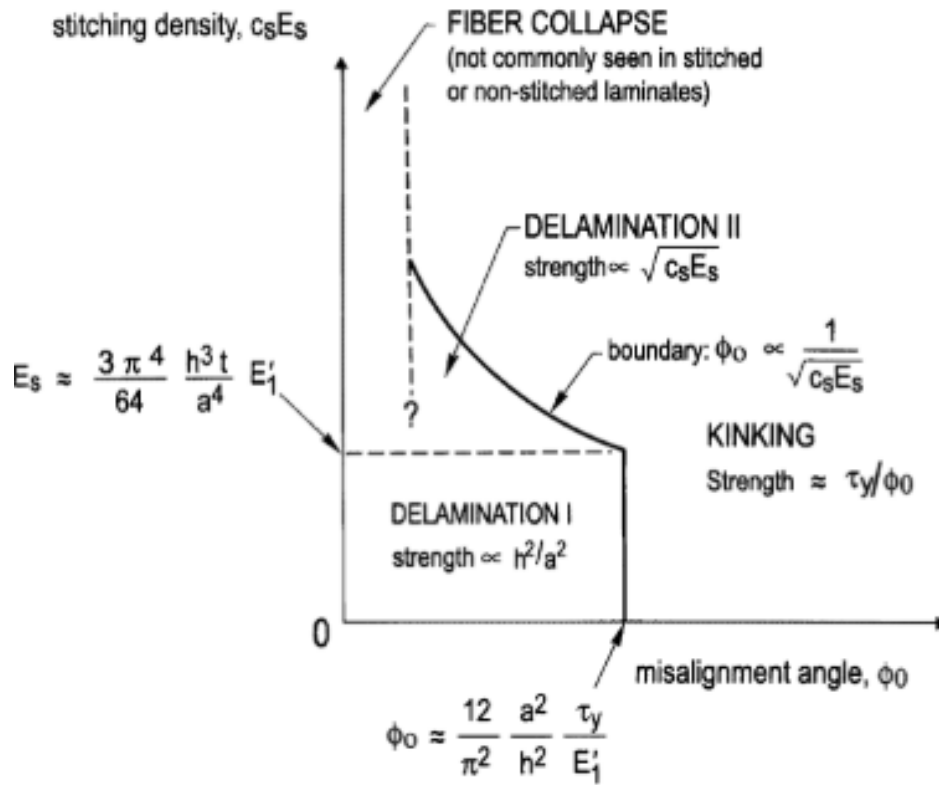


Figure 18: Failure map for stitched laminates as a function of misalignment and stitching density. Image source [97].

CHAPTER 2:
THE COMBINED EFFECT OF TEMPERATURE AND SEAWATER
ON THE COMPRESSION PROPERTIES OF CARBON FIBER
VINYL ESTER COMPOSITES FOR SANDWICH STRUCTURES

This chapter is based on a paper published by Vivek Chawla and Dayakar Penumadu: V. Chawla, D. Penumadu, The combined effect of temperature and seawater on the compression properties of carbon fiber vinyl ester composites for sandwich structures, 0 (2023) 1–19. doi:10.1177/10996362231157002. My contributions include experiment planning and data acquisition, data processing and most of the writing.

Abstract

For naval applications, composite sandwich structures are of significant interest, and are often manufactured using thin (2 to 4 mm) composite facings made from carbon or glass fiber reinforcement, attached to a thick (25 to 50 mm) section of PVC cellular foam or balsa wood-based core materials using a suitable polymeric resin. In the present study, we focus on the hygrothermal effect on the fiber-dominated compression properties of carbon fiber reinforced vinyl ester resin based polymeric composite (CF/VE), used as “skin” for a polymeric composite sandwich material. Hygrothermal conditioning is achieved by saturating samples in simulated seawater at 40°C. Compression properties are evaluated for coupons extracted along warp and fill undergoing- no conditioning, conditioning till saturation (up to 6 months), and long-term conditioning (2 years). Seawater saturation yields in up to 12 percent drop in compression strength with a further 3-4 percent drop resulting from long-term conditioning. No statistically significant modulus degradation is noticed due to short or long-term hygrothermal exposure. The failure mechanism of the warp extracted coupon, which fails in a splitting failure mode originating due to the delamination between the 0/90 interface, or the fill extracted coupon, which fails due to the instability caused by tow micro-buckling, remains

unchanged due to combined exposure (short or long-term) of seawater and temperature. The loss in strength is attributed to the degradation of the fiber-matrix interface, which is validated via conducting single fiber push-in tests with a nominal diameter of 7 micron for conditioned and unconditioned coupons.

Introduction

Fiber-reinforced polymer composites have gained high interest in applications that require a high strength-to-weight ratio[108–110]. Primarily, aerospace[111,112], automotive[110], and sports industries[112] have actively tried to replace conventional materials with carbon fiber-based composites. For naval applications, composite sandwich structures are of significant interest, and are often manufactured using thin (2 to 4 mm) composite facings made from carbon or glass fiber reinforcement, attached to a thick (25 to 50 mm) section of PVC cellular foam or balsa wood-based core materials using a suitable polymeric resin. In the present study, we focus on the characterization of facings made from carbon fiber reinforced vinyl ester resin based polymeric composite (CF/VE), used as “skin” for a polymeric composite sandwich material. The effect of exposure to sea water is investigated by pre-soaking of specimens for target duration at controlled temperature in the water bath. For marine applications, the behavior of CF/VE laminate-based sandwich structures exposed to long term sea water and coupled temperature effects is of current interest. Sandwich structures are often studied for their mechanical response in flexure using three- or four-point loading fixtures and an important mode of failure is the laminate subjected to compression. The effect of seawater on the tensile[4], fatigue [2], and interfacial delamination[3] of CF/VE

composites has been studied in the literature. Directly studying the behavior of these CF/VE laminates in compression is the topic of interest for this study.

The compressive properties of the composite are vulnerable to the test setup and specimen preparation. For a test to be valid, the stress field must be uniform in the gage area with minimal influence of the free edges. The test setup should have less sensitivity to imperfections and a valid failure mode that should happen within the gage region.

Compression properties have been shown to be the function of means of load introduction[69]. The effect of the means of load introduction on the test results is evaluated by examining the results from the Combined loading Compression (CLC) and Illinois Institute of Technology Research Institute (IITRI) fixtures.

An investigation of microscopic failure initiation and its progression is necessary to understand the resulting macroscopic compression properties. Various failure modes have been reported in the literature for compression failure of polymer composites- delamination[58,60], kinking[58,60,71], fiber micro-buckling[58,60][72–74], and in a few cases, fiber failure[58,60]. These failure modes initiate at a microscopic or mesoscopic level, resulting in macroscopic failure. Therefore, the macroscopic failure modes function as an indicator of underlying mesoscopic/microscopic failure mode. For example, a splitting failure mode usually implies delamination as the cause of failure initiation. The failure initiation modes are a function of constituent material properties and the microstructure of the composite under investigation. The mechanical properties' dependency on the microstructure substantiates the difficulties in universal strength-based modeling of composites.

The CF/VE investigated in this study are manufactured using a non-crimp fabric (NCF). NCF-based composites are of interest because of the lower manufacturing and storage cost than the prepreg-based composites. Due to the additional support provided by stitching, the delamination resistance between the stitched interface (0/90 in this study) of the NCF composite is typically higher [91,97]. On the other hand, NCF adds other geometric and material nonlinearity mechanisms in the microstructure of the manufactured composites, such as resin pockets, tow misorientations, stitching, and localized fiber fracture resulting from the stitching process. These sources of nonlinearities can change the failure modes and thus the resulting in-plane mechanical properties. The effect of stitching on mechanical properties has been studied in literature, with most studies finding a significant reduction (up to 20 percent) of in-plane mechanical properties[91,93,97,113].

Water transport for composite materials immersed in water is usually caused by diffusion and absorption. The absorption happens through the voids, micro-cracks, and gaps between the fiber/matrix interphase [114]. A connected fiber/matrix imperfect interphase acts as capillaries and increases the permeability of the composites to a variety of fluids. Moisture saturation can induce matrix swelling and plasticization- this often occurs in matrices of relatively high hydrophilicity [115]. Swelling introduces negative pressure on the matrix caused by being bounded by the almost undeformed fibers, which results in residual radial stresses that can lead to interfacial de-cohesion. *Plasticization* reduces the glass transition temperature of the matrix, T_g , often resulting in the softening [21]. For matrices with low to moderate hydrophilicity, swelling and plasticization have minor

effects, but hydrolysis can induce polymer embrittlement[115]. Moisture saturation has been shown to cause degradation in in-plane mechanical properties[98]. Understanding the compression behavior requires understanding mechanisms of failure that depend upon the micromechanical properties and microstructure. Interfacial shear strength (IFSS), a measurement of the bonding between the fiber and matrix, has been shown to affect the tensile[56,98], compression[59,98] and impact properties of the composites. Moreover, seawater saturation causes a significant reduction in the interlaminar shear strength resulting from additional routes for water uptake developed due to microcracking and debonding [116,117]. The hygrothermal effects on the Fiber/Matrix interfacial strength is of prime importance in understanding the hygrothermal effects on the compression properties [98,118–120]. In this work, the authors investigated the combined impact of seawater and temperature upon the fiber-matrix interface and their effect on failure modes and, thus, the resulting compression properties.

Materials

The reinforcement investigated in this study is Devold AMT AS stitched bonded fabric designated LT650-C10-R2VE. This is an equibiaxial Non-Crimped Fabric (NCF) produced using Toray's T700 12 K carbon fiber (diameter $\sim 7\mu\text{m}$) tow with a vinyl ester compatible sizing. The matrix used is Dow Chemical's DERA-KANE 520A-40, a brominated vinyl ester formulated for the Vacuum Assisted Resin Transfer Molding (VARTM) process. The composite is manufactured using the VARTM process, for which the setup and cure time-temperature profile is described by Shivakumar [121]. The panel is cured for 72 hours at 25.6° C and then ramped at 0.11° C/min for 7 hours to 71.1

° C where it is post-cured for another 20 hours before cooling down at 0.56° C/min. Five 1” by 0.5” sections are extracted in warp and fill. Burn-off experiments were performed in a vacuum for the extracted sections. Table 3 shows the results of burn-off tests carried out in an inert atmosphere. No significant differences in volume fraction are obtained between the warp and fill coupons, with a standard deviation of less than 1 percent obtained between samples. The volume fraction obtained is higher than the one reported by Shivakumar using the areal density measurements. High-magnification optical images showed that there were no dry fiber regions or voids. VARTM is an attractive process because it offers a cost-effective methodology for manufacturing large complex parts and thus is attractive for naval applications. The fabric is stitched with 14g/sqm polyester knitting. Stitching has been shown to substantially improve the interlaminar fracture toughness in modes I and II and damage tolerance but with significant degradation in the in-plane properties[91,97]. The composite panels are fabricated using a 4-ply symmetric fabric layup, resulting in the layup of [0/90]_{2s} and [90/0]_{2s} in warp and fill, respectively. The total thickness of the panels obtained varies by around ±5%, with an average thickness of 2.7mm. On the other hand, the variation between the average thickness obtained between coupons varies by around ±1.75%, with an average thickness of 2.7 mm. The details of the fabric and the fabricated composite panel is shown in Figure 19a and Figure 19b. The consequence of the VARTM process is that the air side (the surface exposed to the vacuum bag) shows a much higher surface roughness than the Mold side. The average surface roughness (S_a) obtained using Keyence VK-X250k laser confocal microscope for the side A and B (Figure 19b) of the composite panel under investigation

is 11.3 μ m and 63 μ m, respectively. The higher surface roughness value obtained for the air face is representative of the variation in curvature because of vacuum bagging, i.e., the flatness. The higher variation between the total thickness of the panel compared to the average thickness of the coupons is attributed to the higher surface roughness.

The coupons are cut along warp and fill. Henceforth these coupons are referred to as warp and fill extracted coupons, respectively. The sea-water saturated coupons are prepared by soaking the samples in simulated seawater at 40⁰ C. Simulated seawater is prepared by mixing coarse sea salt (NaCl) with deionized water until the specific gravity of 1.022 of the resulting solution is achieved. The Combined Effect of temperature and seawater is then evaluated upon the compression properties of CF/VE composites. It has been shown[5] that the CF/VE studied in this work saturates in the controlled temperature and seawater environment after two months. Example weight gain vs square root time curves are shown in Figure 20. More details about the kinetics of Fickian diffusion of seawater [5] and diffusion coupled with wicking within the vinyl ester matrix can be found elsewhere[114]. Simulated seawater is reintroduced every 2-4 weeks to prevent excessive change in the system's density, i.e., the salt concentration in water. Ten warp and fill extracted coupons are soaked for six months, while five warp and fill cut coupons are soaked for two years. Henceforth, these coupons are short-term and long-term soaked coupons, respectively. Additionally, five 1” by 10” CF/VE coupons (manufactured using the same processing parameters) that have been soaked for 15 years (same aging conditions as the short-term and long-term soaked coupons, i.e., simulated seawater at 40°C) are extracted from a different panel. These coupons are cut into 10mm *10mm

sections and polished along the warp and fill face to examine the local microstructural changes due to extreme long-term exposure to seawater. Similarly, a pure resin (Vinyl Ester) coupon saturated for 15 years is also extracted to examine the degradation in mechanical properties of Vinyl Ester subjected to extreme long-term exposure.

Methods

Compression Testing

Compression test setup and procedure are done per ASTM D6641[122] using the Combined Loading Compression (CLC) fixture. The load is transferred to the sample using end loading combined with the shear loading to ensure efficient stress transfer and failure in gage length. MTS 810 test system with a 100 kN load frame setup is used for compression testing. The details of the test setup and sample dimensions are shown in Figure 19c. The samples are precision cut using a grinding wheel equipped with a diamond blade. Alignment of samples within the fixture is achieved using a laser level. The surface in contact with the platen is critical to effectively transfer the load when the sample is subjected to compression. Sample ends are grinded using an automatic polisher with 320 grit to achieve optimal contact with the platen.

DIC Validation

Compression testing requires strain measurement on both faces of the coupons to eliminate the effect of bending that may arise due to misalignment in the test setup[122]. Two Digital Image correlation (DIC) systems- GOM Aramis with 12 MP cameras and Correlated solutions VIC 3D with 1.4 MP cameras- are used to evaluate the strain on either face of the coupon. DIC offers spatial strain resolution and thus the zones of strain

concentration which can be a valuable tool in determining the zones of failure initiation and consequently the failure propagation. However, the accuracy of the measured strain via DIC is a function of the DIC setup calibration. Therefore, the measured strain requires validation. Two sets of experiments are conducted to validate the strain obtained via DIC - 1) Compression testing using DIC (VIC 3D) and strain gauge, 2) Compression testing using VIC 3D and GOM Aramis- measuring strain on the side B (Figure 19b) during compression testing. Side B is chosen for validation because of the higher surface roughness and thus a higher probability of poor correlation for DIC setup. Figure 21a shows an excellent agreement between the strain obtained via strain gauges and the VIC 3D setup. Figure 21b shows the results obtained for the two DIC setups measuring strain on the same face. The results in Figure 21b are calculated by defining a representative strain gauge area and an effective extensometer for both setups. The strain measured via a representative strain gauge is an average strain for each sub-volume within the defined area. In contrast, the strain is calculated by measuring the change in length of the effective extensometer, which is only a function of endpoint displacements. It was observed that the choice of location and length of the extensometer significantly changes the strain obtained, which is a direct consequence of the high strain gradient on the face of the sample. Thus, the strain measurements in this study use the representative strain gauge.

Effect of torque on test results

Test setup can play a significant role in efficient load transfer and thus the resulting compression properties. Care must be taken to ensure that the failure happens within the

gage region with efficient load transfer. The torque used to constrain the sample for the CLC fixture can have a constraining effect on the sample and thus the resulting compression properties. Three dry samples extracted in warp and fill for each torque condition (20lb-in-35lb-in) are tested using the CLC fixture to understand the torque effect. Side faces were not tabbed for any of the torque conditions. The resulting stress-strain plots are shown in Figure 22a and Figure 22b, while the results are reported in Table 4. All but one warp cut coupon corresponding to a 35 lb-in. Torque (Figure 22a) failed within the gage area. The torque for the fill extracted coupon is varied between 20lb-in. And 30lb-in. No correlation in strength, modulus, or the resulting stress-strain curve is observed as a function of torque. 30lb-in. Torque showed the maximum average strength and was chosen for further testing. Furthermore, since no failure was observed at the ends, the side faces were not tabbed for the further tested CLC coupons.

Role of Fixture on test results

The stress field developed during compression testing is sensitive to the loading mechanism. Various fixtures have been proposed to calculate the compression properties of polymer composites. These fixtures can be broadly characterized into three categories – End-loaded, Shear-loaded, and Combined-loaded fixtures. End-loaded fixtures have decreased in popularity because of the higher probability of failure within the fixture. IITRI (Illinois Institute of Technology Research Institute) fixture is a compression testing fixture that transfers the load via shear loading. An advantage of using the IITRI fixture is that the flatness at the end of coupons has little effect on the resulting compression properties as the load is transferred through the side faces. Side faces for IITRI coupons

are tabbed using Garolite (G10) and bonded using epoxy resin with hardener (5 to 1 by weight) and glass filler to prevent stress concentration while the side faces of CLC coupons are not tabbed because of the gage failure observed for un-tabbed coupons while evaluating the effect of torque. A displacement rate of 1.5 mm/s is chosen for IITRI testing as per [123]. Five dry coupons cut in warp and fill tested for IITRI and CLC fixture. All coupons failed in the gage region. Table 5 shows the resulting mechanical properties for both fixtures. The compressive strength obtained via the CLC fixture is higher than that obtained via the IITRI fixture. This result indicates the inefficient transfer of load from the faces through the sample for the IITRI fixture, which might be due to the difference in surface roughness of the faces or due to the inherent material unsymmetry present because of the local differences in microstructure of the fabric. Henceforth, the compression properties are reported using the CLC fixture.

Results

Fifteen dry coupons, ten short-term soaked coupons, and five long-term soaked coupons, extracted in warp and fill, are tested using the CLC fixture. As previously stated, the coupons are tested with 30lb-in. Torque. Typical stress-strain curves for dry and seawater-soaked warp and fill cut coupons are shown in Figure 23. Face 1 and 2 correspond to the specimen's strain on the opposite faces (Mold and Air face). The average of the two strains is the desired value since the amount of bending due to sample misalignment does not affect the average strain.

Thin laminates under compression are prone to buckling. The minimum thickness required to avoid Euler buckling can be estimated by the equation 2.1[123]. Taking a

conservative approach and assuming a modulus of 50 GPa with compressive strength of 600 MPa gives a minimum thickness of 1.7mm for a gage length of 13mm, which is smaller than the thickness of CF/VE being investigated. Moreover, the stress-strain curve validates the absence of global buckling as there is no evidence of instability. Even though the global buckling is absent, there is significant bending in fill coupons. The presence of constant bending in the fill coupon implies the nonlinearity arising from material imperfections rather than a systematic misalignment in the test setup. A closer examination via optical microscopy revealed a higher degree of misorientation in fill coupons (Figure 23), perhaps indicating bending due to geometric nonlinearity.

$$h \geq \frac{1}{0.9069\sqrt{\left(1 - \frac{1 \cdot 2F^{CU}}{G_x}\right)\left(\frac{E^l}{F^C}\right)}} \quad -(2.1)$$

The summary of compression strength and compression modulus obtained for dry aged and sea-water saturated coupons is shown in Figure 24 and *Table 6*. Compression modulus decreases between 1.35-2.1 percent and 0.9-1.3 percent for warp and fill extracted coupons, respectively. The higher value of compression modulus for the long-term soaked coupons compared to the short-term soaked coupons perhaps indicates the insignificance of the two data sets. A student t-test comparison between the short-term and long-term soaked warp samples results in a Z value of 0.47, indicating a less than 50 percent confidence interval of the difference between the two data sets. On the other hand, the difference between dry aged and saturated warp coupons shows a greater than 80 percent confidence interval. Thus, the authors conclude a 1.35-2.2 percent decrease in compression modulus of warp coupons due to combined exposure to seawater and

temperature. There is no significant change in modulus between the long-term and the short-term saturated warp coupons. Fill coupons show a relatively lower decrease with a higher standard deviation in modulus. Thus, it is difficult to statistically state any reduction in fill coupons compression modulus due to long-term hygrothermal conditioning.

On the other hand, strength shows a significant decrease between the dry aged and saturated coupons. The strength decreases by 12.3 and 12 percent for warp and fill extracted short-term soaked coupons with a further reduction in strength by an additional 3.1 and 4.2 percent when conditioned for two years. Another interesting observation can be made from *Table 6*. The standard deviation corresponding to the compressive strength of fill coupons increases with long-term exposure to seawater, suggesting that some fill coupons are more prone to strength degradation than others, perhaps an indicator of change in failure mechanisms.

Discussion

Modes of failure for dry aged and saturated coupons

Compression failure is not only the function of the material properties of reinforcement, interface, and matrix but is also largely dependent upon the microstructure of the composite under investigation. Macroscopically, failure modes can indicate the fundamental cause of microscopic/mesoscopic failure initiation. Figure 25 shows the macroscopic failure modes observed for dry warp and fill extracted coupons. Splitting is observed as the macroscopic failure mode for all warp cut coupons with delamination between the 0/90 layers, suggesting failure governed by the fiber-matrix interface. Fill

coupons show kink bands in the post-failure microscopy and a high degree of matrix cracking.

To investigate the underlying failure mechanisms, the edges of warp and fill extracted samples are polished using the Buehler MetaServ 250 auto polisher. In-situ imaging under compression is done to observe the evolving microstructure of warp and fill cut coupons. The coupons are tested till 90 percent failure load and imaged using Keyence VHX-7000 to monitor any zones of failure initiation. The misorientation ($\emptyset$) is characterized by calculating the tangent inverse of equally spaced points distributed across the tows of samples (Figure 26a). The maximum misorientation ($\emptyset_{\max}$) calculated before loading and before failure for fill extracted coupons increases from 4.1° to 5.2° , respectively, as seen in Figure 26a. The increase in misorientation is indicative of tow micro-buckling. The finding is consistent with the computational study done by Wisnom et al., showing that NCF compression strength is controlled by 0° tow geometric instability arising at mesoscale and accompanied by resin shear plastic flow[59]. The coupons exhibit no microstructural changes via optical microscopy until the failure load is achieved. At this point, there is a catastrophic failure arising from the overall shear of the coupon. The post-failure microscopy shows kinking, matrix-cracking, and delamination as the failure mode. Warp extracted coupons do not show significant changes in microstructure during compression testing. Though, optical microscopy (Figure 26b) of coupons tested to 90 percent failure load revealed delamination at the edges of the coupon providing further evidence of failure to be controlled by the fiber-matrix interface with delamination as the failure initiation mode.

Sea-water saturated samples are taken out of their controlled environment and are immediately speckled (for DIC measurements) and tested. Therefore, it is not possible to understand the failure evolution of saturated samples via polishing. However, DIC can be used to understand the failure initiation and evolution of these coupons. An instantaneous change in out-of-plane deformation could indicate failure initiation and subsequent propagation. Thus, out-of-plane velocity quantifying the change in out-of-plane deformation is defined as per equation 2.2. Macroscopically, saturated warp extracted coupons fail in a splitting failure mode with a reduction in strength, indicating a decrease in interfacial strength of CF/VE due to long-term exposure to seawater. Figure 27a and Figure 27b show the failure evolution via DIC and the resulting stress-strain curve obtained for a saturated warp cut coupon. The failure initiates at the edges via delamination and then propagates longitudinally and transversely until failure.

$$\frac{dw}{dt} = (w_{i+1} - w_i) * \eta \quad - (2.2)$$

Saturated Fill cut coupons show high variation in strength. Thus, the effect of saturation upon fill extracted coupons cannot be captured by just understanding the failure evolution of one coupon. Out-of-plane velocity is used to understand the failure evolution of fill cut coupons (Figure 28). Like the warp extracted coupons, the failure initiates at the edge. Unlike the warp cut samples, the failure is localized, and the out-of-plane velocity evolution is radial until the catastrophic failure. Resembling the failure sequence of dry fill cut coupons, this trend suggests the cause of failure localization to be tow micro-buckling.

Figure 29 shows the failure evolution of a saturated fill coupon captured via DIC images. The failure initiates as a combination of tow micro-buckling and delamination. The crack then propagates both transversely and through-thickness, eventually causing failure. The dry and saturated fill cut coupons undergo tow micro-buckling; thus, the mechanical properties in the vicinity of localization and the microstructure dominate the failure. The above evidence of failure evolution alludes to the cause of higher variation in failure strength observed in saturated fill extracted coupons. A lower fiber-matrix interfacial strength in the vicinity of micro-buckling will result in splitting as the failure mode. In comparison, a relatively higher interfacial strength will result in a catastrophic failure, perhaps due to the geometric nonlinearity caused by kinking. The above rationale is augmented by Waas et al., who found kinking and splitting to be competitive failure modes that depend upon mode II fracture toughness and mode-II interfacial strength [71]. To understand the microstructural factors that influence the compression properties of dry and Wet CF/VE coupons extracted in warp and Fill, X-Ray tomography (XCT) with 9 μm voxel resolution is done prior to testing (or soaking for wet samples) for seven dry and five wet short-term soaked warp and fill coupons, respectively. Two of the dry and wet coupons extracted in warp and fill are tested till a ninety percent failure load, and another XCT scan is taken to identify any zones of failure initiation. No apparent failure-initiating zones were observed. It was concluded during the investigation that any evidence of plastic tow micro buckling or delamination, if present, was disguised beneath the voxel resolution of 9 μm . For brevity, those results are not presented here. The remaining five dry coupons and three wet coupons are tested till failure and are used to

characterize the resin pockets. Figure 30 shows the methodology for characterizing the resin pockets.

Firstly, the XCT scan is segmented using the Simpleware software. Then, voxels representing each load-bearing tow are exported to a separate CSV file. The file is then imported to a self-written MATLAB code where, for each load-bearing tow, the edge is characterized at every length increment using a single voxel. Henceforth, this voxel is referred to as centroid. Therefore, there are two centroids for each load-bearing tow, and the distance between the two centroids of the neighboring tows is defined as a resin pocket. The centroid is defined as the mean x and the mean y value at the edge of each tow (Figure 30). The edge is defined by identifying the voxel that yielded more than two voxel jumps in the width (major axis) of the tow with a unit increment in thickness (minor axis). It was observed in the sensitivity study that this definition of edge yielded the most consistent results. Centroid is used to characterize the resin pockets because it considers the shape of the tow (as it accounts for the eccentricity of the ellipse, i.e., the shape of the tow) and eliminates the effect of scan orientation when determining the distance between the two adjoining tows. The centroid is evaluated for every tow and at every voxel along the length of the tow. The results are then averaged to identify the mean resin pocket. The effect of mean resin pockets upon the strength of the dry and wet warp and fill coupons is plotted in Figure 30. A clear trend for the tested warp coupons is noticed for both dry and wet coupons. However, dry fill coupons do not show a trend as a function of resin pockets. On the other hand, the wet fill coupons show a clear trend like

the one obtained in dry and wet warp coupons, perhaps indicating failure dominated by interfacial failure for most coupons.

Effect of seawater upon the fiber-matrix interfacial shear strength

As discussed in the previous section, the decrease in compressive strength for both warp and fill extracted coupons insinuate a decrease in fiber-matrix interfacial properties.

Thus, the authors evaluate the differences in interfacial strength between the dry aged and saturated coupons using the single fiber Push-in method[68][64][124], corresponding to the nominal fiber diameter of 7μm. First, the fibers are statically loaded using the Nanomechanics inc. iMicro Nanoindenter with a displacement rate of 50nm/s using a truncated cone with a 5μm initial diameter and a cone angle of 60°. The resulting load-depth curve is then used to quantify the interfacial strength as per equation 2.3.

$$T_c^{SL} = \frac{S_0 P_c}{2\pi^2 r^3 E_{11}^f} \quad -(2.3)$$

Where S_0 is the stiffness of the linear portion of the load-displacement curve, P_c is the debonding load, E_{11} is the longitudinal fiber modulus (230GPa), and r is the Fiber radius. The initial non-linear portion of the load-depth curve represents the tip contacting the fiber. Once the contact is established, the deformation is elastic until the onset of nonlinearity, expressing a break in the fiber-matrix interface. For the coupons tested, it was found that the slope of the load-depth curve consistently remains linear between 15mN and 25mN. Thus, S_0 is calculated from the slope of the load-depth curve corresponding to the load ranging between 15 to 25 mN. Since there is no apparent debonding load (P_c) in the load-depth curve, P_c is identified using the intersection of the load-depth curve with the 5% offset line of slope S_0 . Therefore, the definition of

debonding load is abstract. Thus, values reported in this study must only act as the qualitative differences between the data sets.

Interfacial strength represents the bonding between the fiber and matrix and thus likely differs from one location to another. Hence, 25 tests are conducted stochastically for each fiber tow that lies within the cross-section of the coupon to capture the range of values of interfacial strength across the cross-section. Each location is then optically imaged to identify the tests for which the tip-maintained contact with the fiber throughout the test. Five fill and warp cut coupons per environmental conditioning are evaluated. Figure 31a and Figure 31b show the optical image of pushed-in fibers revealing interfacial cracking and an example of the obtained load depth curve.

The histogram expressing the range of measured values of fiber-matrix interfacial shear strength for dry aged and saturated coupons is shown in Figure 32. As expected, a peak shift in the normalized probability curve for both warp and fill coupons indicate a loss of interfacial strength due to long-term combined exposure to seawater and temperature. Furthermore, there is a reduction in the distribution width, reducing the standard deviation of the normalized curve, which is perhaps an indication of proportionality between the strength and reduction in interfacial strength.

Degradation in interface due to long-term combined exposure to seawater and temperature is a consequence of chemical degradation and the continual hygrothermal stresses developed due to the disparate coefficient of thermal and moisture expansion between the resin and fiber. Thus, the degradation would only increase with time[125]. Therefore, few coupons conditioned for 15 years are inspected using a Scanning Electron

Microscope (Figure 33). Based on Figure 33, cracking occurs along the tow circumference and along with the stitching. It should be stated that only two out of the various coupons inspected showed cracking of the interface. Fibers within the tow have similar misorientation. Thus, each tow acts like a sub-composite under steady hygrothermal stresses, resulting in the highest residual stresses developing at the tow-matrix interface. Similarly, the degradation due to negative pressure introduced due to swelling of the matrix will be maximized at the tow-matrix interface. Therefore, the fiber-matrix interfacial strength degradation is maximum for fibers at the tow matrix interface. A similar rationale can be followed for the degradation in stitching-matrix interfacial strength.

The degree and effect of plasticization can be analyzed by evaluating the degradation in mechanical properties of the matrix. Therefore, following the similar reasoning as adopted for IFSS, the matrix degradation is evaluated in this study corresponding to two coupons with dry and wet ages of 15 years using Nano-indentation. Nano-indentation was performed using Nanomechanics, Inc.'s iMicro system and a Berkovich tip. The force and displacement measurements were done using a 1000mN actuator with a capacitive gauge and displacement range of 40 μm .

The continuous stiffness method (CSM) is used for determining the mechanical properties as a function of depth. The area function calibration of the diamond Berkovich tip was done using fused silica. Figure 34 shows the result obtained for both samples. Figure 34 shows no degradation in vinyl ester properties due to long-term exposure to seawater. The results are unsurprising since a simple rule of mixture analysis would

conclude that any decrease in indentation modulus would cause a reduction in macroscopic modulus, which is not seen in this study. Thereby the effect of the plasticization of Vinyl Ester on the results is minimal.

Conclusions

In this experimental study, the authors demonstrated the combined effect of long-term temperature and seawater upon the compression behavior of NCF-based CF/VE composites. Compression testing is done using the CLC fixture while the effect of role of fixture in determining the resulting compression properties is evaluated using an IITRI fixture. DIC is used to measure the strain. The following conclusions are made in the study:

1. Coupons extracted along warp and fill shows ~ 12% decrease in compression strength due to sea-water saturation. Long-term (2 years) exposure causes a further 3% and 5% drop in compression strength of coupons extracted along warp and fill, respectively
2. Compression modulus is minimally effected for coupons extracted along warp and fill due to short or long-term exposure to sea water.
3. Coupon extracted along warp macroscopically fails in splitting failure mode initiated by edge delamination which is observed via optical microscopy of 90 percent loaded sample. There is no change in the failure initiation mode for the sea-water saturated coupons, and the measured lower compressive strength is attributed to the loss in interfacial strength.

4. An increase in misorientation is observed just before failure in coupons extracted along fill during compression testing, which indicates tow micro-buckling. The evidence of tow micro-buckling is obtained for the saturated fill coupons via a radial increase of out-of-plane velocity localized at the sample edge before failure. The interfacial strength in the vicinity of the localized deformation becomes a crucial micromechanical property upon which the failure mode and the compression strength are dependent. A higher variation in compression strength of soaked coupons is thus attributed to the variation in interfacial strength in the vicinity of localized deformation.
5. Single fiber Push-in tests for fibers with nominal diameter of $7\mu\text{m}$ are conducted to quantify the effect of long-term exposure to seawater and temperature upon the interfacial shear strength. The results verified a significant drop in interfacial shear strength. Interfacial degradation is maximum for fibers corresponding to the tow-fiber interface.

Appendix 2

Table 3: Fiber Volume fraction from Burn off tests.

	Fiber Volume Fraction	
	Warp (%)	Fill (%)
Sample 1	64.8	63.2
Sample 2	64.5	62.7
Sample 3	65.9	63.2
Sample 4	65.9	64.4
Sample 5	66.3	64.0
Average	0.655 $\pm$ 0.0076	0.635 $\pm$ 0.0069

Table 4: Effect of torque on fill and warp extracted coupons.

Torque (lb-in)	Warp		Fill	
	Strength (MPa)	Modulus (GPa)	Strength (MPa)	Modulus (GPa)
20	413	51	338.2	53
25	404	54	312.8	55
30	409	52	349.1	52
35	393	53		

Table 5: Comparison of mechanical properties obtained via CLC and IITRI fixture.

Fixture	Warp		Fill	
	Strength (MPa)	Modulus (GPa)	Strength (MPa)	Modulus (GPa)
CLC	453	52.0	373	48.6
IITRI	431	52.5	352	48.3

Table 6: Effect of seawater on compression properties of CF/VE

Conditioning (N)	Warp		Fill	
	Strength(MPa) (Stdev.)	Modulus(GPa) (Stdev.)	Strength(MPa) (Stdev.)	Modulus(GPa) (Stdev.)
Dry (20)	411 (23.4)	51.0 (2.7)	395 (29.9)	50.7 (3.3)
6 months soaked (10)	361 (27.4)	49.9 (2.2)	348 (46.9)	50 (3.0)
2 year soaked (5)	348 (21.5)	50.3 (1.3)	330 (68.4)	50 (2.5)

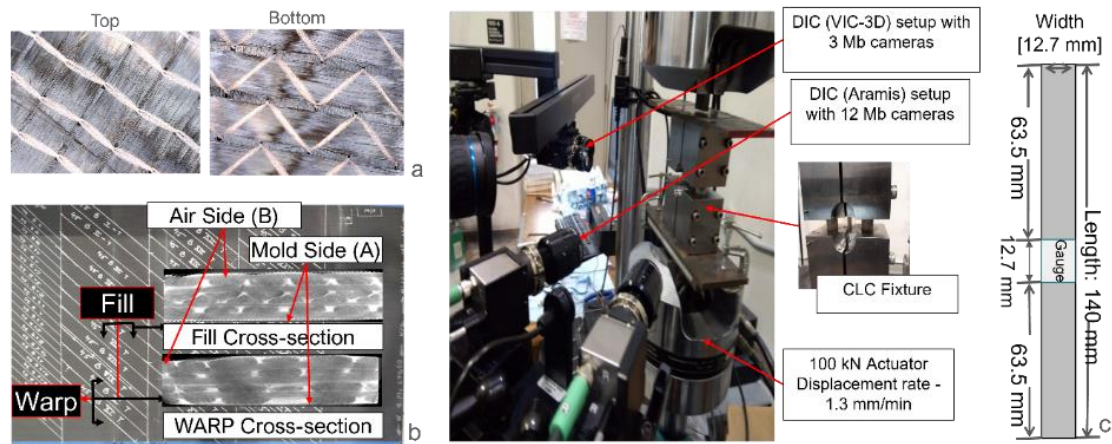


Figure 19: a) DEVOLD LT 650 carbon fiber fabric b) Manufactured composite panel from the fabric c) Test setup and sample dimensions.

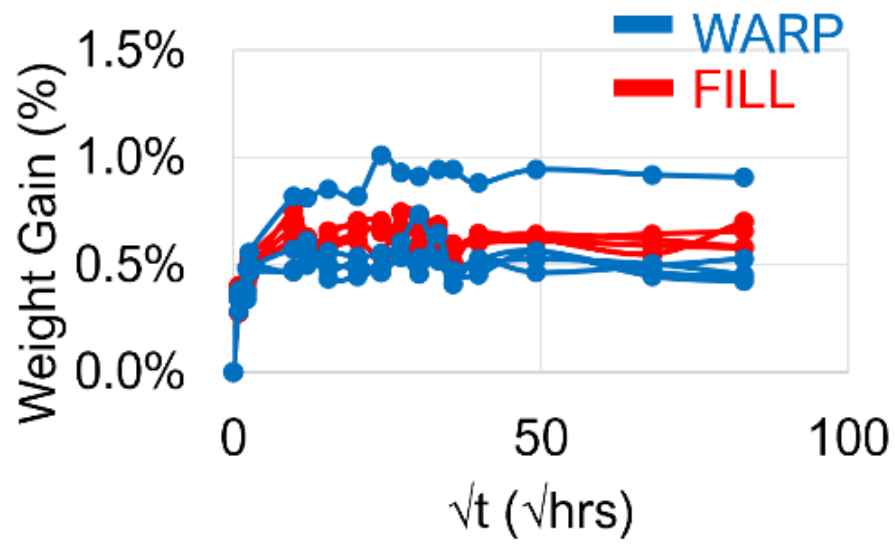


Figure 20: Mass gain due to sea water diffusion vs square root time

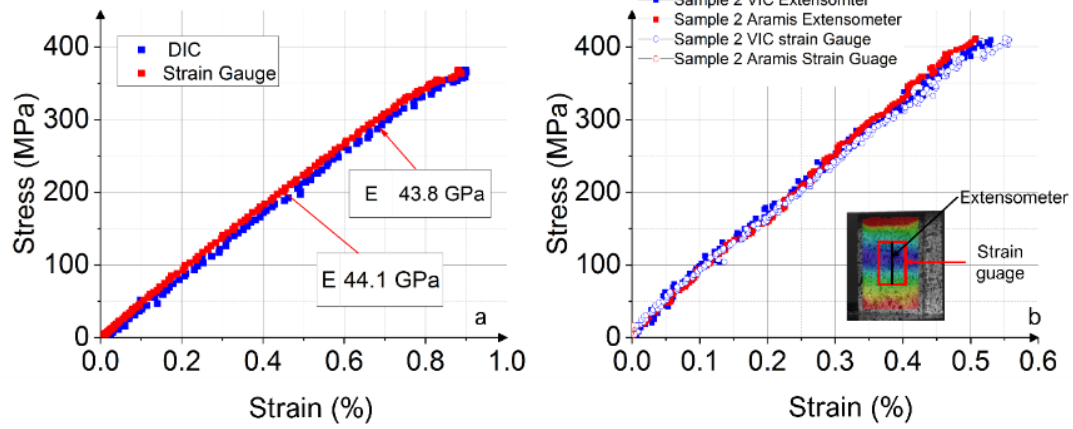


Figure 21: Strain validation by comparing a) VIC 3D and Strain gauges b) VIC 3D and GOM ARAMIS

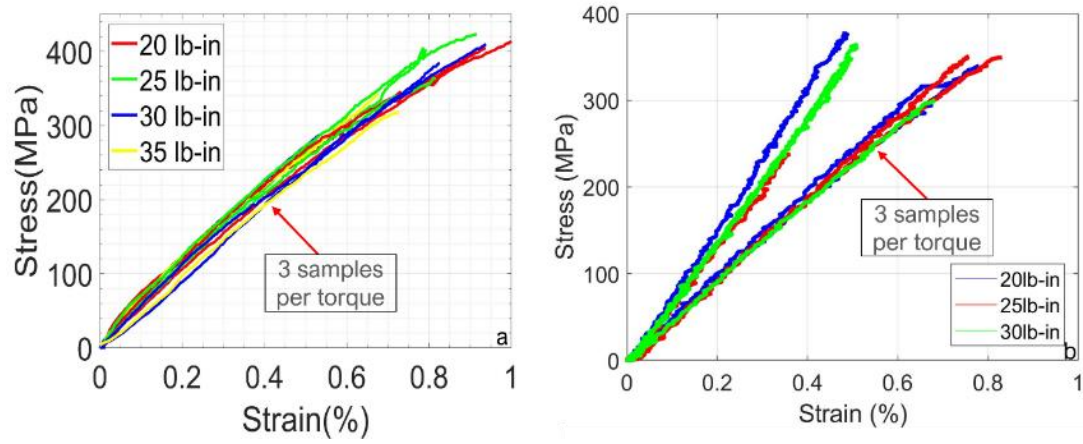


Figure 22: Effect of torque on a) Warp coupon b) Fill coupons.

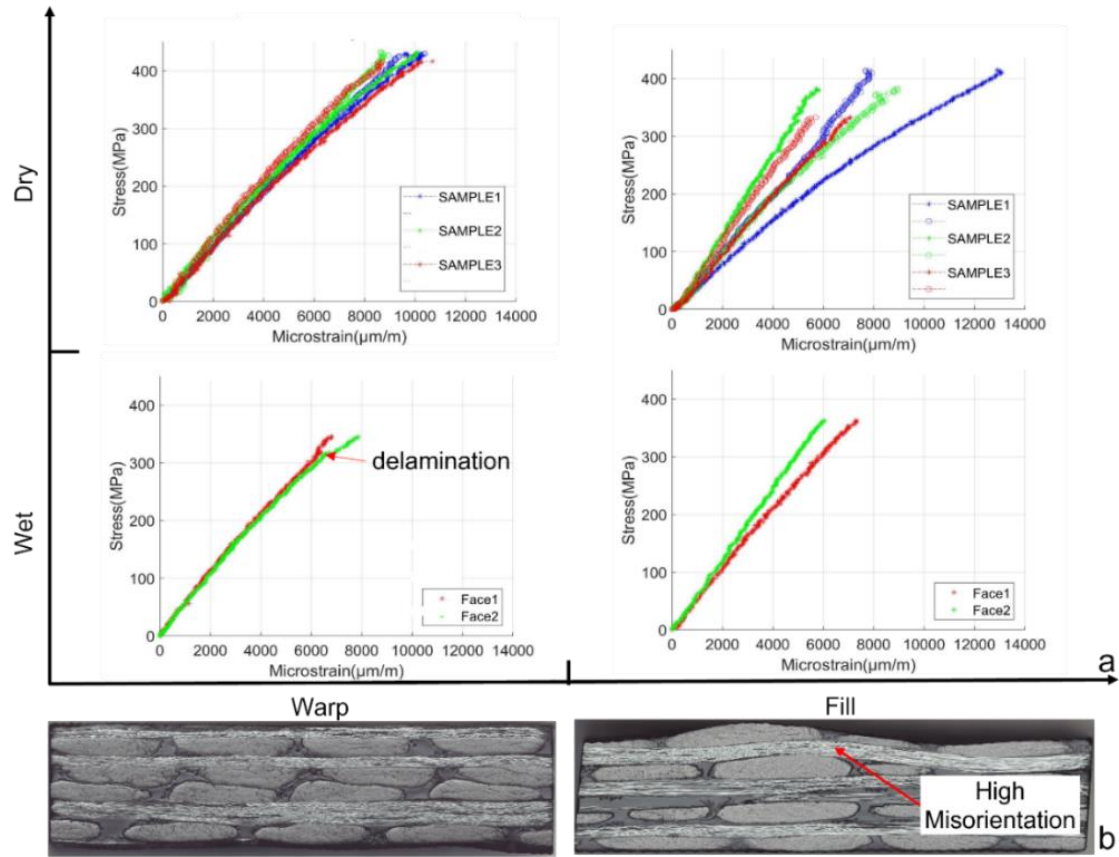


Figure 23: a) Stress-Strain curves for dry aged and saturated warp and fill extracted coupons b) Optical image of fill and warp extracted coupon in the loading direction

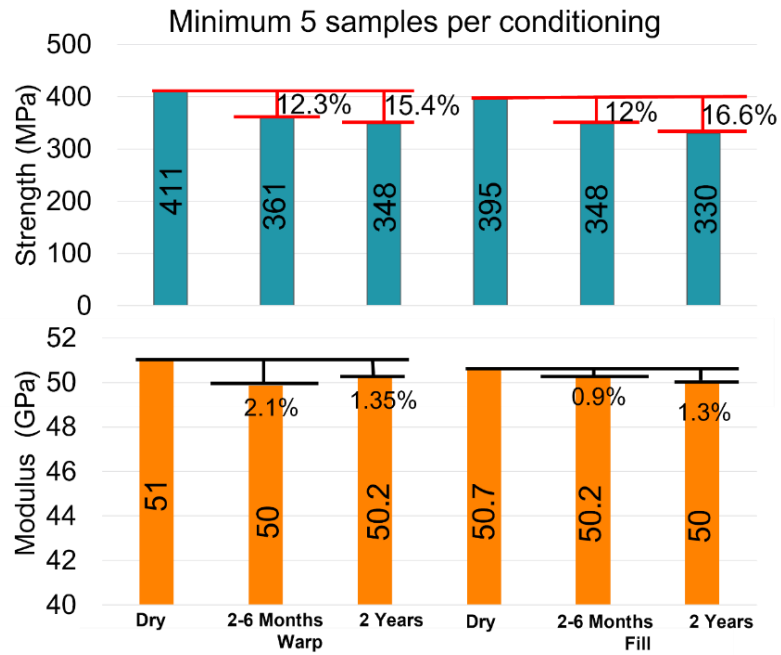


Figure 24: Effect of seawater on the compressive properties of CF/VE

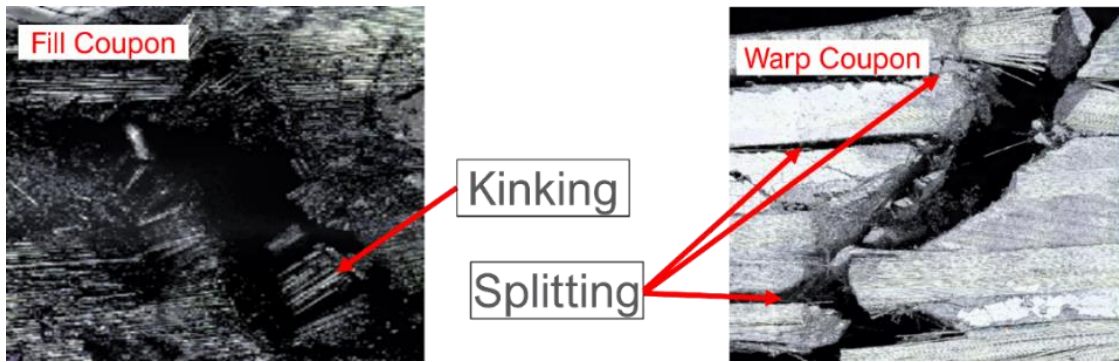


Figure 25: Post failure microscopy of dry warp and fill coupons

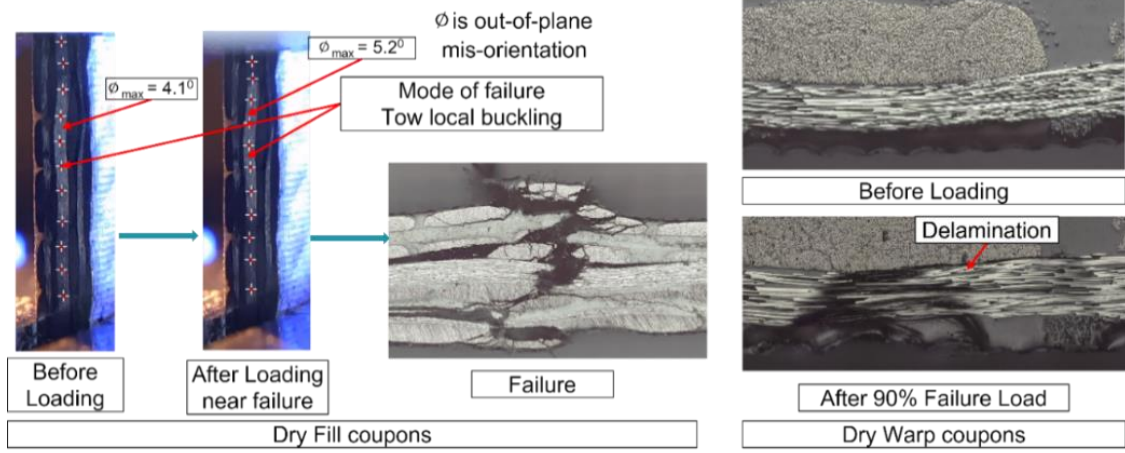


Figure 26: Failure initiation and evolution in fill and warp coupons

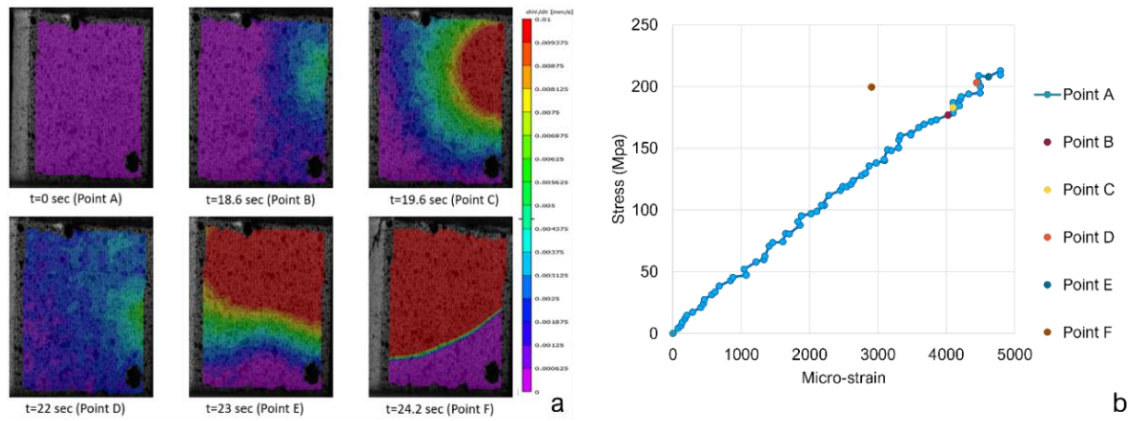


Figure 27: a) Failure evolution in saturated warp extracted coupon using the out-of-plane velocity from DIC, b) resulting stress-strain curve.

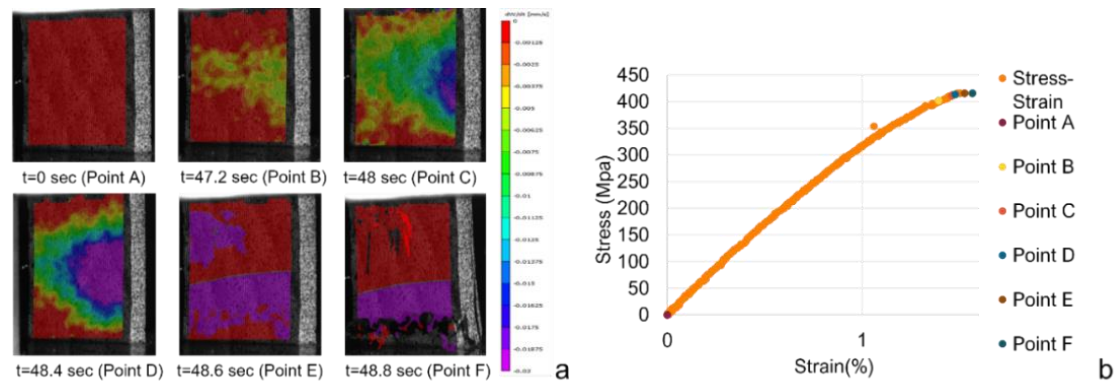


Figure 28: a) Failure evolution in saturated fill extracted coupon using the out-of-plane velocity from DIC, b) resulting stress-strain curve.

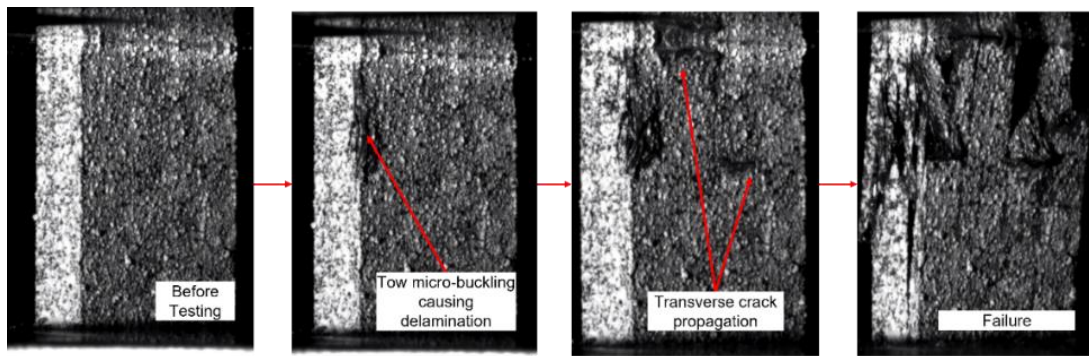


Figure 29: Failure evolution in saturated fill extracted coupon using the DIC images.

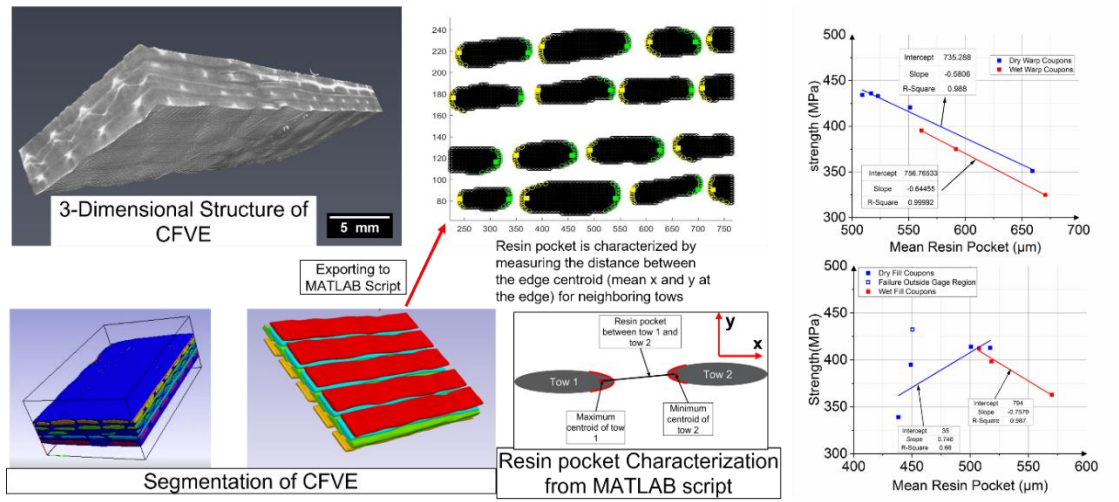


Figure 30: Mechanical Properties as a function of resin pocket

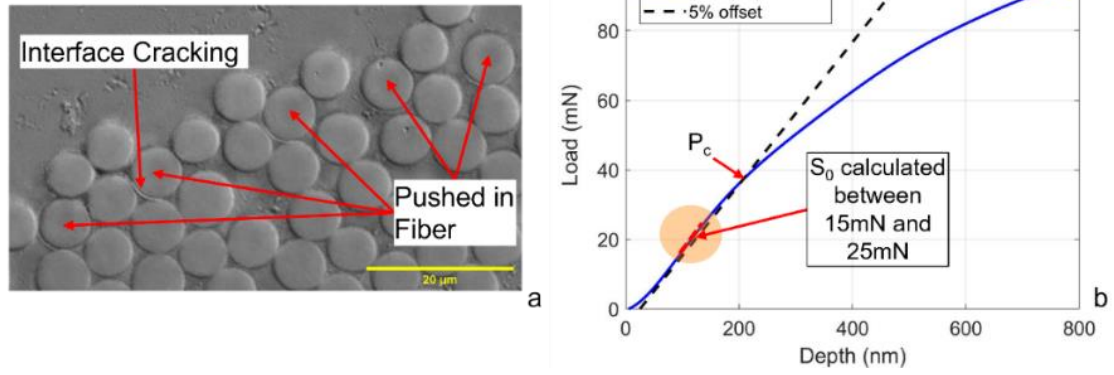


Figure 31: a) Optical image showing pushed in fibers, b) Example of a load-depth curve.

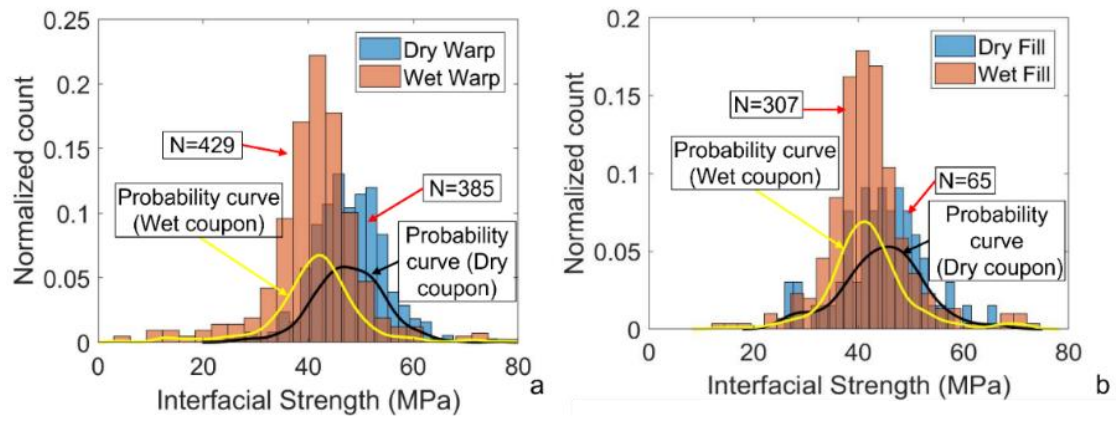


Figure 32: Interfacial shear strength obtained via single fiber push-in tests for dry aged and saturated a) Warp extracted coupons b) Fill extracted coupons.

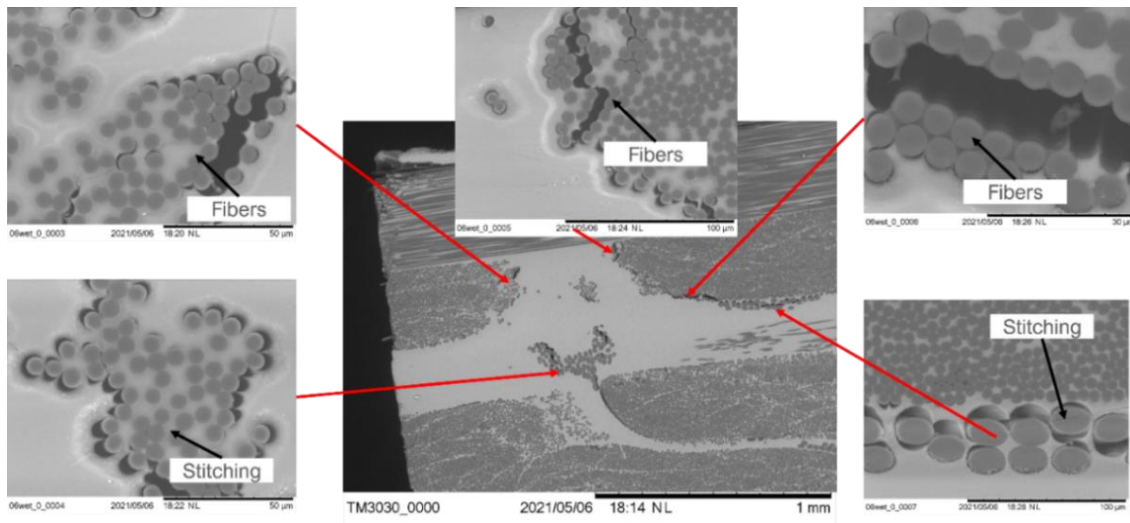


Figure 33: Coupon exposed to hygrothermal conditioning for 15 years.

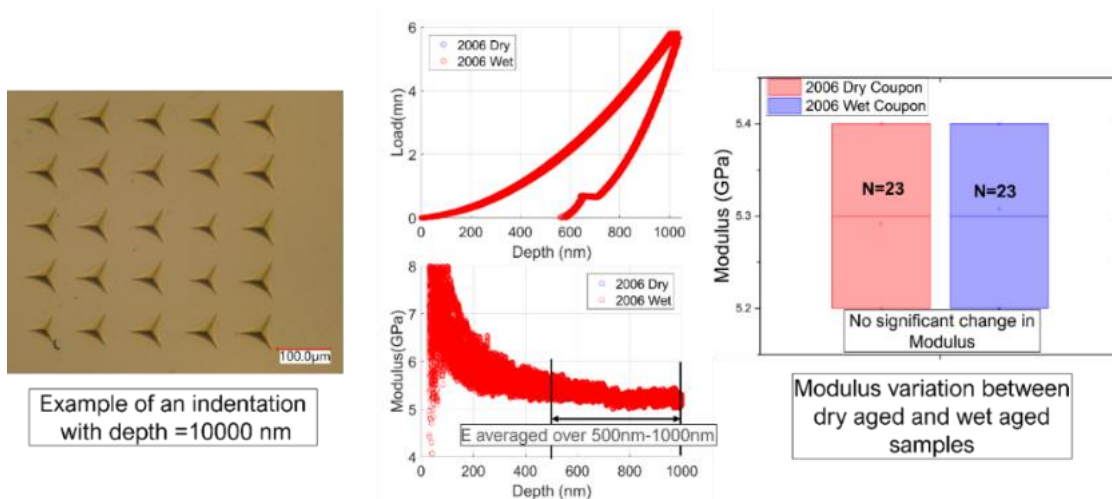


Figure 34: Mechanical properties obtained via nanoindentation of vinyl ester.

**CHAPTER 3: DEGRADATION IN INTERFACIAL SHEAR
STRENGTH OF CARBON FIBER/ VINYL ESTER COMPOSITES
DUE TO LONG-TERM EXPOSURE TO SEAWATER USING PUSH-
OUT TESTS.**

This chapter is based on a paper published by Vivek Chawla and Dayakar Penumadu: V. Chawla, S.B. Puplampu, N.J. Murray, D. Penumadu, Degradation in interfacial shear strength of carbon fiber/ vinyl ester composites due to long-term exposure to seawater using push-out tests, *Compos. Sci. Technol.* 241 (2023) 110131. doi:10.1016/j.compscitech.2023.110131. My contributions include experiment planning and data acquisition, data processing and most of the writing.

Abstract

In this study, single fiber (~7-micron diameter) push-out tests are conducted to evaluate hygrothermal effects on the interfacial shear strength (IFSS) of carbon fiber/vinyl ester (CF/VE) composites. Hygrothermal conditioning is achieved by saturating samples in simulated seawater at 40°C for two years. An investigation has been conducted on the preparation, validity, and interpretation of the push-out test results. First, the authors present a polishing methodology that results in thin films of CF/VE composites in the thickness range of 15 to 120 microns and produces an average 41.2 percent drop in IFSS due to long-term hygrothermal exposure. Using scanning electron microscopy (SEM), we show that during the push-out tests, the failure initiates locally at the zone of minimum bond strength at the bottom (away from the indenter), then propagates along the length of the interface. The influence of radial tensile stresses originating due to bending is found to be negligible. Using the SEM imaging of the pushed-out fibers, we validate the failure of the interface to be the primary source of failure. The associated results are found to depend on the thickness of the interface. We then reevaluate the results using the Weibull distribution, knowing that the failure mechanism is analogous to the weakest link theory.

The results show a 25.5 percent drop in the IFSS of the CFVE composite, measured at an infinitesimal scale due to long-term to hygrothermal conditioning at 40°C. A significant drop in IFSS was observed after reheating above glass transition temperature (T_g) and cooling.

Introduction

Fiber-reinforced polymer composite has gained significant attention for its applications in structural components in the aerospace [110,111], automotive [111], marine [2,3], and sports [112] industries. Typically, the fiber volume to interface area ratio varies as a fraction of $r/2$. Thus, a composite material consisting of a large volume fraction of reinforced fibers leads to a large interface surface area per unit volume. The interface transfers the load from the matrix to fibers and thus controls the mechanical performance of the composite. Interfacial shear strength (IFSS), a measurement of the bonding between the fiber and matrix, has been shown to affect the tensile [56,57], compression [58–60], and impact [61][62] properties of composites, whether subjected to static or fatigue loading. Despite the importance of IFSS, there is no consensus about the most accurate technique for characterizing the interface's mechanical properties.

Various tests have been proposed in the literature to evaluate the IFSS. The single fiber fragmentation test [63] is often used, but this has a significant drawback in evaluating the interfacial shear strength of an independently made fiber and matrix system; the ramifications of the manufacturing process are not considered during single-fiber fragmentation. The fiber-matrix system and the interface experience varying proportions of residual stresses depending on the local microstructure, processing conditions, and the

general manufacturing process. Recently, push-out tests [64] [65][66][126], push-in tests [64][67][68], and micro bond tests [127] have been proposed to evaluate the interface. The proposed techniques offer different sample configurations and loading geometries and thus involve disparate stress states at the interface. Micro bond tests involve pulling a fiber out of a bead of the matrix and, similarly to single fiber fragmentation tests, do not consider the effect of local microstructure, processing conditions, and manufacturing process. For push-in tests, where the fibers embedded in the matrix are pushed to cause decohesion, the effect of the surrounding matrix, the applicability of shear-lag model, and the difficulty in identification of load corresponding to the initiation of debonding, results in only qualitative analysis of the interface [128]. Recently, Zhou et al. [129] experimentally showed that the interfacial strength obtained from push-out tests using a simple equilibrium equation can provide reliable measurements of bond strength by comparing the results with single fiber fragmentation tests. Moreover, other studies have successfully used average shear to evaluate the interfacial shear strength [64,130]. Therefore, among these techniques, the push-out technique offers high promise because of its simple mechanical approach and its ability to calculate the interfacial strength of the manufactured composite. The difficulty of thin films preparation required for testing presents the main drawback for push-out tests.

Once a suitable sample is prepared, an individual fiber within the thin sheet of composite is loaded with a flat tip. The fiber first deforms due to the combined fiber and interfacial elastic deformation. The applied force eventually leads to the fracture of the fiber/matrix interface. When all the interfacial bonds break, a catastrophic failure occurs. Then, by

frictional sliding, the fiber is pushed out of the thin sheet. The experiment requires a vacant volume underneath the fiber being pushed out. Depending on the available space, the fiber might undergo bending. To evaluate the IFSS, bending should be minimized to eliminate the effect of radial and hoop stresses on the test results. The effect of bending upon the IFSS can also be evaluated using the push-out tests; however, that is outside the scope of this study. Here, the IFSS is evaluated by calculating the average shear stress τ at the instability load, which is given by:

$$\tau = \frac{P_c}{2\pi r e} \quad -(3.1)$$

where P_c is the critical instability load corresponding to the breaking of all interfacial bonds, r is the fiber radius, and e is the thickness of the material.

The mechanics involved during the fiber push-out is more complicated than the one captured by the simple equilibrium equation 3.1. Failure in push-out tests is not catastrophic but is progressive. In push-out tests, the critical shear stress is first achieved near the zone of load application, causing initial debonding. The debonding then propagates along the length of the interface while frictional sliding occurs in the debonded region. Finally, the load increases until instability occur, at which point the entire length of the fiber gets debonded.

Nevertheless, the average shear stress given by equation 3.1 is used in this study as it has been shown to correspond reasonably well with the fragmentation tests [129]. In this work, the authors first present a polishing methodology to prepare thin films suitable for push-out testing. The deformation mechanism associated with push-out testing is identified, and the effect of thickness upon the interfacial strength is evaluated. The primary objective of

this work is to quantify the impact of long-term exposure to seawater upon the interfacial strength of carbon fiber vinyl ester (CFVE) composite manufactured using vacuum assisted resin transfer molding (VARTM). The details of the manufacturing process can be found in the work by Shivakumar et al. [131]. The sandwich structures made from these composites are under consideration for naval applications by the U.S. navy. From an experimental perspective, this work identifies and answers the challenges associated with conducting and analyzing push-out experiments for polymeric composites where the interfacial shear strength does not represent a value but rather a distribution.

Materials

The composite investigated in this study is manufactured using the Devold AMT AS stitched bonded fabric, LT650-C10-R2V, an equibiaxial non-crimped fabric consisting of Toray T700 carbon fiber with a diameter of 7 μ m. Dow chemical's Derakane 520A-40 brominated vinyl ester resin, formulated for VARTM, is used as the matrix material. The panels are cooled down from a temperature of 71.1 °C at a rate 0.56 °C/min to room temperature during manufacturing. The details of the manufacturing process can be found elsewhere [131]. This composite is being investigated for consideration for naval applications by the U.S. Navy. The interfacial strength is evaluated using dry (unconditioned) coupons and coupons that have been soaked in seawater for two years at a controlled temperature of 40°C (wet coupons). The dimensions of the seawater-soaked coupons are 0.5" x 0.1" x 5.5". The CF/VE samples under investigation saturate after two months [132]. Thus, any degradation evaluated in this study is a consequence of saturation with seawater or the chemical degradation that results from long-term exposure

to seawater. Figure 35a shows an example microstructure of a polished dry coupon. The sample consists of four layers of fabric with an orientation layup of $[0/90]_{2s}$.

Moisture saturation often induces matrix swelling and plasticization. in matrices of relatively high hydrophilicity [115]. Swelling is a phenomenon where the matrix attempts to expand due to seawater absorption but experiences negative pressure due to being bound by the almost undeformed fibers; this results in residual radial stresses that can lead to interfacial de-cohesion. *Plasticization* reduces the glass transition temperature of the matrix, T_g , often resulting in softening [21]. Based on the differential scanning calorimetry (DSC) curves (Figure 36), the T_g obtained for dry and wet coupons is 114 °C and 116 °C, respectively, which means that no plasticization of vinyl ester occurs when exposed to seawater for an extended period of time.

Methods

Focused Ion Beam (FIB) Cut samples.

Notches, ranging from 3 microns to 30 microns, are prepared using a focused ion beam (FIB) to understand the push-out deformation mechanism and to evaluate the IFSS at very shallow depths ($<10\mu\text{m}$) for dry samples. FIB notches are prepared by creating a notch 40 μm in length and ground using a 3nm probe for 30 minutes, followed by a 2nm probe for 10 minutes. The thickness of the notches is measured using scanning electron microscopy (SEM). In case of uneven thickness along the length of the notches, the thickness of the pushed-out fiber is calculated by interpolating the measured thicknesses.

Samples prepared using polishing.

Thin sections (15–150 μm) of the samples are prepared using polishing. Each sample's individual location and thickness are determined using a laser microscope (Keyence VK x250). Due to the non-trivial nature of sample preparation and testing, the authors visit the polishing procedure in detail. The samples are hand polished using a hand grinder, model 160 obtained from E.A. Fischione Instruments Inc (Figure 37a and Figure 37b), and a Buehler MetaServ 250 auto polisher (Figure 37c). First, using a TechCut 4 thin section cutter (supplied by Allied High-Tech Products, Inc), 2mm thin sections are cut from 0.5", *0.1", and *5.5" dry and wet samples. The samples are then mounted on the sample holder of the hand grinder using the high-temperature crystal bond designated as 509 Crystalbond™, provided by Electron Microscopy Sciences®. Exposure to high temperature can alter the chemistry of the samples, so once the crystal bond on the sample holder melts, the system is allowed to cool to slightly below 65°C (just above the glass transition temperature of the crystal bond). The sample is then mounted on the sample holder and quenched to accomplish rapid bonding with no thermal damage to the sample. The mounted sample is ground using SiC abrasive papers obtained from Buehler. The grinding is done sequentially from rough (320) to medium (600) grit, followed by finer grit (1000). At this point, the samples are successively polished using 3 μm and 0.5 mm diamond lapping film, obtained from Allied Tech, Inc. No polishing suspension is used, as it was observed that using the polishing suspension results in uneven sample topography. The observed unevenness could be caused by the variable removal/polishing rate on account of the high gradient in hardness between carbon fibers and vinyl ester.

Once the first face of the sample is polished, the sample is removed from the sample holder. At this point, a U.S. 625-grade mesh gasket is mounted on the sample holder. The sample is mounted back on the mesh (which rests on the sample holder), with its polished face in contact with the mesh. The mounting procedure is analogous to that used prior to the first polishing phase. The use of a mesh improves the odds of successfully removing the sample after polishing. It was observed in prior trials that not using the mesh caused the samples to shear below a certain thickness because the samples sat on a rigid substrate (i.e., the sample holder). The compliance of the mesh causes the samples to bend rather than shear. However, the consequence of using the mesh is a resulting uneven topography of the sample surface. For every push-out test conducted, the thickness of the pushed-out fiber must be identified. For this, the authors accurately measured the fiber's thickness using a Keyence VK 250 laser microscope.

The polishing of the second face follows a similar protocol as the first face with one caveat: only worn-out abrasive paper and diamond lapping films are used in the grinding and polishing. It was observed that using a new abrasive paper or diamond lapping film at a shallow thickness caused the samples to shear. Figure 35b shows an example of a polished thin film mounted on the supporting mesh and ready for push-out testing.

Push-out testing is carried out on a Nanomechanics iMicro nanoindenter with a load capacity of 1000 mN and displacement range of 40 μm . The instrument is equipped with a truncated conical flat tip with an initial diameter of 5.5 μm and a 60° cone angle. The details of the instrument and the tip are shown in Figure 38. Thin sections ranging between 3.6 μm and 30.6 μm are prepared using FIB. Samples with a thickness less than 10 μm are

tested within the SEM using the Nanomechanics NanoFlip instrument with a load capacity of 50mN and a displacement range of 20 μm . This is done because it was observed that the thickness is small enough for the interface to fail within the 50 mN load limit. Testing in SEM allows for precise probing at the center of the fibers, which is required because of the limited number of fibers within the notch.

Push-out testing requires some empty space beneath the sample to allow the fiber to be pushed out. The necessary empty space is created by mounting the samples on a US 625-grade mesh gasket with a spacing of 75 μm (the same as the one used for polishing). The samples are then indented/probed using the flat tip. The samples are loaded at 5 nm/s, 20 nm/s, and 50 nm/s to understand the effect of the displacement rate on the measured IFSS. The testing is conducted with a set of indentation arrays separated by 200 μm within each tow of the prepared sample. Each array consists of 5 by 5 indents separated by 30 μm . For this, 30 μm ($> 4 \times \text{Fiber diameter}$) spacing is used to ensure the results are not affected by neighboring tests. A total of more than 1,000 tests are conducted for each sample. The tests are conducted stochastically within the fiber tows. Successful tests are identified using the post testing microscopy of each array. Laser microscopy is then conducted to identify sample thickness at each successful test location. The number of successful tests thus varies from sample to sample.

Results

In push-out testing, the flat tip contacts the fiber while the interface transfers the applied load to the matrix. The assumption with the test is that for the given thickness, the load required to break the last interfacial bond is less than the load corresponding to the ultimate

shear strength of the matrix. Furthermore, the test is assumed to be quasi-static and therefore assumed to be independent of the loading rate. Hence, before reporting the test results, the authors conduct push-out tests for two samples with loading rates of 5 nm/s, 20 nm/s, and 50 nm/s. The iMicro system has a depth resolution of 0.04nm. Even though it is possible to go slower than 5 nm/s, the time required to evaluate the interfacial strength for a particular sample statistically increases linearly with the decrease in loading rate. For example, assuming the tests are carried out to a target depth of 1,000 nm, the time required to load the fibers increases from 20 seconds to 200 seconds for 50 nm/s and 5 nm/s displacement rates, respectively. For hundreds of tests, the difference in time adds up. Thus, the tests should ideally be performed with the maximum possible displacement rate while maintaining the quasi-static assumption. Therefore, three dry samples are tested at varying displacement rates to evaluate the effect of displacement rate upon the interfacial strength.

Figure 39 shows the effect of the displacement rate on interfacial strength. The two-sided student's t-test comparison of 20nm/s and 50nm/s tests with 5nm/s tests results in a z-value of 1.32 and 0.74, resulting in a confidence interval of 70 percent and 50 percent of significant difference in observation sets. Therefore, based on

Figure 39, there is no significant difference in the measured interfacial strength with the changing displacement rates.

An example load-depth curve obtained via push-out tests of dry samples is plotted in Figure 40a. The resulting interfacial shear strength corresponding to the dry and seawater-soaked samples is shown in Figure 40b. Negligible bending may be observed based on the load-

depth curve because the fibers begin taking on load immediately after loading; thus, the effect of bending upon the interfacial strength is not evaluated. The values are reported for a displacement rate of 50 nm/sec. For each CFVE coupon, the interfacial strength is calculated from a minimum of 50 tests. With most coupons, the number of successful tests was more than 200.

As seen from Figure 40b and Table 7, there is a 41 percent drop in interfacial strength due to long-term exposure to seawater. A decrease in interfacial shear strength as a function of exposure time to water has been reported in the literature [133]; therefore, the above result is not surprising. The higher data scatter for the wet coupons is perhaps an indication of different degrees of local degradation. Even though the results seem plausible, a few important considerations must be reviewed to validate the results. For example, for all tests, it is assumed that the instability load refers to breaking the last interfacial bond, but instability might be a consequence of the matrix's shear failure. As mentioned previously, the thickness of the sample changes from one location to another; thus, in the above results, the interfacial strength is assumed to be independent of the thickness.

The literature shows that the assumption of the invariance of interfacial strength with variation in thickness is valid [65]. However, the observations made in this study indicate the contrary. Figure 41a and Figure 41b show the interfacial strength as a function of thickness for a dry coupon and an example of the set of 25 tests performed at a location within the tow. Based on Figure 41b, there were a few bad tests in which the tip may have been eccentric with respect to the fiber, which may have contributed to the interfacial failure of more than one fiber. Since judging a good test based on the load-depth curve can

be misleading, it is necessary to confirm the individual quality of the tests by means of optical imaging. Figure 41a shows that interfacial strength decreases as thickness increases. The data points in red correspond to the measured IFSS for the FIB cut dry samples. Figure 42 shows the geometry of the notches obtained via FIB cutting and polishing, along with the thickness of the interface. There is no apparent difference in IFSS for the FIB-cut or polished samples. Figure 42e shows the resulting load-depth curve obtained from the push-out testing of the FIB-cut fibers. Like the polished samples, the bending was negligible in the FIB samples. The IFSS represents the maximum stress required to break all the interfacial bonds. Assuming bond strength to vary with a normal distribution, it is reasonable to surmise that at shallow thicknesses, the scatter in the bond strength density will be higher, and thus there should be a high variance in the IFSS. This is demonstrated in Figure 41a.

Conversely, as thickness increases, the variation in bond strength across the length of the interface parallels the overall normal distribution. Thus, the scatter in the measured IFSS decreases as thickness increases. This is shown in Figure 41b. The dependency of the IFSS upon thickness implies an inaccuracy in using average and standard deviations to calculate the difference between the IFSS as corresponding to dry and wet coupons. For example, a sample with a higher average thickness would show a lower IFSS due to the inverse relationship observed between thickness and IFSS. Thus, the results reported in this work require a more elegant treatment to account for sample thickness.

Discussion

Deformation mechanism

The mechanics involved in an ideal push-out test are uncomplicated, provided that uniform shear stress is achieved along the length of the fiber. Assuming a flat cylindrical tip is in contact with a transversely isotropic fiber embedded in an isotropic matrix, the resulting stress stemming from the applied load by a rigid cylinder will result in the shear loading of the interface and the matrix. Because there is a competition between the matrix and interface shear failure, the mode and mechanism of failure must be identified to validate the results. Due to the interface being surrounded by a matrix, it is difficult to observe the failure initiation and evolution.

In this study, the authors address the above issue by altering the geometry of the problem. A $2 \times 12.7 \times 12.7 \text{ mm}^3$ sample is cut from a dry coupon and polished to reveal the microstructure. A $20 \times 20 \times 3 \text{ }\mu\text{m}^3$ notch is then cut using FIB as shown in Figure 42. This notch represents the lowest t/L (t being the thickness and L being the span) ratio investigated in this study, resulting in the maximum bending effects. The fiber at the edge of the notch is then tested using the flat tip, as shown in Figure 43. The testing geometry introduces free edge effects in the mechanics of the problem, thereby increasing the probability of failure initiation at the free surface. Even though the geometry chosen adds another variable in the push-out mechanics, the deformation initiation and evolution should remain the same, provided the stress corresponding to failure at a higher thickness remains lower than the stress required to cause matrix shear failure. The testing is performed at a displacement rate of 20 nm/s to improve the probability of observing the deformation initiation and evolution.

Figure 44 shows the load-depth curve and depth-time curve obtained from the test. To the best of the authors' knowledge, this is the first evidence of capturing the sequence of failures during a push-out test for a carbon fiber-based composite. The failure initiates at the bottom (away from the indenter tip) at around 60 percent of the maximum load at the interface. This initiation of failure at the bottom has been reported in the literature for other materials [134][135][136]. The bottom debonding initiation could either be because of Mode I stresses (developed due to bending) or interfacial shear stresses along the length of the interface [134]. The literature demonstrates that an E_f/E_m (fiber modulus/matrix modulus) ratio of greater than 3.5 results in debonding initiation at the bottom [136][137] because of the higher residual stresses that follows more significant differences in the matrix and fiber modules. Further, the CFVE has an E_f/E_m ratio of around 65. The negative coefficient of the thermal expansion (CTE) of T700 carbon fiber somewhat diminishes the residual stresses. Nevertheless, if the value of the IFSS obtained is highly dependent on the radial tensile stress, the IFSS will increase as thickness increases [134]. This contrasts with the observations from this study.

Kallas et al. [135] showed that a pure shear state can be achieved during push-out testing by maximizing specimen thickness. However, as thickness increases, the probability of failure transitioning from push-out to push-in tests increases, which limits the maximum allowed thickness. Asthan et al. [138] and Chen et al. [136] report $2t/L = 0.75$ (t is the sample thickness and L is the span) to be the critical sample thickness for a successful push-out test. For a span of 75 μm (mesh size), the minimum thickness required for a successful push-out test is 28.13 μm , which satisfies most of the tests conducted for samples made via

polishing. As shown earlier, no considerable differences were observed between the samples made via polishing and the FIB-cut samples. Therefore, results corresponding to all the thicknesses investigated in this study are valid. The failure after initiation propagates along the length of the interface until the ultimate failure load is reached, at which point the stress is high enough to break all the bonds. The initiation of failure away from the loading is significant because if the failure were to commence near the vicinity of the loading, the test results could be a function of load introduction. Knowing that the failure initiates locally on one edge and is not highly influenced by the Mode I stresses, we can conclude that the failure is a consequence of weak local interfacial strength. This failure mechanism is analogous to the assumption of the Weibull “weakest-link” theory, which states that the strength of a chain is the function of the weakest link within the chain [139]. The effect of varying bond strengths along the length of the interface on the IFSS is one aspect of push-out tests that has not been investigated in the literature for any material. The authors address this issue in Section 3.2.2.

The above results highlight the deformation mechanism of interfacial failure in push-out testing. However, for the results to be valid, the interface failure—and not the matrix failure—must be ensured. Thus, we remove a tested sample (same dry coupon from Figure 41) prepared via polishing from the mesh, clean it using acetone, then image using SEM to observe the pushed-out fibers from the bottom end. Figure 45 shows the SEM results of the pushed-out fibers. As seen in Figure 45, there is a clean interfacial break for all the fibers. The clean interfacial break validates the results for push-out tests, as this shows that the failure occurs in the interface only. Figure 46 and Table 8 show the laser image that

corresponds to the same tests, along with the resulting fiber pillar heights. As seen from Table 8, the pillar height measured by laser microscopy is greater than the height expected from the load-depth curve; generally, this discrepancy increases with the height of the micropillar. The above result perhaps indicates the frictional sliding of the fiber after the tip is retracted, thereby confirming the breaking of all the bonds that form the interface. Given that the fiber slides, the height difference is likely a consequence of the higher momentum associated with fibers of a more significant height.

Most fibers show a clean interfacial break. However, some pushed-out fibers located in a tow with a higher thickness ($>60\text{ }\mu\text{m}$) are engulfed in the matrix after failure, as shown in Figure 47. Note that this is the same coupon for which the clean interfacial break was obtained in Figure 45. One possible explanation for this behavior is the shear failure of the matrix. This study's results show an inverse relationship between the IFSS and the thickness of the interface. Assuming the matrix to be homogeneous and isotropic, a higher IFSS at a shallower depth implies a higher probability of matrix shear failure because the matrix's ultimate shear strength remains the same. If this is the case, matrix engulfed fibers should be observed for low thickness push-out tests. However, the observations made in this study are just the contrary. At higher thicknesses, purely interfacial failure (i.e., crack propagation along the interface) requires the fiber to be highly aligned with respect to the loading direction. While a small misalignment would not be a significant concern at shallower thicknesses, with increasing thickness the path of least resistance for a crack propagating along the interface may traverse into the matrix, thereby causing a failure characteristic of the fiber enclosed within the matrix. The IFSS data points corresponding

to this type of failure mechanism are illustrated by a dark outline in Figure 41a. Figure 41a shows no significant difference between the IFSS obtained from the two post-failure classifications. Thus, the data points corresponding to interface failure of the matrix-enclosed fibers are considered valid. The above result is important because it justifies the use of push-out testing for “nearly aligned” fibers in random fiber composites where the alignment can only be guaranteed within a few degrees based on the ellipticity of the fibers.

Interpretation of results

The results are interpreted using the simplest Weibull two-parameter model. Per Weibull’s theory, the chain’s strength is a function of the weakest link, and therefore is inversely proportional to the number of links. Assuming the stress state to be uniform in a large volume of material, the failure will initiate at the location of the weakest unit. Consequently, the overall strength is a function of the weakness of the most prominent flaw. Defects tend to be randomly distributed, and larger volumes have a higher probability of containing a more significant defect, giving rise to size-dependent properties as observed in the deformation mechanism of the push-out tests. As demonstrated by Henstenburg et al.[140], a simple power-law relationship shown in Equation 3.2 is adopted for flaw population intensity ($\mu(\sigma)$).

$$\mu(\sigma) = \frac{m}{\sigma_0 V_0} \left(\frac{\sigma}{\sigma_0} \right)^{m-1} \quad (3.2)$$

where σ_0 , V_0 , and m are positive constants. This choice of $\mu(\sigma)$ yields the Weibull distribution for the IFSS with volume V . Upon integrating, the probability of survival can be obtained via generalized Equation 3.3. If the stress is assumed to be uniform, Equation 3.3 can be reduced to Equation 3.4. The conceptual interpretation of $(1/V_0)(\sigma/\sigma_0)^m$ is the

average number of flaws per unit volume with a strength less than or equal to σ . For two specimens of volume V_1 and V_2 under constant stress σ_1 and σ_2 at failure, the relationship between V_1 , V_2 , σ_1 , and σ_2 can be obtained using Equation 3.4 by assuming an equal probability of failure.

Conflicting results have been reported for brittle materials using the approach of Equations 4 and 5, with most studies finding that the use of Equations 3.4 and 3.5 accurately predicts the size effect [139]. Meanwhile, Yentl et al. [141] identify the issues related to the Weibull modeling of composites. More specifically, they point out that extrapolating results from the tests conducted at length in the order of millimeters to gauge length in the order of micrometers does not translate when using the Weibull equation. Regardless, push-out tests provide the advantage of using the two-parameter Weibull distribution because the results are not extrapolated at different lengths. Rather, results at different volumes are used to fit the Weibull parameters, making the analysis prone to smaller error. However, to use the Weibull distribution for push-out tests conducted at different volumes, Equation 3.4 must be rewritten as Equation 3.6. Evaluating the results this way allows the use of a parameter $\sigma V^{1/m}$, an effective scale parameter, which makes the comparison between the IFSS obtained at different volumes possible. However, this requires the value of the shape parameter (m) to be known *a priori*. This is accomplished iteratively by assuming a value of m , then replacing it with the value of m obtained via the slope of the $\ln(\sigma V^{1/m}) - \ln\left(\ln\left(\frac{1}{1-P}\right)\right)$ curve, where σ is replaced by τ to represent the IFSS. The process is repeated until the error between the assumed and obtained value of m is less than 0.01. For most of the samples, the solution converges in five iterations.

$$P(s) = \exp \left[- \int \left(\frac{\sigma}{\sigma_0} \right)^m \frac{dV}{V_0} \right] \quad -(3.3)$$

$$P(s) = \exp \left[- \frac{V}{V_0} \left(\frac{\sigma}{\sigma_0} \right)^m \right] \quad -(3.4)$$

$$\frac{\sigma_1}{\sigma_2} = \left(\frac{V_1}{V_2} \right)^{-1/m} \quad -(3.5)$$

$$P(s) = \exp \left[- \left(\frac{\sigma}{\sigma_0} \left(\frac{V}{V_0} \right)^{1/m} \right)^m \right] \quad -(3.6)$$

Figure 48a shows an example of the $\ln(\tau V^{1/m}) - \ln\left(\ln\left(\frac{1}{1-P}\right)\right)$ plot for a dry sample. A good correlation (>0.98) is observed for all samples. Here, the value of the Weibull shape represents m , while the Weibull scale parameter represents $tV^{1/m}$. Figure 48b and Figure 48c show the cumulative probability distribution and probability density function plots for dry and wet coupons, respectively. As can be seen from the Figure 48, there is a higher degree of scattering in wet coupons, while the maximum $tV^{1/m}$ required to reach the cumulative probability of failure for wet coupons is lower than for dry coupons. This indicates that long-term exposure to seawater causes the fiber-matrix interface to degrade. The degradation is quantified by reporting the IFSS values at thicknesses of 25 μm , 50 μm , and 75 μm . Figure 49 and Table 9 show the degradation results in the fiber-matrix interface as corresponding to different thicknesses. The degree of degradation increases when thickness ranges from a 27 percent drop at 25 μm to 31 percent at 75 μm . Linear extrapolation results in an IFSS of 73.2 MPa and 54.5 MPa for dry and wet coupons, respectively, with a 25.5 percent reduction in the IFSS due to long-term exposure to seawater at an infinitesimal scale.

As shown earlier, the failure in push-out tests is progressive. As the crack propagates, the debonded region increases and the contribution of frictional stresses increases as the load increases toward instability. Frictional stresses are a function of residual stresses between the fiber and matrix (originating because of thermal expansion mismatch between matrix and fibers). Moisture saturation causes an increase in compressive residual stresses that develop due to the swelling phenomenon. Consequently, the contribution of frictional stresses for the wet coupon is likely higher. Therefore, the degradation in fiber-matrix adhesion is perhaps more significant than the reduction in IFSS reported in this study. However, the extent of the contribution of frictional stress originating due to thermal expansion coefficient mismatch and the swelling generated residual stress requires extensive investigation and is beyond the scope of this study and a topic of further research.

Effect of Reheating

Two dry and two wet coupons are tested to understand the effect of heating on the IFSS. It has been reported that for higher temperatures testing, the viscoelastic behavior of the interface must be considered[142]. However, for the current testing procedure, all coupons are tested at room temperature. Subsequently one set of samples (consisting of one dry and one wet coupon) is exposed to 80 °C while a second set is exposed to 120 °C. Both sets are kept at their respective target temperatures for 24 hours. The samples are brought to room temperature and allowed to cool down. The 120 °C and the 80 °C samples took 18 and 15 minutes respectively to reach room temperature. The retesting is done near the testing locations selected prior to conditioning to minimize the effects of

location. The 120 °C temperature was chosen as it is just above the glass transition temperature (T_g). Based on obtained results (shown in Figure 50), a significant degradation is noticed for the coupon conditioned at 120 °C, with wet coupons showing more significant degradation. Increasing the temperature beyond the glass transition of a thermoset resin results in an increase in the specific volume of the resin due to the amorphous regions experiencing a liquid-like flow, indicating that the observed IFSS degradation is a consequence of resin-flow-related morphological changes at the fiber-matrix interface. On the other hand, while the wet coupon conditioned at 80 °C show a decrease in IFSS, the dry coupon conditioned at 80 °C shows an increase in IFSS. The alteration in residual stresses because of reheating and cooling and its effect upon the moisture-induced compressive stresses adds to the complexity of the already convoluted problem and therefore requires a thorough treatment which is a topic for a follow-up study.

Conclusion

In the present work, the authors demonstrate the methodology for conducting highly precise single fiber push-out tests with a nominal fiber diameter of 7 μm . The principal obstacle to conducting the push-out tests pertains to the sample preparation, which has been addressed in this study. The methodology presented for preparation resulted in samples with uneven topography and a consistent minimum thickness of less than 20 μm . The results show the dependency of the IFSS upon the length of the fiber being pushed out, indicating that the IFSS cannot be evaluated simply using the average of results; it is necessary to account for thickness effects as well. FIB polishing showed that the results

are not affected by polishing procedures, and the deformation mechanism of the push-out process was examined. We observed that failure initiates at the weakest bond, then propagates. At shallower thicknesses, a clean interfacial break was observed. For tests corresponding to higher thicknesses, some of the pushed-out fibers were enclosed in the surrounding matrix; we attributed this to a slight misalignment of the fibers with respect to the loading axis, which caused the crack to propagate through the matrix at the point of instability. We then used the Weibull distribution to analyze the results because the failure mechanism followed the weakest link chain failure. We modified the Weibull equation to compare results that corresponded to different volumes, which allowed us to correctly account for the size effects. The results show a 26.9 percent, 29.7 percent, and 31.3 percent drop in the IFSS of CFVE composite with thicknesses of 25 μm , 50 μm , and 75 μm , respectively, due to hygrothermal conditioning at 40°C. Reheating and cooling experiments show a significant decrease in the interfacial shear strength of CF/VE when exposed to a temperature greater than the glass transition (T_g). The impact of residual stresses upon the calculated IFSS is found to be significant; the full extent of this impact is a topic of further study.

Appendix 3

Table 7: Average result obtained for 5 dry and wet coupons.

Sample	Dry (Number of tests)	Wet (Number of tests)
	Strength (MPa)	Strength (MPa)
Sample 1	67.6 ± 11.8 (84)	44.9 ± 10.8 (217)
Sample 2	68.5 ± 11.3 (494)	47.3 ± 11.4 (69)
Sample 3	69.9 ± 5.12 (61)	24.2 ± 6.55 (54)
Sample 4	60.5 ± 10.2 (201)	34.4 ± 13.1 (113)
Sample 5	58.0 ± 15.4 (436)	40.1 ± 12.5 (314)
Average	64.9	38.2
Stdev.	5.3	9.2

Table 8: Height difference resulting from fiber sliding calculated via load-depth curve and via laser microscopy.

Test	Load-Depth curve-	Measured Pillar	Difference
	based height (nm)	height (nm)	
1	3625	3927	302
2	5445	5977	532
3	4720	5270	550
4	4188	4850	662
5	4071	4484	413
6	3721	4371	650
7	3603	4226	623
8	4208	4518	310
9	4012	4663	651
10	2731	3143	412
11	3966	4702	736
12	4857	5619	762
13	6326	7044	718
14	4063	4477	414
15	4628	5480	852
16	4870	5245	375
17	3406	4204	798
18	902	1180	278

Table 9: Average results obtained as a function of depth using Weibull Parameters.

	Dry					Wet				
	Scale	Shape	25μm	50μm	75μm	Scale	Shape	25μm	50μm	75μm
Sample 1	140.7	5.4	77.1	67.8	62.8	126.1	3.8	60.9	52.0	47.5
Sample 2	109.6	5.6	61.7	54.5	50.7	132.7	4.4	64.1	54.8	50.0
Sample 3	110.7	4.8	62.3	55.0	51.2	72.0	4.8	37.0	32.0	29.4
Sample 4	133.3	4.2	69.9	60.9	56.1	101.7	4.0	45.1	37.9	34.2
Sample 5	127.0	5.0	66.6	58.0	53.4	118.5	2.5	39.7	31.4	27.3
Average			67.5	59.2	54.9			49.3	41.6	37.7
Stdev.			6.3	5.4	5.0			12.4	11.1	10.4

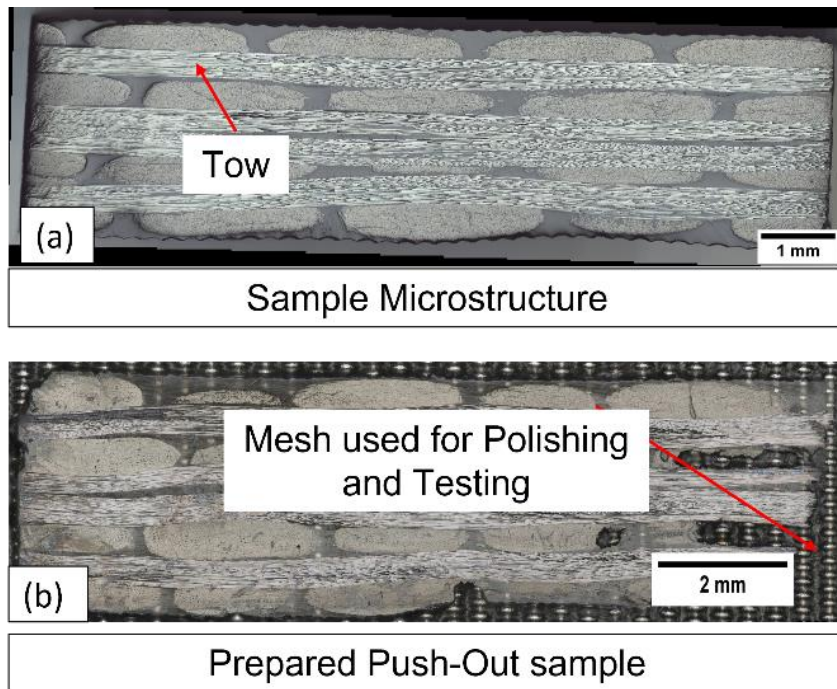


Figure 35:a) Sample Microstructure, b) A prepared push out sample

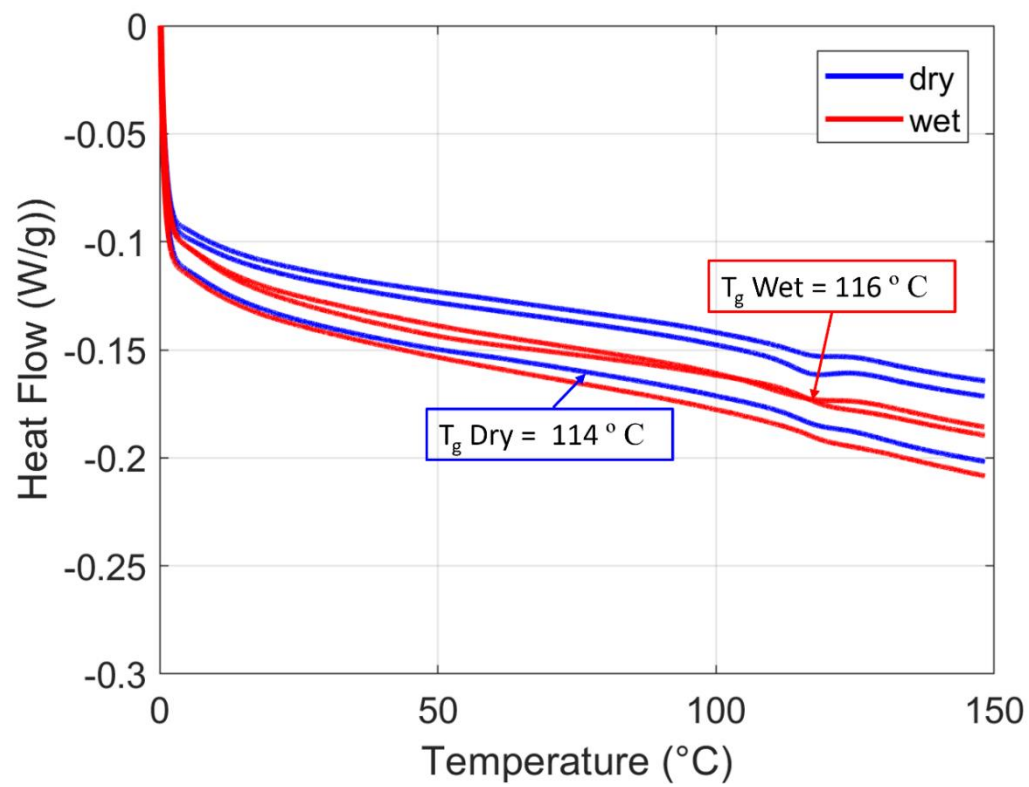


Figure 36: Differential scanning calorimetry (DSC) curves for Dry and Wet CFVE coupons.

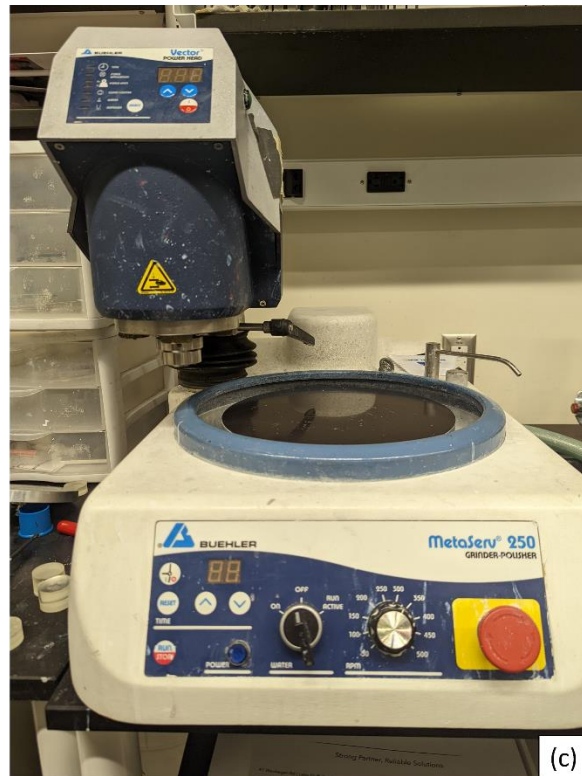
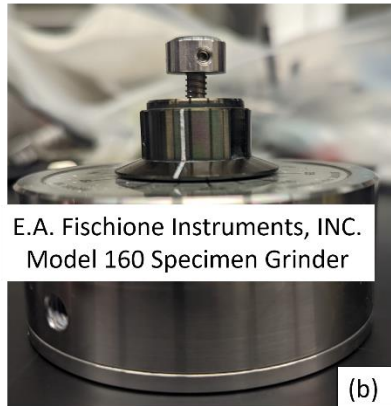
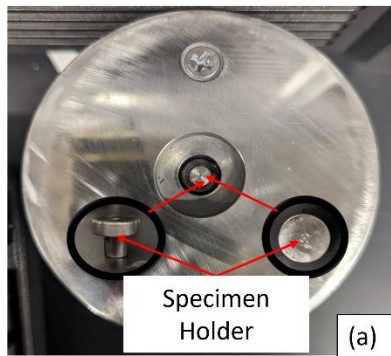


Figure 37: a), b) Specimen grinder used to prepare thin films, c) Auto-polisher used for polishing.

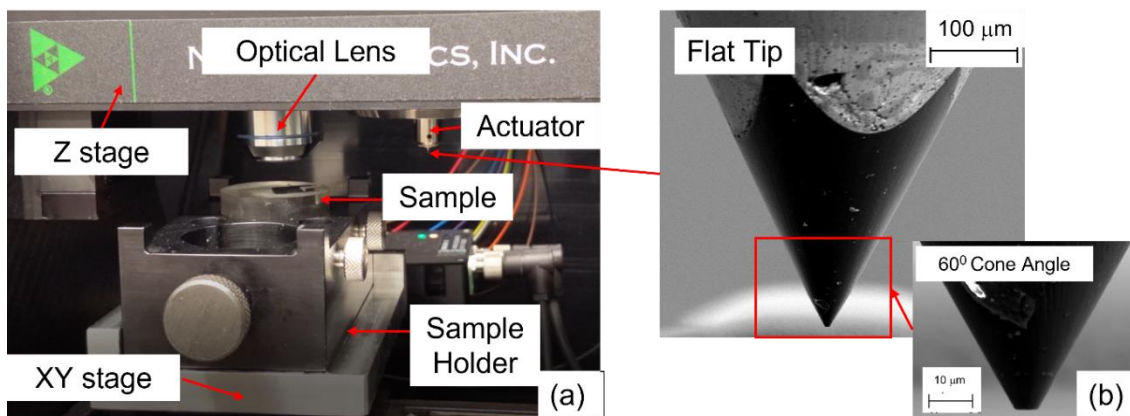


Figure 38: a) iMicro Nanoindenter system, b) Diamond flat conical tip used for Push-Out tests.

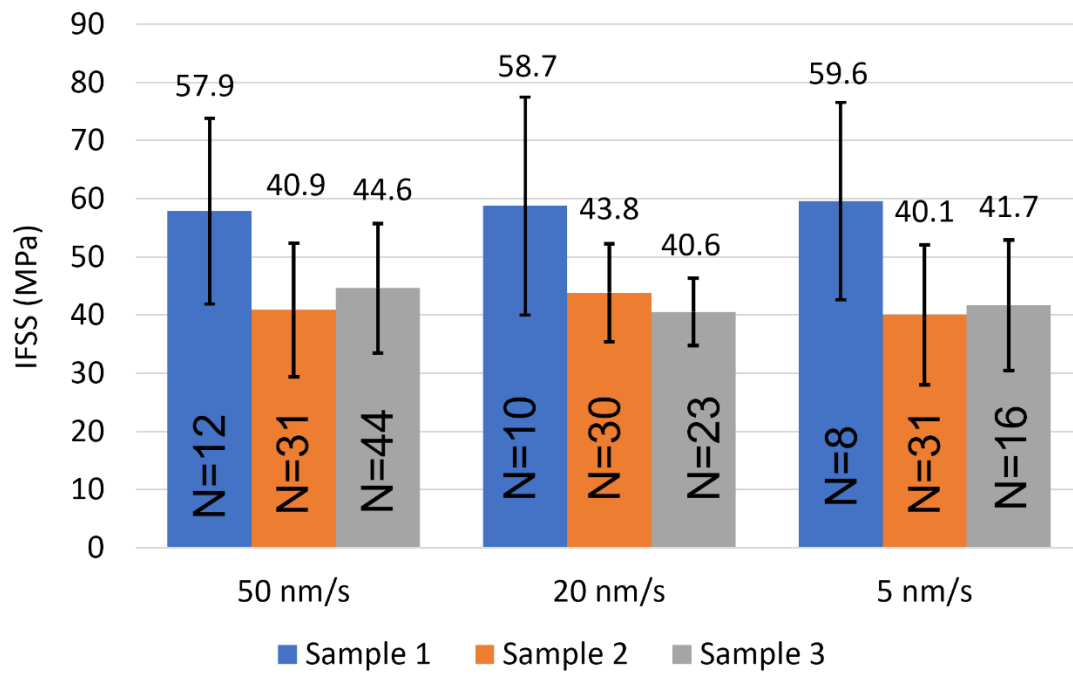


Figure 39: Effect of displacement rate upon the IFSS. N is the number of tests.

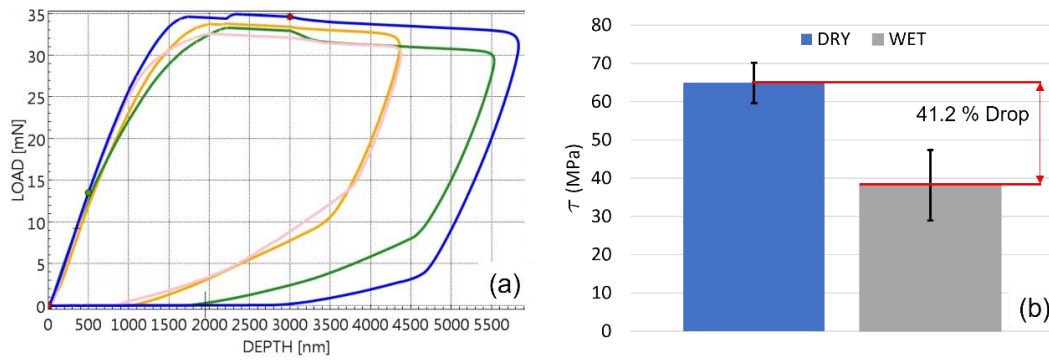


Figure 40: a) Load-Depth curve corresponding to successful push-out tests, b) IFSS obtained for dry and wet samples.

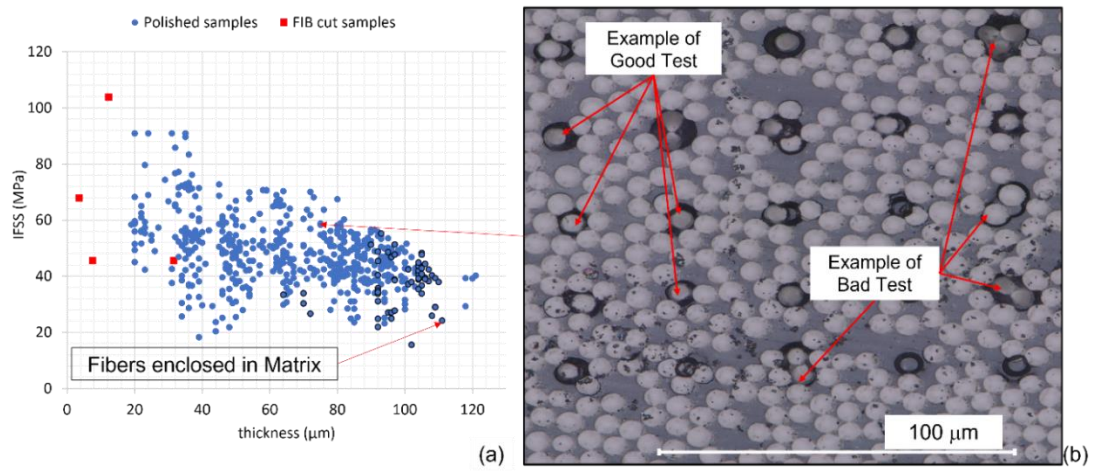


Figure 41:a) IFSS as a function of depth for a dry sample, b) Optical image of an array showing push-out tests.

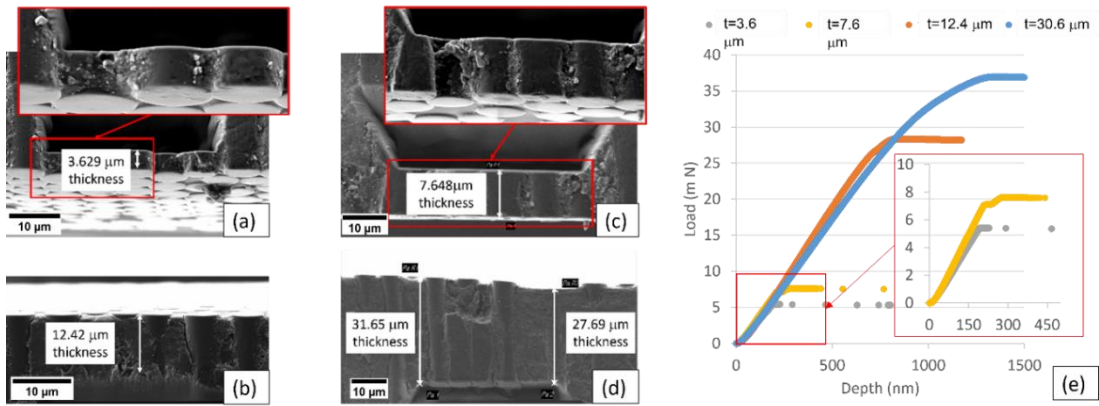


Figure 42: Prepared notches of thickness a) 3.6 μm , b) 7.6 μm , c) 12.4 μm , d) 30.6 μm using the FIB technique and e) the respective load-depth curve obtained.

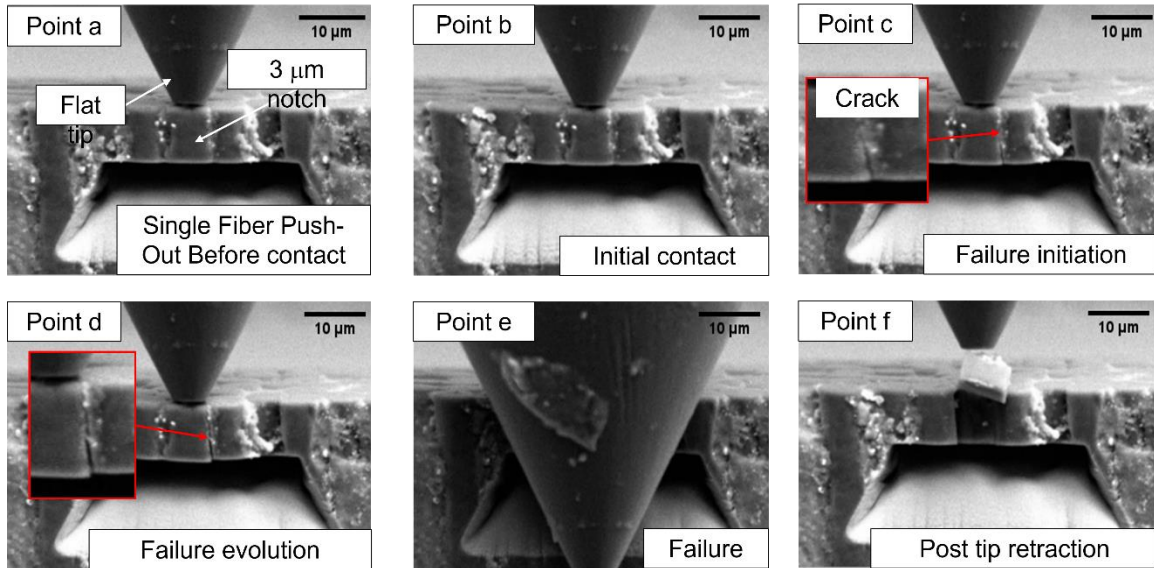


Figure 43: Failure initiation and propagation during single fiber push-out tests.

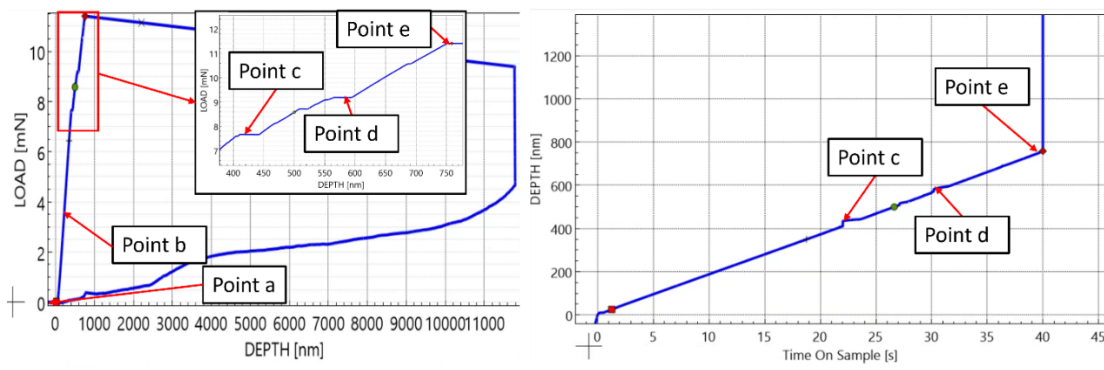


Figure 44: a) Load-Depth curve and b) Depth-Time curve for the notch sample.

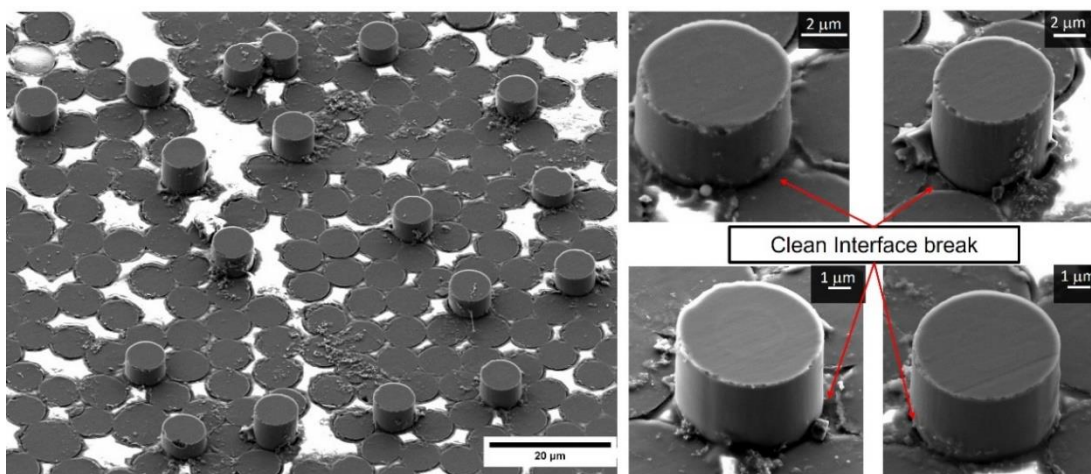


Figure 45: Post-testing SEM imaging of pushed-out fibers obtained after flipping the sample.

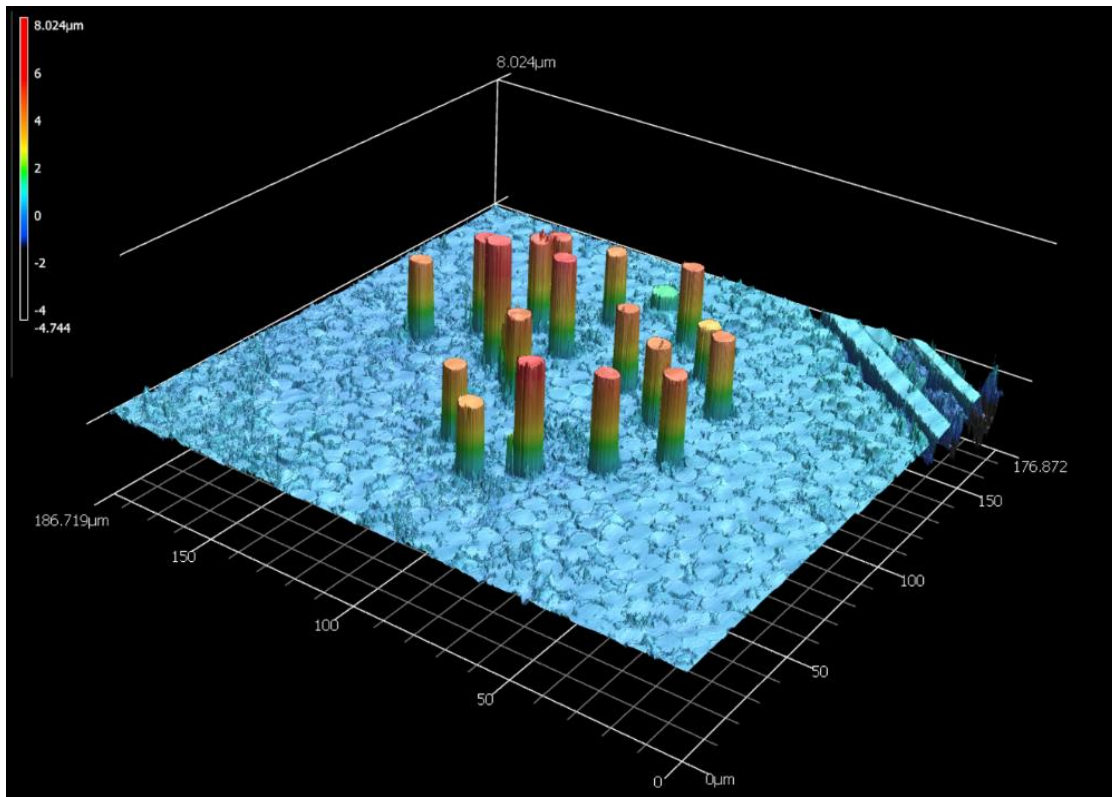


Figure 46: Laser image of the Pushed-out fibers.

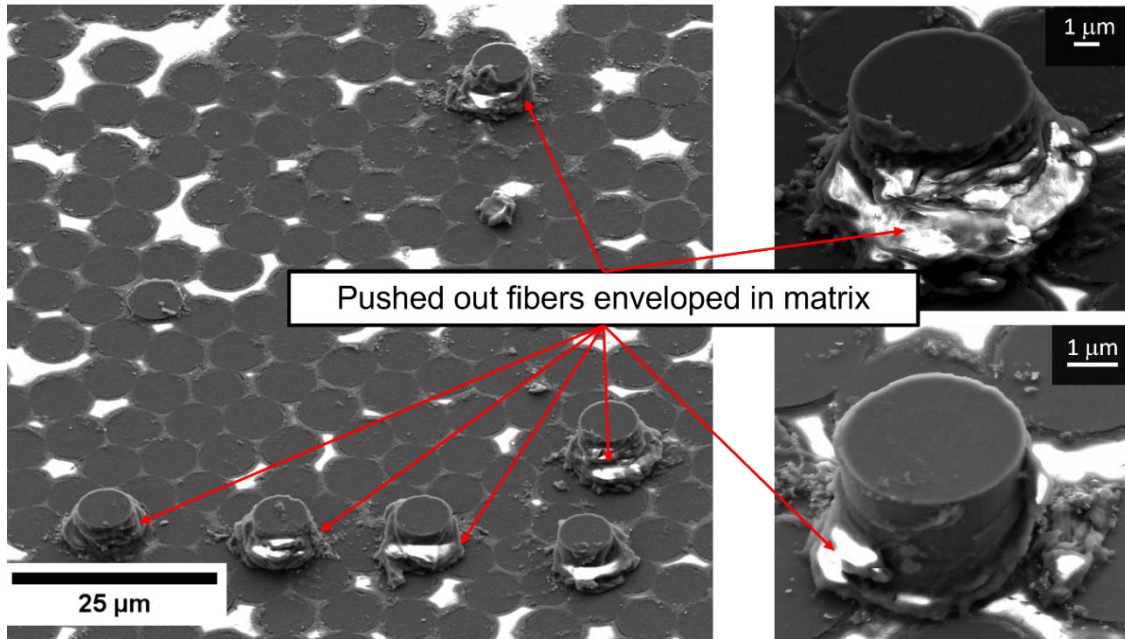


Figure 47: SEM image showing pushed-out fibers enclosed in the matrix.

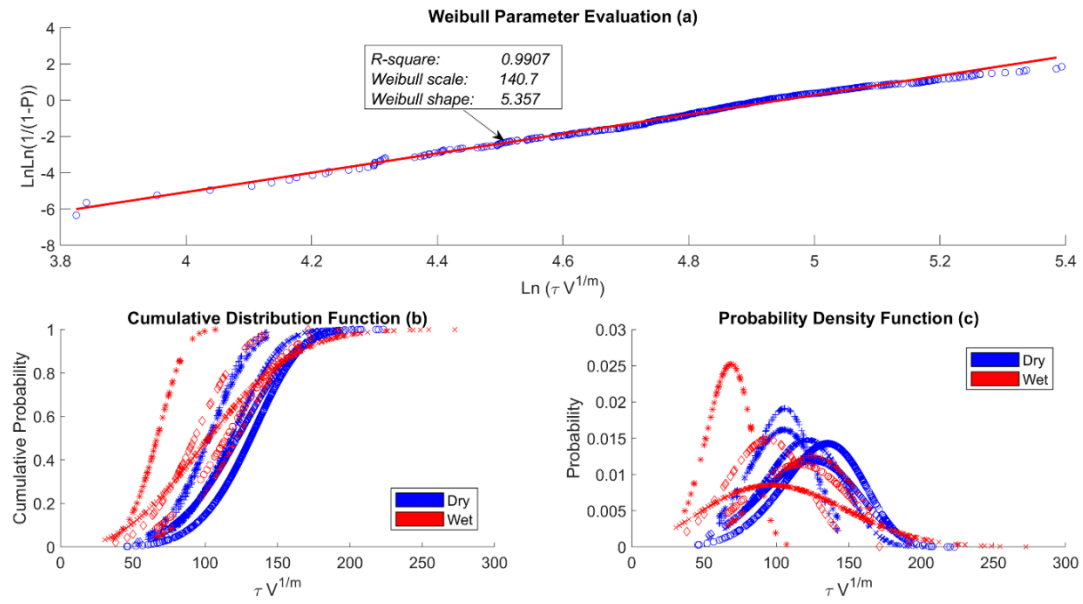


Figure 48: Results obtained using Weibull distribution.

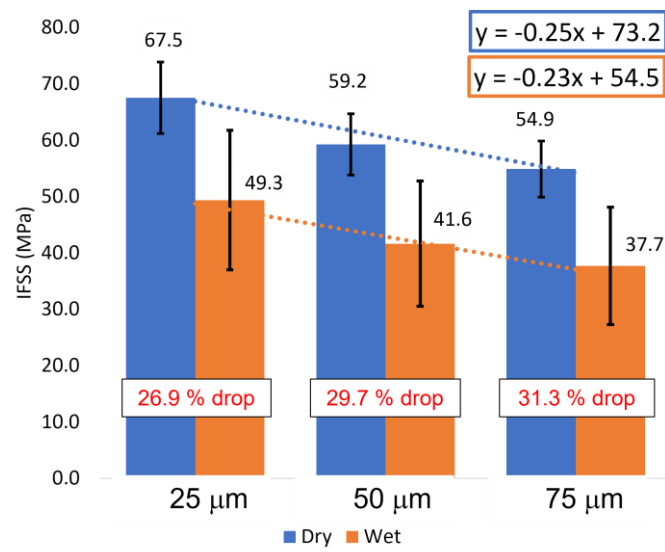


Figure 49: IFSS of the dry and wet coupon as a function of depth based on Weibull parameters.

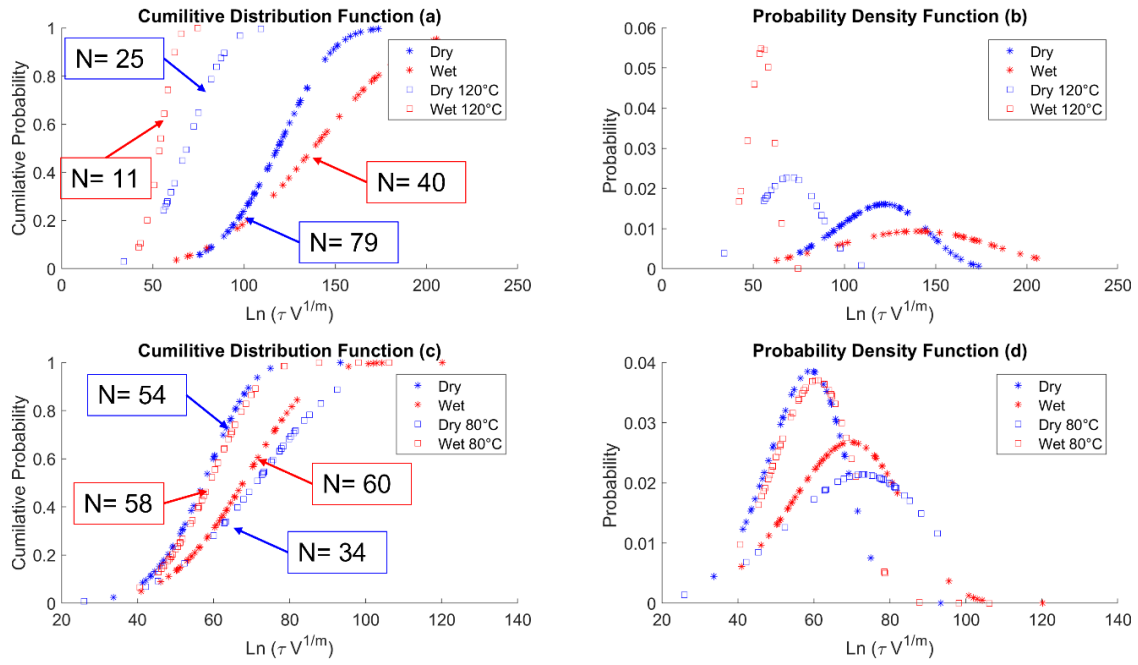


Figure 50: Effect of reheating upon the IFSS. N is the number of tests per sample

CHAPTER 4: NANOINDENTATION TO CHARACTERIZE THE MICROSTRUCTURE OF CARBON FIBER.

Abstract

Measuring the mechanical properties of a single fiber consolidates our understanding of failure mechanisms in carbon fiber composites. Processing parameters ranging from the type of polymer precursor to the carbonization stage have importance in determining the degree and orientation of resulting turbostratic graphite crystals in carbon fiber. This study addresses the scope, limitations, and challenges associated with precisely analyzing the local mechanical properties of carbon fibers using nanoindentation. The role of fiber-matrix is assessed using the continuous stiffness measurement technique. Results show that at shallow indentation depths ($h < 200\text{nm}$) the interfacial response can be accounted for by conducting push in tests, while at higher depths the fracturing of the interface yields unacceptable results. It is found that energy dissipation during nanoindentation is directly correlated to the local pore size in the carbon fibers. The authors introduce an energy-based parameter, R , which is used to characterize the local crystal structure of carbon fiber. The presented technique offers spatially resolved qualitative estimation of the crystal parameters. The ease of applicability of the technique offers future researchers a means to understand the relationship between processing parameters and crystal structure and consequently the understanding of the failure mechanisms of carbon fiber.

Introduction

Carbon fibers, the most sought-after material in applications requiring a high strength-to-weight ratio, have vastly improved mechanical properties compared to the first carbon fiber manufactured by Sir Joseph Wilson Swan in 1879. The modern-day carbon fiber

can exhibit a tensile strength and modulus of 4 GPa and 400 GPa, respectively [143]. However, due to the high manufacturing and storage cost associated with carbon fiber, applications have been somewhat limited to the aerospace [111,144], automotive [111], and sports industries [112]. In the past decade, there has been a surge in the use of recycled and low-cost carbon fibers [110,145]. Across all areas of application, developing carbon fibers with improved mechanical properties is always of scientific importance. To this day, there remains a gap in understanding the relationship between the processing parameters – used in the manufacturing of carbon fibers – and their effect on the developing microstructure of carbon fibers and therefore, their mechanical properties. To bridge this gap, the localized crystal structure must be quantified as a function of different processing parameters.

Carbon fibers possess non-homogeneous microstructural features across their cross-section and therefore show variation in local mechanical properties. The cause of inhomogeneity – the variation in local microstructure – arises as a consequence of processes ranging from oxidation to carbonization. During the oxidation process – where oxygen molecules from the air combine with the PAN fibers and cause the polymer chains to start crosslinking –, progressive oxidation of the skin seals off the oxygen diffusion to the inner portion of the fiber and hence results in a less cross-linked and more disordered core (skin-core effect [146–150]). The characterization of local microstructural features is crucial in determining carbon fiber quality; however this remains a significant challenge.

If the spatial variation in the mechanical properties of carbon fibers can be correlated to the local microstructure, then, local mechanical testing could be used as a tool to assess the evolving microstructure of carbon fiber as a function of processing parameters.

Characterization by nanoindentation offers an opportunity to measure the local mechanical properties and would help to create feedback that makes the multi-step manufacturing process of carbon fiber both efficient and cost-effective.

At a macroscale, the techniques to measure the mechanical properties of carbon fiber have been well established [46,151]. The reported values of the tensile modulus along the fiber axis for carbon fiber are usually between 200 and 500 GPa. Various techniques, such as tensile [152], bending [153,154], and indentation [145,152,155–157] testing have been utilized to measure the tensile modulus and stiffness of carbon–fiber composites. Few studies in the literature have reported systematic local measurements of the fiber indentation modulus [155–157]. These studies find a significant difference between the modulus measured using nanoindentation [158] in comparison to the macroscopically obtained modulus [46].

While few techniques exist in literature to quantify the local crystal structure of carbon fibers, nearly all methods have their limitations. For example, only overall crystalline structure can be quantified from X-Ray diffraction and the values obtained depend on the choice of parameters in post processing. At the same time, Raman spectroscopy and Transmission electron microscopy (TEM) are time-consuming and cost-ineffective with results highly dependent upon the quality of the samples prepared. In the present work, the authors introduce an energy-based parameter, R , which is used to characterize the

local crystal structure of carbon fiber. The ease of applicability of the presented technique offers future researchers a means to understand the relationship between processing parameters and crystal structure and consequently the understanding of the failure mechanisms of carbon fiber.

Material

Commercially available TORAY T700 carbon fibers are chosen as the primary material for investigation because of the extensive research done upon these fibers using X-Ray scattering [45] and Transmission Electron Microscopy (TEM)[44]. Specifically, for T700 carbon fiber, core stacking height (L_c) and crystallize size (L_a) of 3 nm and 2 nm respectively were observed by transverse cross-section High-Resolution Transmission Electron Microscopy (HRTEM), whereas in the fiber skin, L_c and L_a crystal sizes were 5 nm and 3 nm respectively [44]. Two sets of TORAY T700 carbon fiber samples are used in this study to investigate the effect of interface: carbon fibers embedded in potting epoxy (prepared by mixing EpoxyCure2 resin and EpoxyCure2 hardener in a four-by-one ratio by weight obtained from BuehlerTM), and carbon fibers (TORAY T700) embedded within a carbon fiber vinyl ester composite (CFVE) made using the Vacuum Assisted Resin Transfer Molding (VARTM) process. The samples are potted in a Buehler epoxy mold and polished according to the specific guidelines for polishing composites using Buehler Metaserv 250 Grinder-Polisher. The surface of the epoxy puck is then examined under the KEYENCE VHX7000 optical microscope with a 3.19 MP image sensor to visually inspect whether the surface is smooth enough to be indented. The conclusions made via indentation of T700 carbon fiber are then

validated by extending the results to a wide variety of commercially available TORAY carbon fibers: T300, T400, T800, M40J, and M50J. T300, T400, and T700 correspond to the high-strength standard-modulus carbon fiber, T800 correspond to the high-strength medium-modulus carbon fiber, and M40J and M50J correspond to high-strength high-modulus carbon fiber. The details of the mechanical properties of the fibers can be found elsewhere [45]. For the purposes of this study, these fibers represent the evolution of the microstructure of carbon fibers from the same precursor but manufactured using different processing parameters. The findings of this study are thus limited to carbon fibers made from the same precursor.

Methods

Nanoindentation is performed using the iMicro system from Nanomechanics, Inc. and a Berkovich tip [16]. The force and displacement measurements are conducted using a 1000 mN actuator with a capacitive gauge and displacement range of 40 μm . The actuator has a displacement measurement resolution of 0.04 nm, load resolution of 6 nN, noise floor of less than 0.1 nm, and drift rate of less than 0.05 nm/s. The controller is capable of dynamic excitation frequencies from 0.1 Hz to 1 kHz, with a data acquisition rate of 100 kHz. The iMicro system is mounted on a vibration isolation table. It uses an environmental chamber to minimize thermal variations during testing. Indentation is performed using the Oliver–Pharr method [16], which uses a continuous stiffness method for determining the mechanical properties as a function of depth. A tip area function (A_C) and frame stiffness (K_F) calibrations are done by indenting fused silica, a material with well-known mechanical properties. The samples are loaded dynamically at a 110 Hz with

a 2 nm amplitude to calculate the contact stiffness during the unloading cycle. Total depth (h_t) is calculated by subtracting the frame displacement and drift from the measured depth. Similarly, contact stiffness is calculated by subtracting the effect of frame stiffness (K_F) from measured stiffness. Equation 4.1 is used to calculate the contact depth (h_c), where $\epsilon = 0.75$. ϵ is a parameter that depends on the shape of the indenter and its value is widely accepted for a Berkovich indenter[16]. Once the contact depth is known, the contact area can be determined with the known area function, and equation 4.2 and equation 4.3 can be applied to calculate the reduced modulus and indentation modulus of the samples (assumed to be an elastic half-space), respectively. Since poisson's ratio of carbon fiber is usually unknown, it is assumed to be 0.3 in this study. It can be shown based on Equation 4.3 that there is a weak dependence of the indentation modulus on poisson's ratio. In equation 4.1, h_c is the contact depth, and h_t represents the total depth.

$$h_c = h_t - \epsilon \frac{p}{S} \quad -(4.1)$$

$$E^* = \frac{\sqrt{\pi}}{2 * B} \frac{S}{\sqrt{A_c}} \quad -(4.2)$$

$$E^* = \left(\frac{1 - \nu_s^2}{E_s} + \frac{1 - \nu_i^2}{E_i} \right)^{-1} \quad -(4.3)$$

E^* is the reduced modulus, E_i and ν_i are the young's modulus and Poisson's ratio of the indenting diamond tip, and E_s and ν_s are the Young's modulus and Poisson's ratio of the sample.

Figure 51a shows a typical load-depth curve obtained via nanoindentation for fused silica. The stiffness (S) indicates the slope of the unloading curve. The traditional method of indentation calculates the slope at the maximum load during the unloading cycle and hence provides the modulus value only at one point (maximum depth). The continuous stiffness measurement (CSM) method dynamically loads the elastic half-space, subsequently providing the contact stiffness as a function of depth until the target total depth is reached. Figure 51b shows a schematic of the dynamics of the actuator in contact. The actuator is operated by two leaf springs of known stiffness and damping coefficients. The frame stiffness value is calculated using the indentation of fused silica. Solving the dynamics of the problem gives the value of contact stiffness and contact damping. F_0 and ω correspond to the amplitude of the force oscillation and frequency of oscillation respectively. These are given as the input, while the amplitude of the displacement oscillation z_0 and phase angle ϕ are measured during testing. The term K_f represents the frame stiffness which is calculated using the indentation of fused silica. CSM works based on the assumption that dynamic unloading relieves elastic pressure and that unloading, and reloading does not change the indentation process.

The indentation is carried out at a constant strain rate of 0.2/s, where the strain rate is defined as the ratio of the time derivative of the load ($\dot{P}$) and the load (P). It has been shown [21] that the hardness measured in the indentation testing approaches a constant value if the strain rate is held constant. Hence, keeping the strain rate constant gives the advantage of obtaining rate independent results for materials that show creep. An array of

indents is made on the samples, and their exact locations are determined via optical microscopy using the Keyence VHX7000 optical microscope.

Results

Indentation of carbon fiber

Examples of the load-displacement and modulus-depth curves obtained for the T700 carbon fiber embedded in epoxy and vinyl ester are shown in Figure 52. The interpreted values are averages from a minimum of 25 indentations and are reported in Table 1. The tests are run at a constant strain rate of 0.2/s. An array of 7×7 indents separated by 10 times the target depth of the indent is made for each sample. A separation distance of $10 \cdot h_{\max}$ is chosen to avoid the effect of indents interfering with each other. The target depths chosen per sample are 200 nm, 500 nm, and 800 nm, with each indent separated by 2 μm , 5 μm , and 8 μm respectively. The modulus and hardness values reported in Table 10 are the average of modulus values between 150 nm–200 nm, 300 nm–500 nm, and 600 nm–800 nm for a target depth of 200 nm, 500 nm, and 800 nm respectively. A consistent trend for all fibers: the modulus decreases as the depth increases. The carbon fibers for shallower indentation depth showed an elastic stress-strain curve. It is well established in literature that the elastic modulus of T700 carbon fiber is ~ 230 GPa. However, the value obtained via nanoindentation is ~ 70 GPa. This result is consistent with the literature [156,157,159,160] and highlights the challenge of evaluating tensile modulus using nanoindentation. Interestingly, while the load-depth curve shows negligible permanent deformation, there is a difference in the hysteresis loop energy between the loading curve and the unloading curve, indicating some energy dissipation.

Figure 53 shows the optical microscopy corresponding to a 500 nm indentation for both samples. Though, at higher depths (500 nm and 800 nm) a permanent deformation can be seen in the load-depth curves of the carbon fibers, no residual indents are observed based on optical microscopy (Figure 53). On the other hand, the indents on the matrix are clearly visible. Since there is no observable permanent deformation, the measured indentation hardness for carbon fiber is not a valid indicator of carbon fiber hardness. The indentation of carbon fibers is complicated by the presence of surrounding matrix as well as the fiber-matrix interface. The effects of this additional compliance (arising due to matrix and interface) must be accounted for during indentation. Henceforth, we call the combined stiffness of fiber, matrix, and interface assembly the interfacial stiffness. Since the stiffness is calculated by dynamically unloading the tip (Figure 51b), the measured contact stiffness can be assumed to be the combined stiffness response of carbon fiber during indentation and the interface stiffness connected in series. This assumption has been shown to work well in eliminating the effects of frame stiffness in typical nanoindentation experiments as well as the substrate compliance in thin film measurements [161]. The combined response is thus given by Equations 4.4 and 4.5,

$$h_{measured} = h_{fiber} + h_{interface} \quad -(4.4)$$

$$\frac{1}{S_{measured}} = \frac{1}{S_{fiber}} + \frac{1}{S_{interface}} \quad -(4.5)$$

where h_{fiber} and S_{fiber} are the indentation depth and indentation contact stiffness of the fiber, while $h_{interface}$ and $S_{interface}$ are the combined depth and stiffness response of the fiber, matrix, and interface assembly i.e., the interface depth and interface stiffness.

Equations (4.4) and (4.5) can be rearranged to give the fiber indentation depth and

stiffness if the stiffness of the interface is known. Since the stiffness is related to modulus implicitly, a sensitivity study is conducted to investigate the effect of fiber-matrix-assembly compliance upon the modulus-depth curve obtained for carbon fiber. For a 200 nm indent, the error in the calculated fiber modulus can be as high as 60% for $S_{\text{interface}} = 2S_{\text{measured}}$ or close to zero for $S_{\text{interface}} \gg S_{\text{measured}}$. Thus, evaluating the order of magnitude of interfacial stiffness ($S_{\text{interface}}$) is necessary to validate the nano-indentation results.

The evaluation of the fiber-matrix-interface assembly stiffness (interfacial stiffness) can be done by testing the fiber in compression using a flat cylindrical tip. This methodology, referred to as push-in test, is often conducted in literature to quantify the interfacial shear strength [64,68]. Figure 54a shows an SEM image of a truncated cone used to conduct the push-in tests. Figure 54b shows an example load-depth curve obtained via push in tests. The initial part of the load-depth curve corresponds to the flat tip engaging with the fiber. Unlike the Berkovich tip, the depth required for a flat tip to engage with the fiber is more correlated to the flatness of the tip rather than the surface roughness of the material. After the engaging of the tip, the slope of the load-depth curve corresponds to the interfacial stiffness. Since equations 4.4 and 4.5 assume a constant interfacial stiffness, it becomes necessary to remain in the elastic zone and hence the load corresponding to the selected indentation total depth, should be kept below the non-linearity onset load P_c (Figure 54). The interfacial stiffness ($S_{\text{interface}}$) is calculated for TORAY T700 carbon fiber embedded in a vinyl ester resin and an epoxy potting resin.

Table 11 shows the interfacial properties obtained for the two sets of samples. The results are an average of a minimum of 10 tests. During 200 nm deep nano-indentation testing (Figure 52), the maximum stiffness measured is 47,619 N/m which gives a 4.22 interfacial stiffness to maximum measured stiffness ratio (for an interfacial stiffness value of 201,000 N/m). Based on the sensitivity study, the error in the fiber indentation modulus is ~25 percent if the interface stiffness is not accounted for.

The interfacial stiffness can be easily accounted for by defining an equivalent frame stiffness defined by equation 4.6 which implies replacing the K_f (~3240000 N/m) in Figure 51b with $S_{equivalent}$.

$$\frac{1}{S_{Equivalent}} = \frac{1}{K_f} + \frac{1}{S_{interface}} \quad -(4.6)$$

Since the exact interfacial stiffness cannot be determined for the specific fiber being indented, it becomes necessary to assume an interfacial stiffness. Assuming $S_{interface} = 200,000$ N/m, a sensitivity study is carried out evaluating the error corresponding to the ‘true’ interfacial stiffness ranging between 150,000 N/m to 250,000 N/m. Figure 55a shows the fiber indentation modulus obtained as a function of depth corresponding to the range of interfacial stiffness values. At 200 nm, as shown in Figure 55, $\pm 25,000$ $S_{interface}$ variation leads to a maximum error of ~5%; similarly, a $\pm 50,000$ $S_{interface}$ variation leads to a maximum error of ~10%. Therefore, provided the indentation depth is small enough, an approximate value of interfacial stiffness can be used. Henceforth, we assume $S_{interface} = 200,000$ N/m and only report results corresponding to a maximum depth of 200nm.

Spatially resolved mapping of carbon fiber properties

To investigate the variation in the modulus across the cross-sections of the carbon fibers, indentation is performed using the NanoBlitz technique. NanoBlitz is a high-speed indentation testing technique that allows for rapid measurement of mechanical properties. This technique works by applying a specified target load to the sample and measuring the resulting indentation depth and contact stiffness, which are then employed to calculate the modulus and hardness value using the Oliver–Pharr method[16]. Based on the load-depth curve, a load of 3 mN, corresponding approximately to a depth of 150 nm, is chosen for the carbon fibers. The spacing between the indents is chosen to be 1.5 μm to avoid strain field effects from adjacent indents. Figure 56 shows the resulting contour plot revealing the core-sheath behavior of carbon fiber.

Discussion

Deep (>500nm) CSM indentation of carbon fibers.

While the shallow indentation ($h_t = 200 \text{ nm}$) testing did not show any permanent deformation based on the load-depth curve, the deep indentation ($h_t \geq 800 \text{ nm}$) of the carbon fibers showed permanent deformation. To understand the cause of permanent deformation, additional testing with a target depth of 800 nm is conducted. Optical images of the surface before and after indentation are taken. Figure 57 shows three fibers before and after indentation. Cracking at the fiber–matrix interface after testing could be seen. No indentation marks are seen on the surface of the fibers. Based on this evidence, the resulting residual depth (h_f) seen in the load-depth curve is a direct consequence of the “pushed-in” fibers due to the breaking of the fiber–matrix interface. This result is consistent with the literature, where a flat tip is used to push on the fiber until the

interface breaks and the resulting load-depth curve is employed to obtain the interfacial properties of the fibers [64,68].

Shallow (<200nm) CSM indentation of carbon fibers.

Nanoindentation is performed using an array of 15×15 indents with a target depth of 200nm and 1.5 μm spacing between indents using the CSM technique. The modulus is reported at 100nm. Figure 58a and Figure 58b show the optical image and corresponding contour map for indentation modulus for the fiber. The core-sheath structure is apparent from the contour plot. The resulting load-depth curve and modulus-depth curve are shown in Figure 58c and Figure 58d, respectively. The results for carbon fiber are divided into three regions: Region A—the edge of the carbon fiber, Region B—the sheath region-between the edge and the core, and Region C—the core of the carbon fiber. Region C is identified by selecting any indents that fall within a 1.5 μm -radius circle, originating at the center of the fiber. Region B comprises any indents that fall within an annulus with inner and outer radii of 1.5 μm and 3.5 μm respectively. Similarly, Region A is identified by an annulus with 3.5 μm and 5 μm inner and outer radii respectively.

The modulus curves for Region C remain constant with depth. The modulus-depth curves for Region B show a repeated pattern where the modulus values decrease exponentially as the depth increases. The modulus–depth curves for Region A show a range of values. Most of the values start at a very low modulus (~ 5 GPa) and then, depending on the distance from the nearest fiber, either increase in value with depth when the tip contacts the fiber or remain constant if the fiber is at a far enough distance. There are few indents for which the modulus values start at approximately 40 GPa and then decrease linearly

with depth. This behavior can be explained by the scenario in which the tip first makes contact with the fiber, then as the depth increases, a portion of the tip exceeds the fiber surface boundary and contacts the matrix thus decreasing the modulus. Other indents in Region A start with a high modulus value (75–90 GPa) and then decrease exponentially with an increase in depth. For these indents, the tip maintains contact with the fiber throughout the indentation, and thus they show modulus-depth behavior resembling that of Region B indents.

To understand the indentation response of carbon fiber in the B and C regions, the authors investigated the recovered energy during nanoindentation. Quantification of recovered energy is done by defining a parameter R which evaluates the unloading energy normalized to the applied energy as per equation 2. The parameter R for Region C (core) and Region B (sheath) is evaluated for indents with target depth of 200nm, 100 nm, 50nm, and 10nm to determine the effect of depth upon recovered energy. Indentation is performed with and without dynamic loading. The results are reported in Figure 58f.

$$R = \frac{\Sigma(\Delta P \Delta h)_{Unloading}}{\Sigma(\Delta P \Delta h)_{Loading}} \quad -(4.7)$$

Figure 58e shows the contour map obtained for recovered energy (R) for 200nm indentation tests. Based on Figure 58e, the recovered energy is higher in the fiber's core than in the sheath. The result can be qualitatively observed in Figure 58c inset, where the Region C unloading curve closely follows the loading curve. Based on Figure 58f, the recovered energy stabilizes after around 100nm indentation depth independent of the loading condition. There are no significant differences between the recovered energy obtained via dynamically or statically loading the fibers other than perhaps an earlier

stabilization of recovered energy using dynamic loading. The results suggest that energy loss is a continuous process as the percentage of the energy dissipation remains the same throughout the indentation depth.

Role of microstructure in indentation

Recovered energy distribution gives insight into the deformation mechanism of carbon fiber undergoing indentation. Jenkins [162] explained a similar energy loss behavior for reactor-grade graphite using the friction block model, which assumes connected Hookean (spring) and Voight (friction block) elements, to show that frictional sliding between the grains is the reason for energy dissipation. Given the displacement prescribed by a rigid frictionless triangular pyramid, it is likely that alongside frictional sliding, there must be some amount of transverse displacement and nano-buckling of graphene layers constrained by weak van der Waals forces. Wang et al. [163] observed nano-buckling as the primary deformation mechanism under Atomic Force Microscopy (AFM) indentation using in situ TEM. For T700 carbon fibers, larger pore and crystal sizes have been identified in the sheath compared to the core [44]. The core represents a region dominated by a poor degree of crystallinity with smaller crystal size, pore size, and stack height [44,45]. The core also features higher misorientation and large regions of amorphous carbon [45]. A consistently higher energy loss in the sheath may be a direct consequence of bigger local crystal and pore size. Small crystal size and low stack height lead to a low critical buckling load while smaller pores favor a more efficient packing with large contact area between crystals requiring a higher load for transverse deformation and frictional sliding. On the other hand, large crystal size, and stack height

result in higher critical buckling load but large pore sizes lead to a relatively inefficient packing.

If the tip is sharp enough and the depth is low enough, irrespective of the indentation location, there would be plastic deformation at the start of indentation. As the depth is increased, deformation in the core is dominated by nano-buckling and a low critical buckling load leads to a low modulus measurement. The closely packed structure in the core makes shearing and frictional sliding difficult. Additionally, amorphous carbon may act as an obstacle for dislocation motion thus almost no plastic deformation is observed. For an indent carried out in the sheath, initial deformation is also dominated by nano-buckling. However, high critical buckling load due to crystal structure, leads to a high initial modulus. The presence of relatively large pores indicates smaller contact areas between crystals and facilitates frictional sliding. With increasing indentation depth, a sufficiently high load is reached causing shearing between crystals and a decrease in measured modulus. This frictional sliding is the source of the observed additional energy loss in the sheath. The elastic strain energy stored in the buckled crystals is released during unloading thereby resulting in no permanent deformation.

(Figure 58d). The schematics of the deformation mechanism is shown in Figure 59. The inference of the above argument is that recovered energy (parameter R) could provide qualitative estimation of the crystalline parameters if the relationship governing energy loss as a function of crystallinity is identified.

To validate the above hypothesis, the authors investigated five additional carbon fibers (T300, T400, T800, M40J, and M50J) obtained from the same precursor but subjected to

different processing parameters. These are the same fibers used in the study by Meek and Penumadu evaluating the effect of average crystalline parameters upon carbon fiber's strength, modulus, and stiffening behavior under tension [45]. As previously mentioned, these fibers represent the evolution of the microstructure of carbon fibers. As shown in Figure 60, all but T700 carbon fibers have a 'kidney bean' cross-section due to manufacturing conditions. Figure 61 shows the optical image, modulus map, and recovered energy map for the five fiber types under investigation. The contour plot limits are adjusted for each fiber type to highlight variations within the fibers. The core-sheath structure is again apparent in modulus and recovered energy maps. The correlation between indentation properties and crystalline parameters can only be justified if it remains invariant irrespective of the fiber type under investigation.

Figure 62a and Figure 62b show the average recovered energy and the average modulus values obtained for different fibers as a function of average pore size according to [45]. The error bars correspond to one standard deviation from the average. A strong correlation is attained for recovered energy as a function of pore size, demonstrating the relationship between pore size and dissipated energy. Meek and Penumadu argued that heat treatment at higher temperatures results in bigger local pore size and, consequently, the crystal size and stack height increases - a conclusion derived by evaluating the relationship between average pore and crystal sizes, and processing parameters of carbon fibers under investigation. Assuming the conclusion to be accurate, the findings of this study uphold their argument and validate it since the recovered energy is consistently higher within the core of the fiber in comparison to the sheath- a mechanism occurring

within the fiber. More importantly, the argument implies that perhaps one parameter is needed to qualitatively characterize the crystal structure within the carbon fibers. The average indentation modulus remains relatively unaffected from fiber to fiber (Figure 62b), and thus a poor correlation is obtained between the crystal parameters and indentation modulus. Based on the presented hypothesis, the result is unsurprising as a bigger stack height and crystal size would effectively increase the contact stiffness though the increase would then be compensated by larger pore sizes.

Figure 62c shows the recovered energy for different fibers as a function of absolute distance from the center of the fiber with piecewise linear regression. The center of the fiber is identified by manually selecting the center from the contour plots. Fibers T300, T400, and T700 show very similar behavior. A linear decrease in recovered energy as one recedes from the center is followed by constant recovered energy in the sheath before a further reduction in the recovered energy towards the edge. Fibers T800, M40J, and M50J show a similar trend with different values. The core for these fibers show bigger pore sizes compared to the core of T700 (or T300 or T400) carbon fibers. The recovered energy decreases linearly in the sheath for all fibers before saturating towards the edge.

Conclusions

Mechanisms are proposed to explain the lower indentation modulus seen in the core and sheath of carbon fiber by considering the deformation being controlled by out-of-plane shear and transverse deformation and nano buckling of graphene sheets of carbon fiber. Based on the calculation of recovered hysteresis energy between the core and sheath, it is found that the energy recovered is a function of the pore size, which is a function of the

degree of crystallization. This finding has enormous implications as it provides an opportunity to understand the effect of localized crystal parameters on carbon fiber's mechanical performance and the relationship between processing parameters and crystal structure.

Appendix 4

Table 10: Elastic modulus and Hardness values obtained for T700 carbon fiber in different potting medium.

Sample	Maximum Depth of	Modulus (GPa)	Hardness (GPa)
	Indentation (nm) (Averaged over)		
Carbon fiber in potting epoxy	200 (150 -200)	62.2 (5.13)	4.96 (0.386)
	500 (300 -500)	51.4 (2.37)	4.43 (0.762)
	800 (600 -800)	47.2 (4.10)	4.33 (0.381)
Carbon fiber in vinyl ester	200 (150 -200)	64.2 (6.22)	7.12 (0.41)
	500 (300 -500)	57.8 (7.53)	5.74 (0.755)
	800 (600 -800)	48.8 (5.52)	5.19 (0.866)

Table 11: Interfacial properties for TORAY T700 carbon fiber in potting epoxy and composite

Sample	Interfacial Stiffness (N/m)	Onset of Nonlinearity (mN)
Carbon fiber in Vinyl Ester	201000 (20700)	39 (3.25)
Carbon fiber in Potting epoxy	189000 (18100)	23 (4.22)

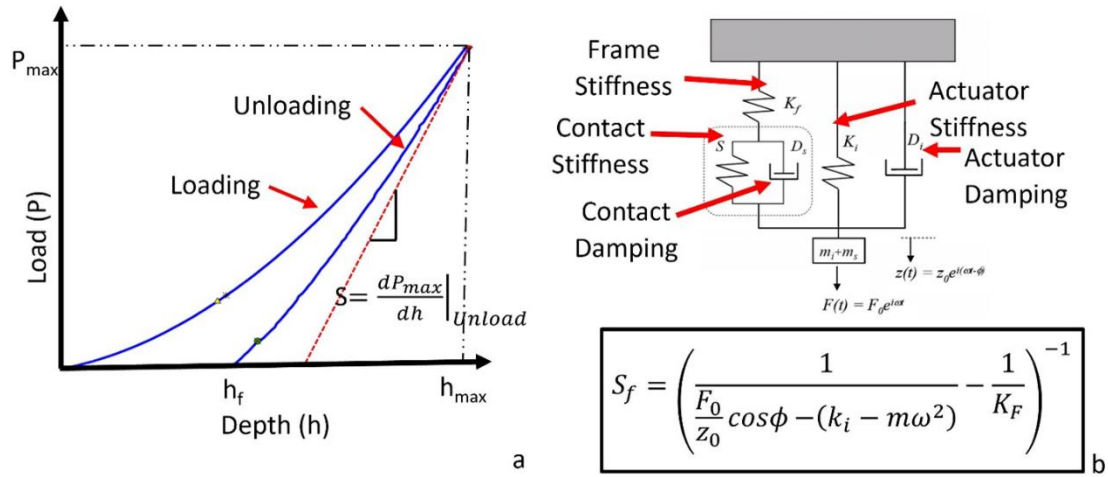


Figure 51: Typical Load-Depth curve from Nanoindentation b) Dynamics of contact in Continuous Stiffness Methods (CSM)

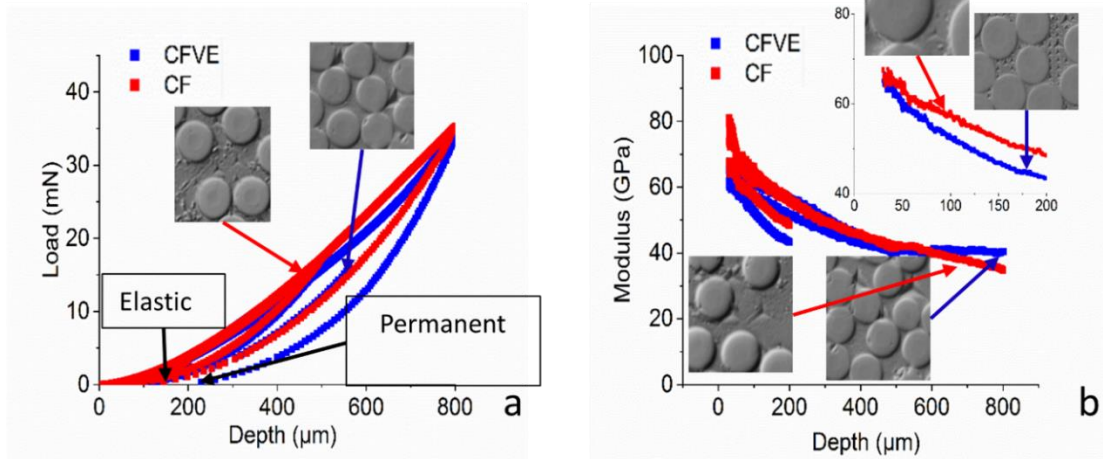


Figure 52:a) Load depth curve b) Modulus depth curve obtained for T700 carbon fibers.

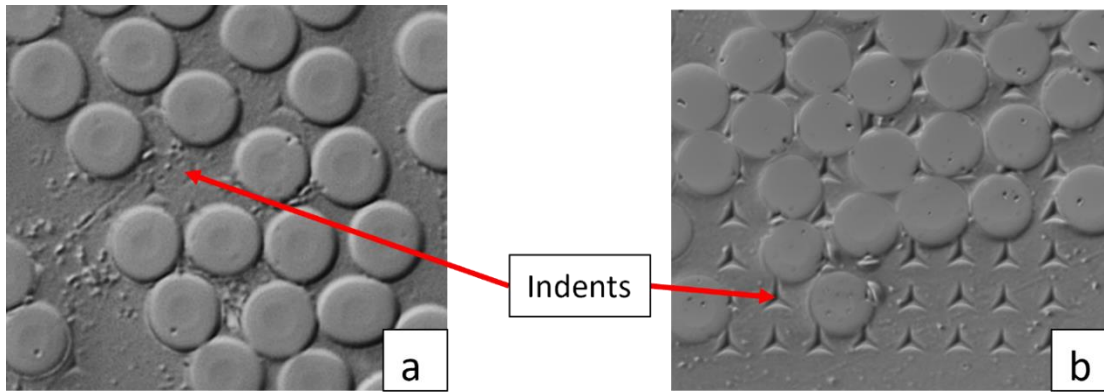


Figure 53: Optical image showing the 500 nm indentation of a) T700 carbon fibers in epoxy matrix, b) T700 carbon fibers in Vinyl ester matrix.

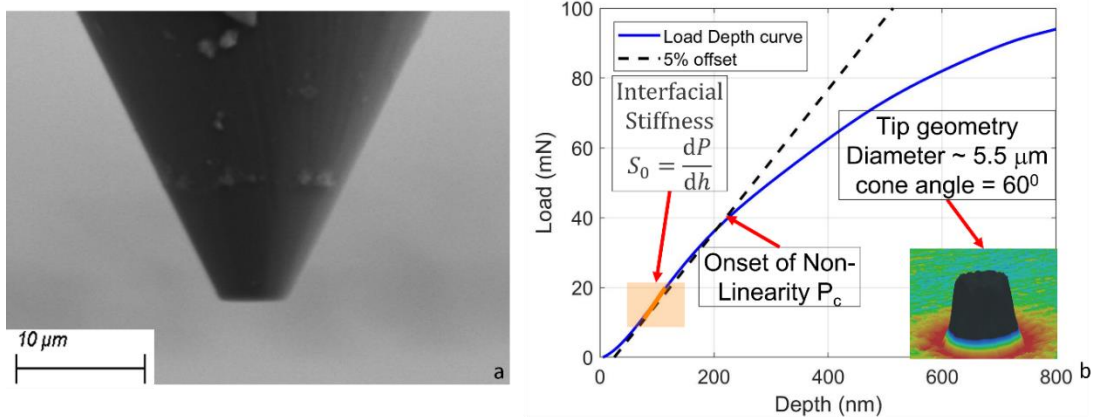


Figure 54:a) Geometry of the tip b) Load-Depth curve obtained via Push in tests.

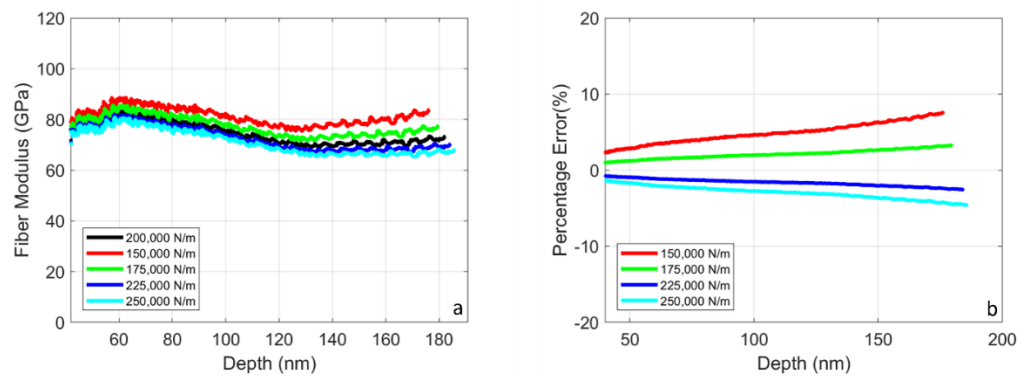


Figure 55: a) Effect of interfacial stiffness upon the calculated Fiber indentation modulus
b) Error in the calculated modulus assuming an interfacial stiffness of 200000N/m.

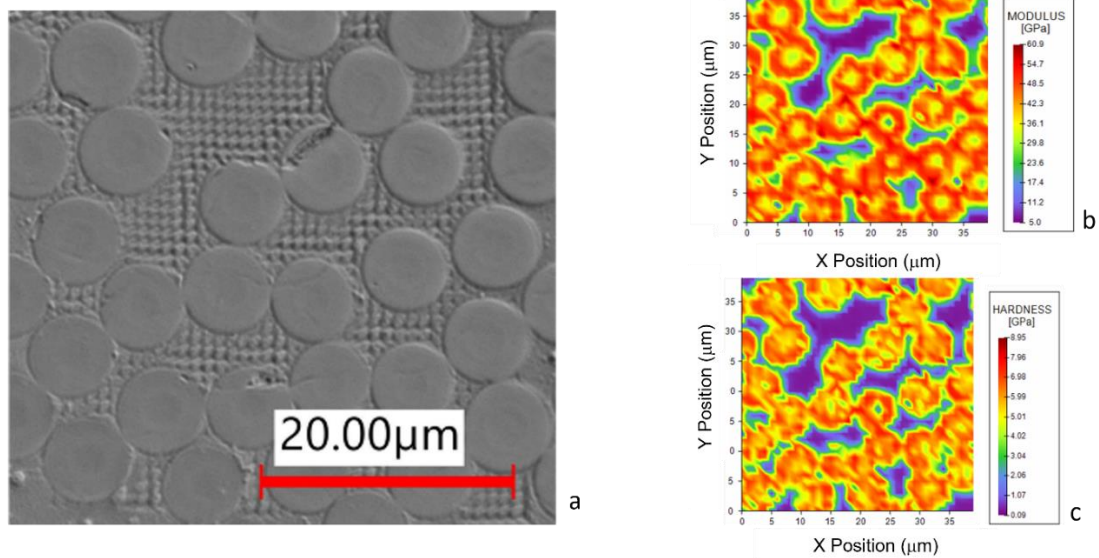


Figure 56: Spatial variation in modulus and hardness for different fibers

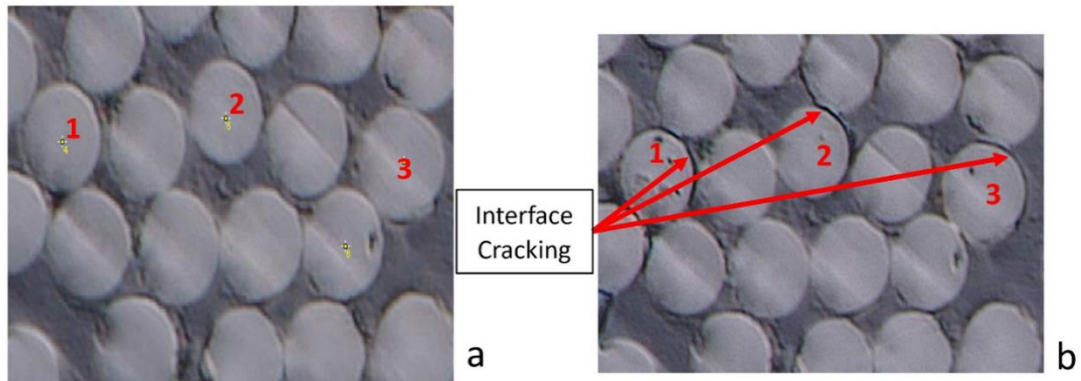


Figure 57: Optical images of CFVE a) pre indentation b) post indentation.

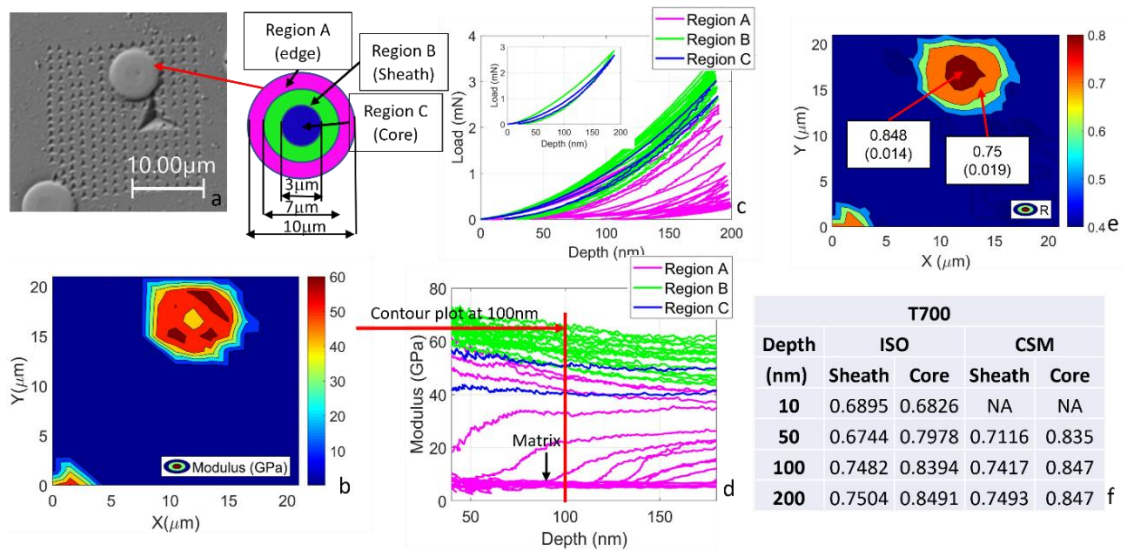


Figure 58: Nanoindentation response of TORAY T700 carbon fiber a) Optical Image b) Modulus Map at 100nm, c) Load-Depth curve, and d) Modulus vs. Depth curve e) Recovered energy map for 200nm indentation f) Recovered energy as a function of depth and dynamics.

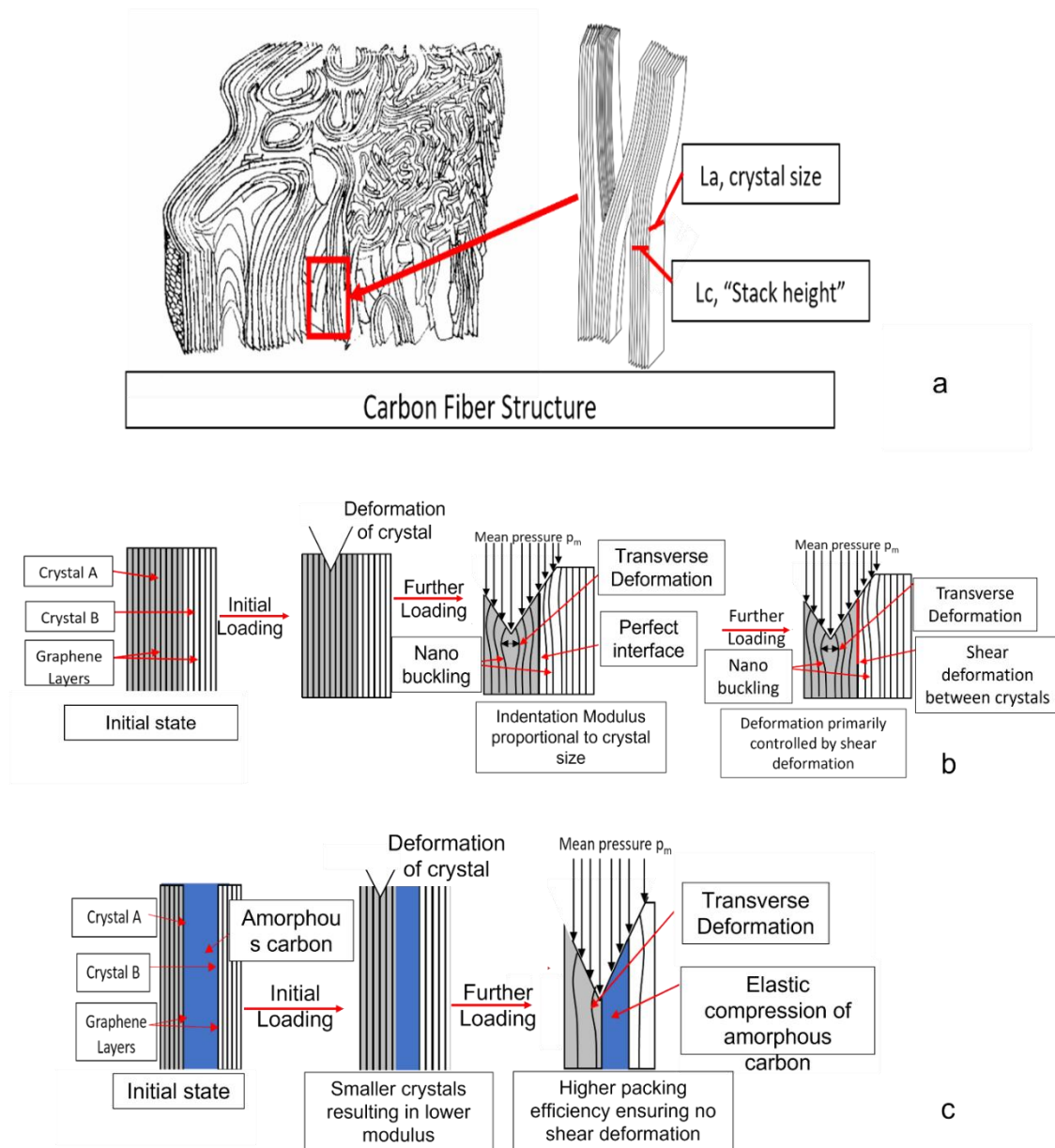


Figure 59: a) Structure of carbon fiber, b) Schematic of the deformation of carbon fiber during indentation with region dominated by crystalline carbon with larger crystals, c) deformation in region dominated by amorphous carbon and smaller crystals.

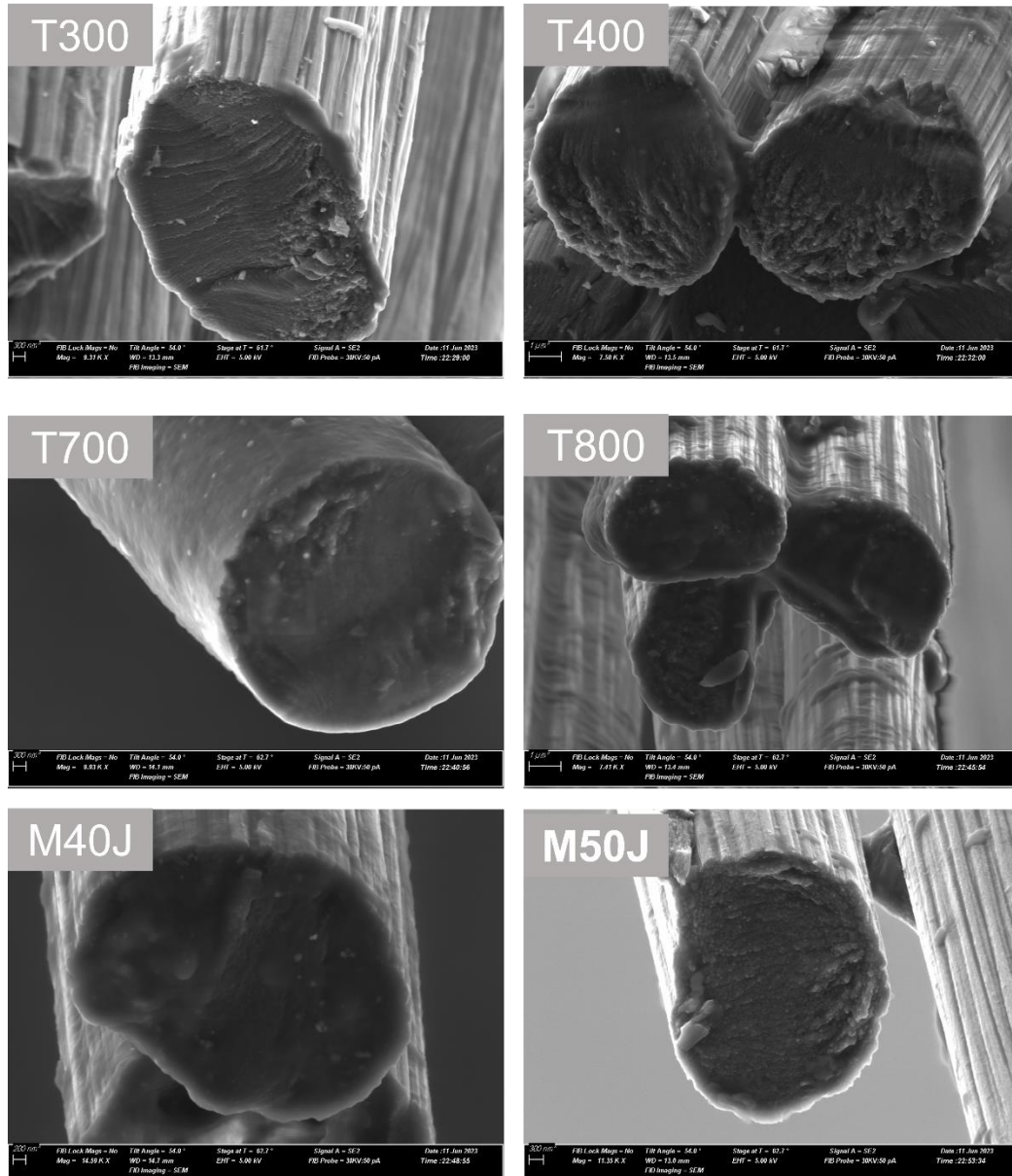


Figure 60: SEM micrographs of T300, T400, T700, T800, M40J and M50J Carbon fibres.

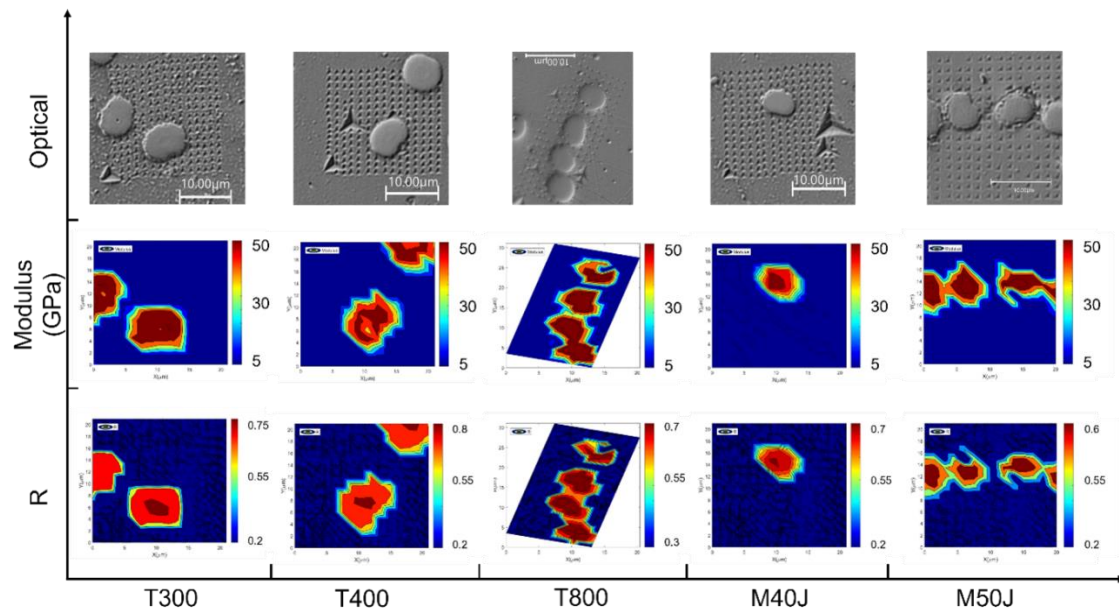


Figure 61: Modulus and Recovered energy maps for different TORAY carbon fibers.

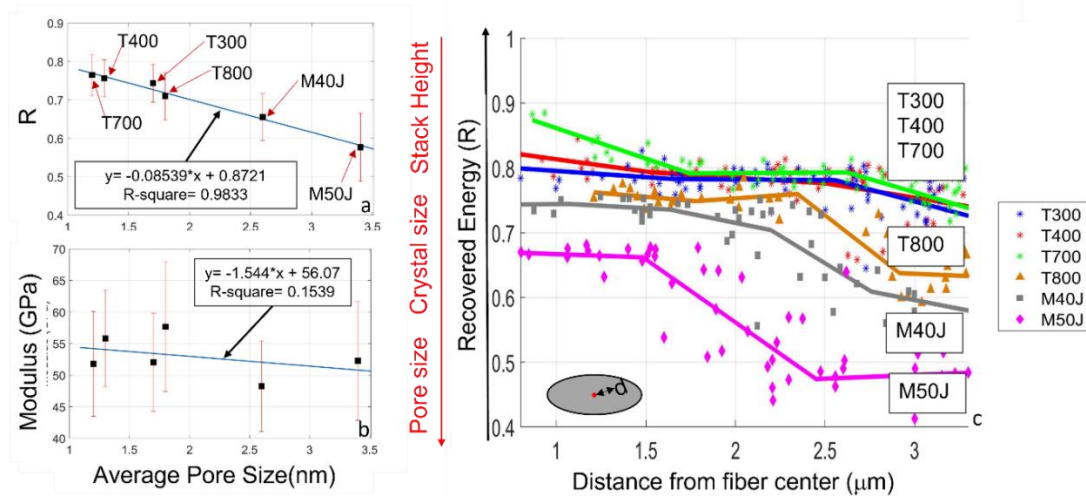


Figure 62: a) A strong correlation between recovered energy as a function of pore size, b) weak correlation for modulus as a function of pore size c) Development of pores, crystal size, and stack height obtained using recovered energy as a function of distance from center.

CHAPTER 5: SPLITTING MODE-I FRACTURE TOUGHNESS OF CARBON FIBERS USING NANOINDENTATION

Abstract

In this study, we conduct a thorough experimental and computational investigation to extend the pillar splitting technique, developed initially for ceramics, to brittle fibers in reinforced composites. In pillar splitting methodology, micropillars with circular cross-sections are tested to evaluate the load required to cause instability. The fracture toughness of the material, using the parameter γ via the cohesive zone finite element method (CZFEM), is correlated with the instability load. In reinforced composites, a unique opportunity arises: the existence of already present micropillars (reinforcing fibers). To successfully apply the pillar splitting technique, the authors investigate the effects of fiber/matrix assembly and the shape of the fiber. This study focuses on evaluating the fracture toughness of different-grade Toray carbon fibers. The minimum height required to avoid matrix effects is equal to the diameter of the reinforced fiber for a perfect interface. In contrast, the required protruding height is reduced to zero for a weak fiber–matrix interface. A new parameter, β , is introduced to quantify the deviation of the cross-sectional shape from circularity. An effective γ is then evaluated and used in the pillar splitting experiments to correlate the instability load to Mode I fracture toughness. Finally, the results are validated experimentally, and the Mode I fracture toughness is evaluated for a range of Toray PAN carbon fibers. It is found that fracture toughness reduces as the modulus of the carbon fibers increases.

Introduction

Carbon fibers as reinforcements in fiber reinforced-polymer (FRP) composites have seen substantial growth in diversified applications, such as aerospace, automotive, and sporting goods industries [164–166], due to their high strength-to-weight ratio. The

success of these applications will further be enhanced as a result of the developing advances in high quality strong and stiff fibers[164], improved understanding in surface functionalization and interphase science[165], and recent explosion on integration into additive manufacturing methods[166]. As the demand for lightweight and energy-efficient materials surges, the application of carbon fibers is predicted to rise continuously. Recently, improvements in the production and quality of low-cost recycled carbon fiber have unlocked a wide array of alternative domains for carbon fiber applications [167,168]. The Office of Naval Research is currently exploring the use of carbon fiber sandwich structures for large sea vessels [1,128,131]. Thus, there is a critical need to evaluate and understand the mechanical properties of carbon fibers. Typically, the failure of FRP composites is catastrophic, whether subjected to tensile or compressive loading[2,128,169]. The failure often initiates due to matrix cracking and ends with a fiber rupture caused by a fiber fracture. Therefore, the fracture toughness of the single-fiber phase is directly associated with the fracture resistance of the multi-phase composite. Typically, nominal carbon fiber diameter ranges between 6 μm and 7 μm , and due to the scale involved, it is not easy to evaluate single fiber mechanical properties [46]. Due to these difficulties, little work has been done to measure the fracture behavior of single carbon fiber. Linear elastic fracture mechanics (LEFM) is often used to evaluate the fracture toughness and critical energy release rate for most brittle materials[47]. Using LEFM, Mode-I fracture toughness can be estimated by Equation 1:

$$K_{1c} = \sigma_f Y \sqrt{\pi \cdot a_c}, \quad \text{-(5.1)}$$

where K_{IC} is the Mode-1 stress intensity factor, σ_f the tensile strength, a_c is the flaw size, and Y is the geometrical correction factor [47]. Unfortunately, Equation 5.1 requires a priori knowledge of the flaw size, which is difficult to evaluate for small-diameter fibers, such as carbon fibers. To overcome this drawback, fracture toughness is often calculated using the mirror-zone size relationship, where the critical flaw size to mirror zone (defined by the smooth region around a flaw of the fractured surface) ratio is assumed to be constant and is calculated empirically. Recently, a new technique is developed by Morishita et al. [48] to measure fracture toughness directly using focused ion beam (FIB)-milled notches [48–50]. The technique is extended by Kant et al.[47] to Toray T700 Polyacrylonitrile (PAN) carbon fibers having an average diameter of 7 μm . Although highly accurate, the time-consuming sample preparation and the intricacy required to measure fracture toughness justify the development of an alternative technique. In this work, the authors use the values reported by Kant et al. [47] to be the source of validation for the developed methodology.

Evaluation of fracture toughness using elastic/plastic indentation has been a topic of interest in past decades[36,38,170]. It is widely accepted in the literature that the cracks form below the indented surface and propagate along the corners of the indenter edges. These cracks that form can be characterized as lateral, Palmquist, median, radial, or cone cracks. A detailed description of the definition of these cracks can be found elsewhere[35,171]. Earlier work in understanding the crack initiation and profile involved a scientific community debate. For example, Lawn and Evans[36] argued that the initiation of median cracking due to Vickers indentation depends upon the size of the

flaw. On the other hand, Hagan [38] argued that the location of the intersection of the dislocation slips is the region where the crack initiates. Recent advances in computational capabilities have shown that the type of crack that originates during the indentation depends upon the elastoplastic properties of the material under indentation. Brittle materials show a median cracking, while ductile materials show a Palmquist-type cracking. Therefore, it has been shown that the Lawn, Evans, and Marshall model works well for brittle materials as the median crack profiles are obtained during indentation. For long cracks (large crack lengths compared to flaw size), the simplified Lawn-Evans-Marshall model can be reduced to Equation 5.2 [29]:

$$K_c = \alpha \sqrt{\frac{E}{H} \frac{P_{max}}{c^{3/2}}} \quad -(5.2)$$

Through a series of works, Johannis et al. [30,41] have shown, using cohesive zone finite element simulation (CZ-FEM), the development of median and Palmquist cracks during indentation and the evaluation of stress intensity factors to the corresponding cracks. More importantly, for purposes of this study, they have addressed the advantages and limitations of simulating the indentation cracks using CZ-FEM [30] which is discussed in more detail in section 2.3.

Indentation cracking [28,34,41,172–174] and the pillar splitting technique [27,33,107,173] are two proposed methodologies for measuring fracture toughness using nanoindentation. In indentation cracking, the sample is loaded with a sharp pyramidal diamond tip, resulting in cracking of the material under investigation. The crack length is then measured by imaging, and LEFM is used to evaluate the fracture toughness.

However, due to the geometric constraints of reinforced fibers (diameter < 20 µm for glass fibers and diameter ~ 7 µm for carbon fibers) and the relatively vast volume of material required for the indentation cracking tests, the application of indentation cracking for reinforced fibers is not possible. The pillar splitting tests method was introduced by Sebastiani et al. [107] to overcome the limitations of the indentation cracking techniques (i.e., residual stresses, substrate influences, and, in some cases, geometric limitations to calculate the fracture toughness). In the pillar splitting technique, micropillars are often prepared using FIB milling. Using a Berkovich or sharper indenter, the pillars are then indented at the center. The pillars are loaded until instability is reached, at which point, the pillar splits into three equal fragments. The instability load is used to determine the fracture toughness based on the pillar radius (Equation 5.3 [107]):

$$K_c = \frac{\gamma \cdot P_{Instability}}{R^{3/2}}, \quad -(5.3)$$

where K_c is the critical fracture toughness, $P_{Instability}$ is the instability load, R is the radius of the micropillar, and γ is a material dependent constant determined using cohesive zone finite element method (CZFEM). In their earlier work, Sebastiani et al. [27,107] showed that while the coefficient γ (Equation 5.3) does not depend on the individual elastic modulus and hardness values; it is only dependent upon the modulus-hardness ratio (E/H). This property of γ being only a function of E/H ratio has been shown to be valid for a range of K_c (0.8-8 MPa m^{3/2}) and irrespective of the pillar radius. The origin of Equation 5.3 stems from a simple dimensional argument, therefore there is no physical meaning for the parameter γ . Regardless, γ considers the role of the shape of the tip and material properties in equating the left side and right side of Equation 5.3.

However, the property of γ being influenced only by the E/H ratio has its origin in the classic Lawn-Evans-Marshall (LEM) model (Equation 5.2) where in case of long cracks the fracture toughness of the material is only dependent on the maximum load, the crack length, and the E/H ratio. The minimum radius of the micropillars required for pillar splitting is a function of the material's hardness. Pillar splitting testing, however, involves complex preparation of the samples. Often, the micropillars are prepared by milling the sample under consideration using FIB in a circular pattern. The probe size of the beam is then reduced to obtain a finely polished micropillar. Not only is the preparation of each micropillar taxing, but the damage caused by the FIB beam at the pillar edges could also influence the evaluated fracture toughness. In addition, multiple tests are required to calculate statistically significant fracture toughness; thus, the time and cost associated with FIB milling add up. Reinforced composites, however, offer the possibility of preexisting micropillars, and simple polishing techniques can be used to prepare micropillars of the desired height required for fracture toughness evaluation.

The geometry of continuous fibers in FRP composites typically exhibits an almost infinite aspect ratio (l/d) with a surrounding low stiffness polymer matrix, resulting in a geometry that presents a unique opportunity for pre-existing micropillars. In this work, the authors present a modified pillar splitting technique to evaluate the fracture toughness of reinforced fibers and explore the advantages and challenges that arise due to reinforced fiber geometry.

Experimental Details

Pillar Preparation

Toray PAN-based carbon fibers are used as this work's primary material. The pillar preparation is done by clamping a tow of carbon fibers between two metal blocks to ensure the verticality of the fibers. A hollow pipe is then placed around the straight tow protruding from the metal blocks and filled with Crystalbond™ 509 supplied by Electron Microscopy Sciences. Once the crystal bond is cured, the metal blocks are removed, thereby exposing the lower portion of the mounted fibers. The system is then placed in a cylindrical mold and filled with epoxy obtained from Buehler™, prepared by mixing EpoxyCure2 resin and EpoxyCure2 hardener in a four-by-one weight ratio (Figure 63). The samples are hand polished (from the side with crystal bond) using a hand grinder, model 160 obtained from E.A. Fischione Instruments Inc. Epoxy-based pillar preparation is done by grinding (320 grit paper), polishing, and inspecting the samples at regular intervals until the desired thickness is achieved (measured using a Keyence VK x250 laser microscope). The samples are soaked in an acetone solution within a vacuum desiccator for two minutes to liquefy residual crystal bonds. Compressed air and cotton swabs are then used to remove the crystal bond, thereby revealing the micropillars. Next, the height of the pillars is remeasured. If the pillars are too tall, more crystal bonds are added, and the grinding/polishing process is repeated until the desired height of the micropillars is achieved.

Other than the micropillars, carbon fibers are mounted in two more resin systems: epoxy resin and Crystalbond™ 590. The mounted samples are polished using the specific guidelines for polishing composites using Buehler Metaserv 250 Grinder-Polisher. The

surface of the fibers after polishing is examined using a KEYENCE VHX7000 optical microscope.

Nanoindentation Testing

Nanoindentation testing is done under ambient conditions using the iMicro system (Figure 64) by NanoMechanics Inc. The system is housed in an environmental chamber on a vibration isolation table. Modulus and hardness evaluation uses a Berkovich (65.3° cone angle) diamond tip following the Oliver–Pharr formulation [16,17], while the Cube corner (35.3° cone angle) diamond tip is used for Pillar splitting experiments (Figure 64). Both tips are acquired from Synton-MDP.

As mentioned, the γ parameter is needed to evaluate fracture toughness in pillar splitting experiments. For this purpose, an E/H ratio is required. Conventionally, E and H values are obtained from indentation testing using a Berkovich tip [29,33]. For carbon fibers, the modulus obtained via indentation (~55 GPa for T700) [158] does not coincide with the SFTT-evaluated elastic modulus (~250 GPa for T700) [46]. Using the lower E values obtained from nanoindentation testing results in convergence difficulties in the simulation due to the large depth required to reach the instability load needed for γ evaluation. γ being a parameter that is only dependent on the E/H ratio, we combine the modulus evaluated using SFTT [45,46] with the E/H ratio from nanoindentation to determine the hardness value. The above choice of E and H is controversial. However, it is confirmed that this choice of E and H did not change the value of γ calculated for a specific case of T700 carbon fiber using the properties obtained from nanoindentation. Those results are provided in supplemental information. The γ obtained also corresponds well with the

study by Ghidelli et al. [27]. Indentation testing uses a continuous stiffness measurement mode with a strain rate of 0.02/s. The elastic modulus and hardness are averaged over at least 25 tests. The modulus and hardness are averaged for depths between 100 nm and 150 nm. Carbon fibers are locally anisotropic; thus, the properties used in this work are an average of the resultant properties from a minimum of five tested fibers. Table 12 shows the hardness and modulus values used for the carbon fibers under investigation. Poisson's ratio has been shown to minimally affect the indentation modulus[16] while having no effect on hardness; thus, it is chosen to be 0.25 in this work. Tip area function and frame stiffness calibration are performed before testing using the standard fused silica reference sample according to the Oliver–Pharr method [16].

Finite Element Analysis

Finite element analysis with cohesive elements is performed using ABAQUS software. The cube corner pyramidal indenter is assumed to be rigid. Unless explicitly mentioned, all the simulations performed in this work exploit the 6-fold symmetry of the indenter. The carbon fiber is locally anisotropic and inhomogeneous and therefore the propagating cracks experiences disparate spatial mechanical response. However, similar to previous work by Kant et al. [47], we assume the carbon fiber to be isotropic thereby considering the average mechanical response. Figure 65 shows the Abaqus model assembly. Cohesive elements are employed by offsetting the mesh nodes to obtain zero-thickness cohesive nodes with two faces. One face of the cohesive element is tied to the pillar. At the same time, symmetric boundary conditions are applied to the other faces of the cohesive elements and the micropillar's symmetric plane (Figure 65). Therefore, the crack is

constrained to grow within the defined cohesive plane, as observed experimentally and in previous studies [41,107]. The base of the pillar is fixed, and the contact between the indenter and the fiber is assumed frictionless. The fiber is assumed to be perfectly plastic, and more than 20,000 full integration elements (C3D6 and C3D8) are employed in the mesh corresponding to the fibers. The constitutive behavior of these elements is defined by the elastic modulus, E , Poisson's ratio, ν , and a mises yield strength, Y , as shown in Table 12. Yield strength, Y , is obtained by parallel elastoplastic simulations to match the corresponding value of hardness, H , as previously done in the literature [175].

The cohesive zone model with bi-linear traction-separation-based cohesive elements (COH3D8) is used to represent crack propagation phenomenologically. Although cohesive elements do not correctly model crack initiation, crack propagation and instability load are correctly estimated using the cohesive zone model [28,41,107].

Cohesive elements are defined through elastic stiffness, S , which remains constant until the maximum cohesive strength, σ_c , is reached. Upon further loading, the elastic stiffness decreases linearly such that the total area under the traction-separation curve corresponding to the deformation equals to the critical Mode-I energy release rate, G_{IC} .

The Maximum quadratic nominal stress damage (MAXS) damage criterion for the onset of debonding and fracture energy is used for crack nucleation [107]. The initial separation of cohesive elements is set to zero, and the cohesive planes are placed on the prospective crack planes. Thus, crack growth is constrained to the defined plane. The cohesive elements' constitutive behavior is described by four material properties: the Mode I critical energy rate, the cohesive strength, the cohesive stiffness, and the viscosity

corresponding to viscous regularization. Assuming plane strain, the fracture toughness, K_{IC} , is related to the critical Mode I energy release rate, G_{IC} , as shown in Equation 5.4, based on LEFM. Therefore, the inherent assumption in the simulation is that, for the crack to propagate, the Mode I stress intensity factor at the crack tip needs to be equal to the linear-elastic plane strain fracture toughness, K_{IC} . This assumption has been shown to correspond well with experimental results in the literature [29,30] Mode II and Mode III energy release rates, cohesive stiffness, and cohesive strength are set well above the Mode I parameters to ensure that these modes do not influence the results, as has been done in past studies [29,41].

$$K_{IC} = \sqrt{\frac{G_{IC} E}{1 - \nu^2}} \quad -(5.4)$$

$$\rho = \frac{\pi}{8} \left(\frac{k_1}{\sigma_c} \right)^2 \quad -(5.5)$$

The size of the process zone (ρ), defined by the size of the plasticity region at the crack tip to avoid stress singularity, in LEFM depends on the fracture toughness, K_{IC} , and the maximum cohesive strength, σ_c , given by Equation 5.5, as per Dugdale [41]. As has been shown in the literature [30,41], a minimum of three cohesive elements within the process zone are required to capture the developing stress state [28]. Unless otherwise specified, this work employs a minimum of five cohesive elements within the process zone. For the simulation to correctly represent crack propagation, the minimum radius of the pillar must be at least 10 times the size of the process zone [41]. At the same time, the height of the pillar should be at least twice the radius of the pillar. For all simulations studied in this work, the pillar radius is set to be at least 10 times the size of the process zone.

Unless otherwise specified, the height of the pillar is set to be equivalent to the diameter of the pillar.

Results

Evaluation of γ

For a given pillar radius and fracture toughness, the simulation outputs an instability load.

These values are used in Equation 5.3 to determine γ . Figure 66 shows the crack growth geometry before and after failure for Toray T700 carbon fiber. The crack grows radially until the crack tip recognizes the free surface, at which point, the crack grows

instantaneously, resulting in instability. The cohesive strength (σ_c), pillar radius (R), and critical energy release rate (G_{IC}) input for different fibers are shown in Table 13

Using Equation 5.4, the value of the critical energy release rate is chosen such that the calculated fracture toughness is close to 1 GPa (reported value of range of carbon fibers [176]). Table 13 shows the value of γ obtained for different grade Toray carbon fibers.

The value of γ increases with an increase in the E/H ratio; these results are anticipated, as has been shown by Sebastiani et al. [27]. γ values presented in Table 13 can be used for a wide range of reinforced fibers with E/H ratios between 9.4 and 13.3, as the values can be linearly interpolated in that range, as discussed in previous studies [27]. However, to implement these results experimentally, the challenges associated with the fiber/matrix assembly must be identified and resolved.

Effect of Matrix Upon Pillar Splitting Results

In a typical FRP composite, reinforcing fibers are surrounded by a polymer matrix. To evaluate the influence of the surrounding matrix on fiber pillar testing, simulations are

carried out by varying the elastic modulus and hardness of the matrix. Figure 67 shows the meshed assembly used to evaluate the effect of the matrix on the pillar splitting results. As in the setup in Figure 65, only the one-sixth model is considered. The height of the fiber-matrix assembly is extended to 25 times the diameter of the fiber. Increasing the height any further did not change the results of the simulation. Ideally, cohesive elements should be applied to the height of the whole fiber; however, this results in extensive computational time. To reduce computational time, the fiber is divided into a substrate portion and a pillar portion. These two parts are connected to each other using tie constraints. Cohesive elements are applied only to the pillar portion of the fiber. The height of the pillar is chosen to be twice the diameter, with one-half protruding above the matrix surface. No difference in the simulation results is observed with increasing the pillar height beyond twice the diameter.

The surrounding matrix has a radius that is six times the radius of the fiber, and the contact between the fiber and the matrix is defined by the tie constraint. The fiber-to-matrix modulus ratio (E_f/E_m) and the matrix-modulus-to-matrix yield strength ratio (E_m/Y_m) are varied between simulations, and their effect on the instability load is determined.

Figure 68 shows the resulting load-depth curve for various E_f/E_m and E_m/Y_m ratios with a perfect interface. As the E_f/E_m or E_m/Y_m ratio increases, significantly more deformation is needed to reach the same load compared to the free-standing (no surrounding matrix) fixed pillar. The result is predictable, as the combined effect of a lower matrix modulus or matrix yield strength would be to lower overall indentation stiffness. However, as can

be seen from Figure 68, the instability load remains invariant as a function of matrix compliance. Sebastiani et al. [32] reported similar behavior for ceramics with different substrates.

Minimum Aspect Ratio (h/R) of the Pillar

Additional simulations are carried out where, by changing the height of the substrate fiber, the protruding height, h (Figure 67), is varied to understand the effect of the aspect ratio (h/R) upon the evaluated fracture properties. The matrix modulus and yield strength are set to be 3 GPa and 0.200 GPa, respectively, representing the properties of potting epoxy often used for preparing samples for polishing. Based on the results obtained (Figure 69), the value of γ changes significantly as a function of protruding height.

Assuming the value of γ obtained for $h/R = 2$ to be the true value, the error corresponding to a case of no protruding height can be as high as six percent, while the error corresponding to a $h/R = 1$ is less than one percent. The results signify that a minimum protruding height-to-diameter ratio of 1 is required to evaluate the fracture properties correctly. These results are expected because Sebastiani et al. [32] reported an increasing error as a function of a decreasing h/R ratio. For the case of $h/R = 0$, two additional simulations with surface-based cohesive behavior (interface) between the fiber and the matrix are performed. More specifically, the splitting load is evaluated for Mode II nominal stress of 10 GPa ($G_C = 0.1 \text{ GPa}\cdot\mu\text{m}$) and 10 MPa ($G_C = 0.0001 \text{ GPa}\cdot\mu\text{m}$) representing “extremely strong” and “weak” interface, respectively. The introduction of the interface significantly changes the simulation behavior: the error in the evaluated value of γ reduces to less than two percent for the strong interface, while it becomes

negligible for the case of the weak interface. The above results are promising, as they imply that, provided the interface between the fiber and matrix is “weak,” the pillar splitting methodology can effectively be conducted without the preparation of micropillars. Of course, this requires experimental validation, which is addressed in Section 3.2.2.

Effect of Shape of Reinforced Fibers upon Pillar Splitting

The abovementioned methodology for evaluating fracture toughness is very limited to circular fibers, and it requires that the indentation be conducted at the center of the fiber. Carbon fiber diameters are approximately 7 μm , and achieving perfectly concentric indentation is a challenge. Furthermore, carbon fibers often come in elliptical and “kidney bean”-shaped cross-sections. Therefore, there is a need to expand the above methodology to any arbitrary shape or indentation location. Perhaps an additional parameter quantifying shape is required. From an experimental perspective, this would make the toughness evaluation more involved; however, a two-parameter approach is typical of nanoindentation experiments. To understand the effect of shape, we start with relatively simplistic cases of twofold symmetry with respect to the shortest crack axis. In an ellipse with different a/b ratios (special case of the circle with $a/b = 1$), an arbitrary geometry can be generated by indenting at a point within the ellipse away from the center defined by the distance e , at an angle θ from the x-axis (Figure 70); the orientation of the minimum crack with respect to the x-axis is defined by the angle φ . For the 2-fold symmetric simulations under consideration, we start with cases corresponding to $\theta = \varphi = 0$. An E/H ratio ~ 9 is considered, while the minimum crack length, $R_{\min}$, is set to 10

μm . The base circle (radius = $R_{\min}$) is kept constant across all simulations to minimize the mesh effects on the instability load. Indentation is always carried at the center of the base circle. For these cases of $\theta = \varphi = 0$, $a = e + R_{\min}$. The size of the cohesive elements is chosen such that there are three cohesive elements within the process zone.

Figure 70 shows the normalized load (normalized with respect to the instability load of the base circle) depth curve obtained for the base circle, a circular geometry with an $R_{\min}/e$ ratio of 0.5, and an elliptical geometry with $a/b = 0.5$ and $e = 0$. Since the measurement of the instability load corresponds to the crack tip identifying the presence of a free surface, it is reasonable to assume that the instability load would primarily be a function of the minimum radius of the crack path (i.e., $R = R_{\min}$ in Equation 5.3). Since $R_{\min}$ is kept constant, the resulting instability load is expected to be the same for all three simulations. However, based on Figure 70, a significant variation in γ ($\sim 1/1.4$) is observed even though $R = R_{\min}$ is assumed in Equation 5.3.

Substituting $R_{\min}$ in Equation 5.3 and using the same γ calculated from the one-sixth symmetric model would result in a significant error while evaluating γ for every shape, and eccentricity is unrealistic. Therefore, a correction shape factor is required in Equation 5.3. For all simulations, it is observed that the crack growth remains symmetric until the instability load.

To understand how the input mechanical properties affect the error in instability load, simulations are carried out to vary the mechanical properties of the fiber and the input fracture toughness. Additional simulations are carried out to understand the effect of scaling the problem while keeping the same shape (changing $R_{\min}$ and scaling

accordingly). The results are reported in Table 14. No significant deviation as a function of mechanical property or scale is observed. Hence, it is concluded that the error in γ is only a function of the cross-sectional shape. The small deviation between the values of γ is attributed to the relatively coarser cohesive elements used in the simulations (three cohesive elements per process zone).

Discussion

Extension of Pillar splitting to an arbitrary shape

Any error function that correlates the γ evaluated for a shape with two-fold symmetry to the γ of a circle with radius = R_{min} should represent the deviation of a shape from circularity. Therefore, the error function (β) in the form of Equation 5.6 is chosen and plotted against γ/γ_{circle} . A conceptual interpretation of Equation 5.6 is that, R being the distance from the point of indentation to the perimeter along the direction defined by an arbitrary angle ψ , the parameter $\left(\frac{R-R_{min}}{R_{min}}\right)$ represents the normalized deviation from circularity. Simultaneously, the parameter $e^{m\psi}$ determines the contribution of the calculated deviation at an angle ψ . Therefore, the exponential term (with a negative coefficient) allows for reducing the effect of the region away from the crack tip.

$$\beta = \int_0^{\pi} \frac{1}{\pi} \left(\frac{R - R_{min}}{R_{min}} \right) e^{m\psi} d\psi \quad -(6)$$

A sensitivity study is carried out to understand the effect of m upon the evaluated β and, subsequently, the γ/γ_{circle} evaluated from the simulations. The value of m varies incrementally by 0.25 between -2 and 2, and the correlation between the evaluated β and γ/γ_{circle} is scrutinized. Figure 71 shows β/β_{max} (normalized β) vs. γ/γ_{circle} plots as a

function of m . For conciseness, only three values of m are shown. A poor correlation is observed for cases of $m > 0$, which is obvious, as $m > 0$ implies a significant contribution to the error as one moves away from the minimum crack axis. More interestingly, the best correlation is obtained for the specific case of $m = 0$ with a linear variation of β . From an experimental perspective, this is a highly encouraging result, as no cumbersome methodology is required to evaluate β because it can be rewritten as Equation 5.7. Equation 5.7 involves measuring the minimum radius corresponding to the fracture and the cross-sectional area of the shapes defined by $\pm 180^\circ$ from the minimum crack plane ($A1$ and $A2$ in Figure 71), which can easily be measured using open-source software, such as ImageJ [177]. The maximum error between the simulation and the trendline in Figure 71 is less than 2 percent. Therefore, given $0.2 < \beta < 2$, one can calculate the γ for a two-fold symmetry problem using the parameterized trendline. Interestingly, it is observed that the intercept of the trendline ($\beta = 0$, γ corresponding to the base circle) is closer to 0.9 than 1 ($A1 = \text{Area}_{\text{Base Circle}}$). Equation 5.7 assumes that instability is a function of the geometry defined by $\pm 180^\circ$ from the minimum crack plane. However, this assumption becomes invalid in the case of the center indentation of the base circle, as instability is only a function of $\pm 60^\circ$ of the minimum crack plane. Therefore, the γ evaluated using parameter β would not be reduced to the case of circular geometry with center indentation.

$$\beta = \frac{\sqrt{A1} - \sqrt{\text{Area}_{\text{Halfcircle}}}}{\sqrt{\text{Area}_{\text{Halfcircle}}}} = \frac{\sqrt{A1} - \sqrt{\frac{\pi}{2} * R_{min}^2}}{\sqrt{\frac{\pi}{2} * R_{min}^2}} \quad -(5.7)$$

The above methodology only works for shapes with half symmetry. To understand how an unsymmetric geometry affects the results, two additional simulations are carried out, the first corresponding to the superposition of $R_{\min}/e=2$ and base circle ($e=0$) and the second corresponding to the superposition of $R_{\min}/e=2$ and $R_{\min}/e=0.5$ (Figure 72). Considering that we are in the LEFM regime and the propagating crack tip experiences equal and opposite forces at the crack front, a simple thought experiment reveals that the resulting instability load would be the weighted average of the two instability loads. Table 15 shows the instability load corresponding to all cases and the weighted averages. Excellent agreement is seen for both cases based on the areal-weighted averages, confirming the hypothesis.

Based on the above results, the problem of pillar splitting for an arbitrary shape can be solved by defining a $\gamma_{effective}$. We define $\gamma_{effective}$ based on Equation 5.8, in which the γ_1 and γ_2 correspond to the γ of the area of the shape defined by $+180^\circ$ and -180° from the minimum crack radius, where the individual γ_i is defined as per Equation 5.9 (Figure 71).

$$\frac{1}{\gamma_{effective}} = \frac{1}{A_1 + A_2} \left(\frac{A_2}{\gamma_1} + \frac{A_1}{\gamma_2} \right) \quad -(5.8)$$

$$\gamma_i = (0.906 - 0.1138\beta_i) \gamma_{circle} \quad -(5.9)$$

Validation

T700 carbon fibers obtained from Toray industries are experimentally investigated to validate the technique's applicability to carbon fibers. These fibers correspond to the same fiber used by Kant et al. to evaluate Mode I fracture toughness using nanofabricated

notches [47]. Three Toray T700 carbon fiber samples—an epoxy matrix with $h/D > 1$, an epoxy matrix with no protruding height ($h = 0$), and a crystal bond substrate with $h = 0$ —are fabricated. Figure 73 shows an example load-depth curve obtained from one of the tests, with the inset showing the fracture surface of a T700 micropillar and a specific case of $h = 0$. For cases of $h/D > 1$, the fragments of remnant fibers were rarely found. The load-depth curve shows an increase in load until instability is reached, which agrees with the simulation results and previous studies. Kant et al. reported a value of $1.73 \text{ MPa}\cdot\text{m}^{3/2}$ as the average Mode I fracture toughness, while the fracture toughness varies roughly between 1.5 and $2 \text{ MPa}\cdot\text{m}^{3/2}$. An excellent agreement between the fracture toughness reported by Kant et al. and the proposed technique is attained for the crystal bond and epoxy ($h/D > 1$) matrices. At the same time, slightly higher values are obtained for the epoxy matrix with $h = 0$. The excellent agreement between the two techniques validates the assumption that E/H values obtained from the nanoindentation of carbon fibers can be used to evaluate Mode I fracture toughness. This result is unsurprising, as the stress field experienced by the fiber undergoing nanoindentation would be similar to that experienced during fracture toughness evaluation due to the similarity in tip geometry. The above validation eliminates the requirement of preparing micropillars, which, from an experimental perspective, is highly productive. It should be noted that CrystalBond™ 590 is soluble in acetone. Therefore, if necessary, micropillars could be easily created using acetone to expose the fibers.

Fracture Toughness of Carbon Fibers

Given the applicability of the technique, in-situ pillar splitting (M40J fiber with $\beta < 0.1$) is performed within a scanning electron microscope to observe the deformation behavior during pillar splitting of micropillars (Figure 74). First, the cube corner tip approaches the micropillar, and the initial deformation of the pillar is similar to an indentation experiment. No buckling of the micropillar is observed. As the depth increases, three identical cracks 120° apart (based on post-testing microscopy) from each other are formed until an increment in load causes instability. Post-testing imaging of the micropillar showed a 120° fragment of the remnant fiber (Figure 74).

Experiments are performed to evaluate the fracture toughness of different grade Toray carbon fibers. The tests are performed with a displacement rate of 50 nm/s. Only cases corresponding to $\beta > 0.2$ and $R_{\min} > 1.5 \mu\text{m}$ are considered for all the kidney bean-shaped fibers. Figure 74 shows the properties obtained for different grade carbon fibers using micropillars. A good correlation with the literature is seen for T300 carbon fiber [178]. It should be noted that a separate study was done to additionally validate the shape parameter using E-glass. Even though the results showed good correlation between the experimentally obtained $\gamma_{\text{effective}}$ versus the $\gamma_{\text{effective}}$ evaluated using the simulation, the center indentation of fibers showed high variance. Therefore, those results are not presented. Figure 75 details the procedure developed in this study, with the example showing the evaluation of fracture toughness of T400 carbon fibers with CrystalBond 590 as the substrate. First, optical imaging is done, then the fibers are indented using a cube corner tip. The optical microscopy is redone after testing. The before and after testing images are overlayed so that one fraction of the remaining fiber matches the intact fiber.

Subsequently, the evaluation of A_1 , A_2 , and $R_{\min}$ is done. Equations 5.7, 5.8, and 5.9 are then used to calculate the $\gamma_{\text{effective}}$, which is used in Equation 5.3 along with $R_{\min}$ to evaluate the fracture toughness. Even though the fracture toughness, based on nanofabricated notches, of T400, T800, and M40J is not reported in the literature, an opposite trend of decreasing fracture toughness from standard modulus (T700, T300, and T400) to intermediate modulus (T800) to high modulus (M40J) carbon fiber is observed in this study in comparison to what has been reported in the literature for other carbon fibers [178]. The opposite trend is not a consequence of pillar splitting methodology, as it has been shown to correspond well with ceramics and quartz [33,107].

Carbon fiber's crystalline properties (pore size, crystal size, and stack height) increase as one moves from standard to intermediate to high-modulus carbon fibers [45]. Moreover, the porosity of the sheath is reported to be higher than that of the core [44]. Therefore, a decrease in fracture properties could arise due to the increased porosity of the high-modulus carbon fibers. In pillar splitting methodology, the crack develops along the axis of the fiber (splitting the fiber cross-section into three parts); therefore, the effect of local porosity is higher. As the porosity increases, the crack propagates along the path of least resistance, resulting in lower fracture toughness for high-modulus carbon fibers with high porosity. For standard modulus carbon fibers, the amorphous core (location of fracture initiation) with insignificant porosity has a negligible effect on the reported properties. On the other hand, in the nano-notch technique, the crack propagates perpendicular to the fiber axis. Therefore, the properties obtained correspond to cracks traversing the graphene planes, resulting in higher fracture toughness. Hence, the discrepant trend

observed in this work is a consequence of the transverse isotropy of carbon fibers. To the best of the authors' knowledge, these are the first reported values of fracture toughness in the splitting mode. The methodology mentioned in this work can be further extended to evaluate the fracture toughness of fibers with cracks propagating perpendicular to the fiber axis by performing experiments in the transverse direction. However, this would require a volumetric shape parameter to account for non-cylindrical pillars, which is beyond the scope of this study and is a topic of further investigation.

Conclusion

In this work, a thorough experimental and computational investigation is conducted to extend the technique of pillar splitting to brittle fibers in reinforced composites. In the pillar splitting methodology, micropillars with circular cross-sections are prepared using FIB and then tested using a triangular pyramid to evaluate the load required to cause the micropillar fracture, which is correlated to the fracture toughness of the material using the CZFEM. First, the authors presented a polishing-based methodology to prepare the micropillars typically required for the pillar splitting technique. A series of computational and experimental investigations are carried out to understand the effects of the matrix, interface, and protruding height of the micropillar on the results. It is found that the matrix does not affect the instability load and only contributes to the depth required to reach the instability load provided an adequate height of the micropillars. The minimum height required to evaluate the matrix-independent results is equal to the micropillar's diameter for a composite with a perfect interface. The introduction of the interface drastically reduces the error in instability load, even for a condition with no protruding

height. Additionally, if the interface failure happens before the splitting failure, the error in the instability load approaches zero. Therefore, the presented methodology becomes elementary, as it eliminates the requirement of micropillars, provided the interface is “weak” and thus offers the simplicity of conducting traditional indentation experiments to evaluate Mode I fracture toughness. CrystalBond™ 590 is shown to be a suitable matrix material for the evaluation of the Mode I fracture toughness of carbon fibers using pillar splitting. Finally, experimental and computational investigations are carried out to extend the technique to an arbitrary shape. A shape correction parameter, β , is defined to extend the constant γ , evaluated for a circular cross-section, to a constant representing an arbitrary geometry. It is shown that the error arising due to an arbitrary cross-section is independent of the mechanical properties. Therefore, the concept of an effective constant, $\gamma_{effective}$, is introduced. The authors recommend that the methodology only be applied to cases with $0.2 < \beta < 2$. Finally, the fracture toughness of different grade Toray carbon fibers is evaluated using the proposed technique, and it is found that the fracture toughness of carbon fibers in the splitting mode decreases with increasing modulus. More specifically, the fracture toughness decreases from 1.67–1.82 MPa-m^{3/2} for standard modulus carbon fiber (T300, T700, T400) to 1.41 MPa-m^{3/2} and 1.03 MPa-m^{3/2} for intermediate (T800) and high modulus (M40J) carbon fibers, respectively. In contrast, the literature showed that, based on nano-notch testing, increasing the modulus leads to increasing fracture toughness. This behavior is attributed to the different resistances a crack faces during propagation, depending on the crack direction with respect to the fiber axis.

Supplemental information

In section 3.1.4, it was found that the crack growth remains symmetric until instability. Therefore, following the effect of shape on the instability load, a case can be made for instability depending only on the geometry defined by $\pm 120^\circ$ (symmetric crack propagation) from the crack plane and be completely independent of the third sector (120° – 240° from the crack tip in Figure 76). Two additional simulations ($a/b = 1$, $R_{\min}/e = 2$ and $E/H = 18$) are performed to understand the effect of the third sector. For the first simulation, the third sector is changed to a circular arc with radius R , defined by the two large cracks, while for the second simulation, it is changed in such a way that the arc becomes tangent to the base circle at two points 30° apart from the two larger cracks. This geometry is referred to as the “3rd sector minimized” geometry. Based on Figure 76, the error in γ , corresponding to the effect of the third sector, is significant.

Appendix 5

Table 12: Mechanical properties of carbon fibers under consideration

	Modulus (GPa)	E/H	Hardness (GPa)	Poisson's Ratio	Yield Strength (GPa)
T300	230	9.6 ± 0.4	24.0	0.25	12.5
T400	250	9.4 ± 0.3	26.6	0.25	13.4
T700	240	9.4 ± 0.3	25.5	0.25	12.9
T800	294	10.5 ± 0.5	28.0	0.25	12.7
M40J	377	13.0 ± 0.6	28.3	0.25	11.5

Table 13: Finite element input and output modeling parameters

	T300	T400	T700	T800	M40J
σ_c (GPa)	0.64	0.64	0.64	0.64	0.64
G_{IC} (GPa-μm)	0.0021	0.0020	0.0020	0.0017	0.0013
R (μm)	8.00	8.00	8.00	8.00	8.00
K_{IC} (MPa $\text{m}^{3/2}$)	1.02	1.02	1.02	1.02	1.02
P (mN)	7.16	7.13	7.12	6.86	6.65
γ	0.539	0.541	0.542	0.561	0.580

Table 14: Effect of shape on instability load

$\frac{\gamma_{actual}}{\gamma_{Base\ Circle}} = \frac{P_{Base\ circle}}{P_{actual}}$			
Geometry ($\theta = \phi =$	E/H~18	E/H~9	E/H = 18
0)	K = 0.85 MPa m ^{3/2}	K = 0.85 MPa m ^{3/2}	K = 1.96 MPa
	R = 10 μm	R = 10 μm	m ^{3/2} R = 5 μm
Base Circle (e = 0)	1	1	1
Circle R _{min} /e = 4	0.886	N/A	N/A
Circle R _{min} /e = 2	0.821	0.827	0.818
Circle R _{min} /e = 1	0.792	N/A	N/A
Circle R _{min} /e = 0.5	0.688	0.702	0.703
Circle R _{min} /e = 2/3	N/A	0.734	N/A
Ellipse a/b = 0.5 e = 0	0.864	0.859	0.868
Ellipse a/b = 2/3 e = 0	N/A	0.894	N/A
Ellipse a/b = 0.5 R _{min} /e = 5	N/A	0.827	N/A

Table 15: Effect of superposition

Case	Instability Load (P)	Half Circle Area (A)	$\frac{A_2 P_1 + A_1 P_2}{A_1 + A_2}$
e = 0	52.8	157.1	N/A
e = 0 and R_{min}/e = 2	56.45		56.34
R_{min}/e = 2	64.3	353.4	N/A
R_{min}/e = 0.5 and R_{min}/e = 2	66.5		66.6
R_{min}/e = 0.5	75.8	1413.7	N/A

Table 16: Fracture toughness of different grade carbon fibers

Carbon Fiber	Epoxy Substrate $h/D >$	Crystal Bond substrate $h =$
	1	0
	(MPa-m ^{3/2})	(MPa-m ^{3/2})
T300	NA	1.67 ± 0.16
T400	NA	1.82 ± 0.15
T700	1.75 ± 0.21	1.74 ± 0.24
T800	NA	1.41 ± 0.22
M40J	0.99 ± 0.11	1.03 ± 0.17

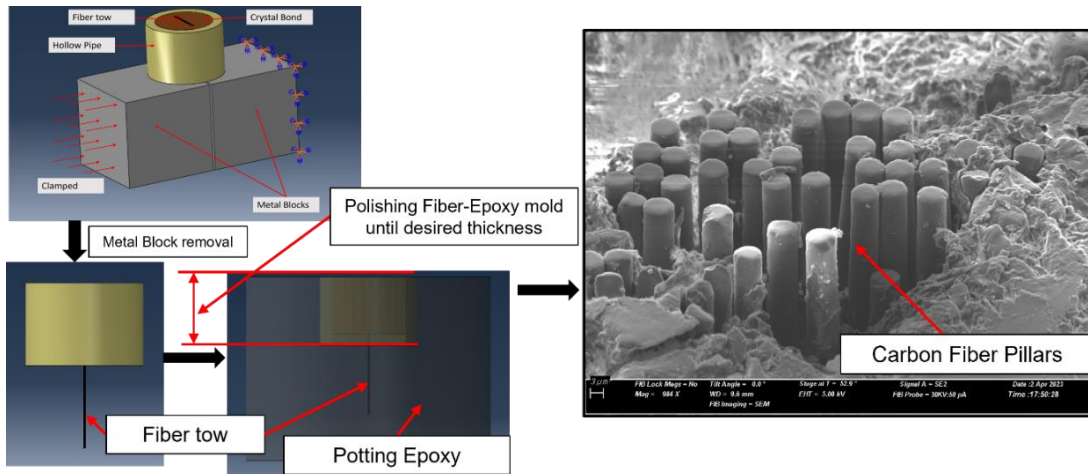


Figure 63: Schematic showing preparation of polishing-based micropillars.

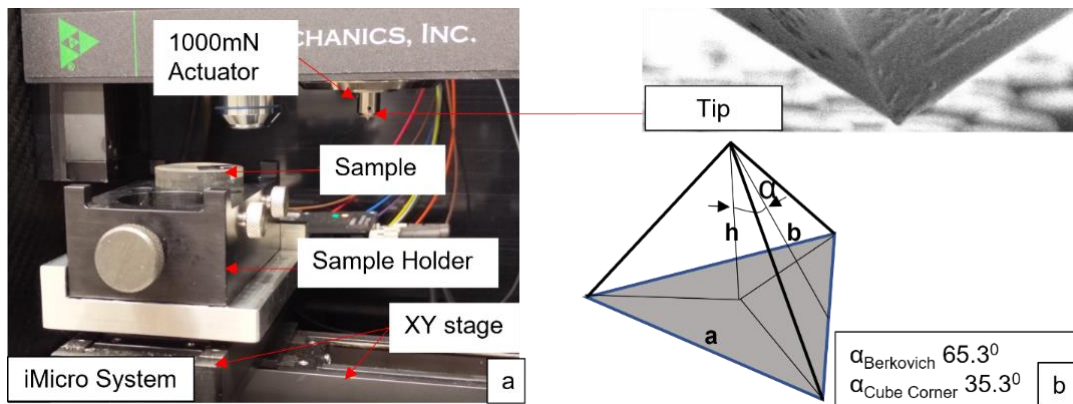


Figure 64: a) iMicro Nanoindentation system, b) Tip Geometry

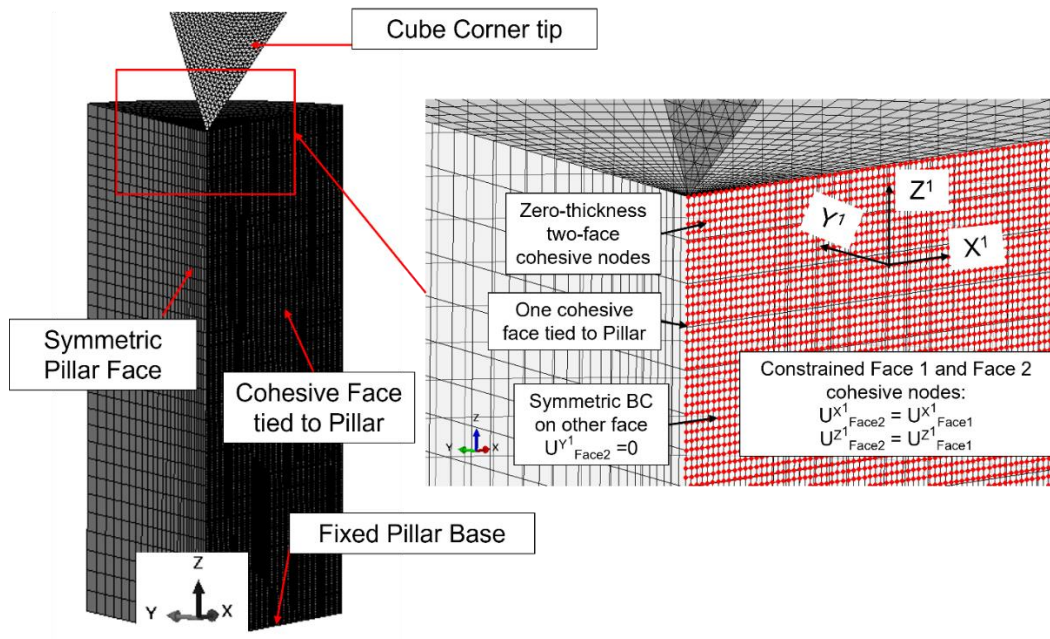


Figure 65: Six-fold symmetric cohesive-zone Finite Element Setup

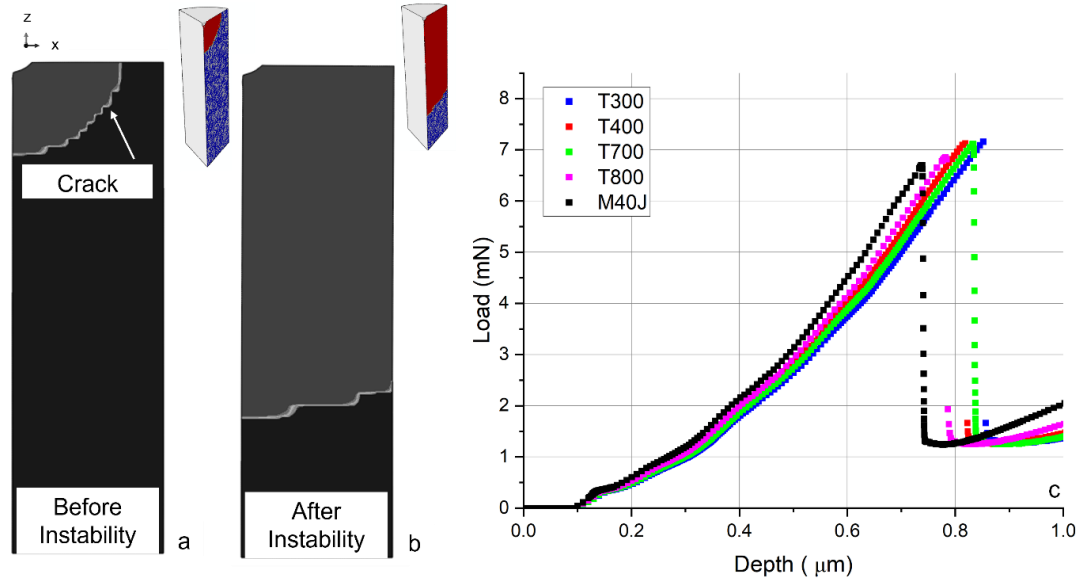


Figure 66: Evolution of median cracking a) before instability, b) after instability, c) load-depth curves for different fibers.

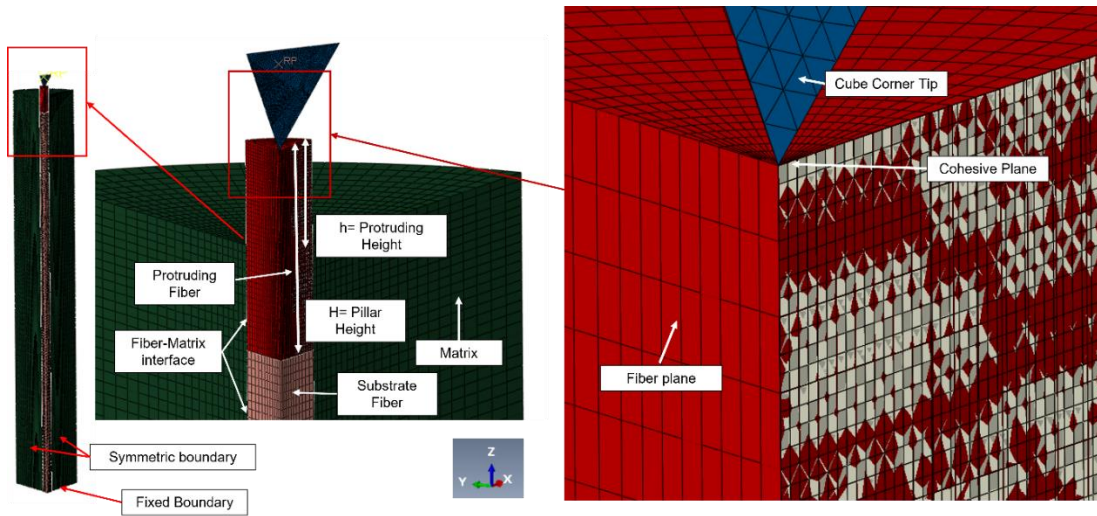


Figure 67: Cohesive zone Finite Element setup to evaluate the effect of substrate and protruding height upon the Finite element results.

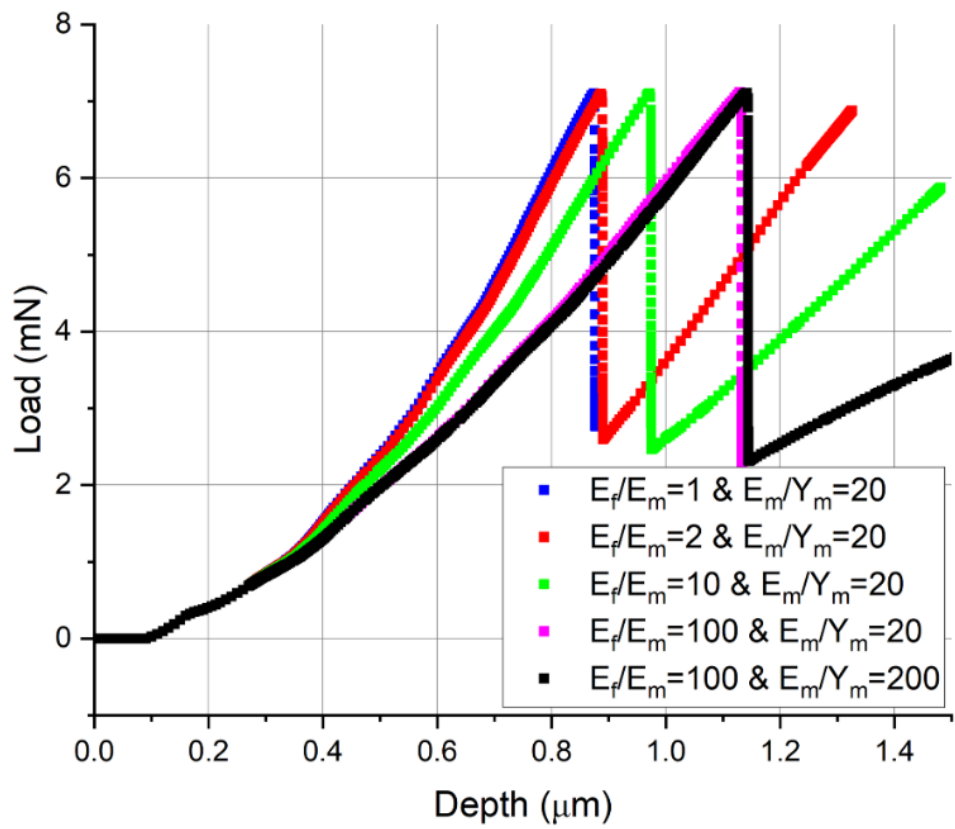


Figure 68: Effect of matrix on load depth curve.

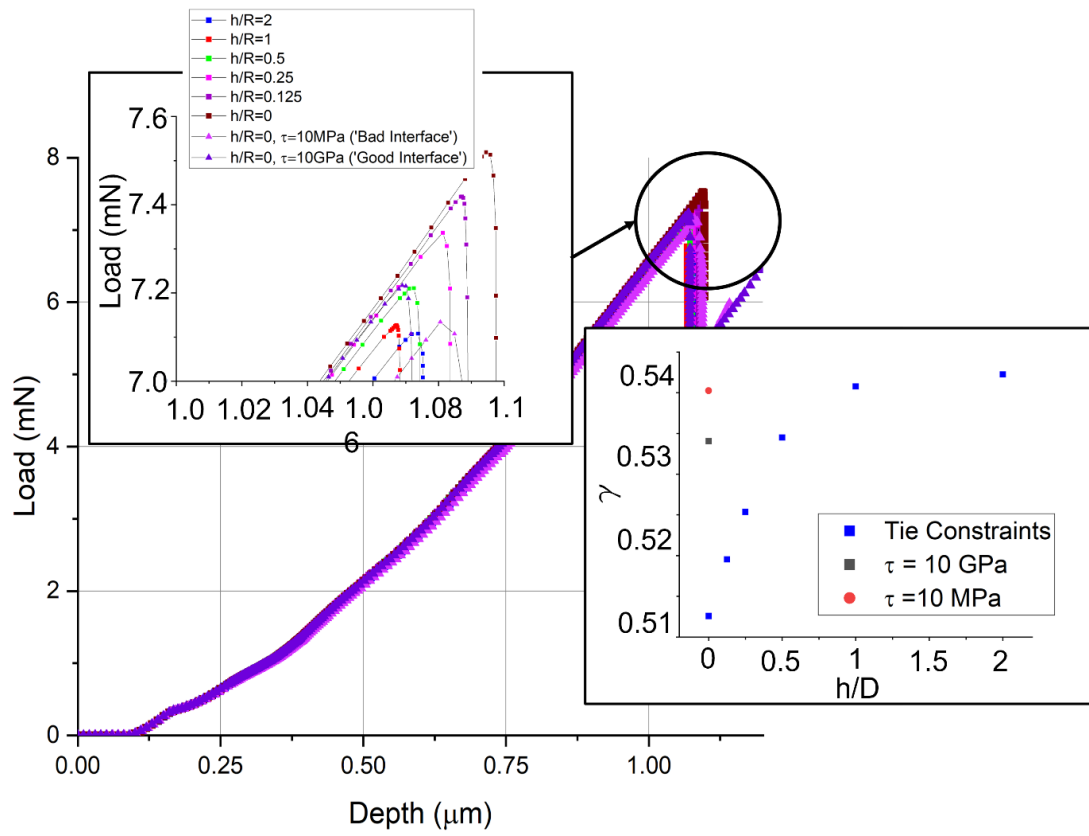


Figure 69: Instability load as a function of protruding height (h/D) and the role of interface.

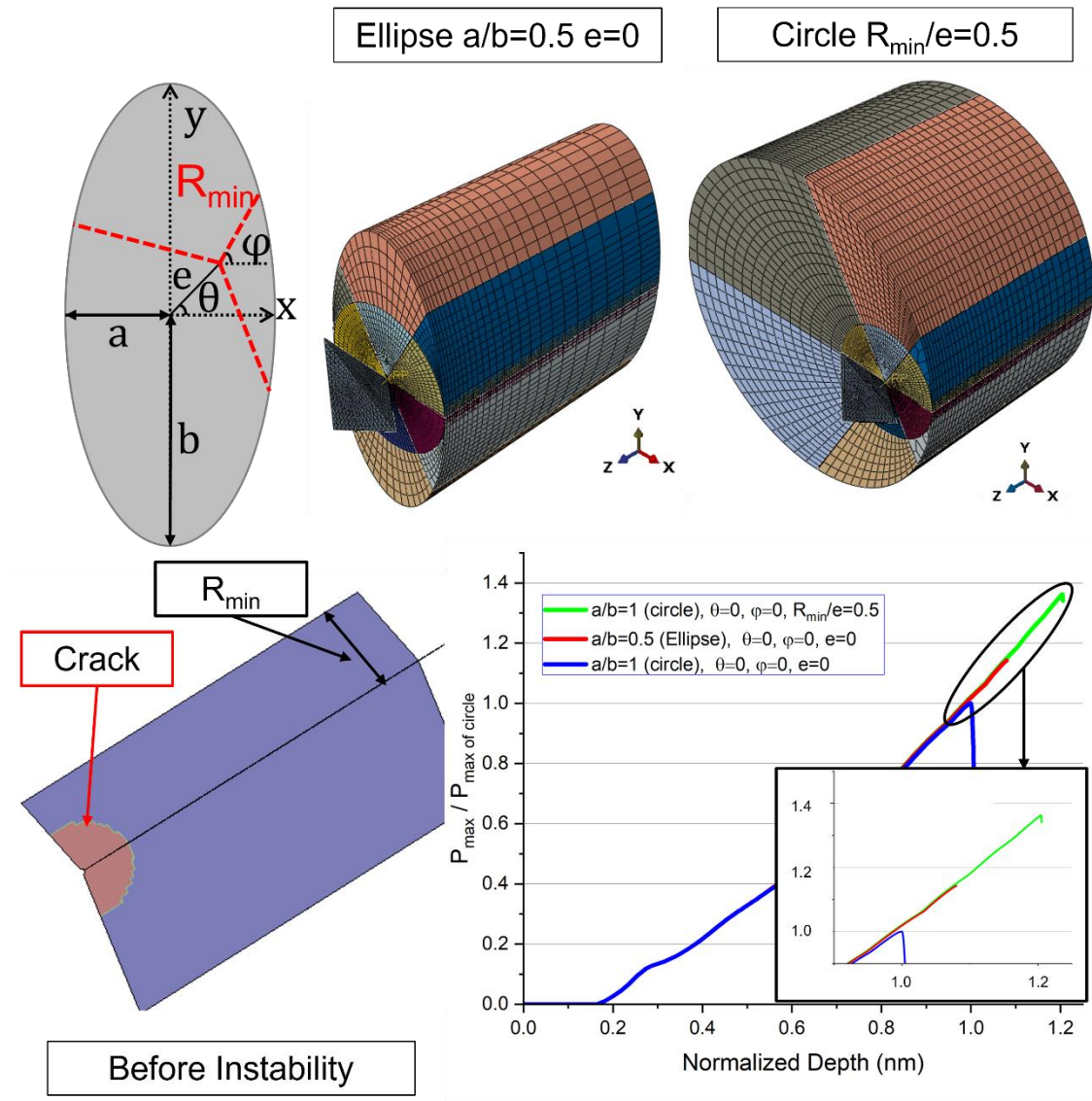


Figure 70: Effect of varying the cross-sectional shape from a circle to a shape with two-fold symmetry upon the instability load.

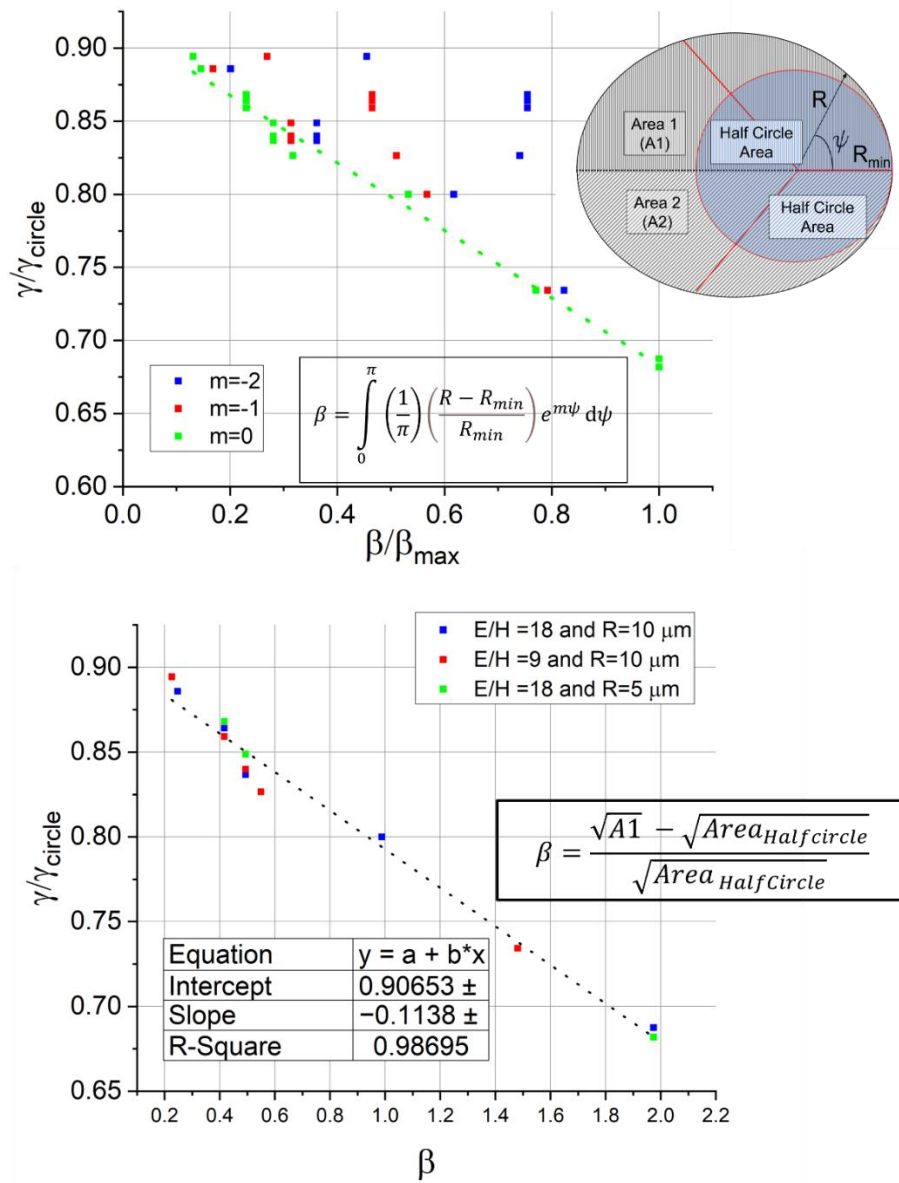


Figure 71: Error ($\gamma/\gamma_{\text{circle}}$) as a function of shape parameter (β)

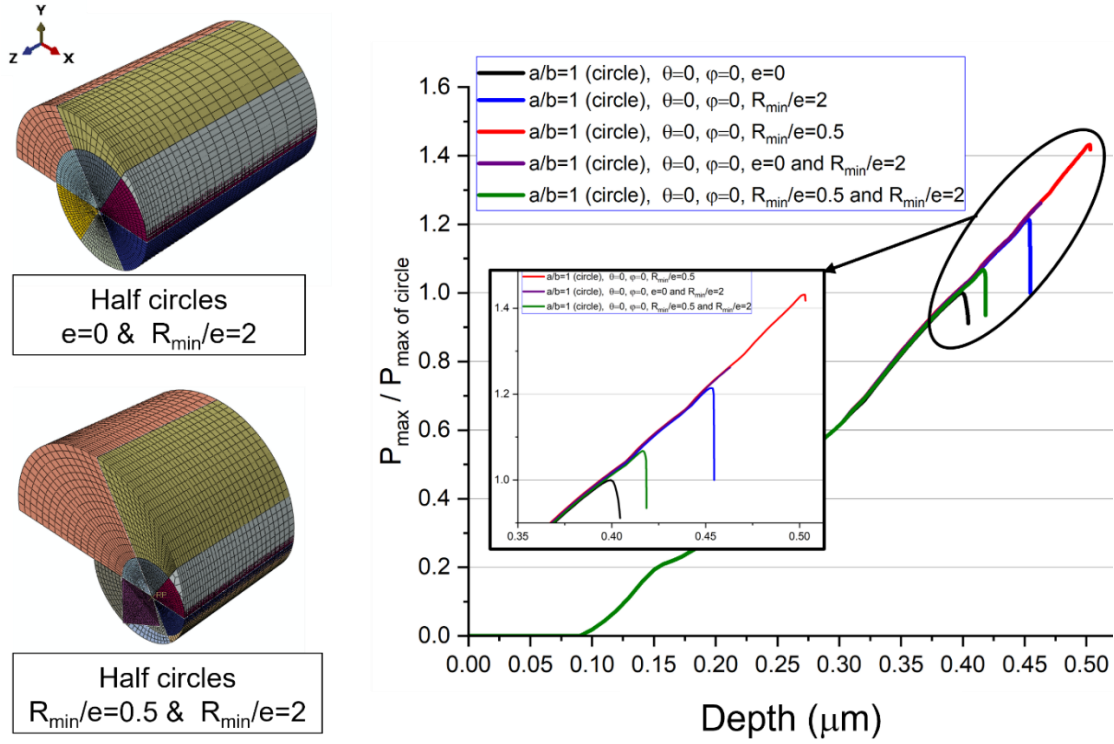


Figure 72: Applicability of superposition for an unsymmetric cross-section (unsymmetric with respect to crack axis)

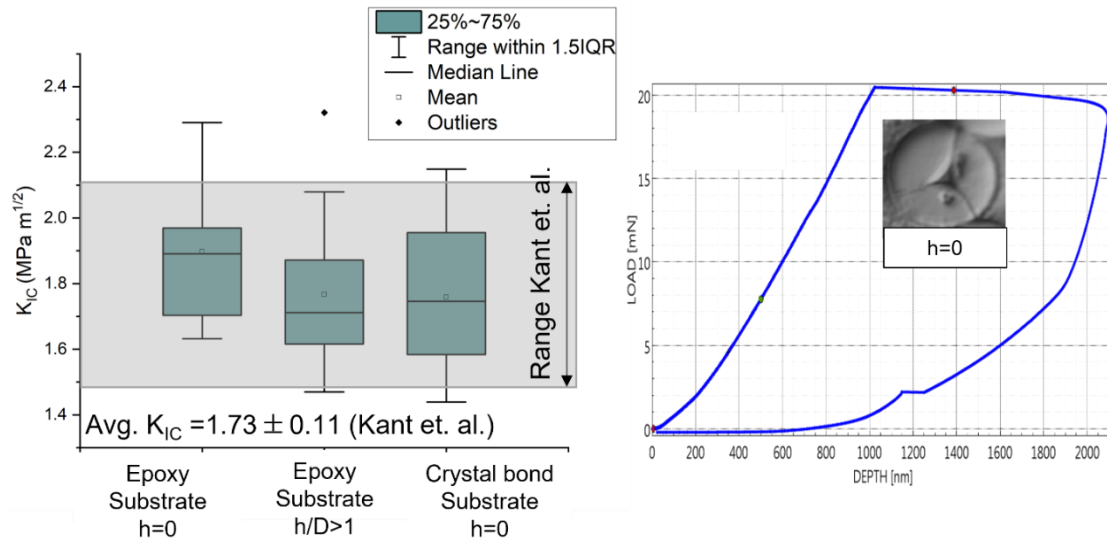


Figure 73: Effect of protruding height and interface upon the Pillar splitting of TORAY T700 carbon fibers

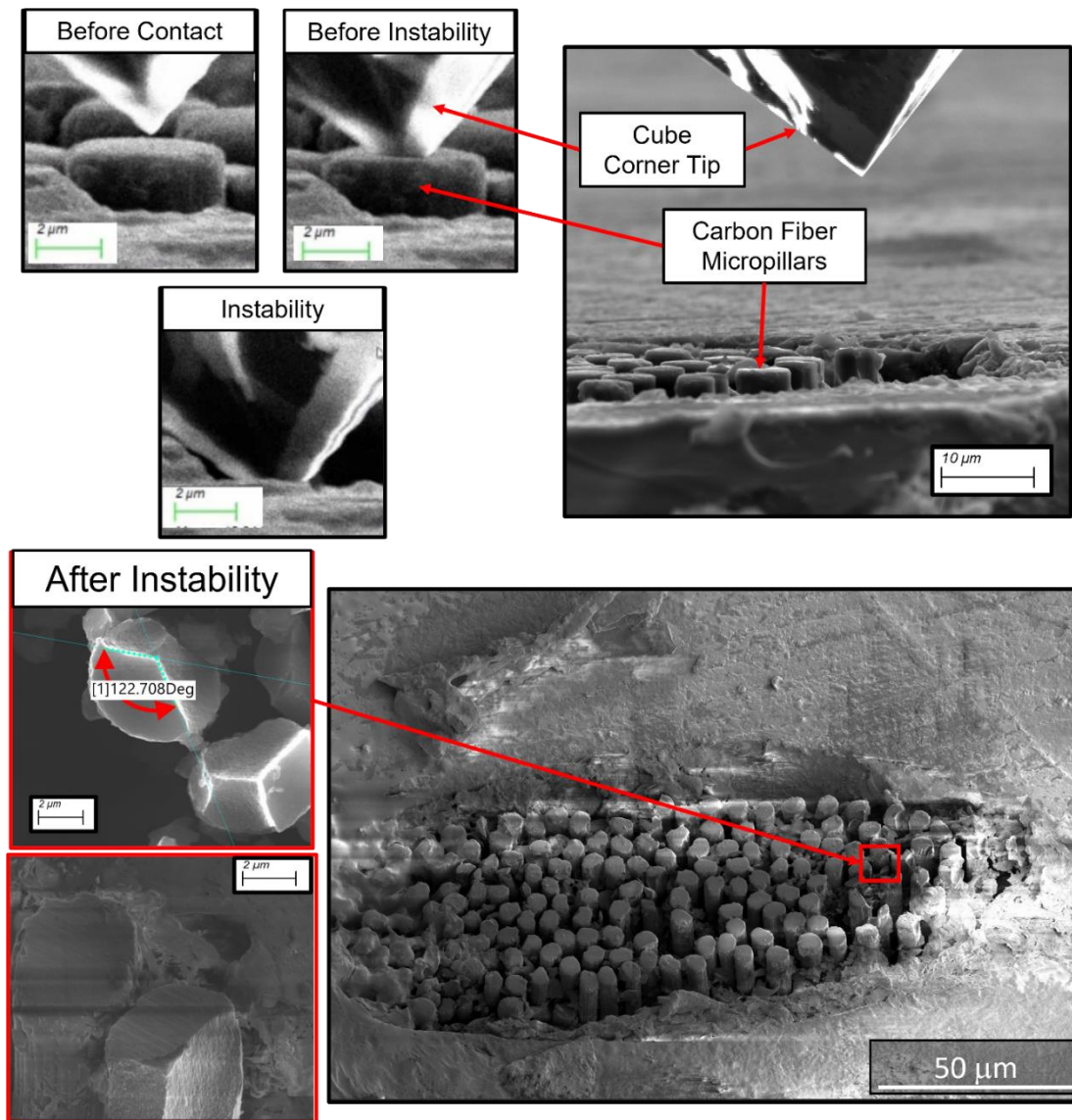


Figure 74: In-situ Pillar splitting of M40J TORAY carbon fiber

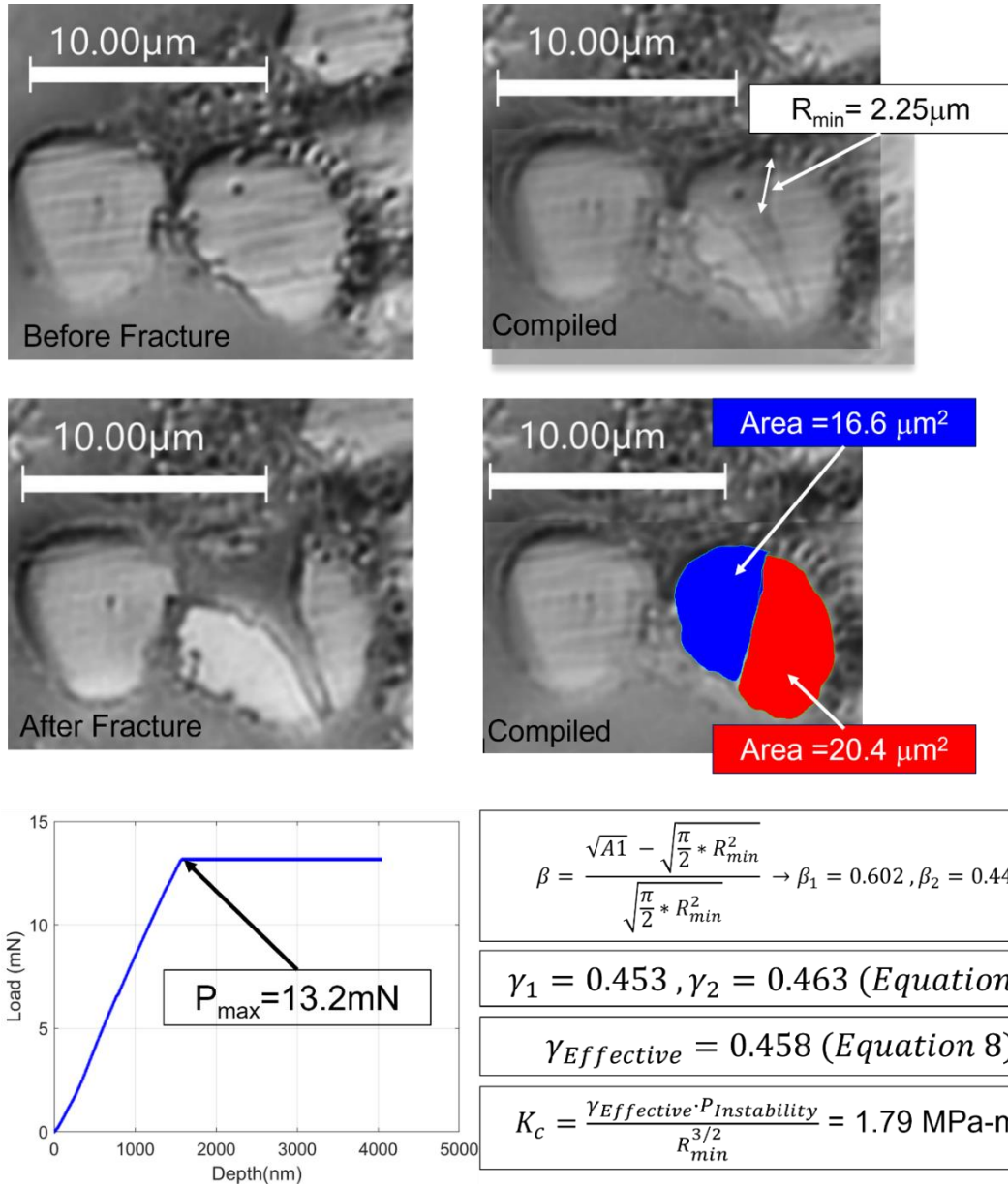


Figure 75: An example of the presented methodology showing fracture of T400 carbon fiber and the evaluated fracture toughness.

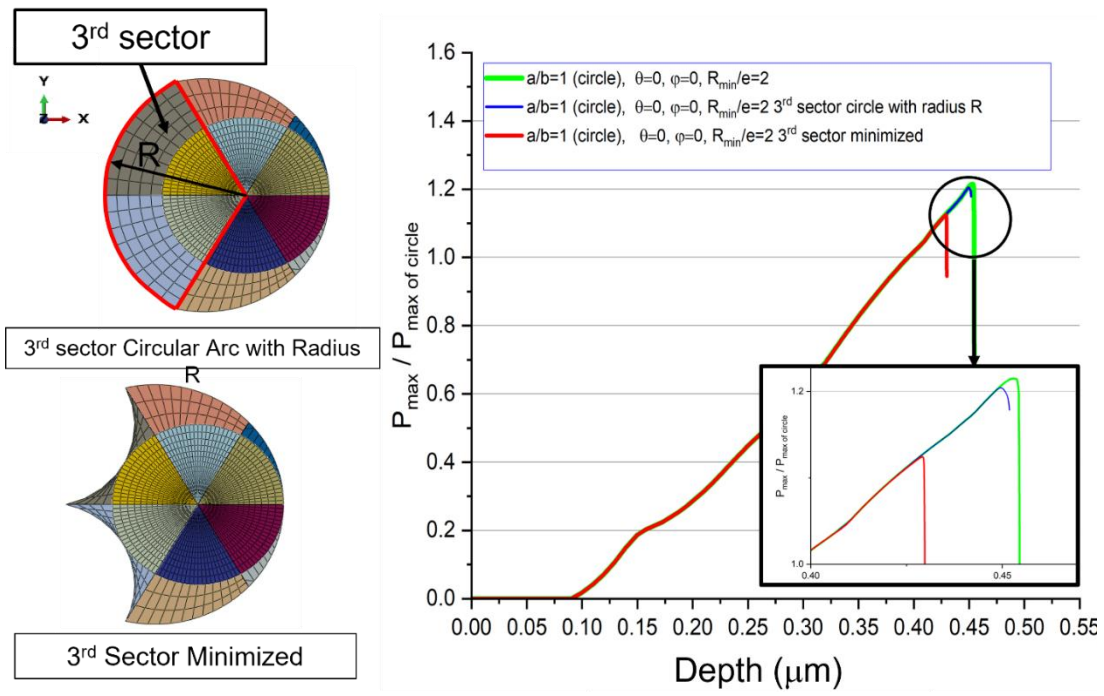


Figure 76: Role of the third sector upon the error in instability load

**CHAPTER 6: EFFECT OF EXTREME LONG-TERM EXPOSURE
TO SEAWATER AND TEMPERATURE FOR CARBON FIBER
VINYL ESTER COMPOSITES- A MULTISCALE INVESTIGATION**

Abstract

In this study, we conduct a thorough multi-scale experimental investigation to understand the effect of extreme long-term exposure to seawater and extreme temperatures on the mechanical properties of carbon fiber vinyl ester composites (CF/VE) and their constituents. Two sets of samples are investigated- the microscale coupons and macroscale coupons. The temperature conditioning corresponds to long-term conditioning at +80 °C, long-term conditioning at -80 °C, and cyclic temperature conditioning in which the samples are taken from +80 °C to room temperature to -80 °C every two days. Due to exposure to extreme temperature, cracks develop along the tow-circumference and the stitching. The crack density is maximum for cyclic conditioned coupons, followed by +80 °C and -80 °C coupons. Generally, wet coupons show higher crack density compared to dry coupons. Higher crack density is observed along the fill cross-section, which is attributed to higher misorientation in the load-bearing tows of the fill cross-section. Micromechanical characterization showed increased interfacial shear strength (IFSS) for +80 °C conditioned coupons, followed by unconditioned and cyclic-conditioned coupons. -80 °C coupons showed the lowest IFSS. Similar behavior is observed for wet coupons that underwent extreme temperature conditioning. Residual stresses follow a similar trend as IFSS for the dry-aged coupons. However, for the wet-aged coupons, it is found that the residual stresses decrease irrespective of temperature conditioning. Thermal aging of the matrix is observed for the coupons that underwent cyclic-temperature conditioning and the coupons that were conditioned at +80 °C. Wet coupons showed similar aging of the matrix. Finally, as a consequence of the increase in IFSS and the increase in glass transition, the macroscopic investigation yielded an

increase in the number of cycles to failure for dry and wet-aged +80 °C conditioned coupons. The increase is found to be more pronounced in wet-aged coupons, attributed to the decrease in residual stresses for wet-aged coupons.

Introduction

Applications of polymer-based fiber-reinforced composites have significantly increased in structural applications as they offer equitable mechanical performance compared to conventional metal-based materials. The lower density provided by the polymer and fiber reinforcements results in a lower overall weight of the composite than traditional structural materials. Therefore, applications where not only impressive mechanical performance is a requirement but also weight is a vital consideration find themselves in a compelling juncture of trying to replace conventional materials with polymer-based fiber composites. The aerospace, sports, and automotive industries have accommodated composite materials for superior performance [164–166]. Recent advances in recycled carbon fibers have introduced a new domain of cheaper carbon-fiber-based composites[144,167,168]. Thus, the applications are projected to surge beyond the current state. Among the advances in composite applications, the Office of Naval Research (ONR) has been trying to implement composite materials for naval-based applications[1,2,128]. The carbon fiber vinyl ester composites are the primary focus of interest due to the strong hydrophilicity of vinyl ester.

Naval crafts are exposed to extreme temperature changes and are immersed in seawater and, hence, are continuously under hygrothermal stresses. The long-term effects of these stresses upon the mechanical and chemical evolution of the composite still need to be

better comprehended. Long-term exposure to seawater has been shown to cause significant degradation in these composites' static and fatigue properties[1,2]. At a microscopic level, it has been shown that long-term exposure to seawater causes degradation in the interfacial shear strength for CF/VE composites[128,179]. Introducing the temperature into the equation will severely affect these results. From a macro-mechanical perspective, it has been shown that composites tend to become stiffer with a decrease in temperature [180,181]. Adams et. al. [182] carried out a study of the effect of cryogenic temperatures upon the storage and loss modulus of a thermoset resin. In their work, they showed that the storage modulus is inversely proportional to the increase in temperature. On the other hand, as the temperature increases, the softening of the thermoset matrix and subsequently the composites has been well reported [183,184]. In this work, a thorough micromechanical characterization is carried out to understand the effects of extreme (>15 years) long-term exposure to seawater. Subsequently, exposure to extreme temperatures is studied. An investigation is carried out to understand the effects of seawater and temperature at a microscale and how the matrix and the interface's microscale mechanical and chemical evolution affects these composites' mechanical performance at a macroscopic level.

Materials

Carbon fiber/Vinyl ester composites are the material of interest in this study. TORAY T700 carbon fibers with vinyl ester compatible sizing are the reinforcements under investigation, while Derakane 510A brominated vinyl ester is the matrix of interest. The fiber reinforcements are supplied as 7K tows stitched together using polyester stitching in

a 0/90 bidirectional layup of carbon fibers forming a Non-crimped Fabric (NCF). Four plies of the fabric are arranged symmetrically for manufacturing. The laminate associated with the fibers and matrix is manufactured using vacuum-assisted resin transfer molding (VARTM). The details of the manufacturing can be found elsewhere[131]. The resulting composite shows a $[0/90]_{2s}$ and $[90/0]_{2s}$ layup in warp and fill direction, respectively. The designation of the warp direction and fill direction corresponds to the panel's length and width, respectively. From VARTM perspective, the warp direction corresponds to the direction where tension is applied while Fill direction corresponds to the direction of resin flow. Based on previous work [2], the maximum degradation is expected in the matrix-dominated fatigue response. Since this study aims to understand degradation caused by extreme hygrothermal effects, $[+45]_{2s}$ laminates (Matrix-dominated failure) are cut from the representative panel for macro-mechanical investigation.

For micromechanical investigation, samples are taken from a panel with a dry age of 15 years. $25.4 * 254 * 2.7 \text{ mm}^3$ coupons are cut from the panel soon (within months) after manufacturing and are exposed to simulated seawater at 40°C . Thus, the coupons investigated in this work (for micromechanical characterization) correspond to the dry and wet age of 15 years. Henceforth, these coupons are called dry and wet samples, respectively. The simulated seawater is prepared by mixing sea salt with distilled water to achieve a specific gravity of 1.022. The seawater is changed every two to four weeks to prevent excessive changes in the sea salt density due to water evaporation. $10*10*2.7 \text{ mm}^3$ sections (Figure 77a) are cut from the dry panel and the wet coupons that has been conditioned for 15 years. The cut sections are exposed to extreme temperature

conditioning. Before temperature conditioning, the two adjacent faces (Warp and Fill face) for each section are polished (Figure 77a). The polishing is done to examine the evolution of the surface microstructure via optical and electron imaging. Thus, before temperature conditioning, each sample is imaged using a Keyence VHX 7000 optical microscope (Figure 77c and Figure 77d) and Hitachi TM3030 Environmental Scanning electron microscope (ESEM), as shown in Figure 77c inset. ESEM scans are done at selective locations.

Three extreme temperature effects are studied- long-term exposure to 80 °C, long-term exposure to -80 °C, and cyclic temperature conditioning in which the samples are moved from 80 °C→ Room Temperature→-80 °C every two days (Figure 77b). The wavelength of one temperature cycle is six days. For each micromechanical investigation coupon, the temperature conditioning is carried out for one year, six months, and one month (Table 17). These coupons are collectively designated as dry or wet temperature conditioned coupons.

Finally, to understand how the micromechanical properties affect the results at the macroscale, nine 25.4*25.4*2.7 mm³ dry and wet [+45]_{2s} coupons are conditioned. For each temperature conditioning, three dry and three wet samples are used. Like the microscale investigation, the conditioning is characterized by long-term +80 °C and - 80 °C and cyclic conditioning. The conditioning is carried out for two months. For macroscale testing, the wet coupons correspond to a wet age of 15 years. On the other hand, the dry coupons have a dry age of 12 years. Since the coupons are taken from two different

panels, any comparison between the dry and wet coupons from a macro mechanical investigation is made with caution.

Methods

Surface characterization

Surface characterization utilizes optical, laser, and scanning electron microscopy (SEM).

The optical microscopy is carried out using Keyence VHX 7000 optical microscope with a magnification range between 100x-6000x. The surface morphology and thickness evaluation is done using the Keyence VK laser microscopy system with a 9nm depth resolution and a maximum magnification of 1500x. Finally, scanning electron microscopy (SEM) employs a Hitachi TM3030 environmental SEM. Thermo-Fischer Helios SEM and Zeiss Auriga SEM are used for higher magnification electron imaging.

Interfacial characterization

Interfacial characterization is carried out using Push-out tests. The push-out tests use a diamond-based 5 μ m truncated cone tip, as is shown in Figure 78. Thin sections from each micromechanical coupon are cut in warp and fill using the TechCut 4 thin section cutter (Allied High-Tech Products, Inc.). The samples are then polished using an E.A. Fischione Instruments Inc. hand grinder so that the final thickness varies between 20-120 μ m. The samples are then bonded (using CrystalBond 509) to a steel mesh (U.S. 625-grade mesh gasket) that is mounted on a cylindrical puck. More details of the test setup can be found elsewhere[179]. The tests are carried out using a displacement rate of 50nm/s. The testing protocol is defined such that the unloading occurs if a maximum target load of 100mN is reached or if instability occurs.

Matrix characterization

Nanoindentation

Nanoindentation is carried out using the iMicro (Nanomechanics Inc.) nanoindenter. The system is installed in an environmental chamber on a vibration-isolating table.

Nanoindentation uses the Berkovich tip (inscribed angle 65.3°) and the Continuous stiffness method (CSM). In the continuous stiffness method, the sample is loaded dynamically, and the contact stiffness is calculated throughout the measured depth, thereby evaluating the modulus and hardness as a function of depth. The samples are loaded to a target depth of 1000nm at an oscillation frequency of 110 Hz with an amplitude of 2nm.

Differential Scanning Calorimetry (DSC)

DSC analysis is carried out using the DSC Q2000 (T.A. Instruments) system with a temperature range of -180 to 725 °C and temperature accuracy of ± 0.1 °C and power sensitivity of 0.2 mW. The scans are done in a nitrogen environment. For all scans, first, the samples are cooled and isotherm at 0 °C. Following the isotherm, the temperature is ramped at 5 °C/min to a final temperature of 150 °C.

Fourier Transform Infrared Spectroscopy (FTIR)

FTIR measurement is carried out using the Spectrum two FT-IR Spectrometer with the diamond crystal. The scans are carried between the wavenumber from 4000 cm^{-1} to 600 cm^{-1} . The scan resolution is set to be 4 cm^{-1} . 16 accumulations are done per measured spectrum.

Results

Evolution of microstructure due to extreme temperature

All the microstructural coupons are polished in warp and fill to understand the microstructure evolution due to long-term exposure to extreme temperatures. The samples are imaged optically and via electron imaging to ensure the absence of any failure modes (cracking) prior to temperature conditioning. After the corresponding conditioning, the samples are again imaged using an SEM and an optical microscope. Figure 79, 80, 81, and 82 show the SEM and Optical images of dry and wet, warp and fill coupons exposed to 80 °C, -80 °C, and cyclic temperature conditioning for one year. Each figure's left and right panel corresponds to the pre-and post-conditioning micrographs. The images corresponding to shorter conditioning times are not presented here for brevity. For all dry samples, irrespective of the conditioning time, the maximum cracking is evident in the cyclic-conditioned coupons, followed by the coupons exposed to 80 °C. Generally, as the conditioning time increases, the crack density increases. Qualitatively, a more significant crack density is observed in fill coupons. Cracking primarily occurs along the circumference of the tows (tow-circumferential cracking) or along the boundaries of the stitches (Figure 79, 80, 81, and 82 for 80°C and cyclic coupons). In cases with higher crack density, the cracks that initiates due to the tow-circumferential cracking and cracking along the stitches nucleate to form a larger crack that traverses through the tow, giving rise to the characteristic through-thickness macroscopic failure mode(see Figure 80-cyclic conditioned sample). This phenomenon is present in all one-year cyclic conditioned coupons except for the dry warp coupons. Other than the -80 °C conditioned dry coupons, the SEM micrographs of all coupons show negative secondary

electron charging (incident electrons getting trapped within the sample) at locations within the tow. At this juncture, the authors argue that the negative charging indicates the presence of the matrix around the fibers within the tow. A deeper examination is required to understand the above phenomenon, which is addressed in section 3.1.1. Although the trends for wet coupons are similar, the density of cracks and the negative charging phenomenon is found to be higher.

Effect on matrix

FTIR spectroscopy is carried out for all the dry and wet pure vinyl ester coupons. The corresponding FTIR spectra of composite coupons showed variance as a function of location. Hence, the corresponding results are not presented. Figure 83 shows the FTIR normalized absorbance vs. wavenumber spectra of the coupons. The normalization is carried out with respect to maximum absorbance peak, as done in the previous studies [17]. Each spectrum in Figure 83 averages three spectra taken per sample at different locations. No significant difference in the OH bonds is noticed between the dry and the wet coupons. The observation is consistent with the literature[185].

DSC scans are taken for all dry and wet composite coupons. The heating rate is set to 5 °C /minute. Figure 84 shows the resulting plots, and the T_g values are reported in Table 19. Two scans are taken for each coupon representative of the conditioning temperature and period. No significant change is recognized between the dry and wet coupons. For all +80 °C and cyclic-conditioned coupons, the glass transition temperature (T_g) increases. An increase in T_g due to thermal aging is a well-reported phenomenon[186,187] that could indicate additional cross-linking or could be a consequence of the elimination of

the monomers. At elevated temperatures ($<T_g$), although the overall cross-linked network is rigid, the mobility can still exist. Odegard et.al. [186] argued that at higher temperature the specific volume would decrease resulting in an increase in the glass transition temperature. Given enough conditioning time at elevated temperature, at some point there would be a constant specific volume due to the presence of strong cross-links that would effectively hold the amorphous structure together. The T_g results for the +80 °C samples show an increasing behavior as a function of the conditioning time, perhaps indicating that a more prolonged exposure would have caused the continual increase in T_g . Not only is there an increase in T_g for +80 °C and cyclic-conditioned coupons, but the enthalpy required to cause the glass transition also increases, which is a direct consequence of an increase in the energy required to cause the rubbery-phase molecular motion that is characteristic of glass transition. The thermal ageing can also be perceived in pure vinyl ester samples that is evident by the yellowing of the resin as seen in Figure 84.

On the other hand, the evaluated T_g for the -80 °C dry coupon remains statistically the same. The -80 °C wet coupon shows a concaving-downward curvature, which is probably caused due to the exotherm caused by water evaporation. Therefore, the -80 °C wet sample (1 year conditioned) is soaked at 55 °C for 48 hours, and two DSC scans are retaken. The results are compared with the DSC scan for a wet coupon. Given the standard deviation obtained for the wet -80 °C coupon, and a relatively small increase in T_g , the authors conclude that there is no significant difference in the glass transition temperature for the wet -80 °C coupons.

Nanoindentation is carried out for dry and wet resin that underwent temperature conditioning for a year. Indentations are carried out at three random locations for each sample. An array of six by six (36) indents is done at each location with a target depth of 1000nm. The distance between each indent is 15 μm (greater than 7*target depth). The indentation and reduced modulus evaluation are done as per the Oliver-Pharr methodology[16,17]. Figure 85 shows the resulting normalized indentation modulus for all the samples. The modulus values are reported at a depth of 800nm. The results show no significant difference in the modulus between any sample.

Effect on Interface

The interfacial effects are characterized using push-out tests. Two tests (one in warp and one in fill) are done per conditioned sample. The details of the methodology can be found elsewhere [179]. The testing is carried out stochastically by conducting tests at a minimum of ten locations, each corresponding to an array of five-by-five push-out flat-tip indentations. For each set of indentations, the thickness is evaluated by conducting post-testing laser microscopy using the Keyence VK laser microscope. An equilibrium equation is used to evaluate the interfacial shear strength (IFSS) given by Equation 6.1, as has been done in past studies[179].

$$\tau = \frac{P_c}{2\pi re} \quad \text{-(6.1)}$$

The Weibull equation, as given by Equation 6.2 [179], is used to characterize the interfacial shear strength as a function of interfacial thickness. In Equation 6.2, m , σ_0 , and V_0 are the shape, scale, and the volume constants for Weibull equation. Use of equation 6.2 requires a known value of m which is accomplished iteratively as per [179].

$$P(s) = \exp \left[- \left(\frac{\sigma}{\sigma_0} \left(\frac{V}{V_0} \right)^{1/m} \right)^m \right] \quad (2)$$

Figure 86 and Figure 87 show the probability and cumulative distribution function using the weibull parameters for the dry and wet, warp and fill coupons respectively. The warp coupons generally show relatively lower IFSS than the fill coupons. The results show a minor degradation in IFSS for the wet coupons. The temperature conditioned coupons show a trend of +80 °C coupons with the highest IFSS, followed by the cyclic and dry/wet coupons. Given the variation between the IFSS of the samples, we attribute slightly lower IFSS values for some of the +80 °C coupons to be the consequence of variation within the samples. The lowest IFSS is identified in -80 °C conditioned coupons. The IFSS evaluated from push-out tests is dependent on the residual stresses, which are a function of the processing, the local microstructure, and the packing efficiency. The effect of residual stresses is higher at higher loads due to the poison's effect. Therefore, the increase in IFSS for +80 °C coupons could be amplified due to higher compressive residual stresses in +80 °C coupons.

Discussion

Failure modes

Based on the fractography results, , two primary cracking zones are characterized in the temperature-conditioned coupons- tow-circumferential cracking, and the cracking along stitches. Figure 88 shows a high-resolution SEM micrograph of a dry +80 °C conditioned coupon showing tow-circumferential cracking. This phenomenon has been reported in the literature for Non-Crimped Fabrics (NCF) based composites[128]. In NCF composites, the in-plane fiber tows infiltrated with the matrix are separated by resin (often referred to

as resin pockets). Fibers within the tow have similar misorientations, and thus, each tow within the lamina acts like a sub-composite separated by resin pockets. Under steady thermal stresses (or hygrothermal for wet samples), each tow with different misorientation would act as a unit; thereby, the highest residual stresses would develop at the tow-matrix interface. Thus, the fiber-matrix interfacial degradation is maximum for fibers at the tow-matrix interface.

Given the above argument, it is reasonable to assume that the tow-circumferential cracking depends on the local tow misorientation and the stiffness gradient between the tow and the polymer matrix. Note that from a fracture propagation perspective, not only the Mode II fracture toughness of the fibers-matrix interface is essential but also the Mode-I fracture toughness. Figure 88 shows a clean fiber-matrix break. The crack propagates along the fiber circumference to the neighboring matrix and, subsequently, the adjacent fiber. These microcracks, when nucleate, result in macroscopic failure modes such as through thickness failure (if the crack propagates through the thickness) or delamination failure (if the crack propagates along the length).

Stitching has been reported to be a favored region for damage initiation [128]. Even though the stiffness gradient between the polyester stitching and the vinyl ester matrix is not as significant as the one between carbon fiber and vinyl ester, the zig-zag morphology of the stitches creates a zone of high-stress concentration. The high shear-stress concentration results in the cracks formation along the stitches (Figure 89).

The locations where negative charging is detected around the fiber-matrix circumference are examined using the scanning electron microscope. Figure 90 shows the SEM

micrographs of the dry and wet coupons. Only one image for the dry coupon (+80 °C) is shown for brevity purposes. As previously mentioned, for the dry coupons, the phenomenon is only identified for the cyclic and the +80 °C conditioned coupons. As expected, the SEM micrographs revealed the matrix's presence around the fibers' circumference. The above phenomenon of matrix protrusion could result from the excessive thermal compressive stresses at the fiber-tow interface resulting in the protrusion of the matrix around the fiber-matrix interface. The result of matrix protrusion would thus result in stress-relaxation. The above argument is augmented by the observation of the above failure mode being present at the locations of medium-higher packing (high residual stresses) or at the tow-matrix interface.

All wet coupons showed the phenomenon of matrix protrusion around the fiber-matrix interface. As shown in Figure 90, the protrusion of the matrix and subsequently the surface degradation for wet temperature conditioned coupons is much higher in comparison to the dry conditioned coupons. The seawater diffusion causes matrix swelling due to the disparate hygro-expansion coefficient between the fibers and matrix. Following the argument for the dry coupons, residual stresses due to matrix swelling and thermal stresses generated at the tow-matrix interface would amplify the above phenomenon, as seen in the +80 °C wet coupons. Water transport in composite materials is usually caused by diffusion and capillarity[114]. The capillary action happens at the voids and the gaps between the fiber and the matrix. For wet coupons soaked at -80 °C, there will be the freezing of water present between the fiber-matrix boundary. The density of ice is lower compared to water. The presence of water between the fiber and

matrix would cause sudden expansion under freezing conditions as the water becomes ice, resulting in the squeezing out of the matrix. Upon reheating (in air) the samples from -80 °C to room temperature, the expansion of the shrank matrix will occur. Given the above argument, the freezing rate would affect the size of the ice crystals. An in-depth study can be conducted to understand the effects of freezing rate and then using the concepts of freeze-drying [188] to preserve the surface morphology. However, that is beyond the scope of this study. The consequence of the above argument and the matrix contraction at -80 °C would be a poor interface, as evident by the values of IFSS for the -80 °C conditioned coupons. The above argument is augmented by the interfacial opening detected in the -80 °C coupons (Figure 90).

Interface and residual stresses

From the fiber-matrix boundary perspective, the +80 °C conditioned coupons correspond to the radially compressive creep at the fiber-matrix boundary. In comparison, the -80 °C conditioned coupons correspond to the compression of the matrix at the boundaries due to shrinkage. In section 2.3, the highest value of interfacial shear strength (IFSS) is identified for the +80 °C, followed by the dry or wet coupons and the cyclic coupons. The -80 °C coupons showed the minimum IFSS. The highest residual stresses are expected for the +80 °C coupons due to the compressive stresses present at the fiber-matrix boundary. To understand the effects of residual stresses, we conduct re-push tests on the pushed-out fibers. Once the push-out testing is concluded, the thin film is dismounted from the mesh. The film is flipped, cleaned using acetone, and subsequently mounted on a steel substrate. Subsequently, the pushed-out fibers are re-tested using the flat tip.

The fibers are loaded at a 5nm/sec displacement rate. Figure 91 shows an example of the in-situ push tests. Before testing, it is confirmed that for the pushed-out fiber, the failure is characteristic of the interfacial failure and not the matrix shear failure. Upon loading, the compression of the free pillar happens until the applied load equates to the resistance from the friction, at which point instability occurs. As the instability occurs, the free pillar gets embedded inside the matrix, causing additional frictional resistance. In situ testing showed that only the compression of the free pillar occurs when instability occurs. At this point, there is a decrease in force due to the momentum associated with fiber. An example load-depth curve is shown in Figure 91. Therefore, the instability load corresponds to the maximum load in the load-depth curve.

A simple mechanistic approach would show that as the thickness of the thin film increases (embedded length of the fiber), the frictional stresses and, consequently, the instability load would increase. Given the applied positive compressive load (P_a), the load at a positive distance x along the fiber-matrix interface would decrease to $P(x)$ due to the frictional shear resistance. The frictional forces are proportional to the radial compressive stresses and would increase with an increase in applied load due to the poison's effect. Following the methodology adopted by Kerans et al. [189], the change in the load at a distance x would be given by:

$$dP(x) = -\tau_f(x)(2\pi r)dx \quad -(6.3)$$

Where, from Timoshenko[190] and Kerans et. al. [189]

$$\tau_f(x) = \mu \left[\sigma_N + k \frac{P(x)}{\pi r^2} \right] dx \quad -(6.4)$$

In equation 6.4, σ_N is the positive compressive residual stress while k is the poisson's effect parameter given by Equation 6.5 for an isotropic material.

$$k = \frac{E_m v_f}{E_f(1 + v_m) + E_m(1 - v_f)} \quad -(6.5)$$

Substituting equation 6.4 in equation 6.3 and integrating would result in the load as a function of interfacial distance as:

$$P(x) = -\frac{\sigma_N \pi r^2}{k} + \left[\frac{\sigma_N \pi r^2}{k} + P_a \right] e^{-\frac{2\mu k x}{r}} \quad -(6.6)$$

Instability will occur when the load at the embedded length (l_e) is zero, i.e., the applied load is equal to the combined effect of the total frictional resistance. Hence, the instability load vs. the embedded length relationship is given by:

$$P_a = \frac{\sigma_N \pi r^2}{k} \left(e^{\frac{2\mu k l_e}{r}} - 1 \right) \text{ or } P_a = P^* (e^{f^* l_e} - 1) \quad -(6.7)$$

Using equation 6.7, an exponential relationship is expected between the instability load and the embedded length (l_e). Given that the r and k are nearly constant between the samples, the coefficients P^* and f^* can be used to quantify the residual stresses and the coefficient of friction between the samples.

Repush tests are conducted for all one-year conditioned dry and wet coupons. High scatter is seen in all coupons (Figure 92), which could result from the variance of the residual stresses within the composites. The development of residual stresses in the composite is a function of local packing, microstructure, and processing. Given the number of variables, many tests are required to characterize the residual stresses for a coupon at a given embedded length (l_e). Given the argument for tow-microcracking, it is reasonable to assume that the residual stresses would also be a function of location within

the composite. For all but the -80 °C dry and wet coupons, a minimum of three locations are tested. Given the limited number of tests and the high scatter in the data, no quantification of the residual stresses or the coefficient of friction can be made. However, a clear trend emerges as a function of temperature conditioning. For the dry coupons, the +80 °C dry sample shows the maximum residual stresses, followed by the dry and cyclic-conditioned coupons. The -80 °C coupons show the minimum residual stresses. The observed trend is similar to the push-out tests. For the wet coupons, irrespective of the type of temperature conditioning, there is a reduction in residual stresses.

Effects at macroscale

As mentioned earlier, to understand the effects at the macroscale, three 254*25.4*2.7 mm³ dry and wet samples cut in $[\pm 45^\circ]_{2s}$ are temperature conditioned. The conditioning is carried out for two months. Fatigue testing is carried out for each sample. Due to the limited number of samples, the study is carried out for only one case of R-ratio of 0.2, frequency of 1Hz, and $\sigma_{max}=80$ MPa as has been done in the previous study [2]. The dry and wet coupons are taken from different panels. CF/VE composites have been shown to have high differences within the panel as well as between the panels[128]. Since the dry and wet samples correspond to different panels, the comparisons made in this study would only correspond to the effect of temperature on the dry and wet samples, while no comparison would be made between the dry and wet samples. Regardless, the tensile and interlaminar shear strength (ILSS) corresponding to the dry and wet-aged coupons before temperature conditioning is reported in Table 20. The tensile properties correspond to the $[\pm 45^\circ]_{2s}$ configuration while the ILSS is reported along Warp (to ensure interlaminar

failure). As can be seen from Table 20, there is a decrease in ILSS, while the tensile strength remains nearly unaffected due to long-term seawater exposure. The negligible difference in tensile strength due to long-term seawater exposure further augments the argument that caution must be made in comparing the results between dry and wet-aged coupons.

Figure 93 shows the plot for the number of cycles to failure for the dry and wet coupons. The error bars correspond to one standard deviation. Interestingly, for both the dry and wet coupons, +80 °C coupons show the maximum strength, followed by the -80 °C coupons. The reduction in the number of cycles to failure is only noticed in cyclic-conditioned dry coupon. The wet temperature conditioned coupons show a higher increase in the number of cycles to failure. Fatigue failure is a stochastic process which is dependent upon the most prominent flaw. Therefore, given the limited number of tests, care must be taken in drawing any conclusions from the above dataset. However, an argument can be made to justify the above counterintuitive results. The failure in $[\pm 45^\circ]_{2s}$ is a dependent on the interfacial shear strength[191]. The increase in number of cycles for +80 °C could stem from the increase in the interfacial shear strength (Figure 87) for the dry conditioned coupons. Similarly, the higher increase in number of cycles for wet conditioned coupons would be a consequence of the increase in IFSS as well as the decrease in the residual stresses at the fiber-matrix boundary.

The normalized-modulus degradation as the function of the number of cycles is shown in Figure 94. The modulus is normalized with respect to the tensile modulus of the dry and wet coupons. The modulus is calculated at every cycle using the stress and strain

corresponding to the peak and minimum stress. Initially, an extensometer is used to record the strain evolution. The extensometer is removed at 2000 cycles for the dry and wet coupons. For the temperature-conditioned coupons, the extensometer is removed at 1000 cycles. The number of cycles for extensometer removal is reduced to ensure that the failure does not happen when the extensometer is attached, as it was expected that the temperature conditioning would reduce the number of cycles to failure. The reported values in Figure 94 are using the LVDT strain. The LVDT strain is validated by comparing the results with the extensometer strain. For the dry coupons, the slope of the modulus reduction is lowest for the +80 °C, perhaps a consequence of the high IFSS of +80 °C coupons. The highest modulus reduction is noticed in the cyclic-conditioned coupons. Cyclic coupons show the highest crack density; therefore, as the number of cycles increases, the number of microcracks that are formed due to temperature-conditioning coalesce, thereby causing higher modulus reduction. Interestingly, the modulus stabilization for the -80 °C and cyclic-conditioned coupons is higher, perhaps an indication of matrix stiffening.

Except for cyclic-conditioned wet coupons, the trend for wet temperature-conditioned coupons is similar to the one for dry temperature-conditioned coupons. The initial modulus for the dry and wet temperature-conditioned coupon is shown in Figure 94 inset. All temperature-conditioned coupons show stiffening. The stiffening for the +80 °C and cyclic-conditioned coupons is perhaps a consequence of the increase in T_g due to thermal aging.

Conclusions

In this study, a thorough characterization is carried out to understand the effects of extreme exposure to seawater and temperature. Seawater conditioning has been carried out for 15 years. After conditioning, the dry and wet coupons belonging to the same panel are conditioned at 80 °C, - 80 °C, and cyclic temperature conditioning. Maximum cracking is evident in cyclic temperature conditioned coupon. The cracking increases with the exposure time. Due to long-term hygrothermal conditioning, two primary zones of crack initiation have been identified- tow circumferential cracking, and the cracking along the stitches. Tow microcracking is hypothesized to happen due to the stiffness gradient (between the tow and the matrix) as well as the morphology of the tows. SEM micrographs revealed the protrusion of the matrix along the fiber-matrix boundaries. The above phenomenon is detected in all but -80 °C conditioned dry coupons. For the +80 °C and cyclic coupons, matrix protrusion is identified to be the consequence of high thermal stresses. For -80 °C coupons, the phenomenon occurs due to the change in the water volume that is present between the fiber and matrix boundary. Interfacial opening is observed in the -80 °C wet coupons.

The micromechanical investigation revealed the thermal aging of the +80 °C and cyclic conditioned coupons for both dry and wet coupons, with the increase being more pronounced in the +80 °C coupons. The increase in T_g is directly proportional to the time of thermal aging. Fourier transform infrared (FTIR) spectroscopy results showed high variance as a function of thermal aging. The results show an improvement in the interfacial shear strength (IFSS) for the +80 °C conditioned coupons. No significant change in the IFSS is evaluated in the cyclic coupons. The -80 °C coupons show a

decrease in IFSS. The above trend is similar irrespective of the dry or wet conditioning. Because of the variability between the samples, no comments can be made on the effect of conditioning time on the IFSS. The pushed-out fibers were tested again to characterize the residual stresses. For the dry temperature conditioned coupons, the maximum residual stresses are found to be in the +80 °C dry coupons, while -80 °C dry coupons showed the minimum residual stresses. For the wet coupons, the residual stresses decreased irrespective of the conditioning temperature.

Due to the high scatter in the number of cycles to failure and the limited number of tests, no statistically significant comment is made on the effect of temperature conditioning on the fatigue properties of carbon fiber vinyl ester composites. Regardless, based on the three data points per conditioning temperature, the highest cycles to failure are seen for the + 80 °C coupons, which are argued to be a consequence of the increase in IFSS and the stiffening of the matrix.

Appendix 6

Table 17: Different conditioning time for each set of samples

Conditioning Temperature	Conditioning Time (Microscale)		
80 °C	52 weeks	26 weeks	4 weeks
-80 °C	52 weeks	26 weeks	4 weeks
Cyclic	60 cycles	30 cycles	5 cycles
Conditioning Temperature	Conditioning Time (Macroscale)		
80 °C	8 weeks		
-80 °C	8 weeks		
Cyclic	9 cycles		

Table 18: Types of samples

Sample Information	Number of samples	
	Dry	Wet
15 year-aged composites	9	9
15 year-aged Resin (Vinyl Ester)	9	9

Table 19: Glass transition temperature as a function of temperature conditioning and the conditioning period

Tg								
Dry					Wet			
Time	Room Temp	80 °C	-80 °C	Cyclic	Room Temp	80 °C	-80 °C	Cyclic
1 Year	112±1.2	122±3	111 ± 0.1	117±1.4	113 ± 0.6	117±0.23	115± 2.7	116±0.4
6 Months	NA	116±1	111 ± 0.1	117±0.73	NA	117±0.04	NA	114±0.5
1 Month	NA	114±3	NA	115±0.75	NA	113±0.34	NA	111±0.9

Table 20: Tensile and Interlaminar shear strength for Dry and wet-aged CF/VE coupons

	Tensile strength (MPa)	ILSS strength (MPa)
Dry	103.6 ± 3.24 (2)	37.6 ± 1.95 (10)
Wet	103.8 ± 5.27 (2)	34.2 ± 3.17 (10)

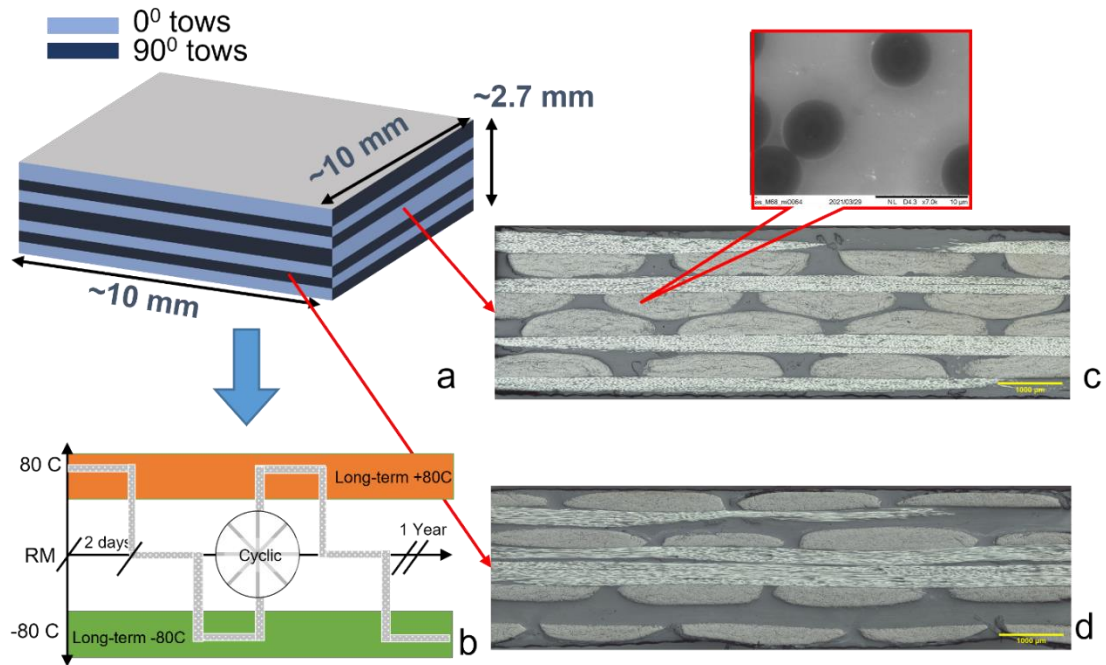


Figure 77: a) Schematic showing the dimensions and polished adjacent faces of a coupon, b) showing the definition of long-term, short-term, and cyclic temperature conditioning of coupons, c), d) examples of the optical images taken prior to temperature conditioning with the inset showing an example of an ESEM image.

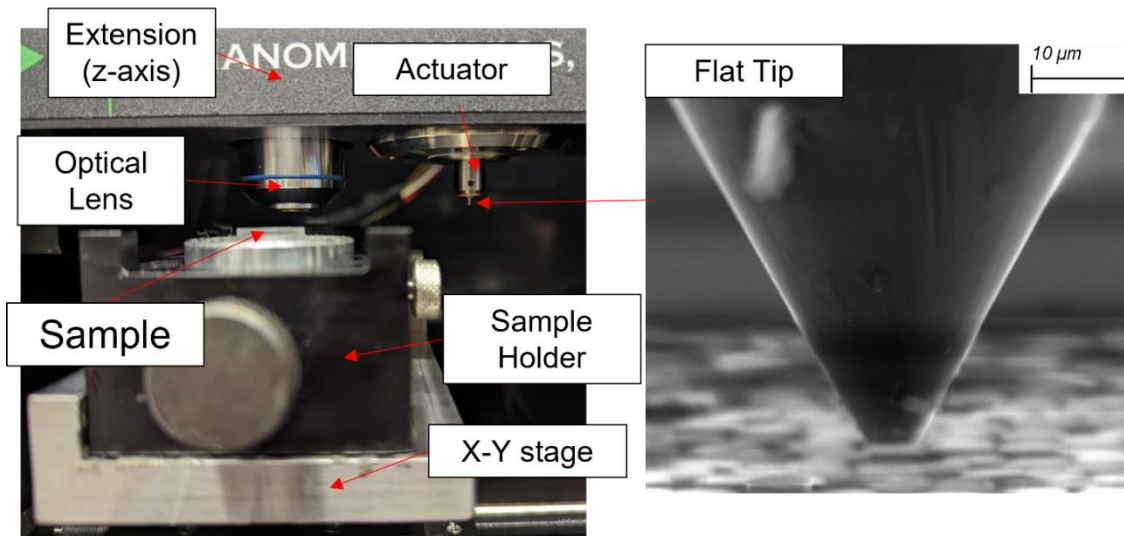


Figure 78: iMicro nanoindenter installed with a truncated cone (flat) tip with $\sim 5 \mu\text{m}$ diameter.

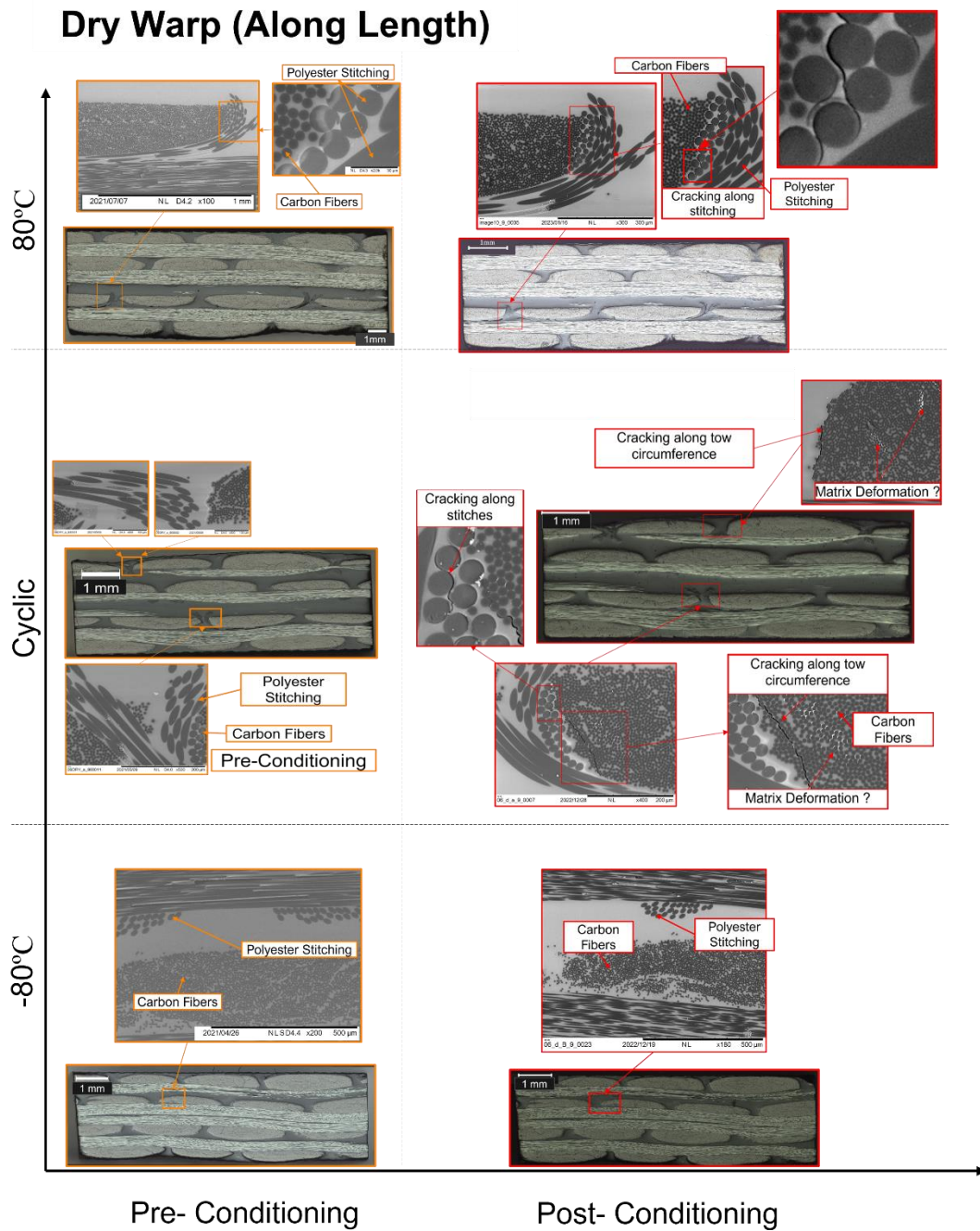


Figure 79: SEM and Optical images of dry warp coupons exposed to -80°C, 80°C and cyclic temperature conditioning for one year. Note the crack initiation along the tow circumference and along the stiches within the composite. -80°C coupons showed almost no cracking. Note that not all zones where cracking is present are shown in the figure. For 80°C and cyclic coupons, electron-charging of the fibers within the tows is detected.

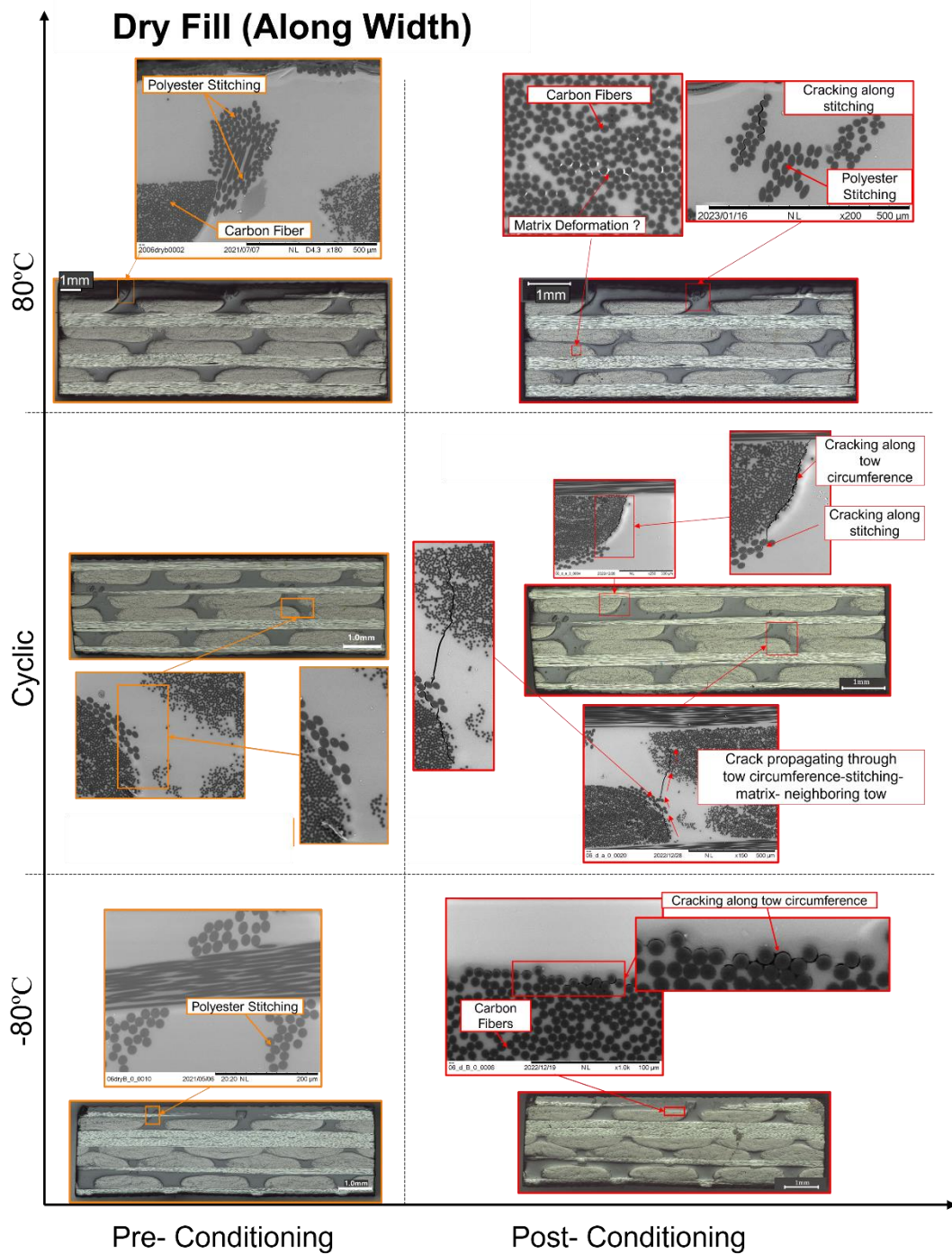


Figure 80: SEM and Optical images of dry Fill coupons exposed to -80°C, 80°C, and cyclic temperature conditioning for one year. The failure modes are similar to the one found for the dry warp coupons. However, the crack density is higher.

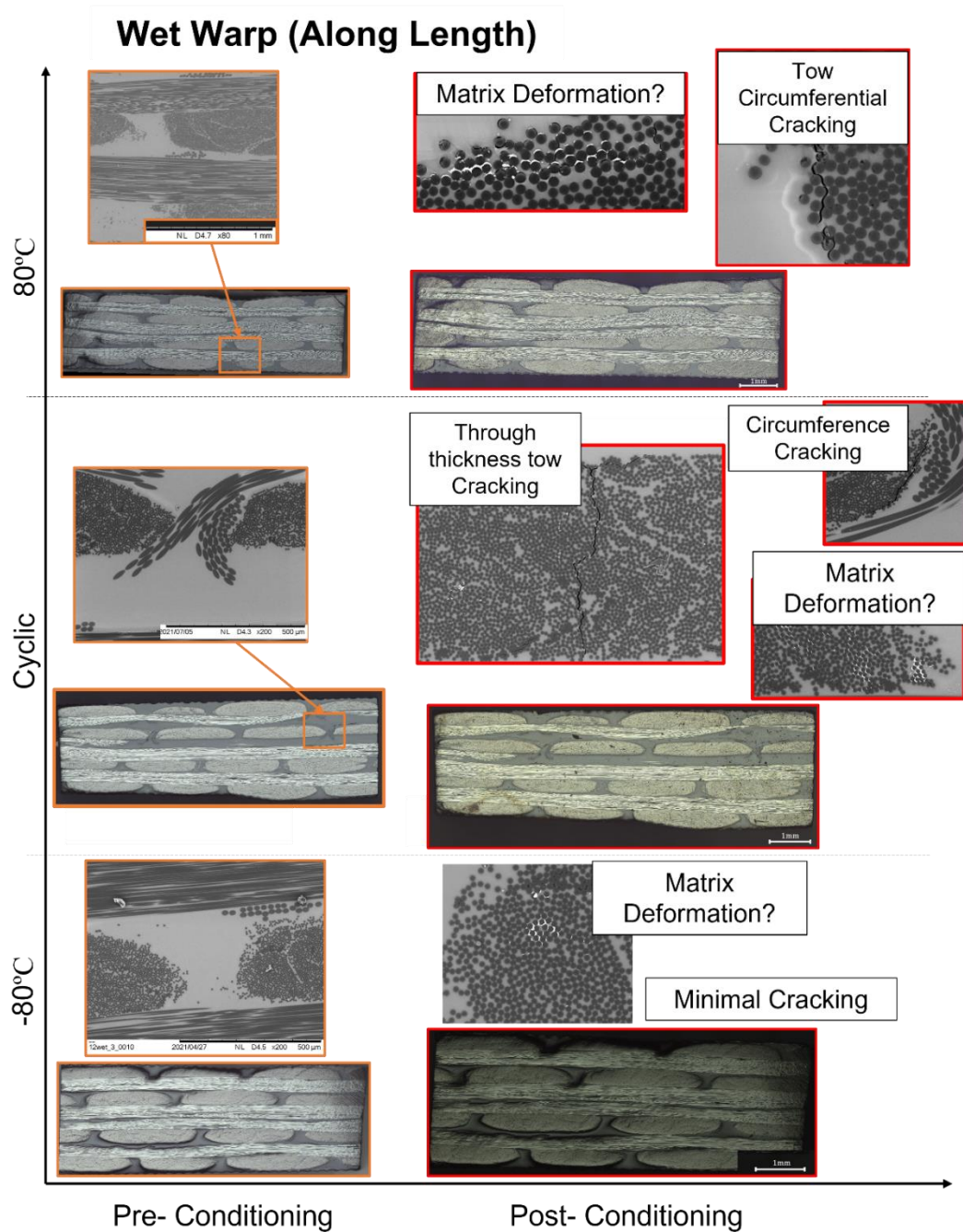


Figure 81: SEM and Optical images of wet Warp coupons exposed to -80°C, 80°C, and cyclic temperature conditioning for one year. Higher crack density is observed compared to the dry warp samples. Interestingly, electron charging is detected in all temperature-conditioned coupons.

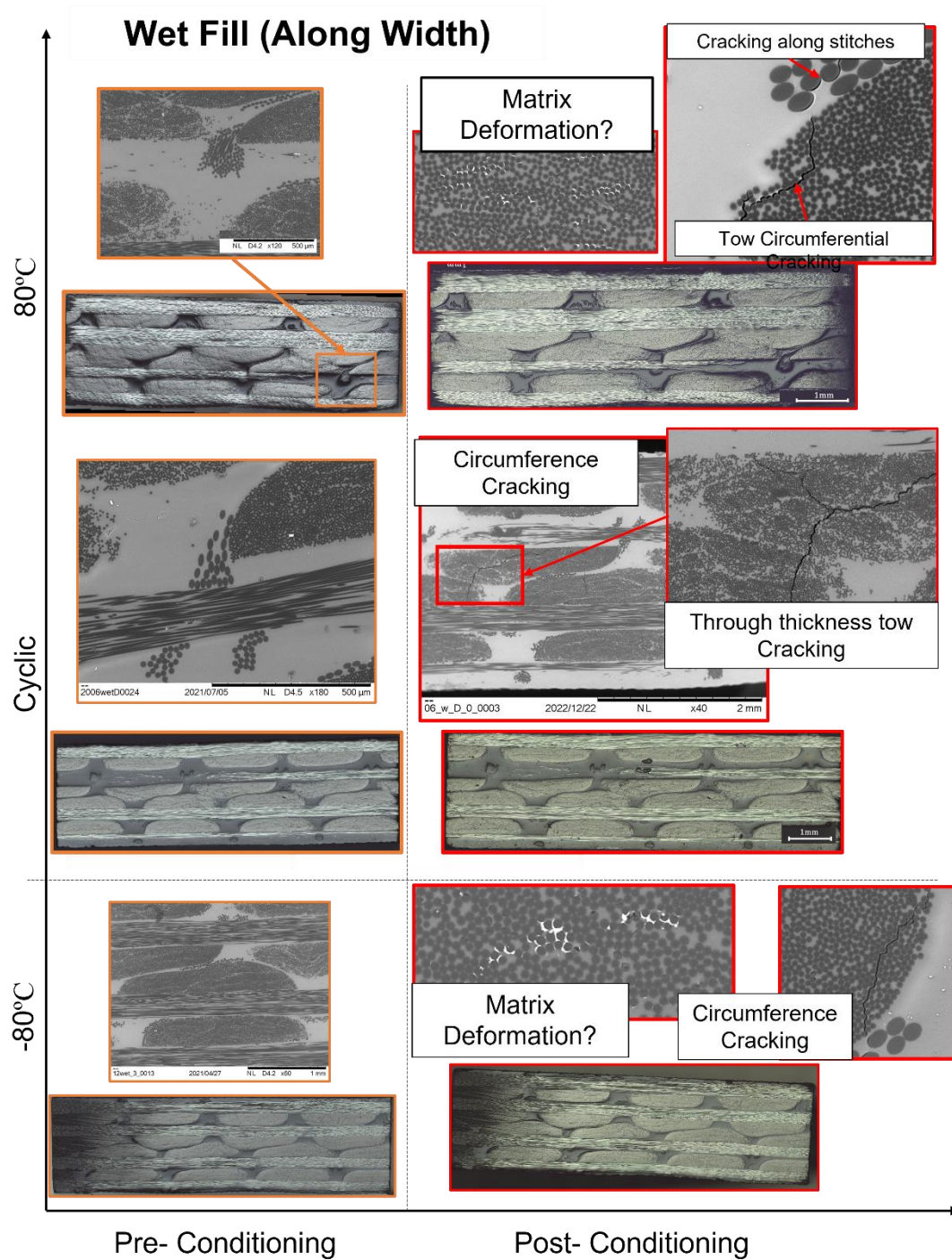


Figure 82: SEM and Optical images of wet Fill coupons exposed to -80°C, 80°C, and cyclic temperature conditioning for one year. The highest crack density is discovered in wet fill cyclic coupons.

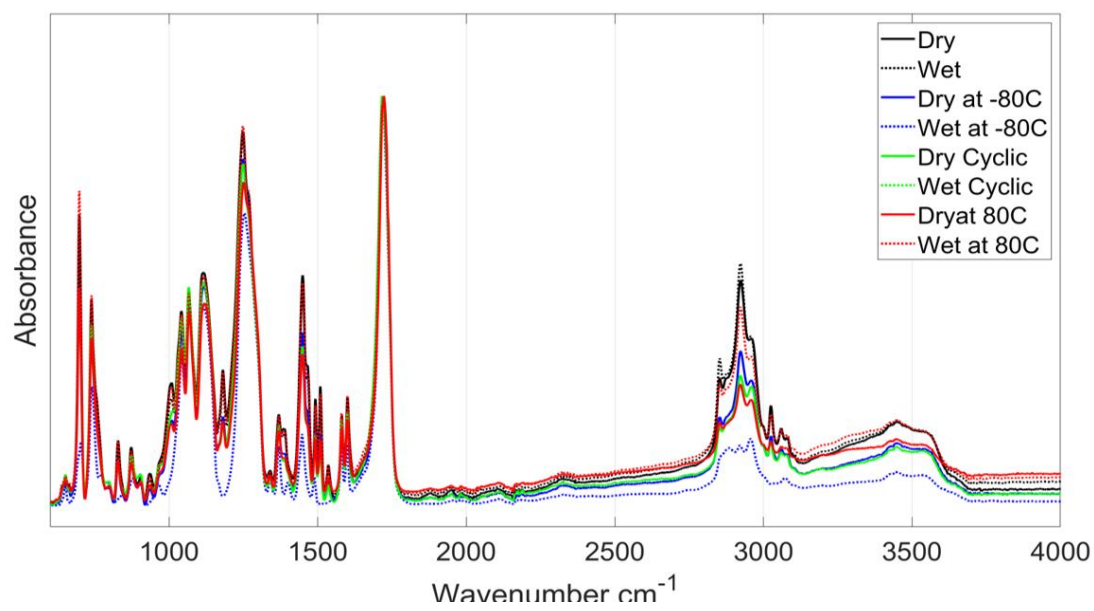


Figure 83: FTIR spectra of dry and wet coupons exposed to different temperature conditioning.

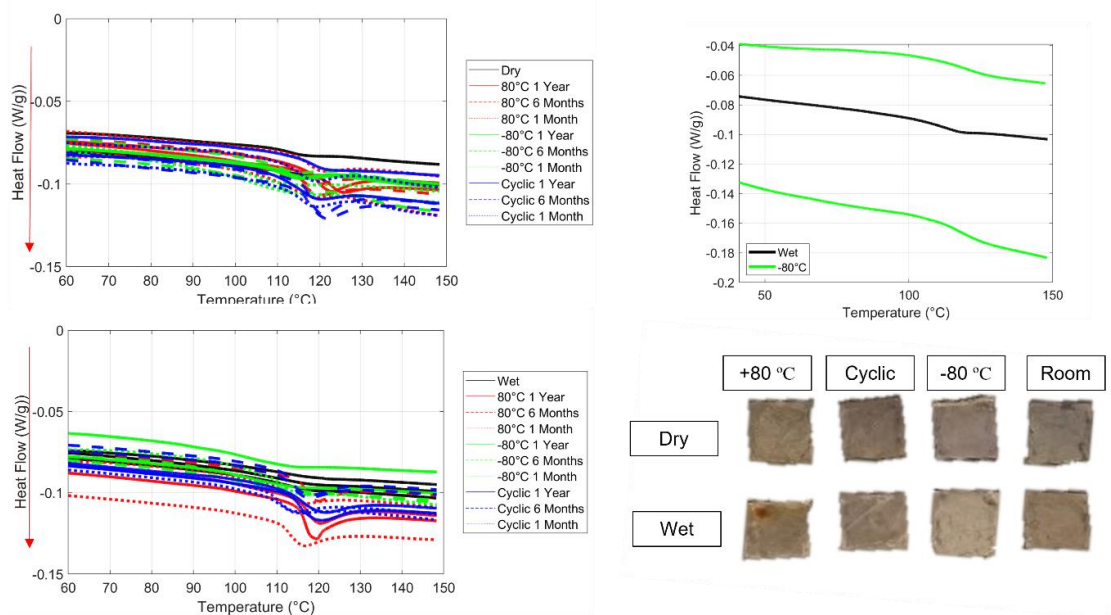


Figure 84: DSC scans for the dry and wet coupons.

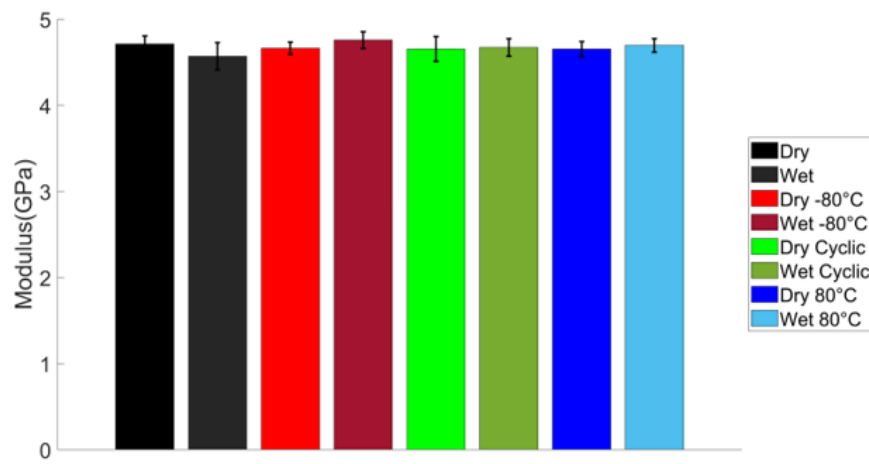


Figure 85: Normalized indentation modulus for different dry and wet coupons.

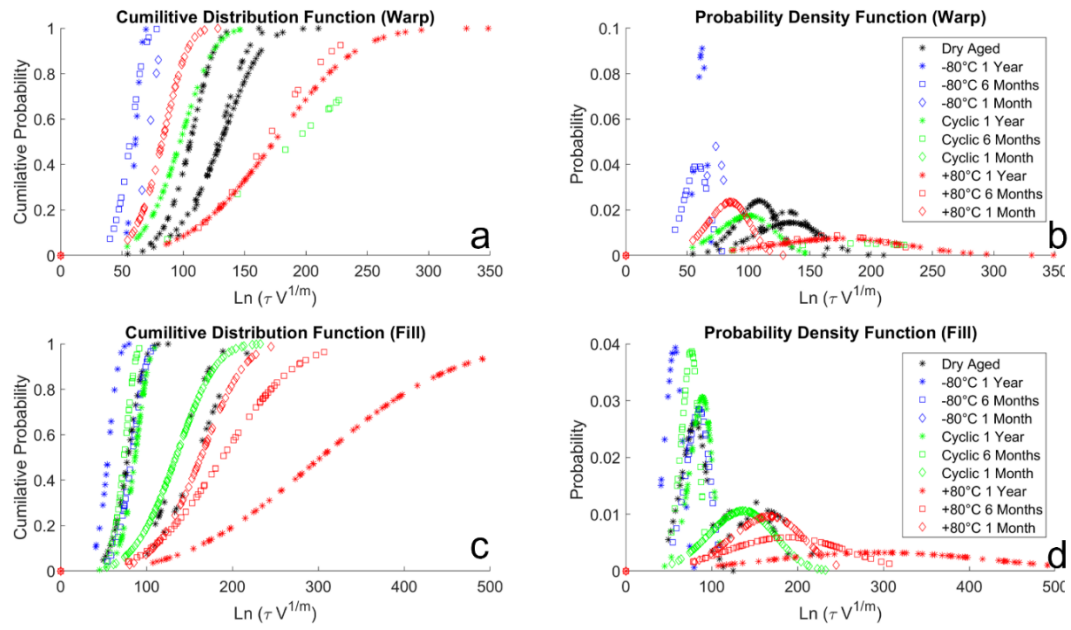


Figure 86: Cumulative and Probability density function of dry temperature conditioned coupons showing the variation of IFSS with respect to interfacial volume using weibull equation.

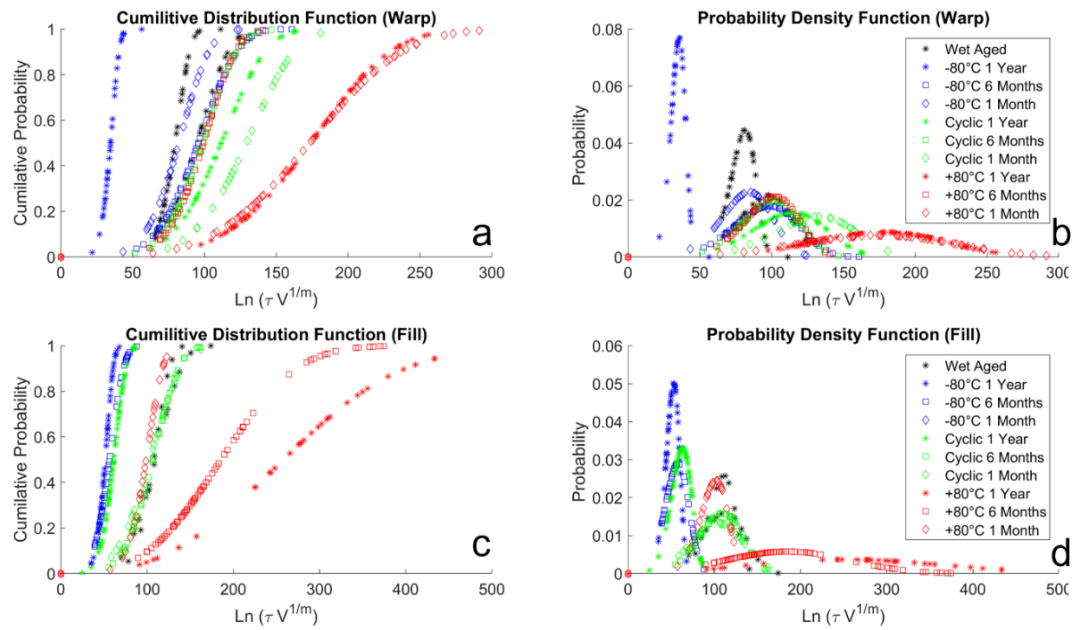


Figure 87: Cumulative and Probability density function of wet temperature conditioned coupons showing the variation of IFSS with respect to interfacial volume using weibull equation.

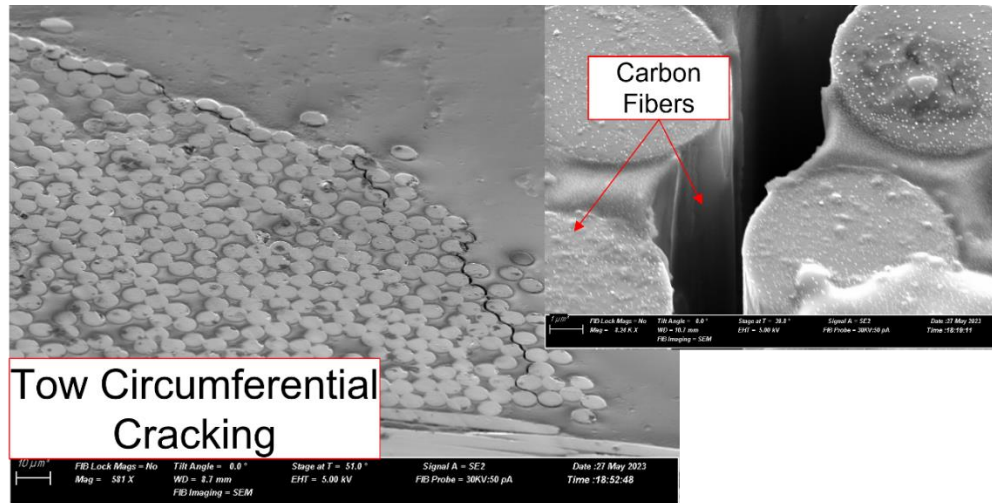


Figure 88: SEM micrograph of a region in a dry sample showing tow-circumferential failure mode.

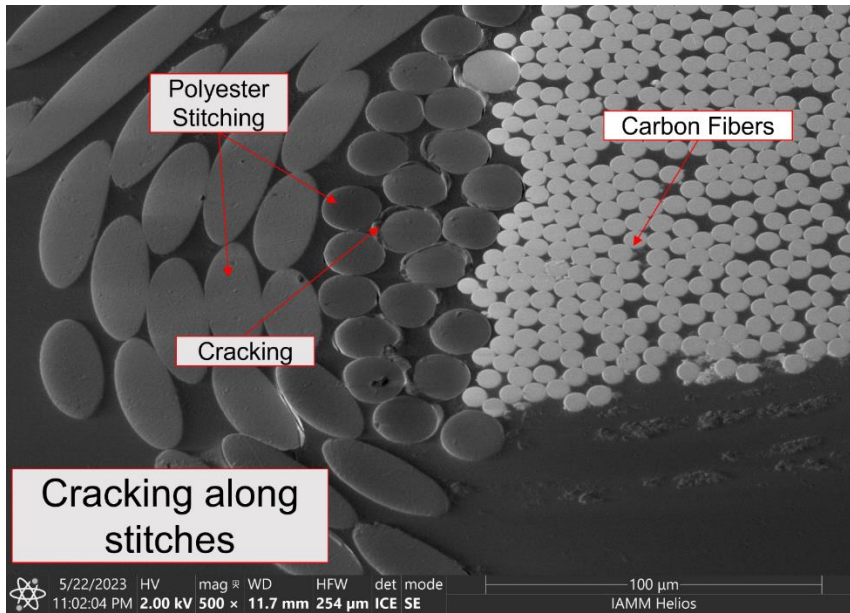


Figure 89: SEM micrograph of a region in a dry sample showing tow-circumferential failure mode.

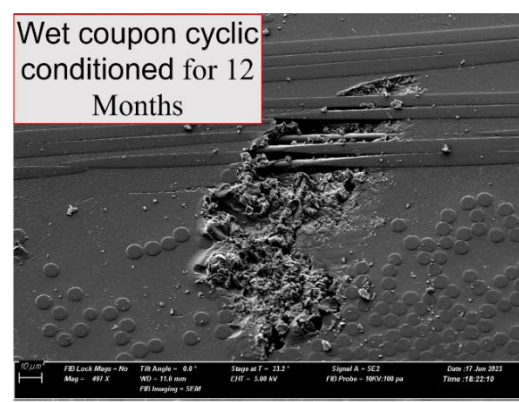
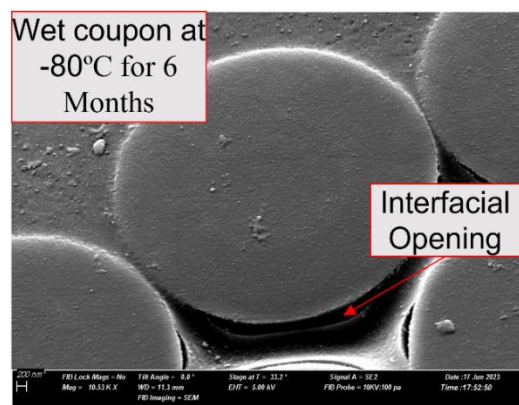
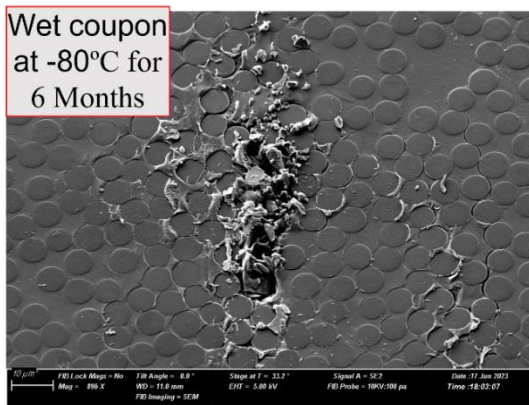
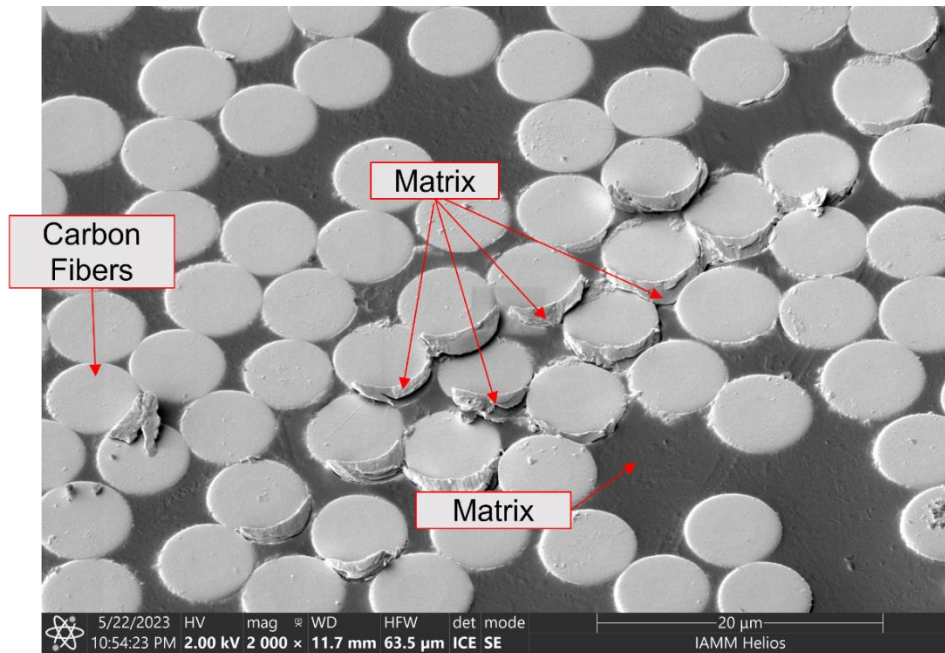


Figure 90: Effect of temeprature upon the matrix in the dry and wet temperature conditioned coupons

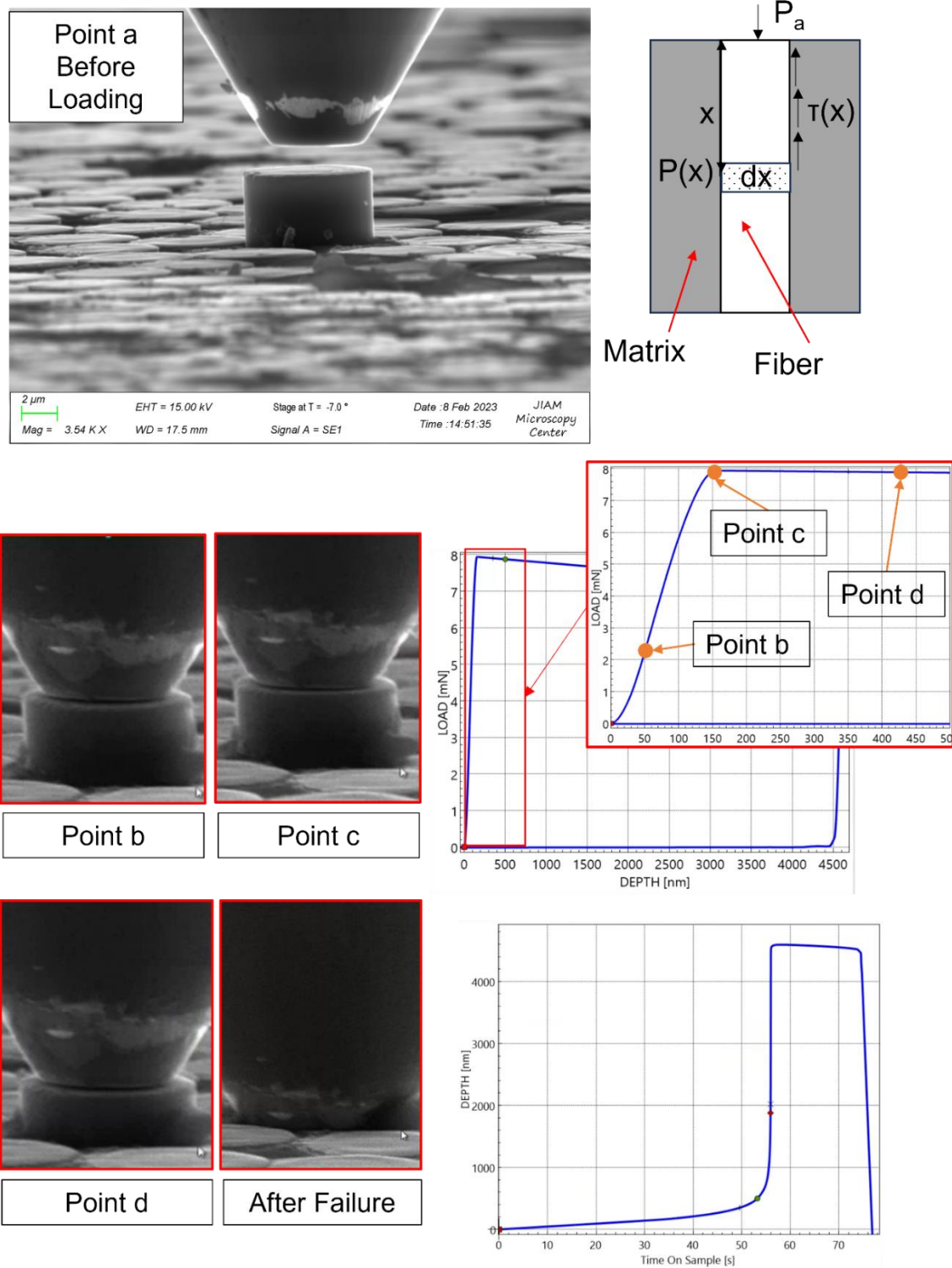


Figure 91: In-situ repush tests of pushed-out fibers to measure the residual stresses.

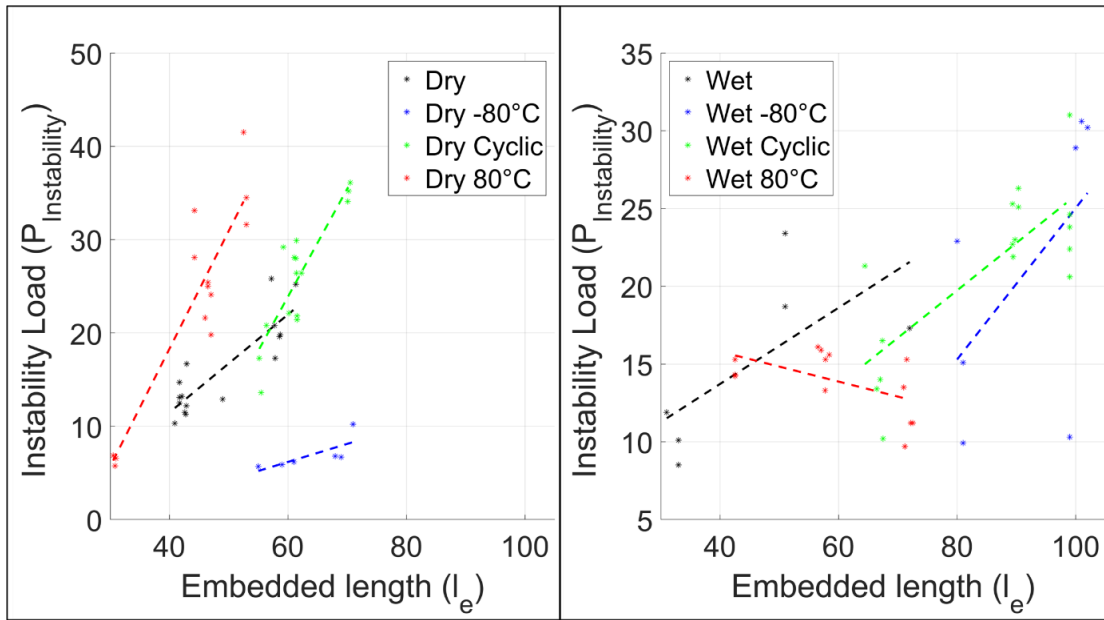


Figure 92: Instability load vs embedded length

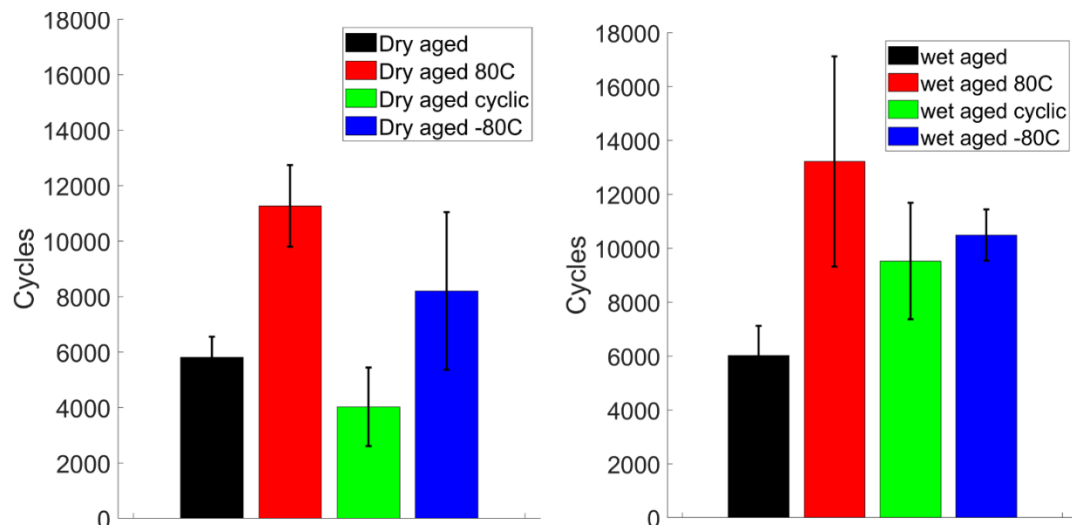


Figure 93: Number of cycles to failure for the temperature conditioned coupons a) Dry, b) wet

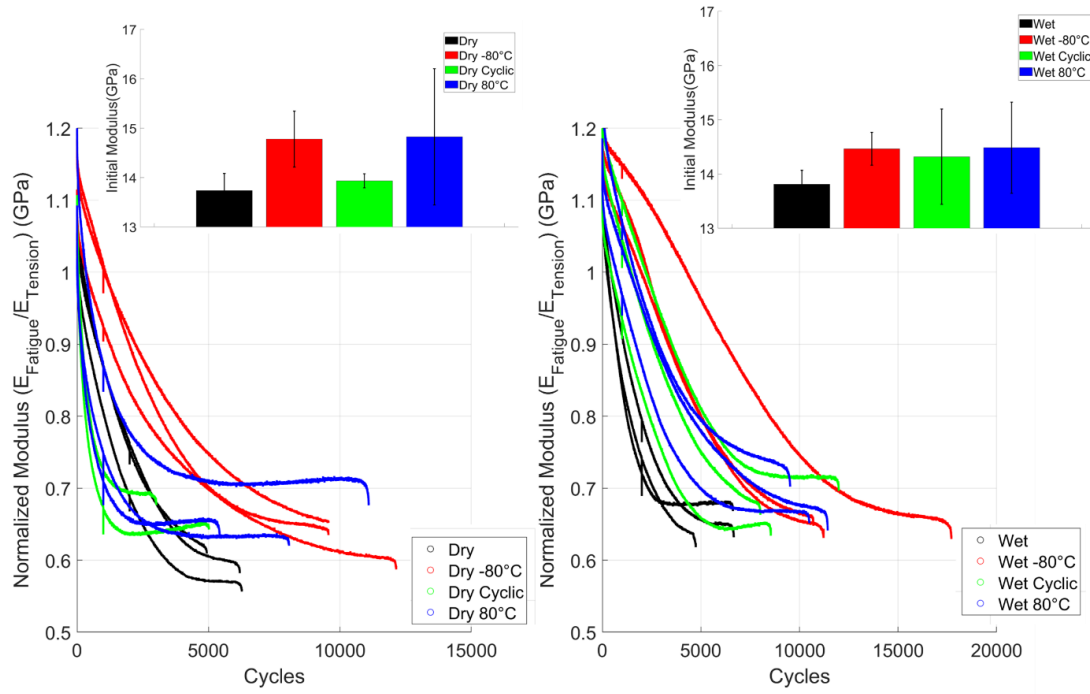


Figure 94: Modulus reduction as a function of number of fatigue cycles for dry and wet coupons underwent different temperature conditioning.

CHAPTER 7: CONCLUSIONS

A suite of techniques for micromechanical characterization of the constituents in polymeric composites were developed. The developed techniques primarily focused on- quantifying the interfacial shear strength (IFSS) while evaluating the effects of residual stresses upon the IFSS- the qualitative estimation of the spatial evolution of carbon fiber 'microstructure' (nanostructure) using nanoindentation- and the evaluation of the splitting mode-I fracture toughness of carbon fibers. The developed techniques were used to understand and evaluate the combined effect of seawater and temperature on the micromechanical and macro-scale properties of carbon-fiber vinyl ester composites. Firstly, an experimental study was conducted in which the authors demonstrated the combined effect of long-term temperature and seawater upon the compression behavior of NCF-based CF/VE composites. Compression testing was done using the CLC fixture and MTS servo-hydraulic system. The strains were measured using Digital Image correlation (DIC). A $\sim 12\%$ and an additional $\sim 4\%$ decrease in compression strength was observed due to short-term (< 6 months) and long-term saturation (~ 2 years) in seawater at 40°C . A new DIC variable was defined ($\frac{dw}{dt}$) that calculates the instantaneous change in out-of-plane deformation. Using the newly defined variable and optical imaging of $90^\circ \sigma_{\max}$ tested warp coupons, it was found that the failure initiation occurs due to edge delamination in warp coupons irrespective of the dry or wet conditioning. For the fill coupons, the failure initiated due to tow-micro buckling and then propagated as a through-thickness failure or delamination. The micromechanical characterization using Push-in tests revealed decreased interfacial shear strength due to long-term exposure to seawater. For the warp coupons, the X-ray tomography (XCT) revealed that the distance

between the tows (size of the resin pockets) was the underlying microstructural parameter that controls the compression strength.

In a series of works, micromechanical characterizing techniques were developed. Firstly, the authors demonstrated the methodology for conducting highly precise single-fiber push-out tests with a nominal fiber diameter of 7mm. The principal obstacle to conducting push-out tests pertains to preparing thin films, which was addressed in the current work. The results showed the dependency of the IFSS upon the interface length. At shallower thicknesses, a clean interfacial break was observed. For tests corresponding to higher thicknesses, some of the pushed-out fibers were enclosed in the surrounding matrix, which was attributed to a slight misalignment of the fibers with respect to the loading axis. A modified Weibull distribution was introduced and used to analyze the results because the failure mechanism followed the weakest link chain failure. Reheating and cooling experiments show a significant decrease in the interfacial shear strength of CF/VE when exposed to a temperature greater than the glass transition (T_g). The impact of residual stresses upon the calculated IFSS was significant.

In the subsequent study, a methodology was proposed to conduct the nanoindentation of carbon fiber by accounting for the combined effects of fiber-matrix-interface assembly. The results show that a modified frame stiffness was necessary to correctly evaluate the contact stiffness in the indentation of carbon fibers. Furthermore, the indentation should be carried out to a maximum depth characteristic of 20 percent of the modified frame stiffness. Mechanisms were proposed to explain the lower indentation modulus seen in the core and sheath of carbon fiber by considering the deformation being controlled by

out-of-plane shear and transverse deformation and nano buckling of graphene sheets of carbon fiber. The modulus values obtained for different grades of carbon fiber were found to be statistically the same. The recovered energy parameter (R) was defined in this study. The parameter was found to be a function of pore size and, consequently, the stack height and crystal size. Unlike the modulus, the above property for the introduced parameter R was found to be invariant irrespective of the type of carbon fiber. The above finding implies that R can be used to understand the effect of localized crystal parameters on carbon fiber's mechanical performance and the relationship between processing parameters and crystal structure. Following the above results, a methodology was developed using computational investigation and experimental validation to extend the technique of pillar splitting to brittle fibers in reinforced composites. Firstly, a polishing-based methodology to prepare the micropillars required for the pillar-splitting technique was presented. Subsequently, a series of computational and experimental investigations were carried out to understand the effects of the matrix, interface, and protruding height of the micropillar on the results. It was found that the matrix does not affect the instability load and only contributes to the depth required to reach the instability load provided an adequate height of the micropillars. The minimum height required to evaluate the matrix-independent results equals the micropillar's diameter for a composite with a perfect interface. The introduction of the interface drastically reduced the error in instability load, even for a condition with no protruding height. Additionally, if the interface failure happens before the splitting failure, the error in the instability load approaches zero. CrystalBond™ 590 was found to be a suitable matrix material for the

evaluation of the Mode I fracture toughness of carbon fibers using pillar splitting. Finally, experimental and computational investigations are carried out to extend the technique to an arbitrary shape. A shape correction parameter, β , is defined to extend the constant γ , evaluated for a circular cross-section, to a constant $\gamma_{\text{effective}}$ representative of an arbitrary geometry. It was shown that the error arising due to an arbitrary cross-section is independent of the mechanical properties. Therefore, the concept of an effective constant was introduced. The authors recommend that the methodology only be applied to cases with $0.2 < \beta < 2$. Finally, the fracture toughness of different grade Toray carbon fibers was evaluated using the proposed technique, and it was found that the fracture toughness of carbon fibers in the splitting mode decreases with increasing fiber modulus contrasting the behavior reported in the literature. The above result was attributed to the different resistances a crack faces during propagation, depending on the crack direction with respect to the fiber axis.

Finally, a thorough characterization was carried out to understand the effects of seawater exposure and temperature on the carbon fiber vinyl ester composites and their constituents. The seawater conditioning was carried out for 15 years. After conditioning, the dry and wet coupons of the same panel were conditioned at 80 °C, - 80 °C, and cyclic temperature conditioning. The effects of temperature conditioning introduced cracking in the samples, with maximum cracking evident in cyclic temperature-conditioned coupons. The cracking tends to increase with the exposure time. Due to long-term hygrothermal conditioning, two primary zones of crack initiation were identified- tow circumferential cracking and the cracking along the stitches. Tow microcracking was hypothesized to

happen due to the stiffness gradient (between the tow and the matrix) as well as the morphology of the tows. SEM micrographs revealed the protrusion of the matrix along the fiber-matrix boundaries. The above phenomenon was detected in all but -80 °C conditioned dry coupons. For the +80 °C and cyclic coupons, matrix protrusion was identified due to high thermal stresses. For -80 °C coupons, the phenomenon occurs due to the change in the water volume between the fiber and matrix boundary. The interfacial opening was observed in the -80 °C wet coupons. The micromechanical investigation revealed the thermal aging of the +80 °C and cyclic conditioned coupons for both dry and wet coupons, with the increase being more pronounced in the +80 °C coupons. Fourier transform infrared (FTIR) spectroscopy results showed high variance as a function of thermal aging. The results showed improved interfacial shear strength (IFSS) for the +80 °C conditioned coupons. No significant change in the IFSS was evaluated in the cyclic coupons. The -80 °C coupons showed a decrease in IFSS. The above trend was similar irrespective of the dry or wet conditioning. Because of the variability between the samples, no comments were made on the effect of conditioning time on the IFSS. The pushed-out fibers were tested again to characterize the residual stresses. For the dry temperature conditioned coupons, the maximum residual stresses were found to be in the +80 °C dry coupons, while -80 °C dry coupons showed the minimum residual stresses. For the wet coupons, the residual stresses decreased irrespective of the conditioning temperature.

Due to the high scatter in the number of cycles to failure and the limited number of tests, no statistically significant comment was made on the effect of temperature conditioning

on the fatigue properties of carbon fiber vinyl ester composites. Regardless, based on the three data points per conditioning temperature, the highest cycles to failure were seen for the + 80 °C coupons, which was argued to be a consequence of the increase in IFSS and the stiffening of the matrix.

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VITA

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