CHARACTERIZATION OF S-GLASS EPOXY COMPOSITE INTERFACE UNDER VARIOUS RATES OF LOADING

by

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ABSTRACT

Glass fiber reinforced epoxy composites are used extensively in military application due to their higher specific stiffness and strength and high levels of damage tolerance and specific energy absorption. When subjected to dynamic loading, a major portion of this energy is dissipated within the composite due to fiber matrix debonding along the interface and localized plastic deformation of the epoxy matrix that occurs at high strain rate. This dissertation involves development of novel experimental methods including carbon nanotube (CNT) based damage sensors to detect interface debonding and characterization of high strain rate resin behavior. A methodology using Finite Element (FE) modeling of the experiments is established to uniquely determine rate dependent Mode II cohesive traction laws of the composite interfaces.

Interface properties were characterized using a microdroplet test specimen at loading rates spanning over six decades of magnitude. At higher loading rates, a tensile Hopkinson bar has been designed that can load the interface in the range of 1-10 m/s. Experimental results on S-2 glass and DER 353 epoxy system and post-failure inspection of the fiber matrix interface showed that the new test method is effective in measuring high rate interface properties of composites. The average interfacial shear strength (IFSS) increased by a factor of 1.6 when the loading rates were increased from 1 μ m/s to 1 m/s.

Crack initiation at the interface was studied by developing a CNT sensor at submicron length scale, which was achieved by modifying the fiber surface morphology through the deposition of CNT using electrophoretic deposition method. As CNTs are coated on a non-conductive substrate, electrically percolating nanotube network is formed in isolation at the interfacial region. This allows for the study of *in-situ* crack initiation at the interface through electrical resistance measurements. Experimental results confirms that crack initiation occurs near the peak load.

To accurately model the microdroplet experiments, rate dependent resin properties were determined over a wide range of strain rates (0.001/s to 12,000/s). To obtain compressive stress strain response up to large strain under high strain rates, a specimen geometry was designed by studying the state of stress in the specimen using FE simulations. High strain rate tests were conducted in a traditional split Hopkinson pressure bar up to a strain rate of 12,000/s over a strain range up to 70%. This specimen geometry overcomes the Hopkinson bar's limitation on maximum attainable strain without altering the bar design. For DER 353 epoxy resin, yield stress increased significantly with applied strain rate and exhibited a bi-linear dependency. Thermal softening was observed under high strain rates at large strains due to adiabatic heating.

A methodology was developed to determine rate dependent traction separation law for composite interface through iterative method by simulating the microdroplet experiments using finite element analysis. A series of parametric studies were conducted by varying peak traction and fracture energy. By matching the peak load, crack initiation time and failure modes from the experiments for three different droplet sizes, a unique set of Mode II traction law parameters are determined for each loading rate. FE results show that both the peak traction and fracture energy associated with the interface are dependent on the rate of loading.

Chapter 1

INTRODUCTION

1.1 Background and Motivation

Fiber reinforced polymer composites have been widely used as lightweight armor for military applications such as ground vehicles and temporary shelters. High specific stiffness, strength and energy absorption makes composites an attractive lightweight alternative to conventional materials. Despite the use of relatively brittle fiber and matrix, polymer composite materials can exhibit high levels of damage tolerance and absorb more energy due to its ability to undergo micro-fragmentation and create a large amount of new surfaces when failure occurs along the fiber matrix interface. The presence of fiber matrix interface, which has the highest potential for the creation of new surfaces, opens an opportunity to tailor the energy absorption capability of the composite material by altering its properties and causing it to fail in a controlled way.

This research is conducted within the framework of mechanism based materialsby-design strategy proposed by an Army Research Laboratory funded Collaborative Research Alliance – Materials in Extreme Dynamic Environment (CRA-MEDE led by Johns Hopkins University, California Institute of Technology, Rutgers University and the University of Delaware) as illustrated in Figure 1.1 for composite materials. During a ballistic impact, a large amount of energy is deposited onto the composite material in a short duration of time. The energy is dissipated by the material through various mechanisms over a range of length scales and time scales. Materials-by-design strategy involves identifying critical mechanisms and seeing it through novel experiments, understanding them through modeling and controlling them through synthesis to design the material. S-2 glass/epoxy has been chosen as a model composite system to study the role of interface and interaction between constituents from atomistic to macro length scales over a range of time scales encountered during a dynamic event. S-2 glass/epoxy resin composites are used as a standalone composite armor or as a backing material in a ceramic composite armor. This dissertation focuses on the study of the S-2 glass/epoxy composite interface at the micromechanical length scale for the determination of interfacial traction separation law needed for higher length scale models within the materials by design framework.



Figure 1.1 Materials by design framework for composite materials uses a multiscale modeling and experimental approach

Glass fibers are commonly used for ballistic applications due to its relatively higher strain to failure. Epoxy, vinyl ester, polyester resins are used as matrix in glass fiber composites for such applications. Epoxy resin is one of the most common thermosets used as the matrix in polymer composites because it offers a balance of properties (mechanical properties, resistance to environmental degradation, thermal stability, etc.), and processablity (low viscosity, low pressure and low cure temperatures).

Glass fiber reinforced composites exhibit higher degree of microcracking and energy absorption under dynamic loading [1]. Fibers are generally coated with sizings to protect them from damages during handling and weaving of fibers. Sizing also helps in the formation of a layer with mechanical and chemical properties that varies continuously from the fiber surface to the matrix through physio-chemical interaction. A wide range of glass fiber sizings for epoxy exists to promote wetting and adhesion that allows interface properties to be designed for ballistic applications [1–3].

During composite processing, a three-dimensional region is formed at the interface between fiber and matrix due to diffusion of the resin and curing agents into the sizing followed by chemical reaction (Figure 1.2). The interface governs the level of interaction between fiber and matrix and affect the overall bulk properties of composite. The properties of interface depend on chemical composition and compatibility between the constituents and the surface morphology of the fiber.

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Figure 1.2 Formation of composite interface (10-100 nm typical) between S-Glass fiber (10 $\mu m)$ and epoxy matrix

A strong bond between fiber and matrix is desirable for structural application but not suitable for ballistic application because such interface will result in low energy absorption due to localized failure. On the other extreme, very weak interface results in no load transfer between fibers, for example in dry fabrics the only interaction is through friction between fibers. When the interface is weaker than resin matrix in shear, energy absorption is dominated by debonding and frictional sliding along the interface over long distances. When the interface is stronger than the shear yield strength of the matrix, energy absorption is dominated by matrix plastic deformation and cracking. Maximum energy absorption may occur when both debonding and matrix plastic deformation occurs (i.e. material by design). Cracks along the interface typically occurs at an isolated fiber break and propagates resulting in fiber pull out, and frictional sliding that contributes additional energy dissipation. Frictional sliding depends on surface roughness, residual stress due to mismatch in coefficient of thermal expansion between fiber and matrix (radial compression is generated in S Glass epoxy after processing). The effects of dynamic loading on the energy absorption mechanisms associated with high strain rate response of the matrix and interface is not well understood.

One of the major requirements for an armor system is to maximize penetration resistance and energy absorption at minimal weight. Energy absorption in composite panel when subjected to ballistic loading occurs through fiber fracture, fiber matrix debonding, fiber pullout, frictional sliding at microscale; whereas, matrix cracking and delamination contribute to overall energy absorption at the macroscale (Figure 1.3). Mechanisms that govern the energy absorption process at the microscale have been found to be more significant than at the macroscale [4]. This provides an opportunity to design composites with desired performance by tailoring the interfacial properties at micromechanical length scale. To achieve this goal, it requires a fundamental understanding of deformation and failure mechanisms involved at multiple length scales when the composite is subjected to dynamic loading. However, experimental techniques are yet to be fully developed, especially at micromechanical level [5]. Furthermore, development of multifunctional interface by using nanofillers such as carbon nanotubes and combining it with conventional mechanical testing can provide insight into the damage mechanisms in the interface [6,7].



Figure 1.3 Energy absorption mechanisms at various length scales

This dissertation focuses on studying the deformation and damage mechanisms of composite interface at micromechanical length scale to develop rate dependent traction separation laws. The traction law describes the constitutive behavior of cohesive zone model, which is used to represent the fracture process zone ahead of the crack tip and debonding of the fiber matrix interface. Key parameters for the traction law are fracture energy and peak traction where softening starts to occur. Various shapes of cohesive relations can be defined based on these two parameters, such as cubic polynomial, trapezoidal, linear softening and bilinear softening [8]. Studies have shown that the fracture toughness and peak tractions are the most important parameters and the shape of the traction law has less influence on the accuracy and predictive capability of the model [9,10]. There are basically two approaches to determine traction separation law. One is direct method where the J-integral is directly determined from experiments such as double cantilever beam (DCB) for Mode I and end notch flexure (ENF) for Model II. Traction laws are calculated using analytical solutions, which are derived based on information regarding crack opening and load displacement response of the specimen. The second approach is an inverse method, where the interface is represented by cohesive elements and traction law parameters are extracted iteratively by accurately simulating and matching the experiments [11,12]. This route in conjunction with novel test methods and in-situ sensing of crack initiation is the approach used in this dissertation.

Dependence of traction law parameters on the rate of loading has been reported in the literature [8,9,13]. For instance, traction law obtained through direct approach for steel adherends bonded with polyurea exhibited strong dependence on the rate of loading [13]. Xu et al. [14] also determined rate dependent model parameters by simulating DCB tests conducted at different strain rates. The rate dependent failure behavior of adhesive bonds was simulated by introducing a Maxwell element to a rate independent cohesive zone model. Wang et al. [15] employed spring and dashpots to introduce viscoelastic factor in the cohesive zone model and simulated DCB tests with metal adhesive (elastic) and rubber adhesive (hyperelastic) structure. Rahulkumar et al. [16] modeled fracture in viscoelastic materials by combining viscoelastic adhesive model with a rate independent cohesive zone model. Marzi et al. [17] used a rate dependent extension of bilinear cohesive model and implemented in commercial FE code LS-DYNA via a user-defined subroutine. Butt joint and tapered DCB tests were conducted at velocities ranging from 10⁻² mm/s to 10² mm/s to determine the Mode I model parameters. Thickness of the S-glass/epoxy composite interfaces considered in this study are in the range of 10 – 100 nm, which makes the direct approach of determining traction law impractical due to the limitations in the instrumentation required to monitor crack growth. Chowdhury and Gillespie [18] predicted Mode I, Mode II and mixed mode traction separation law for silica-silane interface by modeling atomic interactions using molecular dynamics simulation. Swadener and Liechti [19] calculated the fracture toughness of glass/epoxy interface for sandwich specimens by subtracting the plastic dissipation from the total fracture toughness through FE simulation. Sockalingam et al. [11] extracted traction separation law for S-glass/epoxy interface by simulating microdroplet experiments via FEA. However, these studies did not consider the rate dependence of the interface properties. In this study, a bilinear traction law has been assumed and iterative FEA based method has been employed to determine the Mode II rate dependent traction separation law by simulating a microdroplet experiment. Iterative approach requires accurate description of rate dependent resin properties, and information on crack onset along the interface.

As such, the need for traction separation law has motivated studies in the following areas:

i) Development of a physically based methodology to accurately extract rate dependent traction separation law for composite interface.

ii) Understanding of critical energy absorption mechanisms and failure processes involved at interface at micromechanical length scale.

iii) Development of a robust experimental test methods to study the rate dependence of interfacial properties at high rate of loading, which is limited in the literature.

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iv) Incorporation of nanofillers at the interface region for higher energy absorption by creating more tortuous paths for crack growth.

v) Exploitation of the sensing capability of nanofillers to study in-situ damage progression at micromechanical length scale required for accurate traction law determination.

vi) Obtain large strain response of matrix material under high strain rate using Hopkinson bar test technique.

1.2 Research Objectives

The primary objective of this dissertation is to determine strain rate dependent Mode II traction separation law. To achieve this, test methodologies need to be developed for accurate determination of crack initiation at the interface and characterization of rate dependent properties of resin and interface.

The main objectives of this research work are as follows:

i) Through a combination of experiments and finite element modeling, extract the rate dependent traction separation law

ii) Develop an experimental test method for the characterization of interfacial properties at high rate of loading and investigate the variation in interfacial shear strength and energy absorption over a wide range of loading rates

iii) Explore incorporation of nanofillers in the interface for the development of CNT sensor

iv) Study crack onset at the fiber matrix interface using CNT sensors

v) Develop an experimental technique to investigate high strain rate response of resin undergoing large deformation

vi) Develop constitutive model for resin to predict time and temperature dependent stress strain response

1.3 Research Approach

The main objective of this study is to determine rate dependent traction separation law for interfaces in S2-glass/epoxy composite system. The strain rate dependent properties of the constituents obtained from the experiments serve as inputs for the development of accurate FE models (Figure 1.4). A combination of computational and experimental approaches has been taken to understand the interaction between fiber and matrix and extract rate dependent traction separation law. The traction law and the material properties will then be used in models at higher length scales such as representative volume element (RVE) and fiber level tow model to study more complicated interaction between the constituents (see Figure 1.1).



Figure 1.4 Experimentally obtained material properties serve as inputs for microdroplet simulation for the extraction of traction separation law

To develop high rate test method for the characterization of interface properties, Hopkinson bar test method has been adopted [5]. This test method was chosen because of its simple design and potential to obtain material properties at high loading rates with microsecond resolution. The test specimen should be able to provide information on interfacial shear strength, energy absorption during debonding, and during frictional sliding, which can be a major source of energy absorption. Microdroplet test specimen was deemed appropriate as it satisfies all the requirements. Detailed justification for the
selection of this test geometry is presented in Chapter 2. FE analysis was carried out for the determination of optimum specimen geometry to ensure that no dynamic effects are present during loading. Limits on loading rates and specimen geometry necessary for achieving the goal of this study were also quantified through FE analysis. Details on instrumentation are provided and successful high rate interface tests are conducted.

For the development of sensors, carbon nanotubes (CNT) were coated onto the surface of single glass fibers using electrophoretic deposition (EPD) method (Chapter 3). This method was chosen because of its cost effectiveness and versatility in coating particulates onto substrates with complex shapes or surface textures. The thickness of the coating, which can easily be controlled by adjusting the processing parameters of EPD, highly influence the interfacial properties. This chapter concludes with the development of CNT sensor at sub-micron length scale.

There is a great interest in studying crack growth along the interface as it can provide insight into the energy absorption and failure mechanisms. Electrically conductive network formed along the fiber matrix interface through the incorporation of CNT on the surface of glass fiber has been coupled with conventional mechanical tests to study the damage onset at the interface (Chapter 4). Changes in electrical resistance were monitored across microdroplet specimen during the test. As the crack tip reaches the interface region, the CNT network is severed and the electrical resistance begins to increase. With this method, the onset of crack can be monitored along the interface, which is otherwise difficult to achieve through optical methods.

Obtaining accurate matrix properties under different rates of loading is imperative to developing accurate FE models [20]. Split Hopkinson pressure bar (SHPB) test technique was chosen to obtain high rate properties of resin matrix. Chapter

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5 discusses the development of a specimen geometry that overcomes Hopkinson bar's limitation on maximum attainable strain without altering the bar design while maintaining strain uniformity and minimizing radial inertia and frictional effects.

In Chapter 6, the experimental results on compressive properties of resin matrix are subsequently used to develop a constitutive model by employing an incremental approach with strain rate dependence and thermal effects, which can be implemented as user defined material (UMAT) in commercial FE software such as Abaqus.

Chapter 7 presents the methodology to uniquely define traction separation cohesive laws for Mode II interface debonding. A minimum of three droplet sizes are tested for each rate of loading. The experiments are modelled using the measured rate dependent constitutive response of the matrix and a range of traction laws are considered. The unique traction law determination accurately predicts the failure load and failure mode for all drops sizes tested for each rate of loading. In the case of quasistatic loading energy absorption during load/unload cycles is measured and compared to model predictions for additional experimental validation.

1.4 Unique Contributions

A novel test method to directly characterize rate dependent interface properties has been developed using a modified tensile Hopkinson bar and microdroplet specimen. The interfacial shear strength was characterized up to a loading rate of 1 m/s, which is orders of magnitude higher compared to the existing test methods. The interfacial shear strength (IFSS) increased by a factor of 1.6 as the loading rate was increased from 1 μ m/s to 1 m/s. Very few research studies are present in literature which look at tailoring interfacial properties by controlling the CNT coating thickness down to sub-micron level. This can be beneficial in optimizing composite properties for superior performance. In this study, the CNT coating thickness was varied from 400 nm to 2 μ m by adjusting the processing parameters of the electrophoretic deposition method. The coating of 2 μ m resulted in 58% increase in the interfacial shear strength.

The thinnest CNT coating of about 400 nm provided an electrically conductive network along the interface without altering its interfacial shear strength. As such, a sensor for monitoring of crack onset *in-situ* at the interface was developed, which can provide new insight into understanding failure mechanisms.

Hopkinson bar technique is the most common test method to characterize material properties in the range of 10^{3} /s to 10^{5} /s strain rate. The maximum possible attainable strain depends on the duration of the loading pulse and the thickness of the specimen. Without changing the bar design, a specimen geometry was designed through FE analysis, which can increase the maximum attainable strain, while maintaining uniaxial state of stress in the specimen. The rate and temperature dependent constitutive model, which was developed using the experimental results can handle a wide range of monotonic and varying strain rates at temperatures ranging from ambient to above glass transition temperature range.

Finally, a methodology for uniquely determining Mode II rate dependent traction separation law for composite interfaces was established and experimentally validated. This is an important contribution since the literature and our own simulations confirm that many combinations of peak traction and fracture energy can give the same predictions (non-uniqueness). In this study, a physical based approach, which includes

criteria on peak force, failure mode and crack growth along the interface for different droplet sizes has been carried out with accurate rate dependent resin properties to uniquely determine the Mode II rate dependent traction separation law.

Chapter 2

DEVELOPMENT OF HIGH RATE TEST METHOD FOR INTERFACE CHARACTERIZATION

This chapter presents a new test method to directly characterize fiber-matrix interface properties under high rate of loading. Standard test methods available to characterize interface properties are discussed and their feasibility to extend for high rate tests is evaluated. Current state of the art experimental capabilities for interface characterization cannot directly measure interfacial shear strength at high rate of loading. In this study, a tensile Hopkinson bar with a modified incident bar is used to load a microdroplet test specimen to study the high rate properties of interface. Numerical simulations are carried out to design the test specimen geometry and validate data reduction procedures for the dynamic interface experiments. The chapter concludes with experimental results for an S-2 glass/epoxy system and post-failure inspection of the fiber matrix interface, demonstrating the feasibility of the new test method to accurately measure high rate interface properties of composites.

2.1 Fiber Matrix Interface

Fiber matrix interface is formed due to the diffusion and subsequent chemical reaction between the sizing on the fiber and the resin while curing during the fabrication process. By definition, this layer of a finite thickness, which has mechanical, chemical

and physical properties different from those of fiber and matrix, is known as *interphase*. Whereas, an *interface* generally refers to the surface formed at the boundary of fiber and sizing, which is infinitely thin [3].

Typically, glass fiber sizing comprises of coupling agents, film former, lubricant, and antifoam or antistatic agents. Among these components, film former and silane coupling agents play a vital role in determining the mechanical and chemical properties of the interphase. Silane coupling agents promote covalent bonding through thermally activated chemical reaction resulting in the formation of siloxane network with the silanol groups present on the glass fiber surface. This network which spans from the glass surface to the resin provides molecular continuity across the interphase. The primary function of the film former is to protect the fiber surface from damages during handling and weaving. Its chemical composition is generally identical or strongly compatible with the composite matrix resin formulation (i.e. epoxy in this study). An optimum combination of silane coupling agent and film former and its compatibility with the resin formulation can significantly influence the interfacial shear strength, its energy absorption capability and hygrothermal durability of the composites [21,22]. Moreover, the fiber surface roughness can be increased by appropriate choice of film former, which ultimately leads to higher energy absorption during frictional sliding after debonding [23].

Several studies have confirmed the importance of interface on the overall properties of a composite material. Favre and Merienne [24] studied the interface properties of various carbon fiber/araldite resin system at micro and macroscale. It was found empirically that the interlaminar shear strength (ILSS) of the composite was proportional to the square root of interfacial shear strength (IFSS). In another study, Mader et al. [25] showed a linear relation between ILSS of continuous fiber-reinforced composite and IFSS measured through single fiber pull out tests on different carbon fiber/epoxy system. Gao et al. [26] established a linear relationship between the interfacial shear strength (IFSS) obtained from microdroplet testing of a wide range of fiber sizings and punch shear strength of composite laminates fabricated from the same constituents.

A strong bond between fiber and matrix is desirable for structural application, whereas a weak and ductile interface increases the composite toughness and is more suitable for impact and ballistic application [4,27,28]. Energy absorption in a composite occurs through various micromechanisms such as matrix plastic deformation and fiber breakage, fiber-matrix debonding and frictional sliding. At the macroscale, additional energy absorption mechanisms exist such as delamination that occurs between layers during transverse impact. Macromechanical test techniques such as drop weight and dynamic punch shear tests induce damage at all length scales but can provide insight into the role of interface at the microscale on composite properties. Consequently, an opportunity to tailor the interface properties at the nano to micro length scale opens up methodologies to improve composite performance. Characterization methods to directly measure interface properties at the microscale are needed. Incorporating the effects of loading rate on interface properties is of particular importance for impact loading applications of composites.

2.1.1 Characterization methods for composite interface

The first step in the development of high rate characterization method for interface properties is the selection of an appropriate test method. An ideal test method

should yield interfacial strength and the energy absorption associated with complete debonding and frictional sliding. Several techniques are available to quantify the interfacial properties at microscale such as microdroplet test, single fiber fragmentation test, fiber push out and fiber pull out tests [3,29,30]. It is important to note that each test method measures the IFSS which is defined as the average shear stress over the debonded shear area. This value is geometry dependent and the actual shear stress along the interface is non-uniform. Consequently, detailed analysis of the test methods is required to determine the cohesive traction separation laws.

In fragmentation test, a pre-tensioned single fiber is aligned along the center of a dog-bone shaped specimen, which is then filled with resin and cured (Figure 2.1). The resin needs to be transparent such that the fiber can be seen under a microscope. Prior to the test, the specimen might need polishing to improve image quality and prevent premature failure of the matrix due to surface defects. As the specimen is loaded in tension, the fiber will progressively start to fail into shorter and shorter length until a saturation level is reached and the fiber can no longer break. In order to facilitate fragmentation of fibers, the strain to failure of the matrix needs to be at least three times that of the fiber. The progression of failure is observed through a light microscope during the test, and the critical length of fiber is measured after achieving the saturation level. Knowing the critical length, the average interfacial shear strength is estimated using Kelly-Tyson model. This test has the potential for being conducted at higher loading rates. However, the interfacial shear strength is indirectly calculated and this test method cannot provide information regarding energy absorption up to debond and frictional sliding (Table 2.1) and therefore was not considered for this study.



Figure 2.1 Single fiber fragmentation

	Fragmentation test	Pushout test	Microdroplet test
Fiber fracture	X	X	\checkmark
Interface debonding	X	\checkmark	\checkmark
Frictional sliding	X	\checkmark	\checkmark
Rate dependence	+++	+	+++

Table 2.1 Test method selection criteria

Single fiber push out test method for composite materials is basically an adaptation of metallurgical microhardness test (Figure 2.2). The test specimen needs to be thin enough such that the indenter can push out the fiber without damaging or splitting the fiber. Because of the way in which the load is applied, this test method is suitable for only hard fibers such as metal, glass or carbon. Prior to testing, the specimen surface should be polished. During the test, load is applied onto a single fiber using a microindenter and force and displacement response is continuously monitored. Knowing the maximum force at which debonding occurs, the thickness of sample and the diameter of the fiber, the average interfacial shear strength can be calculated. In addition to interfacial shear strength, the energy absorption associated with debonding and frictional sliding can also be measured. However, this method is not chosen in this study because the extension of this test method for high rate characterization is limited as is discussed in section 2.1.2.



Figure 2.2 Single fiber push out test

Microdroplet test method, developed by Miller et al. [31], consists of a single droplet of resin matrix deposited and cured on a single fiber to create a realistic composite interface (Figure 2.3). One end of the fiber is attached to a load cell while a set of knives are used to shear off the droplet such that the failure occurs along the interface.



Figure 2.3 Schematic representation of microdroplet test

Using the force – displacement data (Figure 2.4), the average IFSS can be calculated based on the measured failure load and interface shear area using Eq. (2.1).

$$\tau = \frac{F}{\pi d_f l_e} \tag{2.1}$$

where, τ refers to IFSS, F is the tensile failure load in the fiber at interface debonding, d_f is the diameter of the fiber and l_e is the embedded length of the microdroplet. The average IFSS is geometry dependent and decreases as the droplet size/embedded length increases. Our methodology for traction law determination uses experimental results for drops of various sizes as discussed in Chapter 7.

Energies are normalized to allow for comparison of specimens that may have differences in fiber diameter, gage length and droplet size. Specific energy up to debond is determined by integrating the force-displacement curve and normalizing it by the shear area. However, it should be noted that these force displacement curves include the deformation due to resin plasticity as well. So, the energy absorption calculation includes the contribution from both resin and interface. In Chapter 7, the energy absorbed by each constituent is partitioned using finite element analysis. Also, the calculations for energy absorbed during frictional sliding is only applicable for the quasi-static loading cases since it was not possible to monitor the force response during frictional sliding in dynamic experiments.

Specific debonding energy (Eq. (2.2) and specific energy during frictional sliding (Eq. (2.3) are calculated as follows:

$$E_{deb}^{sp} = \frac{\int_{\delta_i}^{\delta_{deb}} F \, d\delta}{\pi d_f l_e} \tag{2.2}$$

$$E_{fs}^{sp} = \frac{\int_{\delta_{fric,i}}^{\delta_{max}} F \, d\delta}{(\pi d_f l_e) l_e} \tag{2.3}$$



Figure 2.4 Typical force displacement response of a microdroplet experiment (The grey portion in the plot has been omitted from further data reduction)

2.1.2 High rate characterization of interface properties

Most of the tests found in the literature have been conducted only within quasistatic loading regime. Studies focusing on the interface properties due to dynamic loading have been very limited. Tanoglu et al. [32] developed a dynamic interphase loading apparatus to load the interphase through micro-indentation method up to a displacement rate of 3 mm/s. Tests on E-Glass fiber (with different sizing) and epoxy amine systems showed an increase in IFSS, energy absorbed during fiber-matrix debonding and frictional sliding with increase in loading rate. Also, the energy absorption capability increased for the specimens with unsized glass fibers for all loading rates. Other researchers have used the microdroplet test method or its modified version (cylinder test) to study the rate sensitivity of the interface (See Table 2.2) up to about 4 mm/s. Greenfield et al. [33] developed a test method to load a single fiber fragmentation test specimen at high displacement rate of 1250 mm/s, which is the only study found in the literature to conduct micromechanical test in the meters per second range. As mentioned earlier, the interfacial shear strength is indirectly calculated and energy absorption during fiber matrix debonding and frictional sliding is not measured.

In order to characterize the interface properties at higher rate of loading, an experimental setup has been designed, which utilizes a modified version of a tensile Hopkinson bar. The incident bar is modified to load a microdroplet test specimen to directly measure IFSS and the energy absorbed during fiber-matrix debonding.

	Displacement	Test method	Properties
	rate (mm/s)		
Tanoglu et al.	0.3 - 3.00	Dynamic push out	IFSS and energy
[32]		test	absorption
Gao [34]	0.003	Microdroplet test	IFSS and energy
			absorption
Morlin and	0.0002 - 3.33	Cylinder test	IFSS
Czigany [35]			
Greenfield et al.	1,250	Single fiber	IFSS
[33]		fragmentation test	
Current study	0.001 - 10,000	Microdroplet test	IFSS and energy
			absorption

 Table 2.2 Various test methods and displacement rates from literature

2.2 Hopkinson Bar Test Method

A traditional Hopkinson bar consists of an incident bar, a transmission bar, and a striker bar that impacts onto the incident bar to send an input pulse. For compression tests, a striker bar with diameter generally the same as that of the incident bar is accelerated along a long barrel using compressed air and impacts the incident bar to produce a compressive wave. Whereas, for tensile tests, a hollow striker bar is used to strike a flange attached to the end of the incident bar to produce a tensile wave. The input pulse, which is twice the length of the striker bar (in space), propagates along the incident bar at the speed of sound. When the wave reaches the incident bar/specimen interface, a portion of the input pulse is transmitted through the specimen into the transmission bar, while the rest is reflected back to the incident bar. The amount of signal transmitted and reflected depends on the acoustic impedance mismatch and the difference between cross-sectional area between bar and specimen.

Force history in the specimen during the test is calculated from the strain signal in the transmitted bar. Strain rate history in the specimen during the test is calculated from the particle velocities at incident bar/specimen interface and specimen/transmission bar interface. Then, the strain in the specimen is determined by integrating the strain rate history over time. Details regarding the data reduction procedure for traditional Hopkinson bar setup using bar strain is presented in Chapter 6.

Since the specimen considered for this study consists of a monofilament with a nominal diameter of 10 μ m, the transmitted signal will be very weak because of the huge impedance mismatch between the bar and the specimen. One way to account for this difference in cross sectional area is to decrease the diameter of the transmission bar

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to achieve better signal transmission. However, reducing the diameter of the bar can have issues with measuring the strain signal. Traditionally, foil strain gages (gage factor ≈ 2) are used to measure strain in the bar. For cases where the transmitted signal is low, a smaller diameter bar can be used in conjunction with highly sensitive semiconductor strain gages (gage factor ≈ 150). If the diameter of the bar is further reduced, it won't be feasible to apply strain gages. For such cases, alternative methods like an interferometer has to be employed [36,37].

In contrast, for the present study, the transmission bar is replaced by a dynamic load cell, which can measure the force in the specimen directly. A laser sensor is employed to measure the displacement response accurately.

2.3 Development of Tensile Hopkinson Bar

The tensile Hopkinson bar adapted [38,39] for high rate loading of the microdroplet specimen consists of an incident bar with a flange at the end and a hollow striker bar made of 7075-T6 aluminum alloy (Figure 2.5 and Figure 2.6). The incident bar is 6.35 mm in diameter and 1.52 m in length. The outer diameter of the circular flange attached to the end of the incident bar is 12.7 mm. The striker bar has an outer diameter of 12.7 mm and is 203.2 mm in length.

During the experiment, a spring launcher accelerates the striker bar to a target velocity, which strikes the flange attached to the incident bar. A 70 μ m thick soft paper soaked in petroleum jelly is used as pulse shaper to eliminate the high frequency noise generated when the striker bar impacts the flange. A semiconductor strain gage attached on the surface of the incident bar captures the resulting stress waves, which propagate in the direction opposite to the impact direction. A smooth tensile wave with constant

amplitude loads the specimen for a period of about 100 μ s as indicated by the shaded area in Figure 2.7. Velocity of wave propagation in the incident bar calculated based on the monitored signal was about 5000 m/s, which is in good agreement with theoretical value for aluminum.

The tensile force induced in the specimen is directly measured by a fast response quartz piezoelectric load cell (Kistler 9712B5) with a capacity of 22.24 N. It has a frequency response of 115 kHz, which implies that the test duration of 100 μ s is sufficient to collect at least 10 meaningful data points.

Axial displacement at the loading end of the incident bar is monitored using a laser displacement sensor. A laser diode (110 mW output and 660 nm wavelength) with a circular beam is used. The laser beam passes through a beam expander and a line generator, which forms a horizontal laser line. The laser line is passed through the gap between the specimen holder and incident bar, which is collected on the sensor area (75.4 mm²) of the photodetector (DET100A) through a focusing lens. The data acquisition rate was 5 MHz, while the frequency response of the detector was 8 MHz. The laser sensor was calibrated by monitoring the voltage output while changing the gap width with a known distance. The linear relationship between the output voltage and the gap width (Figure 2.8) suggests that the intensity of the laser line is uniform along the length. This relationship was used to calculate the displacement of the loading end of the incident bar.



Figure 2.5 Schematic representation of dynamic microdroplet test apparatus and details on modified end of the incident bar



<image>

Figure 2.6 (a) Miniature tensile Hopkinson bar and (b) Image showing dynamic load cell and laser displacement sensor



Figure 2.7 Typical incident and reflected signal in the incident bar showing specimen loading period



Figure 2.8 Calibration curve for laser displacement sensor ($R^2 = 0.99$)

2.3.1 Calibration of tensile Hopkinson bar

Although laser displacement sensor measures end displacements accurately, other sources of compliance exist and must be accounted for. Calculations of IFSS and energy absorption in a microdroplet test require accurate load and displacement measurement. Our approach is to validate calibration by conducting dynamic tensile tests of single S-2 glass fibers with rate independent axial modulus of elasticity. Single S-2 Glass fiber with a nominal diameter of 10 μ m is glued on to the specimen holder attached to the load cell and the incident bar (Figure 2.9). Load is measured directly and is accurate when dynamic equilibrium is achieved (see Section 3). Dynamic compliance calibration first considers compliance from the fixture and secondly, a dynamic correction factor to provide accurate correction to our fiber standard. Similar dynamic correction measure has been employed in other studies as well [40].

Dynamic tensile tests were conducted on single fibers with a nominal diameter of 10 μ m and gage lengths of 2 mm, 4 mm and 8 mm at a displacement rate of 3 – 5 m/s. The fiber was glued on to the specimen holders attached to the load cell and the incident bar.



Figure 2.9 Specimen holders for dynamic single fiber tensile tests of S-2 glass fiber

Figure 2.10 shows a fairly linear force displacement response up to failure for the S-2 glass fiber with 4 mm gage length (Lg). Since all dynamic tests were conducted within the same range of loading velocity (V), the strain rate (V/Lg) increased with reduced gage length. Higher tensile strength resulted for lower gage length due to both size effect as well as strain rate effects. For the same gage length of 8 mm, the tensile strength increased from 3.7 GPa at 0.002 /s to 4.8 GPa at 500 /s showing strain rate dependency. In the context of interphase testing, higher strength fibers allow larger drops with higher shear areas to be tested without lower probability of fiber failure.

Uncorrected modulus of elasticity for high rate of loading decreased from 92.1 GPa to 59.3 GPa when the gage length decreased from 8 mm to 2 mm (Table 2.3). This is due to the fact that while the fixture compliance is constant, the compliance of shorter gage length fibers decreases. Hence the error in the apparent fiber modulus increases. The influence of fixture compliance decreases at higher gage lengths as described in section 2.4.1.1. Analogous to the quasi static method, the fixture compliance must be accounted for to correct the axial elongation for accurate modulus determination for all gage lengths.



Figure 2.10 Force displacement response of single fiber tensile test with 4 mm gage length (Displacement rate: 3 – 5 m/s)

				Modulus of	Corrected	
Cago	Strain	Tancila	Uncorrected	Elasticity	Modulus	Corrected
langth	Dotos	Strongth	Modulus of	corrected	of	Strain at
(mm)	(1/a)	(CPa)	Elasticity	for Fixture	Elasticity	Failure
(11111) $(1/8)$ (0)	(OF a)	(GPa)	Compliance	(GPa)	(%)	
				(GPa)	$\alpha = 1.28$	
8	500	4.8 ± 0.5	92.1 ± 3.6	112.3 ± 5.3	87.3 ± 3.4	5.5 ± 0.7
4	900	5.1 ± 0.5	80.6 ± 2.5	116.3 ± 4.8	91.1 ± 2.8	5.6 ± 0.7
2	1800	5.4 ± 0.5	59.3 ± 3.7	109.1 ± 13.5	85.7 ± 5.3	6.3 ± 0.9

Table 2.3 Dynamic tensile properties of S-2 glass fibers

2.3.1.1 Determination of fixture compliance

Fixture compliance of the tensile Hopkinson bar was determined in accordance to ASTM C1557. Figure 2.11 shows the apparent compliance ($\Delta L/F$) plotted as a

function of fiber gage length (L_0) normalized by its cross-sectional area (A). ΔL is the displacement measured at the end of the incident bar by laser sensor and F is the corresponding force. Fixture compliance of the system (C_s), given by the intercept of the curve at zero gage length, is 0.189 mm/N. The modulus corrected for fixture compliance now becomes gage length independent. However, the modulus is consistently higher (about 30%) than the known properties of S-2 Glass fiber (Table 2.3).



Figure 2.11 Calculation of fixture compliance from zero gage length intercept of the fitted curve

2.3.1.2 Dynamic compliance correction factor

The modulus of elasticity for longer gage length is over-predicted in the dynamic tests, which has been reported in the literature for a similar dynamic testing system [38]. To ensure accurate displacement measurements a dynamic correction factor (α) is

applied after fixture compliance and gage length effects are accounted for in Eq. (2.4). The corrected displacement is calculated as follows:

$$\Delta L_{corr} = (\Delta L - C_s \cdot F) \alpha \tag{2.4}$$

The compliance calibration factor (α) is chosen such that the corrected displacement would yield the published modulus of our calibration standard (85-90 GPa for S-2 Glass). In this particular case, a value of 1.28 was defined and gives excellent agreement for all gage lengths as presented in Table 2.3. This dynamic correction factor was used in the dynamic microdroplet tests.

2.4 Experimental Work

S-2 glass fibers with (3-glycidoxypropyl) trimethoxy silane coupling agent and epoxy film former sizing obtained from Owens Corning Corporation were used. Epoxy resin DER 353 (Dow Chemical Company) was mixed with bis (p-aminocyclohexyl) methane (PACM-20) curing agent (Air Products and Chemicals, Inc.) at stoichiometric ratio of 100:28 (weight ratio) to form the droplets.

Microdroplet specimens were prepared by laying a single fiber on a tray and depositing a droplet of resin onto the glass fiber using a carbon fiber applicator, which has a single carbon fiber attached to the end of a small diameter rod in order to form a monofilament carbon brush. Carbon fiber was selected for the deposition of droplets due to its high stiffness and small diameter facilitating high quality drops to be placed in the range of 70-200 μ m repeatedly (Figure 2.12).

The microdroplet specimens were then allowed to gel at room temperature for 5 h, followed by curing at 80 and 150 °C for 2 h each. Cured specimens were placed on a

specimen holder, which was attached to the load cell. Embedded length and fiber gauge length was measured under an optical microscope prior to testing, while the diameter of the fiber in the region where the droplet was sheared off was measured after the test. At least 10 valid microdroplet tests for each type of treatment were used for further calculations. The nominal diameter of the S-2 glass fibers considered in this study was 10 μ m. The embedded length of the droplet ranged from 80 to 200 μ m. Gauge lengths between 1 mm and 2 mm were maintained.









(b) Figure 2.12 (a) Scanning electron microscopy image and (b) optical microscopy image of a microdroplet

2.4.1 Quasi-static tests

2.4.1.1 Single fiber tensile test

Quasi-static tensile tests were conducted on single S-2 glass fibers with two gage lengths (8 mm and 25.4 mm) at a strain rate of 0.002 /s to determine the axial modulus, which will later be used for data reduction in microdroplet tests. Tensile tests were conducted using Instron model 5848 MicroTester with 0.020 µm position resolution. A 5 N load cell was used to monitor force in the fibers. Using epoxy adhesive, a single fiber was glued to a cardboard, which was then clamped to the Instron for tensile testing.

S-2 glass fibers exhibited a linear force – displacement response until failure. Total displacement measured by the Instron includes axial elongation of fiber and displacement due to fiber slippage in the adhesive and clamped region. The influence of the compliance during quasi-static testing was quantified analogous to the dynamic loading setup. Compliance arising from the bonding technique diminishes as the gage length increases [41]. For accurate determination of the axial elongation of the fiber, fixture compliance for the quasi-static test setup was determined in accordance to ASTM C1557. Apparent compliance ($\Delta L/F$) was plotted against fiber gage length, and the fitted curve is extrapolated back to zero gage length. Fixture compliance (C_s) for the quasi-static test setup was 0.13 mm/N. Corrected modulus of elasticity was then calculated by correcting the displacement for fixture compliance as shown in Eq. (2.5).

$$\Delta L_{corr} = (\Delta L - C_s \cdot F) \tag{2.5}$$

where, ΔL is the total displacement corresponding to the force (*F*) in the fiber.

The corrected modulus was calculated to be about 85 - 86 GPa, which lies within the range of the published data from the manufacturers [42]. The tensile strength of the S-2 glass fibers for gage lengths of 8 mm and 25.4 mm are 3.7 ± 0.5 GPa and 3.4 ± 0.5 GPa, respectively (Table 2.4). The strength reduction at longer gage lengths is observed routinely in the literature for fiber testing and follows Weibull statistics.

Gage	Strain	Tensile	Strain at	Modulus of
length	Rates	Strength	failure	Elasticity
(mm)	(1/s)	(GPa)	(%)	(GPa)
25.4	0.002	3.4 ± 0.5	4.0 ± 0.9	85.6 ± 4.9
8	0.002	3.7 ± 0.5	4.3 ± 0.5	85.9 ± 3.2

Table 2.4 Tensile properties of S-2 Glass fibers under quasi-static loading

2.4.1.2 Microdroplet test

During the microdroplet test, one end of the fiber was attached to the force sensor and the droplet was then sheared off using a set of knives attached to a motorized actuator. A gap of about 2 μ m between the fiber and the knife edge on each side was maintained. A pan balance (Mettler Toledo PB303-S) with a capacity of 300 g and an accuracy of 0.001 g was used as a load cell. A motorized actuator (Newport VP-25AA) with a resolution of 0.1 μ m was used to load the specimen. Tests were conducted at loading rates of 1 μ m/s and 0.1 mm/s.

For quasi-static loading, test specimen design criteria established by Gao [34] consider fiber strength statistics (smaller gage lengths exhibit higher strength) that places limits on maximum droplet embedded length for a given IFSS to ensure interfacial failure prior to fiber tensile failure (Eq. (2.6)).

$$l_e < \frac{1}{4} \times d_f \times \frac{\sigma_{fiber}}{\sigma_{IFSS}}$$
(2.6)

where, σ_{fiber} is the tensile strength of the fiber and σ_{IFSS} is the IFSS.

For a gage length of 2 mm, fiber diameter of $10 \,\mu\text{m}$ and assuming an IFSS of 50 MPa, maximum droplet size can be calculated based on the failure probability of a fiber with Weibull strength distribution (See Table 2.5). Weibull parameters were obtained from the literature for S-2 glass fibers [43]. Probability of fiber failure increases with increase in droplet size.

Probability of	Tensile strength of	Maximum allowable		
fiber failure	fiber, σ_{fiber} (MPa)	droplet size, l_e (µm)		
(%)	,			
1	1700	85		
2	2000	100		
5	2400	120		
40	4000	200		

 Table 2.5 Calculation of maximum droplet size based on statistical distribution of tensile strength [43]

Microdroplet experiments were conducted on droplet sizes ranging from 70 – 200 μ m. Although the probability of fiber failure is 40% for 200 μ m, due to the size effect on the IFSS, which decreases with increased droplet size, the failure probability of fiber is likely less than 40%. Microdroplets with embedded length up to 200 μ m was deemed acceptable in our experimental design particularly since smaller droplet sizes become increasingly difficult to achieve during specimen preparation. A gage length of 1 – 2 mm was maintained. At least 10 valid tests were considered for further data reduction. Microdroplet specimens exhibited a fairly linear force response until complete debonding, followed by dynamic sliding and a frictional sliding regime (Figure 2.13). During frictional sliding, a fairly constant radial compressive force is

exerted by the matrix on to the fiber due to resin shrinkage during cure and the mismatch in coefficient of thermal expansion (CTE) between fiber and matrix that arises as the specimen cools to room temperature. Fiber surface roughness of the fiber can also contribute to the applied force during frictional sliding. The displacement time plot (Figure 2.14) shows a linear response implying the specimen was loaded at a constant velocity from the beginning. A cross plot of force-time and uncorrected displacementtime yields a force – uncorrected displacement (Figure 2.15). The raw displacement is then corrected for fiber stretching and machine compliance using Eq. (2.5). During this step, the dynamic sliding observed immediately after the peak force is omitted from further data reduction. The resulting force – corrected displacement is presented in Figure 2.16. The force response and shear area of the specimen is then used to calculate the interfacial shear stress (Figure 2.17). The size effect is evident on the IFSS results when plotted against the embedded length (Figure 2.18). The IFSS decreases fairly linearly with increasing droplet size, which is consistent with the findings in literature [29,44].

Since the IFSS is size dependent, an average value of IFSS is calculated for microdroplets with embedded lengths in the range of 70 μ m to 125 μ m for the purpose of comparison with other loading rates. Average IFSS for microdroplets with embedded length 70 μ m to 125 μ m for this specific S-2 glass/epoxy system was calculated to be 49.9 ± 4.7 MPa. Specific energy up to complete debonding and during frictional sliding were 670 ± 220 J/m² and 9600 ± 3100 kJ/m³, respectively. The specific energy up to debond is calculated from the area under the force displacement response. The slope of the force – displacement response is significantly influenced by the gap between knife edge and the contact area between knife edge and the droplet. The amount of

deformation in the resin may also vary with the contact, which ultimately affects the overall displacement measured in the microdroplet experiments. Although the displacement is corrected for fiber stretching and machine compliance, the additional displacement that comes from the plasticity in the resin in the droplet could not be subtracted out from the experimental data. This results in high variability in the corrected displacement, which is reflected in the high standard deviation in specific energy calculations. It should be noted that this specific energy includes the contribution from the resin as well as the interface. Partitioning of this energy is done in Chapter 7 through finite element simulation of microdroplet experiments using accurate resin properties. Specific energy absorbed due to frictional sliding also exhibit high variability in the experimental results. Immediately after the specimen reaches the peak load, dynamic sliding occurs and the droplet shoots out as the strain energy in the fiber is released. It is likely that this dynamic event causes some damage to the inner side of the droplet that is in contact with the fiber. Besides, as the droplet slides along the fiber, any presence of foreign substance on the fiber surface can alter the friction between fiber and droplet, and the force response.



Figure 2.13 Raw force time response for microdroplet experiments at 1 µm/s



Figure 2.14 Raw displacement time response for microdroplet experiments at 1 $$\mu m/s$$



Figure 2.15 Force – uncorrected displacement response for microdroplet experiments at 1 $\mu m/s$



Figure 2.16 Force – corrected displacement response for microdroplet experiments at 1 µm/s



Figure 2.17 IFSS vs. corrected displacement for microdroplet experiments at 1 $$\mu m/s$$



Figure 2.18 IFSS vs. embedded length for microdroplet experiments at 1 μ m/s

2.4.2 Dynamic microdroplet test

Procedure to conduct dynamic microdroplet test includes positioning the knife edges to have a gap of nominally 14 μ m that is slightly larger than the fiber diameter (i.e. the end of the knife edges are 2 μ m from the fiber surface) to load the droplet. On the other end of the specimen, the fiber was glued to the specimen holder attached to the load cell (Figure 2.19). The specimen was preloaded and inspected to ensure the droplet was not loaded eccentrically. A tensile pulse was sent using a hollow striker bar as described earlier to begin the test.

The compliance correction for the microdroplet test must be modified since only one end of the specimen is glued, while the droplet on the other end is loaded by the knife edge (Figure 2.19). Since both ends of the single fiber tests are identical, it is assumed that the compliance due to bonding technique from each end is equivalent. A value of 0.0945 mm/N was used as the fixture compliance (C_s) for the microdroplet test. Then, the corrected displacement (δ) applied to the droplet by the loading knives was calculated using Eq. (2.7). In this equation, the measured laser displacement (ΔL) was corrected for fixture compliance and dynamic compliance correction. The displacement associated with fiber stretching (the second term in Eq. (2.7)) was also subtracted to obtain the droplet displacement used to calculate energy absorption during debonding.

$$\delta = \left(\Delta L - \frac{C_s}{2} \cdot F\right) \alpha - \frac{F \cdot L_o}{A \cdot E}$$
(2.7)

where, $\alpha = 1.28$ and E = 85 GPa



Figure 2.19 Specimen holder attached to the load cell, miniature knife edge attached to the incident bar and microdroplet test specimen

2.5 Specimen Design for Dynamic Loading

Apart from developing the data reduction scheme and displacement correction methods, it is imperative to ensure dynamic equilibrium is achieved in the gage length and interface region during the loading of the microdroplet. During dynamic test, the microdroplet is subjected to compressive stresses as the tensile wave reaches the modified end of the incident bar. Consequently, shear stresses are induced in the fibermatrix interface region, which in turn loads the fiber in tension. A complex series of wave propagation and reflections develop within the specimen.

Finite element modeling of microdroplet (Figure 2.20) was conducted to study the dynamic effects and select appropriate test specimen geometry. A 2D axisymmetric FE model was developed and analyses were done using the commercially available finite element code LS-DYNA 971 [45]. Linear elastic elements were used and perfect bonding was assumed between fiber and droplet. Mesh size of 0.625 μ m was chosen along the droplet length (adjacent to the fiber) to accurately describe the spatial gradients in interfacial stress along the embedded length. Explicit time steps are governed by the higher wave speed of the fiber $(0.00011 \ \mu s)$. A characteristic time is defined based on the specimen geometry and wave speed of the respective materials presented in Table 2.6. For example, the characteristic time for wave propagation along the fiber with a 2 mm gage length is 0.37 µs. Consequently, the numerical model is suitably refined with enough time resolution to study the wave propagation along the fiber and interface. Wave propagation in the fiber gage length and dynamic effects in the interfacial region were investigated for different combination of gage length (2 mm -6 mm) and droplet sizes (100 μ m -200μ m) at different displacement rates (5 m/s to 60 m/s). Force – corrected displacement response for a 100 µm droplet is presented in Figure 2.21. As elastic properties for resin are used, very small displacement is predicted at the failure load. Since the objective of these simulations is to study wave propagation along the interface and fiber for the design of specimen, the use of elastic properties for the constituents is appropriate because it provides the worst-case scenario during a dynamic event due to elastic collision. For more accurate simulation and to obtain realistic displacements in the specimen, rate dependent inelastic resin properties will be used later in Chapter 7.

Properties Unit	Aluminum	S-2 Glass	Epoxy
r toper ties, Omt	knife	Fiber	droplet
Density, gm/cc	2.70	2.49	1.27
Young's modulus, GPa	69.00	86.00	4.3
Poisson's ratio	0.285	0.230	0.35
Bar velocity, m/s	5000	5470	1840

 Table 2.6 Material properties for aluminum, fiber and epoxy [42,46]


Figure 2.20 2D Axisymmetric LS-DYNA model



Figure 2.21 Force displacement response from FE simulation for a 100 μm droplet

When the gage length was reduced for a constant droplet size, the time to achieve dynamic equilibrium in the gage length decreases. Dynamic equilibrium refers to the specimen configuration where the difference between the forces measured by the load cell on one end and the load applied to the droplet by the knife edge at the other end of the gage length is an acceptable small error throughout the duration of the test [47]. For this study, dynamic equilibrium was said to be achieved when this error in forces at the two ends of the gage length (F_1 and F_2 in Figure 2.20) became less than 5%. In general, it took about 4 to 6 wave reflections within the gage length to reach equilibrium. When the gage length was kept constant, the time to reach dynamic equilibrium decreased with increase in droplet size.

When the knife edge, with a much larger mass, comes in contact with the droplet at a certain velocity, the momentum transfer causes the droplet to accelerate to a velocity higher than the knife edge, causing the droplet to momentarily lose contact with the knife edge. Then the droplet starts to decelerate and eventually springs back and comes in contact with the knife edge again. This sequence of event repeats until the knife edges and drop attain the same velocity. The larger drop of higher mass is accelerated to a less extent and hence takes less time to achieve dynamic equilibrium. As such, the combination of the largest droplet (200 μ m) and the smallest gage length (2 mm) was found to achieve equilibrium in the shortest time. However, it should be noted that the probability of fiber failure increases with larger droplet that require higher debonding forces (Table 2.5).

The shear stress and radial stress distribution at different load levels for quasistatic case is presented in Figure 2.22. The load levels correspond to the axial force in the fiber gage length. The coordinates along the interface have been normalized with respect to the total embedded length of the droplet. There is a stress concentration at the loading end of the droplet (present in all of the interface test methods), which decreases to zero at the other end of the droplet. The mechanical loading places the interface under radial tension near the loading end of the droplet. This suggests that the crack initiation near the loading tip is due to mixed mode loading [48,49,6]. Average IFSS represented by the horizontal line in Figure 2.22 shows that peak stress is much higher than average IFSS and hence the peak stress in the traction law should also be expected to be higher as shown in chapter 7.

Figure 2.23 shows the comparison between the quasi-static and high rate loading cases at two load levels for different displacement rates. The state of stress for high rate tests converge to the quasi-static tests when the velocity is 10 m/s or less indicating wave propagation and inertial effects have been minimized. In this case, the data reduction equations presented in Eq. (2.1) - (2.3) can be used for high rate tests. It should be noted that this same rationale is used to establish dynamic equilibrium in compression testing using split Hopkinson pressure bar at high strain rates [50,51].



Figure 2.22 (a) Shear stress and (b) Radial stress distribution along the interface at force level 0.1 N (red) and 0.2 N (black) for quasi-static loading for a 200 μ m droplet



Figure 2.23 Dynamic effects in interfacial shear stress distribution at force level 0.1 N (red) and 0.2 N (black) for droplet size 200 µm and fiber gage length 2 mm at displacement rates (a) 60 m/s, (b) 20 m/s, (c) 10 m/s and (d) 5 m/s

2.6 Results and Discussion

2.6.1 High rate microdroplet experiments

Dynamic microdroplet experiments were conducted on droplets with embedded length ranging from $70 - 125 \,\mu\text{m}$ at an average displacement rate of 1 m/s. Duration of the loading to reach failure load was in the range of $75 - 220 \,\mu\text{s}$. Typical force and

displacement signals are shown in Figure 2.24. The displacement signal increases monotonically while the specimen is being loaded indicating a constant velocity during the test. The load cell vibrates at its natural frequency of 115 kHz immediately after failure occurs. As a result, the frictional sliding between the fiber and the failed droplet could not be captured. However, since droplets were still attached to the fiber after the test, it is possible to reload the specimen to measure the sliding energy.



Figure 2.24 Typical signal recorded during the dynamic microdroplet test. (a) Force signal measured from the piezoelectric load cell, (b) Displacement signal measured from the laser sensor

Post-test inspections were carried out to check the validity of the tests. The specimens were inspected under scanning electron microscope to ensure that the droplet

did not have major fractures within the drop other than the desired interfacial failure near the fiber surface and that the indentation due to knife edge was minimal (See Figure 2.31a). The residual epoxy at the top of the drop (Figure 2.31b), which is the location of crack initiation due to the tensile stresses near the loading end [6], should be localized (See Figure 2.31). Also, to ensure that the failure occurred along the fiber matrix interface region, the surface of the fiber was investigated. Figure 2.31c & d show a fairly smooth fracture surface with a few traces of epoxy. After all these criteria have been met, IFSS and the energy absorbed by the interface were calculated using Eq. (2.1) - (2.2). Again, given the uncertainty in the measurement and correction of the displacement in the specimen that arises from resin plasticity, as discussed earlier, it should be noted that the energy absorption calculations include the contribution of both resin and interface. These energies will later be partitioned using finite element modeling in Chapter 7.

Figure 2.25 and Figure 2.26 show force-time and uncorrected displacement-time response from the microdroplet experiments conducted at 1 m/s. Uncorrected displacement time response shows initial nonlinear region, where the specimen is accelerated to the desired velocity. Then the response remains fairly linear suggesting the specimen being loaded at a constant velocity. Figure 2.27 shows a fairly linear force vs uncorrected displacement response until complete debonding of the interface occurs. Displacements are then corrected for fiber stretching, fixture compliance and dynamic compliance correction using Eq. (2.7). Resulting force and IFSS vs. corrected displacements are presented in Figure 2.28 and Figure 2.29.

IFSS show a decreasing trend with increasing embedded length (Figure 2.30) similar to the quasi-static case. Average IFSS for microdroplets ranging from 70 μ m to

125 μ m increased to 80.6 MPa for high rate loading (1 m/s) from 49.9 MPa at quasistatic loading rate (1 μ m/s). Also, the energy absorbed by the interface up to debond increased from 670 J/m² to 1950 J/m² with increase in the displacement rate (Table 2.7). The extent to which the rate dependent resin properties contribute to this energy absorption calculation will be further assessed by characterizing resin properties in Chapter 5 and through FEA simulation in Chapter 7.

These results suggest that this S-2 Glass/epoxy/sizing system has fiber matrix interface properties that are sensitive to the rate of loading. The coefficient of variation (COV) in the IFSS for quasi-static loading rates are on the lower side (9%) compared to most of the studies reported in literature that can be as high as 33% [30]. However, the COV increases to 15% for the high rate test, which is still within the acceptable range for such test methods. IFSS is sensitive to the gap width and the symmetricity of the droplet loading by the knife edges. Very small differences in the point of contact of the knife edges can cause rotation and bending of the fibers prior to dynamic loading and significantly affect the interfacial shear stress distribution and ultimately IFSS even at quasi static loading rates [52]. To ensure uniform loading, we monitor the bending of the fiber during static preload and adjust the stages holding the knife edges. Another way to reduce such variability would be to use a disk with a concentric hole to load the microdroplet [48]. During dynamic testing, bouncing of the droplet can also be an added source of variability. When there is not enough preloading or if there is a gap between knife edge and the droplet, loading and unloading of the droplet can be seen in the forcetime signal. Such results are discarded before further data reduction.



Figure 2.25 Raw force time response for microdroplet experiments at 1 m/s



Figure 2.26 Displacement time response for microdroplet experiments at 1 m/s



Figure 2.27 Force vs. uncorrected displacement response for microdroplet experiments at 1 m/s



Figure 2.28 Force vs. corrected displacement for microdroplet experiments at 1 m/s



Figure 2.29 IFSS vs. corrected displacement for microdroplet experiments at 1 m/s



Figure 2.30 IFSS vs. embedded length for microdroplet experiments at 1 m/s



Figure 2.31 SEM images of tested microdroplet specimen (a) Debonded microdroplet, (b) Residual epoxy at the loading end of the tested specimen, (c) Fracture surface at the top of the specimen, (d) Fracture surface along the embedded length

2.6.2 Intermediate rate microdroplet experiments

The microdroplet test machine used for quasi-static testing was modified for intermediate loading rates of 0.1 mm/s (Figure 2.32a). The static load cell was replaced with a dynamic load cell (Kistler 9215) and a laser sensor was installed to monitor

displacement response (Figure 2.32 b and c). Figure 2.33 shows a linear response from the calibration of laser sensor.



Figure 2.32 (a) Microdroplet test machine, (b) Dynamic load cell and specimen holder, and (c) Laser line used to monitor displacement in the specimen



Figure 2.33 Laser calibration curve for intermediate rate tests

Raw force time response of microdroplet experiments at 0.1 mm/s is shown in Figure 2.34. Displacement time response shows a linear monotonic increase suggesting the specimens were loaded at a constant velocity (Figure 2.35). For these intermediate loading rates, the force – uncorrected displacement response shows fairly linear increase up to complete debonding followed by dynamic unloading and frictional sliding (Figure 2.36). As the loading rate is increased, the load cell vibrates immediately after complete debonding occurs. As mentioned earlier, the dynamic unloading portion does not contribute to any new insight into the material behavior and hence removed from further data reduction. The displacement response is corrected by subtracting out the fiber stretching and displacement due to machine compliance from the total displacement using Eq. (2.5). The resulting in force vs. corrected displacement response up to complete debonding and frictional sliding due to CTE mismatch is shown in Figure

2.37. IFSS is then calculated by using force in the specimen and the shear area and is presented in Figure 2.38.

Average IFSS for microdroplet sizes in the range of 70 µm to 125 µm increased from 49.9 MPa to 58.4 MPa when the loading rate was increased by 2 orders of magnitude from 1 µm/s (Table 2.7). Assuming interface thickness of 10 nm to 100 nm results in shear strain rates ranging from 10/s to 100/s for 1 µm/s loading rate, which increases to 10^{7} /s to 10^{8} /s range for 1 m/s. More details on shear strain rate estimation are presented in Chapter 7. Differences in the IFSS between loading rates of 1 µm/s, 0.1 mm/s and 1 m/s were found to be statistically significant based on a two-tailed *t*-test with the value of $\alpha = 0.05$. Moreover, the increase in average IFSS is fairly linear with the loading rate when plotted on a log scale (Figure 2.40). Due to the lack of test method for loading rates above 10 mm/s, it was hypothesized in the literature, based on experimental results up to 10 mm/s, that the rate sensitivity would cease to exist at higher loading rates [53]. The mechanism behind loading rate sensitivity was compared to the crazing during fracture of thermoplastics [54]. However, the findings of this study suggest that IFSS is still sensitive to the rate of loading at meters per second range.



Figure 2.34 Raw force time response for microdroplet experiments at 0.1 mm/s



Figure 2.35 Displacement time response for microdroplet experiments at 0.1 mm/s



Figure 2.36 Force vs. uncorrected displacement for microdroplet experiments at 0.1 mm/s



Figure 2.37 Force vs. corrected displacement for microdroplet experiments at 0.1 mm/s



Figure 2.38 IFSS vs. corrected displacement for microdroplet experiments at 0.1 mm/s



Figure 2.39 IFSS vs. embedded length for microdroplet experiments at 0.1 mm/s



Figure 2.40 Average IFSS vs. loading rate for microdroplet specimens with embedded length ranging from 70 μ m to 125 μ m show a linear increase when plotted on a log scale

 Table 2.7 Comparison of experimental results for microdroplets with embedded

 length ranging from 70 – 125 μm

Loading Rate	IFSS (MPa)	Specific energy	Energy during frictional
		debond (J/m ²)	sliding (kJ/m ³)
1 μm/s	49.9 ± 4.7	670 ± 220	9600 ± 3100
0.1 mm/s	58.4 ± 4.9	880 ± 350	10140 ± 5600
1 m/s	80.6 ± 12.1	1950 ± 860	-

2.7 Conclusions

An experimental method for characterizing fiber matrix interface properties at high rate of loading has been developed. The experimental method presented in this study is the first of its kind to characterize fiber-matrix interface properties (i.e. strength and debonding energy) at meters per second range. The experimental setup consists of a tensile Hopkinson bar with a modified end to load a microdroplet test specimen. Finite element analysis was carried out to design optimum specimen geometry including the fiber gage length and droplet size, and acceptable displacement rates within which the specimen would be in dynamic equilibrium. Simulation results showed that the shear stress distribution along the interface would be in dynamic equilibrium up to a displacement rate of 10 m/s. The combination of 2 mm gage length and 200 μ m droplet has the shortest time to reach equilibrium without fiber failure and therefore has the highest loading rate potential. Our experimental set-up was used to test microdroplet specimen with S-2 glass with GPS sizing and DER 353 epoxy system. Experimental results suggest that the average IFSS is sensitive to the rate of loading, which increased by a factor of 1.6 when the displacement rate was increased from $1 \mu m/s$ to 1 m/s. Based the SEM images, it was concluded that the raw displacement could not be accurately corrected due to the presence of resin plasticity in the droplet where knife edge comes in contact. This also resulted in high variability in the calculation of specific energy. Since it was not possible to experimentally separate out the resin and interface displacement, finite element simulation of the microdroplet experiments will be carried out later in Chapter 7 using accurate rate dependent resin properties obtained in Chapter 5 to partition the resin and interface energy contribution.

Chapter 3

DEVELOPMENT OF CARBON NANOTUBE SENSOR FOR MONITORING ONSET OF CRACK AT THE INTERFACE

3.1 Introduction

Preliminary studies [55] have indicated that information regarding the onset of crack growth at the interface is needed for accurate determination of traction separation law. Preliminary modeling results on microdroplet experiments show that different combinations of peak traction and fracture energy can result in the same force displacement but crack initiation might correspond to different load levels. The microdroplet test has been monitored using a microscope in the experimental set-up shown in Figure 2.32a. However, the interface cracks cannot be observed. In this chapter, the use of carbon nanotubes (CNT) have been employed as a potential tool to develop a sensor, which can be used to monitor crack onset at the interface.

Several methods exist to deposit CNTs onto the fiber surface. The ability to control the CNT coating thickness depends on the process adopted to deposit the CNTs. The chemical vapor deposition (CVD) approach is the most commonly used technique to produce CNTs. In general, the extent of decomposition of hydrocarbons and the purity of CNT produced by CVD is associated with higher processing temperature (600

- 1000°C) [56,57]. Several attempts have been made to significantly lower the processing temperature for CVD of CNT [58,59], with temperatures as low as 120°C in some cases for metallic substrates [60]. The lower temperature range $(350 - 490^{\circ}C)$ reported for CVD using glass (or an equivalent surface) [58] as substrates is still high enough for the tensile properties of glass fibers to start degrading and may not yield defect-free CNT coated fibers [61,62]. Harsh deposition conditions and the degree of complexity required during the processing have motivated numerous researchers to explore viable alternative methods to deposit CNTs on structural components [63,64]. Grafting CNTs onto glass fibers can be achieved by different techniques such as dip coating [65–67], spray coating [68,69], and electrophoretic deposition (EPD) of CNTs [70,71]. Although all these approaches are relatively easy to execute and highly scalable, controlling the uniformity and the thickness of the deposited CNT through dip coating and spray coating techniques has been an issue [63,66,72]. EPD is a cost effective and versatile technique to coat particulates onto substrates with complex shapes or surface textures [70,71]. In this method, charged particles, which are homogeneously dispersed in a solvent such as water, are allowed to migrate to a relevant electrode under an applied electric field. Once the charged particles reach the electrode, they coagulate to form a deposit [73].

Recently, some researchers have adopted the EPD approach to coat CNTs on non-conductive substrates like glass fibers [66,74]. EPD of polyethyleneimine (PEI) functionalized CNTs treated using ozone onto E-glass fabric showed significant improvement in the in-plane shear strength and piezo-resistivity of the CNT-coated glass/epoxy laminates [74]. Zhang *et al.* [66] demonstrated the applicability of using EPD to deposit CNTs onto glass fibers for *in situ* damage sensing in a single fiber fragmentation test. Specimens with three individual CNT coated glass fibers were prepared and resistance was measured at either end of the specimen during fragmentation test. CNT coated single glass fibers exhibited electrical properties in the semiconducting range. The authors demonstrated significant change in electrical resistance with each fiber break. No degradation in the tensile strength of the CNT coated fibers was observed, while the IFSS increased by 30%. However, the authors did not explore different coating thicknesses by adjusting the EPD parameters.

Development of a sensor for detection of crack initiation requires the thickness of the sensor to be thin enough such that it does not alter the interfacial shear strength and failure modes, but electrically conductive enough to provide a piezo-resistive response. Although, some researchers have made an attempt to deposit a very thin layer of CNTs onto the surface of glass fibers [68,75,76], no comprehensive study has been carried out to control the thickness and uniformity of the coated film using EPD onto individual glass fibers, although film thickness as a function of field strength was examined for CNTs deposited onto glass fabric [74].

In this chapter, an approach to control the deposited CNT film onto individual glass fibers using EPD has been carried out by investigating the kinetics of the EPD process. Hamaker's law [77] was used to estimate the particle deposition rate. The electric field strength, deposition time and the CNT dispersion concentration were manipulated to investigate the interrelationship between these variables and ultimately

provide control over the quantity and homogeneity of the coating [70,71,78]. In addition, untreated CNTs were also mixed with resin as an alternative approach to monitor crack in the microdroplet specimen. The changes in interfacial properties of EPD fiber and epoxy were investigated using the microdroplet test method. Then an optimum combination of EPD parameter that yields CNT coating, which does not alter the interfacial shear strength, is used for monitoring crack onset by measuring the change in electrical resistance across the specimen, which is presented in the next chapter.

3.2 Materials

Multiwall carbon nanotubes (CM-95, Hanwa Nanotech, Korea) having diameters between 10 and 15 nm and length of 10 to 20 μ m [79] were treated using an ultrasonicated-ozonolysis (USO) method [64,74]. USO treated CNTs were functionalized with polyethyleneimine (H(NHCH₂CH₂)₅₈NH₂, M_w 25000, Sigma-Aldrich, USA) in a sonicator as described in the previous work [64,74]. The pH of the PEI-functionalized CNTs was adjusted using glacial-acetic acid (Sigma-Aldrich, USA) to a pH around 6 [74], which resulted in a zeta potential of the CNTs of around +40 mV [80]. Aqueous dispersions were prepared for EPD with CNT concentrations of 0.5 and 1.0 g/L.

PEI-functionalized CNTs were deposited onto the surface of S-2 glass fibers (Owens Corning Corporation) with γ - glycidoxypropyltrimethoxysilane sizing and epoxy film former. Epoxy resin DER 353 (Dow Chemical Company) was mixed with bis (p-aminocyclohexyl) methane (PACM-20) curing agent (Air Products and Chemicals, Inc.) at stoichiometric ratio of 100:28 (weight ratio) to prepare the droplets.

Figure 3.1 shows amine functional groups in PEI reacting with epoxide group of silane and epoxy, yielding a ring opening reaction, which is then followed by crosslinking reaction with other epoxide groups. Similar reactions occur between amine groups of curing agent and PEI with epoxide group of resin (Figure 3.1). This strong covalent bond formed in fiber – CNT interface and CNT – matrix interface might enhance the load transfer. Epoxy amine from the matrix may still diffuse into the GPS sizing similar to the baseline. The bonding mechanism in the baseline between glass fiber and epoxy in the presence of hardener is the same since the functional group in the hardener is amine.



Figure 3.1 Schematic representation of reaction between amino and epoxide groups (a) Ring-opening reaction with primary amine, (b) Ring-opening reaction with secondary amine and formation of polysiloxane bond, (c) Crosslinking reaction

3.3 Electrophoretic Deposition

EPD was carried out at room temperature in a custom-made apparatus with stainless steel electrodes. S-2 glass fibers were attached with a slight pretension onto one of the two parallel electrodes placed at a fixed gap of 6.7 mm. The entire unit was then immersed vertically in the CNT dispersion and cathodic deposition was carried out

under a constant DC electric field. After the deposition, the fibers were carefully removed from the CNT dispersion and allowed to dry at room temperature.

An expression derived by Hamaker [77] to estimate the quantity of particles deposited over time has been used to study the kinetics of the EPD. Hamaker's law states that the deposit yield, w (kg) is linearly proportional to time, field strength $\frac{dV}{dn}$ (V/m), concentration of particles c_s (kg/m³) and electrode surface area S (m²) as shown by Eq. (3.1)

$$w(t) = \mu c_s \iint \frac{dV}{dn} \cdot dS \cdot dt$$
(3.1)

In Eq. (3.1), electrophoretic mobility μ (m²/(V s)) is a constant related to the properties of the suspension, which is given by Eq. (3.2)

$$\mu = \frac{\varepsilon \,\varepsilon_0 \,\zeta}{\eta} \tag{3.2}$$

Where, ε is the dielectric constant of the liquid, ε_0 (C²/J m) is the permittivity of free space, ζ (V) is the zeta potential of the particles, and η (Pa s) is the viscosity of the liquid.

Following Hamaker, many researchers have studied EPD and observed a linear rate of deposition initially which then starts to plateau [74,81,82]. Based on this observation, modifications have been made to the Hamaker's equation by incorporating the rate of change in the particle concentration of the solution with time or by considering the decrease in the velocity of the particles as a function of deposition time. Both modifications attempt to capture the non-linearity in the rate of deposition for nonconducting particles [82–85]. Despite all these modifications, the actual process of deposition using electrophoresis is very complicated and still not well understood and most of the parameters cannot be quantified accurately [70,71]. Therefore, in this study, the simple linear model developed by Hamaker [77] has been used as a framework to experimentally investigate the interdependence of the processing parameters.

EPD was carried out by varying the processing parameters as presented in Table 3.1. To study the interrelation between the field strength and the deposition time, each of these parameters is reduced individually keeping the CNT concentration constant. For example, in EPD-10.5-15m, only the field strength is reduced by 30% from EPD-15-15m while keeping the rest of the parameters constant. Then for EPD-15-10.5m, only the deposition time is reduced by 30% from 15 min. Similarly, for the last two cases, each of these parameters is reduced by 50% from EPD-15-15m.

Notation	CNT	Field	Deposition Time
	Concentration	Strength	(min)
	(g/L)	(V/cm)	
EPD-1-15-15m	1	15	15
EPD-15-15m		15	15
EPD-10.5-15m		10.5	15
EPD-15-10.5m	0.5	15	10.5
EPD-7.5-15m		7.5	15
EPD-15-7.5m		15	7.5

 Table 3.1 Processing parameters in EPD

3.4 Characterization of CNT Coating

The surface morphology of the CNT coating was characterized using confocal microscopy and scanning electron microscopy (SEM). The thickness of CNT deposition was determined by etching the EPD fiber through-the-thickness using a focused ion beam (FIB) (Zeiss Auriga 60). The uniformity of the coating along the length was quantified by measuring the electrical resistance along the length of the EPD fiber (4 mm). To calculate the electrical resistance a sub femtoamp source meter (Keithley 6430) was used to source a constant voltage of 50 V and measure the resulting current. Both ends of the EPD fiber were attached to the electrodes using conductive silver paste.

3.5 Microdroplet Tests

Microdroplets with virgin S-glass fiber and neat resin were used as baseline. Microdroplet specimens with EPD fibers with neat resin and EPD fibers with epoxy modified with untreated CNTs were prepared (Table 3.2) because both have the potential to be used for crack monitoring by measuring electrical resistance across the specimen. In addition, microdroplets with baseline fibers and epoxy resin modified with untreated CNTs were also considered to study the effect of CNT modified resin on the IFSS. Schematics of interface for baseline with GPS sizing and epoxy resin, and the modified interface with CNT treatment on fiber and epoxy are shown in Figure 3.2. The test machine described in section 2.4.1.2 was used for microdroplet experiments. The three-roll mill method was adopted to homogenously disperse untreated CNTs (0.25% by wt.) in the epoxy resin. A three roll mill (EXAKT-80E; EXAKT Technologies) was used to mix the CNTs with epoxy by progressively decreasing the gap width [86]. For the gap width of 50 μ m, 20 μ m and 10 μ m, the mixture was passed through at least twice. For the gap setting of 5 μ m, the mixture was passed through at least twice. For the gap setting of 5 μ m, the specifics of this procedure and the resulting CNT dispersion are based on a previous study, where CNTs were dispersed in a similar epoxy resin using this calendaring approach [86]. The CNT reinforced epoxy was then mixed with PACM-20 curing agent for the preparation of droplets. Microdroplet experiments were carried out at a loading rate of 1 μ m/s following the procedure described in Chapter 2. At least 10 valid microdroplet tests for each type of treatment were used for further calculations.

A valid test requires that the failure occurs along the interface. As mentioned in chapter 2, glass fiber sizing, which is about 100 nm thick, forms a continuous network from glass surface to resin. Siloxane network formed between glass surface and GPS due to covalent bonding are the strongest. Failure is most likely to occur within the GPS/film former network. With the addition of PEI-CNT coating as potential sensor, failure should occur at GPS/film former network for the test to be valid. Cohesive failure that occurs along the PEI-CNT network or epoxy resin is considered invalid.



Figure 3.2 Schematics of different interfaces (a) Baseline with GPS sizing and epoxy resin, (b) EPD fiber with neat resin, (c) EPD fiber with CNT dispersed in resin and (d) Baseline fiber with CNT dispersed in resin

Notation	Fiber	Resin	
SG/EP	Virgin		
SG-2000nm	1 g/L CNT, 15 V/cm 15 min	Unmodified	
SG-600nm/EP	0.5 g/L CNT, 15 V/cm, 15 min		
SG-400nm/EP	0.5 g/L CNT, 15 V/cm 10.5 min		
	0.5 g/L CNT, 10.5 V/cm, 15 min		
SG-2000nm/EP-CNT	1 g/L CNT, 10V, 15 min	Epoxy + 0.25% CNT	
SG/EP-CNT	Virgin	Epoxy + 0.25% CNT	

 Table 3.2 Notations for various microdroplet specimens

3.6 Results and Discussion

3.6.1 CNT coating and the kinetics of EPD

The confocal images EPD-15-7.5m, EPD-15-10.5m and EPD-15-15m (Figure 3.3 a, c, e) show the process of CNT film development from 7.5 min to 15 min, with a 0.5 g/L CNT dispersion subjected to a field strength of 15 V/cm. The EPD-10.5-15m and EPD-15-10.5m, EPD-15-15m (Figure 3.3 c, d, e) images showed randomly oriented CNTs with uniform thickness around the fiber. When either the electric field or the deposition time was decreased by 50% from EPD-15-15m, the CNT deposition was very thin but non-uniform, showing early stage of the film development (Figure 3.3 a) or agglomerates of CNTs (Figure 3.3 b) attached onto the glass fiber surface. From visual inspection, EPD-15-10.5m (Figure 3.3 c) produced the thinnest uniform CNT coating.



Figure 3.3 Confocal images of S-glass fibers after electrophoretic deposition of CNT (Scale bars are 10 μm in size) (a) EPD-15-7.5m, (b) EPD-7.5-15m, (c) EPD-15-10.5m, (d) EPD-10.5-15m, (e) EPD-15-15m

Figure 3.4 shows SEM images of the EPD fibers, which have been crosssectioned using FIB, showing the carbon nanotube film thickness and morphology. A very uniform PEI-CNT coating on the surface of the glass fiber was observed (Figure 3.4 a). A PEI-CNT film thickness of about 200 nm was measured for EPD-15-7.5m. When the deposition time was increased from 7.5 min to 10.5 min for EPD-15-10.5m, the CNT thickness doubled. With the deposition time doubled to 15 min for EPD-15-15m, the thickness of CNT layer tripled to around 600 nm.





Figure 3.4 FIB images of EPD fiber (a) CNT packing of EPD-15-15m, (b) EPD-15-7.5m with CNT thickness ~ 200 nm, (c) EPD-15-10.5m with CNT thickness ~ 400 nm, (d) EPD-15-15m with CNT thickness ~ 600 nm

Electrical resistance measurement has been used to study the kinetics of EPD in this section. However, it should be noted that being able to measure electrical resistance along the length of the EPD fiber is also important for the detection of crack initiation in the microdroplet specimens. Figure 3.5 shows the electrical resistance measured along the length of the EPD fibers for different cases. As expected, the electrical resistance increased as the deposition time or electric field strength was decreased, which indicates a lower quantity of CNTs. EPD fibers for case EPD-15-10.5m (0.5 g/L CNT, 15 V/cm and 10.5 min) exhibited the most homogenous PEI-CNT coating (Figure 3.5 b), which is consistent with the visual inspection for the same treatments (Figure 3.5 c). To obtain a thinner coating, decreasing the deposition time instead of field strength leads to better film uniformity. It should, however, be noted that the variability in the electrical resistance measurement does not necessarily reflect the overall quality of the coating along the length, since even the smallest of local discontinuity at any point within the length of the fiber can significantly affect the overall resistance measurement.



Figure 3.5 Electrical resistance measurement of EPD fibers – CNT concentration 0.5 g/L (a) At different field strength with constant deposition time of 15 mins, (b) At different deposition times with constant field strength of 15 V/cm

The interrelation between the two parameters (deposition time and field strength) is shown in Figure 3.6. The average electrical resistance has been normalized with respect to the resistance of the EPD fibers for EPD-15-15m (0.5 g/L CNT, 15 V/cm

and 15 min). The abscissa represents the factor by which the parameters were reduced from EPD-15-15m. Decreasing either the deposition time or the field strength by a factor of 0.7 (for example, reducing the deposition time from 15 min to 10.5 min) had the same effect on electrical resistance measurement.



Figure 3.6 Interdependence of processing parameters – Electrode voltage and deposition time in EPD

During EPD, the aqueous solution near the cathode is alkaline due to electrolysis. As the positively charged CNTs approach the cathode it is hypothesized that the PEI deprotonates as a result of increase in the pH of the solution in this region [87,88]. At this moment, the PEI-CNTs would lose their repulsive charge and the dispersion would destabilize, leading to precipitation onto the glass fiber [62,89–91]. At a lower voltage, the electrolytic reactions at the cathode are slower, so initiation of film formation due to precipitation of the destabilized dispersion will occur at a slower rate.
The movement of the particles is then governed by the Brownian motion [89] and the electric field has minimal effect on their motion, which results in the formation of agglomerates before the CNT film formation on the substrate can occur (Figure 3.3 b). CNTs adhere to the substrate due to chemical link between PEI functionalization of CNT and the silane on the fiber surface [62,74]. Comparably, at higher voltage, the deposition rates are faster and such agglomerates are less likely to occur. The sites where initial deposition occur are more favorable for film growth as they become conductive pathways and develop a potential where CNTs will preferentially be absorbed. This can be seen in the early stage of the deposition process for EPD-15-7.5m (Figure 3.3 a), which eventually forms a thin yet very homogeneous CNT film at a longer deposition time of 10.5 min (Figure 3.3 c). The lesser degree of uniformity of the coating observed from electrical resistance measurement when the electric field strength during EPD was lowered (Figure 3.5 a) compared to its counterpart (Figure 3.5 b) can be attributed to the formation of agglomerates during the initial stage of the deposition process.

3.7 Influence of PEI-CNT Coating of IFSS

Typical shear stress vs. corrected displacement for different microdroplet tests are presented in Figure 3.7. Comparison between IFSS for different EPD coating parameters and modification of the resin matrix with CNTs are shown in Figure 3.8 and Table 3.3. The EPD treatment which produced a 2 μ m thick PEI-CNT coating (SG-2000nm/EP) on the fiber surface led to a 58% increase in IFSS (SG-2000nm/EP) (Table 3.3). The IFSS decreased in proportion to the PEI-CNT film thickness from 75.5 MPa

for the 2 μ m thick PEI-CNT coating (SG-2000nm/EP) to 57.7 MPa for 600 nm thick PEI-CNT coating (SG-600nm/EP). The IFSS for the 400 nm thick PEI-CNT coating (SG-400nm/EP) and unmodified epoxy was similar to the untreated baseline sample (SG/EP) (Figure 3.9). No significant changes in the specific energy absorbed up to debonding were detected due to the application of PEI-CNT coating onto the fiber surface.



Figure 3.7 Shear stress vs. corrected displacement for microdroplets with different CNT coating thicknesses



Figure 3.8 Interfacial shear strength of different EPD fiber and epoxy system



Figure 3.9 IFSS vs. CNT coating thickness

70 μm to 125 μm							
	CNT	IFSS	Increase	Specific	Specific		
	coating	(MPa)	in IFSS	Energy:	Energy:		
	thickness		(%)	Debonding	Sliding		
	(nm)			(J / m ²)	(kJ/m ³)		
SG/EP	0	49.9 (9)		670 (33)	9,600 (32)		
SG-2000nm/EP	2000	75.5 (16)	58	770 (44)	15,000 (40)		
SG-600nm/EP	600	57.7 (12)	21	730 (52)	18,000 (49)		
SG-400nm/EP	400	48.0 (15)	0.4	700 (30)	14,000 (40)		
SG-2000nm/EP-	2000	52.5 (14)	10	770 (51)	12,000 (37)		
CNT							
SG/EP-CNT		64.4 (11)	35	1,100 (25)	5,200 (44)		

Table 3.3 Interfacial shear strength and energy absorption of various EPD fiber and epoxy system for microdroplet specimen with embedded length ranging from

Note: Values in parentheses represent coefficient of variation (%).

During the microdroplet experiment, the crack initiates in the interfacial region where the knife edges come into contact with the resin droplet due to the localized stress concentration (Figure 3.11). The crack typically propagates near the matrix-fiber interface in the direction of the applied tensile load before complete debonding occurs. CNT sensors are used for monitoring crack initiation at the interface by measuring electrical resistance across the specimen. More details on CNT sensing are presented in the next chapter. Two scenarios for crack path are shown in Figure 3.10. If the crack grows along the resin the test be considered invalid for interfacial characterization. Crack growth for a valid test case is shown in Figure 3.10b, where the crack initiates below the loading knife edge and propagates through the CNT network and along the interface. This is evidenced by SEM images of the failed specimens as well (Figure 3.11). CNT sensors act as on/off switch, where in this case (Figure 3.10b), the circuit is broken and the electrical resistance goes to infinity as the crack severs the CNT path, providing information on the onset of crack at the interface. The increase in IFSS with respect to increase in thickness of PEI-CNT coating for microdroplets with neat epoxy suggests that the coating thickness may have played a major role in arresting the crack propagation. The fracture surface for the microdroplet sample with the thinner PEI-CNT film (SG-400nm/EP) shows good CNT wetting by the epoxy resin (Figure 3.12 b), suggesting that some resin wetting into the thicker films will have occurred, but penetration to the glass interface would be reduced as the PEI-CNT film thickness increases.



Figure 3.10 (a) Crack growth along the resin would be considered invalid for interface characterization, (b) To be considered a valid test, crack should grow along the interface

While specimens with thickest PEI-CNT coating of $2 \,\mu$ m with neat resin showed a significant increase in the strength, the IFSS decreased from 75.5 MPa to 52.5 MPa for the same coating thickness when the 0.25 wt.% CNT modified resin droplets (SG-CNT/EP-CNT) were used. It may be expected that the addition of 0.25 wt.% CNTs would increase the viscosity of the resin [92] and further reduce the ability to penetrate the PEI-CNT coating, particularly given the drops are formed at room temperature. SEM images of the fracture surface for SG-CNT/EP-CNT specimens show smooth fiber surface suggesting a weaker bond was created because no resin could penetrate inside CNT coating (Figure 3.12 c). It should be noted that in previous studies the use of a very low viscosity resin system cured at 130°C led to very good wetting of the PEI-CNT treated fabrics [74]. The failure modes for the thicker CNT coatings (EPD-1-15-15m), therefore, may indicate that the IFSS results are affected to some extent by the level of resin wetting. However, given there is a significant increase in strength for the thick PEI-CNT film in which the resin was not modified (EPD-1-15-15m), compared to the same film with the CNT-modified resin, there clearly is some resin penetration into the silane coating. Amine functional groups in the PEI could potentially react with the epoxide group of silane coupling agent and the epoxy resin, yielding a ring opening reaction, which is then followed by crosslinking reaction with other epoxide groups [93]. Similar reactions occur between amine groups of curing agent and PEI with epoxide group of resin. This strong covalent bonds formed between the fiber-PEI-CNT and CNT-PEI-matrix interfaces is a critical component of the load transfer process at the fiber/matrix interface.

The addition of untreated CNTs to the epoxy resin used to form the microdroplet led to different levels of improvement in the IFSS depending on whether or not the glass fiber was pretreated with the PEI-CNT film. The sample with the 2000nm PEI-CNT film and CNT-modified resin (SG-CNT/EP-CNT) only showed a 10% improvement above the baseline strength, compared to the sample in which only the CNT-modified resin was used (SG/EP-CNT), a 35% increase in IFSS was measured. However, SEM image of the fracture surface for SG/EP-CNT shows a very rough surface with traces of epoxy and CNTs suggesting a cohesive failure (Figure 3.13 d). Inclusion of CNTs in epoxy could have also increased the yield stress of the matrix resulting in higher IFSS.



Figure 3.11 Typical failure modes (a) SG-2000nm/EP, (b) SG-400nm/EP



(c) Figure 3.12 Wettability between CNT and epoxy (a) SG-2000nm/EP, (b) SG-400nm/EP, (c) SG-2000nm/EP-CNT



Figure 3.13 Fracture surface morphology of microdroplet specimens: (a) SG/EP, (b) SG-600nm/EP, (c) SG-400nm/EP, (d) SG/EP-CNT

Electrical resistance measurements presented in Chapter 7 shows the resistance increasing to infinity near the peak load. However, location of the crack just prior to reaching the maximum load could not be determined. Due to this ambiguity in the crack tip location, the increase in IFSS for specimens with a thick coating of CNT could also be interpreted as arising from the geometry. For example, in case of the microdroplet specimen with 2000 nm thick CNT coating with neat epoxy, if the failure starts on the outside of CNT, and propagates to the fiber surface only after the peak load, then the

effective shear area is higher because of the larger diameter of 14 μ m. This 40% increase in shear area reduces the average IFSS to 54 MPa. Crack seems to have a step at the outer diameter of the coating before moving to the fiber surface. From the electrical resistance measurement alone, it could not be determined at which point during the loading this change in the crack path occurred. Similarly, microdroplet specimens with 600 nm thick CNT coating will have effective diameter of 11.2 μ m and the average IFSS would be reduced to 52 MPa. As such, the apparent increase in IFSS could be due to geometry. Further studies need to be carried out to monitor the location of the crack growth to study the exact mechanism behind the apparent increase in IFSS due to the application of thick coating of CNT.

3.8 Conclusions

This study demonstrated the ability of electrophoretic deposition method to control the thickness of PEI-CNT coatings down to submicron length scale. Hamaker's equation was used to adjust the processing parameters to control coating thickness. The PEI-CNT coatings were found to have a very uniform thickness around the fiber circumference. Decreasing the deposition time proved to be the most efficient way to yield thinner and more homogenous PEI-CNT coatings, as opposed to decreasing the field strength. The effect on the interfacial properties resulting from the application of the PEI-CNT coatings onto the fiber and incorporation of unmodified CNTs into the resin matrix was studied using the microdroplet. Increasing the thickness of PEI-CNT coating resulted in increased IFSS. The combination of glass fiber with the 2 µm thick

PEI-CNT coating and unmodified epoxy resin showed the highest improvement in IFSS with a 58% increase. The higher viscosity of the resin required to form the microdroplets at room temperature compromised the full extent of improvement that may be offered by the PEI-CNT coatings by reducing the level of resin wetting through the film, particularly as the film thickness increased. Improvement in the IFSS due to incorporation of CNT seems promising and need to be further investigated.

The EPD treated fibers exhibited good electrical conductivity, which has the potential for the CNT-modified fibers to be used as distributed sensors in the study of damage initiation at the fiber-matrix interface. Microdroplet specimens SG-400nm/EP with 400 nm thick PEI-CNT coating was found suitable for sensing as it shows no change in IFSS compared to the baseline and will be used for detecting crack onset at the interface in the next chapter.

Chapter 4

MONITORING CRACK GROWTH ALONG THE INTERFACE USING CARBON NANOTUBE SENSORS

4.1 Carbon Nanotubes as Sensors

Among many advantages of using carbon nanotubes (CNT) in composite materials, such as enhanced mechanical properties as depicted in the previous chapter and electrical properties for engineering application [94,95], its ability to sense damage accumulation in composite materials has garnered considerable attention, especially in the area of structural health monitoring and for the study of micromechanics of composite materials [68,95,96]. CNTs have been used to form electrically conductive networks, which when disrupted changes the electrical pathways. Since the CNTs are three orders of magnitude smaller than the microcracks of interest in composites, the disruption or even small deformation induced in the CNT network is sensitive enough to cause changes in the electrical resistance measurement, which can be used to interpret the onset and growth of damage in the composite. CNTs have been successfully infused into the matrix in fiber reinforced polymer composites to tailor the mechanical properties as well as for the investigation of matrix dominated failure mechanisms [86]. While dispersing CNTs into the matrix does help in studying the damage induced during matrix cracking and delamination; crack monitoring in the fiber-matrix interface cannot be achieved by this approach.

Few studies have been carried out to monitor damage accumulation in the interface by incorporating CNTs. Rausch and Mader [97] demonstrated the potential of using multiwall CNTs for in situ damage sensing of interface at macro scale. Glass fiber yarns were coated with CNTs via aqueous coating approach. Controlled cyclic loading in tensile mode were conducted on glass fiber reinforced composite specimens with polypropylene matrix. Zhang et al. [75] employed electrophoretic deposition (EPD) to coat a thin conductive network of CNTs on to a single glass fibers surface and then used the functional interface in a fragmentation specimen with three individual CNT coated glass fibers embedded in the matrix [98]. They demonstrated abrupt changes in electrical resistance with successive fiber break. Such experimental results when coupled with numerical simulation can provide a better understanding of the interactions between fiber and matrix via interface.

Previous chapter demonstrated the manipulation of processing parameters of EPD method to control the CNT coating thickness. IFSS, as measured through microdroplet tests, increased with an increase in the thickness of CNT. Microdroplet specimens prepared with EPD fibers with 400 nm CNT coating formed through a combination of optimum parameters (0.5 g/L CNT, 15 V/cm 10.5 min) and neat resin did not alter the IFSS from the baseline (glass fiber/epoxy) while still exhibiting the electrical properties at semiconducting range. This microdroplet specimen is used to investigate the crack initiation at the fiber matrix interface during the test. The CNT sensor acts as an on/off switch which provide information regarding the onset of crack at the interface. This information will subsequently be used in microdroplet simulation to extract unique traction separation law for interface with S-2 glass fiber with GPS sizing and epoxy resin.

4.2 Electrical Resistance Measurement Across the Specimen

A two wire technique was used to measure the change in electrical resistance across the specimen (Figure 4.1). A constant source voltage of 50V was applied between top and bottom of the specimen. A Keithley 6430 sub-femtoamp remote sourcemeter was used to measure the change in current flow across the specimen. A silifex wire was connected to the specimen using silver paint. If the failure occurs along the resin (Figure 4.2a), the change in electrical resistance would be minimal. In the microdroplet specimen, increase in electrical resistance occurs due to a) disruption of CNT network in the fiber gage length (See Figure 4.1) when subjected to tensile load and b) when the crack reaches the interface region and cuts through the CNT network (Figure 4.2b). The magnitude of resistance change when the crack reaches the interface region is much higher compared to the ones arising from tension in fiber gage length. This is because the crack propagating to the interface severs the CNT network.



Figure 4.1 Measurement of electrical resistance across the microdroplet specimen for crack growth monitoring



Figure 4.2 (a) Crack growth along the resin would have minimal change in electrical resistance measurement and would be considered invalid for interface characterization, (b) To be considered a valid test, crack should grow along the interface. Electrical resistance significantly increases as the crack disrupts the CNT coating

4.3 Single Fiber Tensile Tests

Tensile tests on single EPD fibers were conducted to study the change in electrical resistance across the fiber when subjected to monotonically increasing load. Tests were conducted on single EPD fibers with a 4 mm gage length at a loading rate of 0.001/s. An Instron model 5848 MicroTester was used for the tests. A 5 N load cell was used to monitor the tests.

Figure 4.3a shows change in resistance and tensile load as a function of time. The change in resistance is about 4% when the axial strain in fiber is 2.5%. Change in electrical resistance is apparent from the beginning of the test and is almost linear to change in axial strain as shown in Figure 4.3b. These results show that the sensor network remains conductive over a realistic range of axial strain in the fiber gage length that is expected during the microdroplet test. The vertical spike in the resistance measurement at the end of the data signifies the circuit is open and the resistance goes to infinity because the CNT network has been severed.



Figure 4.3 (a) Load and change in electrical resistance vs. time, (b) Change in resistance vs. axial strain for single EPD fibers

4.4 Monitoring Crack Growth Through Electrical Resistance Measurement

For microdroplet specimens, the bottom portion, which is CNT coated fiber, hanging freely below the droplet is immersed into a pool of conductive silver epoxy (Figure 4.1). The part holding this pool of epoxy is attached to the actuator such that it moves at the same velocity as the knife edges. As such, the portion of the specimen below the droplet remains stress-free with no change in electrical resistance during the experiment. The only change in electrical resistance, therefore, arises from damage accumulation due to stretching of fiber in the gage length and inside the specimen and due to the tearing of the CNT sensor in the interface region just beneath the tip of the droplet where knife edges come in contact.

For microdroplet specimens with 400 nm thick CNT coating, no significant changes in electrical resistance is observed until the failure load is reached (Figure 4.4 a and b). Almost immediately after the crack reaches the interfacial region (point B), complete interface debonding occurs. The change in electrical resistance till point B is very low. The specimens shown in Figure 4.4 a and b have gage lengths of 1.8 mm and 1.3 mm. An axial load of 100 mN and 200 mN would cause an axial strain of 1.5% and 3%, respectively. Assuming resistance change is linear with gage length, this corresponds to resistance change of about 2% and 5%, respectively, shown by the dotted lines in Figure 4.4. This suggest that the resistance change up to point B is mostly due to fiber stretching. The resistance increases abruptly suggesting the crack has started tearing up the CNT network at the interface region. However, as the crack tip location was not monitored, and it is not clear whether the CNT network near the loading end (Figure 4.2b) is broken at the initiation where the resistance increases rather slowly or during propagation where it seems instantaneous because of the limitation in capturing frequency. Further investigation of this sequence is carried out in detail in Chapter 7. Based on the load and resistance change vs. time plot, we can conclude that failure occurs at the moment when the circuit is broken, suggesting the crack speed from point B to non-loading end of the droplet is very fast and the crack growth is unstable and

could not be captured with the 10 Hz sampling rate. Information on crack onset and its corresponding load level will be used as an input in the FE simulation to extract traction separation law.



Figure 4.4 Force and electrical resistance vs. time for (a) 77 µm droplet and (b) 179 µm droplet, and their respective SEM micrographs in (c) and (d) showing failure surfaces of microdroplet specimens with a 400 nm thick CNT coating

4.5 Conclusions

A technique to monitor crack onset at the interface in a microdroplet specimen has been developed. This method includes creating an electrically conductive network in the interface region using CNT coating. Electrical resistance was measured on top and bottom of the specimen to monitor crack onset in the interfacial region. Based on the change in electrical resistance and post-failure inspection through SEM images, load corresponding to the onset of interface debonding was determined.

For a 400 nm coating of CNT, which did not alter the interfacial shear strength, the crack initiation time coincides with complete debonding. This suggests that once the crack tip reaches the interfacial region, it becomes unstable and propagates almost instantly to the other end of the specimen leading to complete debonding. This study demonstrates a unique ability of CNT to monitor crack onset at the interface inside a specimen, which is generally not feasible through optical methods. These experimental evidences on crack onset will be used in the finite element simulation to obtain a unique traction separation law for composite interfaces.

Chapter 5

EXPERIMENTAL INVESTIGATION OF STRAIN RATE RESPONSE OF AN EPOXY RESIN UNDERGOING LARGE DEFORMATION

5.1 Introduction

For accurate determination of strain rate dependent traction separation law and for the determination of energy absorbed by resin and interface for energy partitioning, microdroplet experiments need to be simulated using accurate strain rate dependent properties of the constituents. In Chapter 2, the elastic properties of the S Glass fiber were found to be independent of strain rate. Strain rate dependent properties of the interphase in glass/epoxy with γ -glycidoxypropyl-trimethoxysilane sizing studied experimentally using a microdroplet test specimen loaded in a tensile Hopkinson bar has been presented in Chapter 2 where the average IFSS and energy absorption were found to be rate dependent. During microdroplet experiments, resin beneath the knife edges undergo large compressive deformation as evidenced by the SEM images presented in Chapter 2. Strain and strain rate in the resin are maximum near the loading end and diminishes towards the unloaded end of the microdroplet. Resin properties over a wide range of strain and strain rates need to be generated experimentally. In this chapter, compressive properties of epoxy resin have been determined at quasi-static loading rates using Instron testing machine. To obtain large deformation response at high strain rates a split Hopkinson pressure bar is used as the loading apparatus. An optimal specimen geometry determined using FE simulations has been employed to maintain uniform strain and minimize the effects of radial inertia and bar-specimen friction.

Typical stress strain response of glassy polymers show non-linear increase in stress until yield, which is followed by softening, plastic flow and hardening at large strain [99–101]. Pure viscous flow takes place momentarily when the material yields and this process is dependent on the applied strain rate [99]. At large strain, chemical cross-linking and network entanglement results in material hardening [102] and ultimately bond breakage leads to catastrophic failure. Since the mechanisms behind the rate dependence of yielding is different from strain hardening, the scaling law for yielding cannot be applied to the entire stress strain curve at different strain rates [102,103].

High strain rate compressive properties are generally characterized using split Hopkinson pressure bar (SHPB) technique at strain rates ranging from 10^2 /s to 10^4 /s [47]. The working principle for the compression bar is similar to the tensile Hopkinson bar mentioned in Chapter 2, where the specimen is loaded using an acoustic wave produced by a striker bar. The difference is in the size of the specimen that can be tested. The tensile Hopkinson bar was designed for testing fibers with diameters in micrometer length scale. Whereas, the SHPB setup is more appropriate for macromechanical tests with specimens in millimeter length scale.

Unlike quasi-static tests, the duration of high rate tests is determined by the width of the loading pulse, which limits the maximum strain that can be attained during the test. One approach to load the specimen to large strains using this technique is to use long bars. However, during data reduction process, correction for wave dispersion

needs to be considered, which is caused by waves travelling at different velocities corresponding to their frequency components [104]. Typically, incident and transmission bars up to about 2 meters in length do not have problems with data reduction due to wave dispersion. Besides, larger lab space is required to accommodate long bars and precise machining and alignment of such long bars can become an issue.

This chapter presents a test method for the characterization of large strain response of polymeric materials under high strain rate using SHPB through design of specimen geometry using our existing equipment (having total bar lengths of approximately 4 m). Finite element analysis is employed to design the specimen geometry by studying the state of stress in the specimen under compressive loads. Based on the FE analysis, epoxy specimens with optimal geometry were fabricated and tested using SHPB. Strain rate dependent resin properties will then serve as input in the FE simulation of microdroplets for accurate extraction of traction separation law.

5.2 Experimental Work

5.2.1 Quasi-static compression test

Quasi-static compression tests were conducted on a standard specimen geometry to establish a baseline stress-strain response for the epoxy. The quasi-static test uses right cylindrical specimens with an aspect ratio of 1:1 (thickness:diameter, H_s/D_s), which were prepared by core drilling 4.5 mm thick resin plates. Specimens were placed between two rigid parallel platens and compressed under displacement control. Petroleum jelly was applied to the specimen/platen interface to minimize friction and

barreling of the specimen [105]. True stress and true strain were calculated using Eq. (5.1) and (5.2) assuming the material is incompressible.

$$\sigma_T = \frac{P}{A_0} \left(1 + \frac{\delta}{l_0} \right) = \sigma_E (1 + \varepsilon_E)$$
(5.1)

$$\varepsilon_T = \ln\left(1 + \frac{\delta}{l_0}\right) = \ln(1 + \varepsilon_E)$$
 (5.2)

Where, P, δ, A_0 and l_o are applied force, change in thickness, original crosssectional area and original thickness, respectively. σ_E and ε_E are engineering stress and strain, respectively.

A 30 kN load cell was attached to an Instron testing machine. By varying the displacement rates, tests were conducted at strain rates of 0.001/s, 0.01/s, 0.1/s and 1/s. At least five tests were conducted for each strain rate. Machine compliance of the test setup was also determined, which is later subtracted from the raw displacement during data reduction.

5.2.2 High rate tests using Split Hopkinson pressure bar

Traditional SHPB (Figure 5.1) was adopted for the characterization of dynamic compressive response of epoxy resin. Aluminum 6061 was used for incident, transmission and striker bar, which were precision machined and centerless ground. Material properties and geometry of the bars are presented in Table 5.1.

During the test, the striker bar is accelerated along a long barrel using compressed air and impacts the incident bar. A compressive wave, which is twice the length of the striker bar (in space), propagates along the incident bar at the speed of sound (c_0). When the wave reaches the incident bar/specimen interface, a portion of the input pulse is transmitted through the specimen into the transmission bar, while the rest

is reflected back to the incident bar. The amount of signal transmitted and reflected depends on the acoustic impedance mismatch and the difference between crosssectional area between bar and specimen.

Strain gages attached to the incident and transmission bar measure the incident, transmitted and reflected strains. The incident pulse triggers the data acquisition system and the data was collected at a rate of 5 MHz. A pulse shaper was placed at the end of the incident bar to modify the input pulse and to filter out the high-frequency noise that is generated from metal to metal contact. The surface of the pulse shaper and specimen was lubricated with petroleum jelly to reduce bar-specimen interfacial friction during radial expansion of the specimen and for better acoustic transmission.

Parameter	Notation	Value
Incident bar length	L_{IB}	1.824 m
Transmission bar length	L_{TB}	1.826 m
Striker bar length	L_{SB}	0.406 m
Incident bar diameter	D_{IB}	12.69 mm
Transmission bar diameter	D_{TB}	12.69 mm
Striker bar diameter	$D_{\scriptscriptstyle SB}$	12.69 mm
Elastic modulus of bar material	$E_{\scriptscriptstyle B}$	69 GPa
Density	ρ	2700 kg/m ³
Velocity of sound in the bar	C _o	5056 m/s

Table 5.1 Split Hopkinson pressure bar

The following assumptions are made for the Hopkinson bar data reduction [47,50]: (i) one – dimensional stress wave propagation, (ii) planar interface between bar and specimen, and (iii) dynamic equilibrium of the specimen during the test. The first assumption is satisfied by having a bar with a very high aspect ratio (L/D > 20) [47]. The second assumption is met through precision machining. The establishment of

dynamic stress equilibrium can be determined experimentally by calculating the Rvalue, which is defined as the ratio of the stress difference between the specimen at the specimen/bar interface on both sides and the mean specimen stress. R-value can be determined from the bar stresses by synchronizing the incident, reflected and transmitted pulses as follows:

$$R(t) = \frac{\left|\frac{(\sigma_I + \sigma_R) - \sigma_T}{(\sigma_I + \sigma_R) + \sigma_T}\right|}{2}$$
(5.3)

Where $(\sigma_I + \sigma_R)$ denotes the net stress in the incident bar and σ_T is the stress in the transmission bar at the specimen/bar interface. Once these assumptions have been met, strain rate, strain and stress in the specimen for each time increment are calculated as follows:

$$\dot{\varepsilon}(t) = \frac{2c_o}{H_s} \varepsilon_R(t) \tag{5.4}$$

$$\varepsilon(t) = \frac{2c_o}{H_s} \int_0^t \varepsilon_R(t) dt$$
(5.5)

$$\sigma(t) = E_B \frac{A_B}{A_S} \varepsilon_T(t)$$
(5.6)

Where, $\varepsilon_R(t)$ and $\varepsilon_T(t)$ are strains associated with reflected and transmitted pulse, respectively. H_s is specimen length, A_B and A_S are cross-sectional area of bar and specimen, respectively.

As discussed earlier, there are mainly two different ways to achieve large strain response under high strain rate loading - either by changing the bar dimensions or by altering the specimen geometry. In this study, the specimen geometry has been modified to accurately determine large strain response with the current bar set-up. Reducing the specimen thickness, H_s increases the strain rate, $\dot{\varepsilon}$ and strain, ε (Eq. (5.4) and (5.5)). However, the aspect ratio of the specimen should be maintained to avoid multiaxial loading, which requires reducing the diameter of the specimen. Specimens with smaller cross-sectional area results in lower impedance (ρcA) and most of the incident pulse is reflected back resulting in low signal transmission due to increased mismatch in acoustic impedance. For example, if the condition presented in Eq. (5.7) is met, then the impedance in the bar and specimen is matched and all the signal is transmitted through the specimen. In this case, there is no reflected pulse and the specimen does not accumulate any deformation since $\varepsilon_R(t)$ is zero in Eq. (5.5).

$$(\rho cA)_{bar} = (\rho cA)_{specimen} \tag{5.7}$$

Ideally, the impedance of the bar should be higher than that of specimen such that the magnitude of the reflected pulse is about half of the incident pulse. So, if the cross-sectional area of the specimen is significantly reduced then the transmission bar diameter should also be decreased proportionately for better acoustic transmission, which again requires setting up new set of bars and possibly strain gages with higher sensitivity. In this study, finite element simulations are carried out to identify an optimum specimen geometry, which can achieve large strains under compression at high rate of loading using the existing setup while maintaining equilibrium (R-value is negligible) and a uniaxial state of stress and strain throughout the duration of the test. This specimen design can be easily adapted to other existing bar configurations and other test materials.



Figure 5.1 Schematic of a traditional split Hopkinson pressure bar

5.3 Specimen Design for High Rate Tests

A quarter symmetric FE model of an epoxy disk (Figure 5.2 a) was developed and analyses were conducted using commercially available FE code Abaqus. Elastic perfectly plastic material model was used with an elastic modulus of 3.0 GPa and a yield stress of 100 MPa. Displacement was applied to a rigid platen to load a circular specimen up to an engineering strain of 80%. Reaction force on the platen and the nodal displacements at the edge of the specimen was monitored to obtain the forcedisplacement response. True stress-strain response of the specimen was then calculated using the reaction force and the cross-sectional area assuming no change in density of the material.

True strain was calculated from the imposed uniform platen displacement and instantaneous specimen thickness. This averaged stress strain response mimics the experimental data reduction and is used as a baseline to assess the magnitude of the stress gradients in the sample as a function of aspect ratio and effects of friction between the sample and the platens.



Figure 5.2 Schematic representation of (a) cylindrical specimen and (b) donut specimen

First, the effect of different coefficients of friction (μ =0, 0.01 and 0.05) was studied for a constant aspect ratio (H_s/D_s) of 0.1. A thickness (H_s) of 0.5 mm was maintained for all cases. Stress-strain response for frictionless contact yielded the same result as the model input and averaged baseline response (i.e. elastic perfectly plastic). For μ = 0.01, which is closest to the lubricant (petroleum jelly [105]) used in our experiments, the simulation results show slight stiffening in the post-yield true stressstrain behavior (Figure 5.3a). When the coefficient of friction was increased to 0.05, the apparent yield stress increased by 25% over the baseline, which is consistent with the findings in the literature [106]. Increase in the friction coefficient restricts the radial growth of the specimen, which results in increased stresses at the center of the specimen. A new specimen design should minimize the effects of friction by allowing radial growth during through thickness deformation.



Figure 5.3 True stress strain from FE simulation of cylindrical specimens (a) Different coefficient of friction ($\mu = 0, 0.01, 0.05$) and constant aspect ratio ($H_s/D_s = 0.1$), and (b) Different aspect ratios ($H_s/D_s = 0.1, 0.2, 1$) and constant coefficient of friction ($\mu = 0.01$)

Then, simulations were carried out to study the effect of aspect ratios ($H_s/D_s = 0.1, 0.2, 1$) with a constant friction coefficient of 0.01 (slightly higher in the plateau region than the frictionless baseline as shown in Figure 5.3a). Stress-strain plot presented in Figure 5.3b shows the slope of the curve in the plateau region at large strain increases (compared to the baseline) as the aspect ratio is decreased from 1 to 0.1 due to non-uniform stress. For the aspect ratio of 1 and friction coefficient of 0.01, the curve is essentially the same as the frictionless baseline (this confirms that the geometry used in quasi-static loading is accurate).

The lower aspect ratio exhibits higher axial stress values at the center of the specimen (r=0) as shown in Figure 5.4. This non-uniformity in the stress distribution is reduced by increasing the aspect ratio as evidenced by the axial stress contours on the specimen surface (Figure 5.4) at 60% engineering strain. For $H_s/D_s = 0.1$, the maximum stress was 147 MPa at the disk center (versus the average axial stress of 100MPa), which decreased to 105 MPa for $H_s/D_s = 1$ at this location. Note that increasing aspect ratio

shifts the location of maximum axial stress from the center to outer diameter and is very localized at the surface. Consequently, a H_s/D_s ratio close to one is an optimum geometry to minimize friction effects and stress gradients. These results are consistent with the specimen geometries reported in the literature [107] for testing in the lower range of strain rates.



Figure 5.4 True axial stress contours on the cylindrical specimen surface with coefficient of friction of 0.01 and different aspect ratios (a) $H_s/D_s = 0.1$, (b) $H_s/D_s = 0.2$ and (c) $H_s/D_s = 1$

Since our objective is to characterize material properties subjected to high rate of loading at large strains up to failure using the standard SHPB set-up given in Table 5.1, the specimen geometry must be modified. To achieve high strains and high strain rates under dynamic equilibrium conditions, a thin sample is required. Maintaining the 1:1 aspect ratio reduces the cross-sectional area significantly to the level that the area ratio between bar and specimen becomes so large that the transmitted signal cannot be measured (forces drop to such low levels that strains in the bars cannot be measured accurately). One approach is to reduce the thickness to levels needed to achieve desired strain and strain rates and increase the diameter to increase the specimen cross-section to maintain sufficiently high forces/strains in the bars. This corresponds to a low aspect ratio geometry that exhibits non-uniform axial loading and is sensitive to friction as shown above. Our solution to this problem is to design a low aspect ratio sample of constant thickness with a hole at the center of a thin specimen (i.e. donut) to remove the stress concentration that occurs at the center. Such specimen geometry has been utilized by Song et al. [108] to minimize the effect of radial inertia in soft specimen while conducting Hopkinson bar tests. While testing a gel rubber, a spike-like feature was observed at the beginning of the stress strain curve. Numerical and analytical studies showed that this feature is due to the extra axial stress caused by multiaxial state of stress at the center of the specimen. Similarly, Chung et al. [109] observed oscillations in dynamic stress strain response for cylindrical specimen when tested using Hopkinson bar due to rapid hydrostatic pressure buildup at the center of the cylinder. Consequently, a ring specimen was employed to resolve the issue. This geometry has also been used for the investigation of friction effects in the Hopkinson bar compression tests [110].

To prove out this design for the determination of large strain response under high strain rates, the specimen was modeled using the same epoxy properties. The specimen geometry (Figure 5.2b) has an aspect ratio of 0.1, (thickness of 0.5 mm and outer diameter of 5 mm) and inner diameter of 3 mm that is easy to machine. The net cross-sectional area of the new specimen geometry is 64 times greater than the 1:1 aspect ratio for this thickness (and only 36% smaller area than the disk without the center hole). This geometry works well with the bar configuration presented in Table 5.1. FE results for donut specimen with coefficient of friction of 0.01 show a very uniform stress distribution in the specimen with axial stress of 100 MPa (equal to the average axial stress) at the outer edge (see Figure 5.5). Frictional effects are also minimized with the new specimen geometry, where the maximum axial stress is 108 MPa at the inner edge of the specimen as opposed to 147 MPa for cylindrical specimen with the same aspect ratio of 0.1 and coefficient of friction of 0.01. For high rate tests, donut specimens were prepared by core drilling the epoxy plates. The outer surface of the donut specimen was then polished with fine grained sandpaper.



Figure 5.5 True axial stress contours of the donut specimen with 0.5 mm thickness, 5 mm outer diameter and 3 mm inner diameter with coefficient of friction 0.01 shows minimized stress gradients

5.4 **Results and Discussion**

5.4.1 Quasi-static compression test

Raw force displacement response at a strain rate of 0.001/s for DER 353 epoxy resin is shown in Figure 5.6. Deformation due to machine compliance for load level up to 6 kN has also been plotted alongside for comparison. This curve was obtained by conducting the test at the same loading rate without the specimen. Deformation arising from machine compliance is subtracted from the raw displacement for further calculations. To ensure the lubrication provided by petroleum jelly is sufficient and no barreling occurs at large strain, optical images were captured during compression tests at 0.001/s strain rate at strains shown by red dots in Figure 5.7. Optical images show minimal barreling (Figure 5.8). The effect of barreling was quantified by measuring the maximum diameter at the center of the specimen and the minimum diameter near the loading ends using ImageJ software. Table 5.2 shows the difference in diameters due to barreling near failure load is only 3.3%.

True stress-strain response for strain rates 0.001/s to 1/s is presented in Figure 5.9. No evidence of dynamic effect (i.e. oscillations in the material response) was observed up to the maximum strain rate of 1/s, since the velocity of the crosshead was 4.5 mm/s, which is much smaller compared to the wave velocity in resin material. The overall trend of the stress-strain response is similar for all four strain rates and is typical of glassy polymers [32–35] – initial non-linear increase in stress is observed until the yield point is reached, which is followed by strain softening, plastic flow and strain hardening. Pure viscous flow takes place momentarily when the material yields and this process is dependent on the applied strain rate [32]. Although strain hardening at large

strains is present in all cases, the hardening slope decreases as the strain rate is increased from 0.001/s to 1/s due to increase in specimen temperature. At the lowest loading rate (0.001/s), there is ample time for the heat generated due to plastic deformation to be dissipated by conduction through the loading platens and by convection through the air. As such, the entire duration of 0.001/s strain rate test is carried out under isothermal conditions. However, as the rate of loading increases, the time for heat dissipation decreases, resulting in specimen temperature increase and material softening. At large strain, stretching of the cross-linked network and entanglements results in material hardening [36] and ultimately bond breakage leads to catastrophic failure.



Figure 5.6 Raw force-displacement response of DER 353 resin at 0.001/s strain rate and machine compliance (in red)



Figure 5.7 True stress strain response for DER 353 resin at 0.001/s with red dots showing the points where optical images were captured to observe possible barreling



Figure 5.8 Optical images of DER 353 epoxy specimen undergoing compression test exhibiting minimal barreling at large strains

Frame	\mathbf{d}_{\min}	d _{max} (at center)	% difference		
1	4.50	4.50	0.0		
2	4.77	4.78	0.2		
3	5.05	5.09	0.8		
4	5.15	5.24	1.7		
5	5.45	5.58	2.3		
6	6.08	6.28	3.3		

 Table 5.2 Effect of barreling in diameters of cylindrical specimens during compression test



Infrared (IR) camera was used to monitor the change in temperature at the surface of the specimen during the test. For ambient temperature test, the infrared image of the epoxy resin is close to black prior to loading (Figure 5.10). This ensures that the
emissivity of specimen is close to 1. No significant change in the specimen temperature was found for the lowest strain rate (0.001/s). Whereas the surface temperature increased to about 50°C at failure for 1/s strain rate test (Figure 5.10). This observation implies temperature effects on stress-strain response of this epoxy are important and will be considered in the next chapter.

Elastic modulus was calculated at the initial linear portion of the stress strain curve between 0.1% and 0.3% strain. Yield is defined as a point in the stress strain curve where the slope $(d\sigma/d\varepsilon)$ becomes zero for the first time. Both elastic modulus and yield stress increase with strain rate. Here, it should be noted that the elastic modulus and yield stress are only a function of strain rate because the temperature rise is negligible until yielding occurs where plastic work increase and is converted to heat. For strain rates higher than 0.01/s, the effect of temperature and strain rate on the post-yield behavior of the epoxy resin are coupled and have opposite effects (strain rate increases post-yield behavior while temperature rise decreases this behavior). Failure occurs through formation of cracks in the specimen at around 70% true strain where the stress drops abruptly. Strain to failure was found to be insensitive to the applied strain rate.



44°C, 56% true strain 56°C, 70% true strain **Figure 5.10 Rise in surface temperature of resin specimen at 1/s strain rate**

5.4.2 High rate compression test

High rate tests were conducted on the donut specimens and cylindrical specimens. Typical signals in the incident and transmission bar for donut specimen are shown in Figure 5.11. An incident pulse with a fairly constant amplitude is sent as an

input. Specimen failure occurred within first loading pulse, which is evident from the "dip" in the transmitted pulse.



Figure 5.11 Typical incident, reflected and transmitted signal from SHPB. The dip in the transmitted pulse denotes specimen failure

The first step in the data reduction process of a Hopkinson bar test is to check the validity of assumptions (mentioned in section 5.2.2) during the test. By synchronizing the pulses, R-values are calculated, which decrease to 10% within 25 μ s of loading for both cylindrical and donut specimens (Figure 5.12). This suggests the dynamic stress equilibrium has been established and Eq. (5.4) - (5.6) are applicable for the determination of stress, strain and strain rate of the specimen. Another key requirement for a valid test is the attainment of uniform strain rate throughout the test, which is evidenced by the strain rate profiles in Figure 5.13a.



Figure 5.12 Development of stress equilibrium in (a) cylindrical and (b) donut specimens. R-values are represented by the scattered plot



Figure 5.13 (a) Strain rate profile showing uniform loading until failure (b) True stress strain at strain rates from 1000/s to 12,000/s showing rate dependent yield stress and thermal softening at large strain

Donut specimens with outer diameter 4.7 mm, inner diameter 3 mm and thickness 1 mm were loaded to failure at strain rates of 5000/s and 12,000/s. Due to the non-linear nature of the applied strain rate, average values at the plateau region of the

strain rate profile is used as the representative strain rates. The maximum achievable strain and strain rate is governed by the specimen thickness. Therefore, to obtain stress-strain response at lower strain rates, the specimen thickness was increased to 4.5 mm. With the increased thickness, a cylindrical specimen with the aspect ratio of one could be used and a good transmitted signal is acquired since the impedance mismatch is reduced due to larger ratio between bar and specimen cross-sectional area (Eq. (5.7)). Cylindrical specimens were loaded at strain rates of 1,000/s and 2,300/s. No failure occurred for these strain rates, and unloading occurred at a strain level of around 25% - 35%.

Yield stress increased from 85 MPa at 0.001/s strain rate to 220 MPa for 12,000/s strain rate. Yield stress varies bi-linearly as a function of strain rate when plotted on a semi-log scale (Figure 5.14), which suggests that more than one type of molecular segmental motion are involved at higher strain rates [111]. It has been hypothesized that only alpha relaxation, which is associated with rotational freedom in the segments between crosslinks, is involved at lower strain rates. Whereas, at higher strain rates, since there is less time for the polymer chains to reorient and slide, side chain motion also gets activated resulting in beta relaxation [112], which occurs at about 100/s strain rate for the epoxy resin DER 353 considered in this study. Such behavior is commonly modeled using Eyring type equation [99,113].



Figure 5.14 Yield stress vs. strain rate shows bi-linearity on a semi-log scale

Strain hardening is completely absent for the high rate tests (Figure 5.13b) likely due to adiabatic heating that counters strain hardening with material softening. As mentioned earlier, tests conditions remain isothermal at the lowest strain rate (0.001/s), becomes coupled at intermediate strain rates (> 0.01/s) and then become adiabatic at the highest strain rates. IR camera could not be used to monitor the temperature rise in the specimen during Hopkinson bar tests due to limitations in the frequency response of the camera. The IR camera can capture the specimen temperature at a maximum frequency of about 10,000 Hz. This results in about one frame every 100 μ s, which is equal to the entire duration of the high rate test.

The test condition of the compression tests was categorized as adiabatic or coupled by determining the ratio of thermal diffusion time and test time. Thermal diffusion time can be estimated by the following relation [114]:

$$t_d \approx \frac{L^2}{2(k/\rho c)} \tag{5.8}$$

Where *L* is the distance from the center of the specimen to the nearest heat sink (loading platens). *k* is thermal conductivity (2.092 J/(m s K), ρ is density (1150 kg/m³)

and c is specific heat capacity of the epoxy specimen (1.11 kJ/kg K). For a 4.5 mm thick specimen, thermal diffusion time is 1.54 sec. Test time can be calculated based on strain rate. Assuming the strain to failure is 0.7 the duration of the test is approximately:

$$t_{test} = \frac{0.7}{\dot{\varepsilon}} \tag{5.9}$$

For isothermal test condition, the ratio $\tau = t_{test}/t_d$ is much greater than 1. If $\tau \ll 1$ then adiabatic conditions exist, and if the ratio is close to 1, then test conditions are coupled. Estimates presented in Table 5.3 show that the test is coupled between strain rates 0.1/s and 10/s. Specimens subjected to higher strain rates are classified as adiabatic.

Strain rate (1/s)	Test time (s)	τ	Test condition
0.001	700	453	Isothermal
0.01	70	45.3	Nearly isothermal
0.1	7	4.53	Coupled, nearly isothermal
1	0.7	0.453	Coupled
10	0.07	0.0453	Coupled, nearly adiabatic
100	0.007	0.0045	Adiabatic
1,000	0.0007	0.0005	Adiabatic
10,000	0.00007	0.00005	Adiabatic

 Table 5.3 Estimation of test condition based on heat transfer in the specimen

The rise is specimen temperature can be estimated from the general energy balance equation:

$$\rho c \dot{T} - k \nabla^2 T = \beta \sigma_{ij} \dot{\varepsilon}_{ij}^p - \alpha (3\lambda + 2\mu) T_0 \dot{\varepsilon}_{kk}^e$$
(5.10)

Where ρ is density, *c* is specific heat capacity, *T* is absolute temperature, *k* is thermal conductivity. β is inelastic heat fraction, α is coefficient of thermal expansion, λ and μ are Lamé elastic constants. For adiabatic condition, the thermal conduction

term is negligible. The thermoelastic heating also is negligible compared to the heat generated due to plastic work, which simplifies equation (5.10) to:

$$\Delta T = \frac{\beta}{\rho c} \int_{\varepsilon_{y}}^{\varepsilon} \sigma d\varepsilon$$
(5.11)

Assuming all the plastic work is converted to heat, the specimen temperature can rise beyond 80°C (Figure 5.15). Thermal softening in the stress-strain curves become more apparent at around 55% true strain for 5000/s where the estimated specimen temperature reaches about 70°C. For strain rate of 12,000/s, softening occurs at even lower strains (around 40%), which suggests that the material may have reached the glass transition (T_g) region. To determine the T_g of the epoxy resin, dynamic mechanical analysis (DMA) was carried out on right cylinder specimens (6 mm diameter and 1.8 mm thick) in shear mode at 1 Hz frequency over a temperature range of 25°C – 180°C while maintaining a constant shear stress of 1.77 kPa. Figure 5.15b shows the T_g range, the beginning of which is marked by an abrupt change in the storage modulus at around 70°C spanning to about 100°C. One concludes that both of the higher strain rates induced temperatures exceeding the glass transition temperature of the DER epoxy.

For lower strain rates (0.001/s - 1/s), failure occurs at around 70% true strain indicated by a sudden decrease in stress; however at high strain rates, the specimen temperature rise above T_g and the material transforms to complete rubbery state at that strain level. As such, there is no specific failure strain measured at high strain rates. Thermal softening effects due to adiabatic heating at high strain rate become more pronounced for polymers with low T_g . It is important to obtain accurate material properties for the development of accurate constitutive model by isolating the temperature and strain rate effects. The model which is developed in the next chapter accounts for heat generation in the material and coupling of strain rate and temperature effects.



Figure 5.15 (a) Estimated rise in specimen temperature due to adiabatic heating for DER 353 resin at 5000/s strain rate, (b) Temperature sweep from DMA test shows a T_g range of about 70°C to 100°C

5.5 Conclusions

Strain rate dependent mechanical properties of DER 353 epoxy resin subjected to quasi-static (0.001/s - 1/s) and high rate (1000/s - 12000/s) compression loading have been investigated at ambient temperature. Using FE simulation, a specimen geometry was designed by studying the state of stress in the specimen with different aspect ratios, when subjected to compression. Stress-strain response was obtained at large strain under high strain rates thereby eliminating the need to have longer bars. Validity of the high rate experiments was verified by checking the establishment of dynamic equilibrium in the specimen during the test.

Yield stress showed bi-linear dependence on strain rate suggesting multiple molecular segmental motions are involved at high rates. Stress-strain response at lower

strain rates showed post-yield softening followed by plastic flow and strain hardening. With increasing strain rate, the hardening slope reduces due to rise in specimen temperature, which was observed using an infrared camera at strain rate of 1/s. Thermal softening became more noticeable at higher strain rates where adiabatic heating caused stress-strain slope to become negative. At large strain, the material became rubbery rendering the failure strain to become indistinguishable. This signifies the importance of incorporating thermal effects in developing a full constitutive model, which is present in the next chapter. Accurate constitutive models for the epoxy matrix is required for the accurate determination of strain rate dependent cohesive traction separation laws of the interface.

Chapter 6

CONSTITUTIVE MODEL FOR STRAIN RATE DEPENDENT LARGE DEFORMATION INELASTIC BEHAVIOR OF AN EPOXY RESIN

6.1 Introduction

Major part of the energy dissipation in composite occurs through interface debonding, localized yielding and cracking of matrix. As these events occur at the nano to micromechanical length scales, it becomes extremely difficult to isolate all the mechanisms involved solely through experiments. Therefore, various experimental methods are often used in conjunction with finite element modeling to gain a better understanding of deformation and failure mechanisms involved in polymer composites subjected to various loading scenarios [115,116]. For example, during an event of tensile failure in the fiber direction in fiber-reinforced polymer composites, failure initiates in the form of fiber breaks due to relatively lower strain to failure of fibers [117]. Individual fiber breaks are dynamic failure events that can trigger rate dependent interphase debonding and localized rate dependent resin plasticity. Once a critical number of fiber breaks locally cluster together, the composite fails catastrophically. Such behavior makes it extremely important to understand the localized damage, such as matrix yielding, microcracking and interfacial debonding that accompanies fiber breaks, in order to accurately predict the failure of these composites and ultimately

design better composites [118,119]. Fiber breakage within a composite is a highly dynamic process even when the applied loading rate in the composite is in quasi-static range [119–121]. When a fiber breaks, stress wave propagation occurs due to the dynamic release of stored elastic energy in the fiber and the local strain rates in the matrix reaches about 10^{6} /s and then rapidly drops to the macroscopic far-field strain rate in quasi-static range ($\sim 10^{-3}$ /s) as the dynamic effects subside. This event occurs within an extremely short time-span of around 50 nanoseconds in glass-epoxy composites [120]. Moreover, since the matrix is locally subjected to large plastic strains at high rates, adiabatic heating and thermal softening are likely to occur in the vicinity of fiber breakage. In order to accurately capture the progression of damage accompanying a fiber break using micromechanical FE models, there is a need to formulate a temperature and strain rate-dependent constitutive model for the epoxy matrix spanning from 10^{-3} /s to 10^{6} /s that can handle abrupt changes in strain rate and rapid loading and unloading.

Another important input to these micromechanical FE models of composite failure is the interfacial rate-dependent traction law that governs the interaction between fiber and matrix. These traction laws are extracted from FE modeling of the microdroplet experiments [5,11,55] in Chapter 7. During these experiments, the epoxy droplets are subjected to large strains with strain rates varying spatially within the droplet, until dynamic debonding occurs along the interface. Localized shearing of the matrix and rapid unloading that follows debonding are similar to the mechanisms described earlier. Again, accurate description of constitutive behavior of epoxy resin is required for numerical modeling of our microdroplet experiments and for the extraction of accurate strain rate dependent cohesive traction separation law of the interface as discussed in Chapter 7.

In Chapter 5, the general constitutive behavior of glassy polymer under monotonic compression loading is shown to consist of initial increase in stress-strain up to yield followed by post yield softening and strain hardening at large strain. For the prediction of the initial stress-strain response of polymers, significant contribution has been made by Mahieux and Reifsnider [122] in developing temperature dependent stiffness model, which was later modified by Richeton et al. [123] to include strain rate dependency as well. Other researchers [124–126] have used viscoelastic models using different combinations of spring and dashpot to predict the non-linear stress strain behavior up to yield when subjected to monotonic loading.

In amorphous glassy polymers, pure viscous flow takes place momentarily during yielding and this process is dependent on applied strain rate and temperature [111,127]. Eyring equation is commonly used to predict strain rate and temperature dependent yield stress, which is treated as a thermally activated process [128,129]. The molecular segmental mobility during yielding has been proposed to be similar to the ones during glass transition suggesting that the applied stress essentially reduces the T_g of the material to the test temperature until yielding occurs [99]. Roetling [111,113] proposed that more than one type of molecular segmental motion (α and β relaxation) is involved and the total stress is the sum of stresses carried out by various processes. Mulliken and Boyce [130] adopted a similar approach to capture the transition in yield behavior which is manifested by bilinear relation of yield stress with strain rate when plotted on a log scale. They also developed a physically based constitutive model consisting of spring and dashpot with α and β components to describe hardening at large strains. Richeton et al. [131] extended the capability of Eyring's model to predict the

yield stress beyond glass transition temperature by correlating the yield behavior to the secondary relaxation.

The exact mechanism behind strain softening that occurs immediately after yielding is still unclear [99]. This behavior has been attributed to the formation of localized shear bands and changes in structure (activation volume and internal viscosity) of the material [132,133]. Parallels have been drawn between the softening phenomenon in polymers and thixotropy in colloidal systems [99]. Post yield softening behavior has been described analytically by several researchers using damage models. Nemes and Spéciel [134] developed continuum damage model to describe rate-dependent response of composite laminates under dynamic loading. Frantziskonis and Desai [135] modeled strain softening by treating it as a result of non-homogeneity in the deformation and stress fields. Breemen et al. [136] modified elasto-viscoplastic Eindhoven Glassy Polymer (EGP) model to incorporate strain rate and temperature dependent strain softening in solid polymers.

Strain hardening has been linked to network density (via chemical crosslinking or network entanglement), molecular chain reorientation and alignment [99–103]. Mechanisms behind strain rate and temperature dependence of strain hardening is different from yielding [103]. Arruda et al. [114] modeled strain hardening by decomposing inelastic deformation into non-dissipative internal back stress component, and the remaining dissipative plastic work contributing to heat generation. Pan et al. [137] determined inelastic heat fraction and used multiplicative factors to incorporate thermal softening at high strain rate in their constitutive model. While modeling the hardening behavior, especially at high rates of loading, it is important to consider thermal softening due to adiabatic softening as strain rate and thermal effects are often coupled.

Polymeric materials are also known to exhibit stress relaxation when the displacement is held constant after being subjected to a certain strain rate, where the material relaxes towards an equilibrium state. Time-dependent standard viscoelastic spring and dashpot models work well in describing the relaxation process in polymers [124,125]. Bergstrom and Boyce [138] modeled this behavior by using two networks in parallel – one captures the equilibrium state and the other predicts the time-dependent deviation from the equilibrium, which is based on reptational motion of molecules.

In the previous chapter, test methods were developed to experimentally characterize high strain rate properties of polymer resin over large strains. Hopkinson bar (10³/s to 10⁴/s strain rate) tests on DER 353 epoxy resin exhibited thermal softening resulting in complete absence of hardening at large strain, which led to the experimental investigation on temperature effects presented in this chapter. Also, stress relaxation tests at different loading rates were conducted to determine model parameters for the development of a comprehensive constitutive model. In this chapter, an algorithm based on an incremental approach to predict full stress-strain response for an epoxy resin subjected to compressive loading is developed, which includes estimation of rise in specimen temperature to predict thermal softening. Model predictions for different loading/unloading scenarios, strain rate jumps and stress relaxation are presented.

6.2 Development of Constitutive Model

Constitutive models for dynamic behavior of glassy polymers that account for all aspects of loading scenarios, as mentioned in the previous section, is limited in the literature. Arruda et al. [114] developed a strain rate dependent viscoelastic-viscoplastic constitutive model that accounts for temperature and thermomechanical coupling over large strain of glassy polymers. Thermal softening in the material model was predicted based on the concept that a part of inelastic deformation contributes to strain hardening, which is not dissipative, and the remaining portion contributes to heat generation due to plastic work. However, model predictions were done below glass transition temperature and only up to a strain rate of 0.1/s. The Bergstrom and Boyce model [138] was developed for the prediction of strain rate dependent large strain response of elastomeric materials like rubber and biomaterials. The model is also applicable for glassy polymers above glass transition temperature, where the material behavior is rubber-like. The model decomposes the material response into equilibrium stress state and timedependent deviation from the equilibrium state. The model can predict large strain response for cyclic loading, stress relaxation and creep.

Mulliken and Boyce [130] developed a constitutive model that can predict high strain rate (10^4 /s) response of glassy polymers by taking into account different molecular motions that become active at different frequency regimes. However, thermal softening of the material due to adiabatic heating, which is a very important aspect of the material response at high strain rate, was not taken into consideration. Chen and Zhou [139] modified the Ludwig equation, which first term in the Johnson Cook model to account for the strain-softening portion of the stress strain curve. Model predictions were done from quasi-static to Hopkinson bar strain rate range, and the yield stress was

accurately predicted over this range. However, this constitutive model is only applicable for small strain prediction. Pan et al. [137] also modified the first term of the Johnson Cook model to account for the post yield softening, plastic flow and strain hardening. The effect of temperature and strain rate were incorporated using multiplicative terms. Thermal softening was included for high strain rate prediction, where a strain increment method was implemented to estimate the rise in temperature. However, the model was still limited to below glass transition temperature range.

Richeton et al. [140] developed a three-dimensional constitutive model to describe large strain response of glassy polymers at high rates and above T_g where the material enters rubbery region. Predictions were done up to a strain rate of 6500/s. Although it is a robust constitutive model, stress relaxation was not included in the model and it was noted by the authors that the adiabatic heating at high strain rates was not properly described. One reason could be due to the use of same value of inelastic heat fraction over the entire range of plastic strain, which might not be the case for most polymers [141].

In this chapter, a constitutive model is developed that is valid for a wide range of strain rates (from 10^{-3} /s to 10^{4} /s) and temperatures (from ambient to above T_g) including thermal softening at high strain rates. As such, this model considers the change in the state of the polymer from glassy to rubber-like as the temperature of the material rises above T_g. The model can also handle abrupt changes in loading rates, including zero strain rate, i.e. stress relaxation.

The algorithm developed for the description of viscoelastic constitutive relationship is depicted in the flowchart presented in Figure 6.1. Strain – time profile and the initial temperature of the material serve as initial conditions for the calculation.

At each incremental time step, strain rate, stress and temperature are calculated and updated for use in the subsequent increments. First step is to categorize if the material is being loaded or unloaded, or if the deformation is held constant (stress relaxation). If the strain rate is negative, stress value is reduced at a slope equal to the modulus based on the unloading strain rate and current temperature. If the strain rate is zero, relaxation occurs and the reduction in stress value is calculated based on the previous known positive strain rate, current temperature and strain level. For positive strain rates, it should be determined whether the material has yielded. Then, relevant equations are applied for the calculation of stress depending on whether the material is in elastic or plastic state. For high rate of loading, thermal softening has been incorporated through the estimation of heat generation due to plastic work and the assumption of adiabatic heating.



Figure 6.1 Flowchart showing the algorithm for time and temperature dependent normal stress strain response based on compression loading with incremental approach

6.2.1 Decomposition of stress strain response

A typical stress strain response of DER 353 resin subjected to monotonic compression loading exhibits initial increase in stress until yield followed by post yield softening, plastic flow and finally strain hardening at large strains (Figure 6.2). The model decomposes the stress-strain response into elastic and plastic regimes based on the yield stress, which is defined as a point $(d\sigma/d\varepsilon = 0)$ where pure viscous flow takes place momentarily (Figure 6.2). Stress strain response up to yield as a function of strain

rate and temperature is described using a spring and dashpot model. Eyring type equation is used to predict strain rate and temperature dependent yield stress. For the prediction of post-yield behavior, the plastic flow direction obtained at different temperatures is used.



Figure 6.2 Stress strain curve is decomposed into elastic and plastic regime. Three different sets of equations are used to model elastic and plastic portion of the curve, and yield stress

6.2.2 Determination of yield function

Accurate determination of yield stress and strain is very crucial in the development of constitutive model as it links the elastic and plastic portion of the curve. For each incremental step, it needs to be determined whether the material is in elastic or plastic state for the given strain rate and temperature. First, yield stress is calculated using Eyring equation and elastic trial stress is calculated using viscoelastic model for the given condition ($\dot{\varepsilon} \& T$). If the elastic trial stress is less than the yield stress, then the material is still in elastic region, and the stress value is updated with the elastic trial

stress. However, if the elastic trial stress is greater than the yield stress, the material has yielded and the yield strain is calculated. Subsequently, plastic strain is determined and the elastic trial stress is replaced by plastic trial stress.

6.3 Determination of Model Parameters

In this section, experimental work for the determination of strain rate and temperature dependent stress strain response and stress relaxation behavior are presented. The experimental results are then used to determine the model parameters.

6.3.1 Stress-strain response for monotonic loading (strain rate > 0)

6.3.1.1 Experimental determination of strain rate dependent properties

Strain rate dependent properties of DER 353 epoxy resin determined using Instron testing machine for lower rates and split Hopkinson pressure bar for higher rates have been presented in previous chapter. True stress-strain response for strain rates 0.001/s to 1/s is presented in Figure 6.3a. At least five specimens were tested at each strain rate. The overall trend of the stress-strain response is similar for all four strain rates – initial increase in stress is observed until the yield point is reached, which is followed by strain softening and plastic flow. The initial slope of the stress strain curve slightly increases with strain rate. There is a significant effect of strain rate on the yield stress, which increases from 85 MPa at 0.001/s to 220 MPa at 12,000/s strain rate. At higher strain rates, specimen gets less time to dissipate the heat generated due to plastic work, resulting in rise in specimen temperature. Thermal softening at high strain rates (5,000/s and 12,000/s) result in complete absence of strain hardening at large strains (Figure 6.3b). Estimation of specimen temperature assuming complete conversion of plastic work into heat energy shows that the resin enters glass transition temperature at around 45% - 50% strain level, and becomes completely rubbery when it reaches about 70% strain.



Figure 6.3 Stress strain response of DER 353 resin at 25°C and strain rates of (a) 0.001/s to 1/s shows typical post yield softening and strain hardening, (b) 1000/s to 12,000/s shows thermal softening at large strain due to adiabatic heating

6.3.1.2 Experimental determination of temperature dependent properties

Thermal softening of the polymeric materials due to adiabatic heating at high strain rate is inevitable, especially for materials with low T_g . Temperature dependent response of the material needs to be considered to develop a comprehensive constitutive model. Dynamic mechanical analysis was carried out using Mettler DMA 861 for the determination of T_g . Experiments were conducted on right cylinder specimens (6 mm diameter and 1.8 mm thick) in shear mode at 1 Hz frequency over a temperature range of 25°C – 180°C while maintaining a constant shear stress of 1.77 kPa.

When considering the mechanical aspect of a material, T_g based on storage modulus is used in general. Figure 6.4 shows the T_g range, the beginning of which is marked by an abrupt change in the storage modulus at around 70°C spans to about 110°C. Above 110°C, the material becomes completely rubbery and the storage modulus drops to a very small value.

To obtain full stress-strain response from ambient temperature till the end of the T_g range, quasi-static tests were conducted at strain rates of 0.001/s, 0.01/s and 0.1/s on right cylinder specimen under isothermal conditions at 25°C, 50°C, 70°C, 80°C, 90°C, 100°C, 110°C and 120°C. At least five replicates were tested for each test temperature. Yield stresses at different strain rates and temperatures are presented in Table 6.1. Figure 6.5 shows that yield stress, modulus and compressive strength are significantly affected by temperature. At the T_g range, yield stress drops significantly above 70°C as the material behavior becomes more rubber-like. The post yield softening also begin to disappear at 80°C. Above 100°C, there is no definite yield point $(d\sigma/d\varepsilon = 0)$ and the material behaves more like an elastomer exhibiting strain hardening.

Temperature	Strain rate	Yield stress (MPa)
25°C	0.001/s	85.1 ± 0.4
	0.01/s	94.6 ± 1.1
	0.1/s	104.7 ± 1.1
50°C	0.001/s	75.4 ± 1.8
	0.01/s	86.3 ± 2.1
	0.1/s	95.7 ± 3.6
70°C	0.001/s	69.2 ± 1.5
	0.01/s	82.0 ± 2.4
	0.1/s	89.4 ± 3.1
80°C	0.001/s	32.1 ± 0.8
	0.01/s	50.6 ± 1.6
	0.1/s	58.1 ± 1.9
90°C	0.001/s	13.5 ± 0.5
	0.01/s	28.9 ± 1.0
	0.1/s	40.3 ± 1.4

 Table 6.1 Strain rate and temperature dependent yield stress



Figure 6.4 DMA results showing T_g range (~70°C to 110°C)



Figure 6.5 Temperature dependent stress strain response under isothermal condition at a strain rate of 0.001/s

Strain rate effects on stress strain response of epoxy resin at 100°C, 110°C and 120°C, where the material behaves like rubber, was studied to understand the rate dependent scaling law. For 100°C, Figure 6.6a shows the transformation of the material response from rubber-like at 0.001/s to glass-like at 0.1/s, exhibiting initial linear increase in stress strain followed by a distinct yield point. For 110°C at 0.1/s, similar trend is observed as for 100°C but to a lesser degree (Figure 6.6b). Whereas for 120°C, strain rate effect had minimal effect on stress strain response (Figure 6.6c). The overall stress strain profile at higher strain rate is similar to the one at 0.001/s strain rate. Therefore, for strain rate dependent scaling purposes, the post-yield portion of the stress strain curve can be vertically shifted.





Figure 6.6 Stress strain response for DER 353 epoxy resin at strain rates 0.001/s, 0.01/s and 0.1/s at temperatures (a) 100°C, (b) 110°C, (c) 120°C

Stress strain response under 0.001/s strain rate for temperatures at 120°C and 150°C are identical (See Figure 6.7). Epoxy resin at these temperatures exhibits a pure elastic rubbery behavior. At this temperature range, the material is essentially at equilibrium state throughout the loading and does not exhibit any time dependent deviation, i.e. no stress relaxation or strain rate effects. In addition, load unload cyclic tests done at 0.001/s strain rate and 120°C shows no plastic deformation (See Figure 6.8). This phenomenon is further corroborated by the DMA results above T_g where the storage modulus representing the elastic component of the material drops to about 5 MPa and remains constant till 200°C (Figure 6.9). Whereas the loss modulus, which represents the viscous component, drops to zero, suggesting only elastic component remains. Such temperature dependent behavior above T_g for glassy polymers have been reported in the literature [140,142,143]. The transition from rate dependent glassy material to elastic rubber above T_g has been attributed to temperature dependent

viscosity in spring and dashpot models [144]. The time dependent component of the material arises from the viscosity of the dashpot. As the viscosity decreases, the material behavior becomes more elastic in nature. As the temperature is increased further above T_g , rate dependence can only be seen at much higher loading rates. This behavior can be incorporated in the constitutive model by predicting the temperature and strain rate dependent yield stress using Eyring type equation as will be discussed in later sections.



Figure 6.7 Stress strain response at 120°C and 150°C tested under a strain rate of 0.001/s show identical behavior



Figure 6.8 Load unload tests at 0.001/s and 120°C for DER 353 epoxy resin shows complete recovery up to a strain of 60%



Figure 6.9 Storage and loss modulus for DER 353 epoxy resin above T_g

6.3.1.3 Prediction of stress strain response up to yield point

Analytical solution for a viscoelastic standard linear solid model subjected to monotonic loading (Eq. (6.1)) have been calibrated using experimental results to predict stress strain response up to yield as a function of temperature and strain rate. Eq. (6.2) and (6.3) predict the temperature dependent elastic modulus of the spring. Strain rate effects have been incorporated in the model by using a scaling factor, $r(\dot{\varepsilon})$ which is based on strain rate dependency of the elastic modulus of the material (Eq. (6.4)). Fitting parameters are presented in Table 6.2. A comparison of experimental and model prediction of stress strain response subjected to 0.001/s strain rate at different temperatures is presented in Figure 6.10.

$$0 < \sigma < \sigma_{y} \qquad \sigma_{e}(\varepsilon, \dot{\varepsilon}, T) = \tau \cdot E(T) \cdot r(\dot{\varepsilon}) \cdot \dot{\varepsilon} \cdot \left(1 - \exp\left(-\frac{\varepsilon}{\tau \dot{\varepsilon}}\right)\right) \qquad (6.1)$$

$$T \le 343 K \qquad E(T) = m_T T + c_T \tag{6.2}$$

$$343K < T < 373K \qquad E(T) = A_T \exp\left(-\frac{T}{B_T}\right) + y_T \qquad (6.3)$$

$$r(\dot{\varepsilon}) = a_{SR} + b_{SR} \dot{\varepsilon}^{c_{SR}} \tag{6.4}$$

τ (sec)	50
m_T (MPa/K)	7750.7
c_T (MPa)	-15.73
A_T (MPa)	4.88×10^{11}
	18.1
y_T (MPa)	-494
a_{SR}	1.083
b_{SR}	0.043
C _{SR}	0.299

 Table 6.2 Curve fitting parameters



Figure 6.10 Curve fitting of pre-yield portion of the stress strain curve at different temperatures

6.3.1.4 Prediction of yield stress

Yield stress varies bi-linearly as a function of strain rate when plotted on a semilog scale (Figure 6.11), suggesting more than one type of molecular segmental motion are involved at higher strain rates [111]. Alpha relaxation, which is associated with rotational freedom in the segments between crosslinks, is involved at lower strain rates. Whereas, at higher strain rates, since there is less time for the polymer chains to reorient and slide, side chain motion also gets activated resulting in beta relaxation [112], which occurs at about 100/s strain rate for the epoxy resin DER 353 considered in this study.

Yield stress as a function of strain rate and temperature is modeled using Eyring type equation [99,113]. For the determination of the Eyring model parameters (Eq. (6.5)), the yield stress vs. strain rate curves are decomposed into alpha and beta relaxation processes. The model parameters activation volumes (v_{α} and v_{β}), activation energies (E_{α} and E_{β}), pre-exponential factors ($\dot{\varepsilon}_{0,\alpha}$ and $\dot{\varepsilon}_{0,\beta}$) and model constant (C_{α} and C_{β}) are then determined for the particular process (α and β contribution). For the prediction of the yield stress above T_g , WLF equation is incorporated in the Eyring equation (Eq. (6.6)) as proposed by Richeton et al. [131]. Although T_g occurs over a range of temperature, a single temperature (70°C) corresponding to the initial point in the transition range is used in the equation. 70°C was chosen because of the abrupt drop in the yield stress observed from the quasi-static tests (Figure 6.13) as the material enters T_g range. Model parameters presented in Table 6.3 were obtained using yield stress for test temperature of 25°C over a strain rate of 0.001/s to 12,000/s and then predictions were made for higher temperatures. Strain rate dependent yield stress predicted above T_g (at 80°C and 90°C) are in good agreement with the experimental findings (Figure 6.12). Eyring model predictions for temperature dependent yield stress at strain rates 0.001/s and 0.1/s also show good correlation with the experimental data (Figure 6.13).

$$T < T_g \qquad \qquad \sigma_y(\dot{\varepsilon}, T) = \sum_i \frac{2kT}{v_i} \sinh^{-1} \left(\frac{1}{C_i T} \frac{\dot{\varepsilon}}{\dot{\varepsilon}_{0,i}} \exp\left(\frac{E_i}{kT}\right) \right) \qquad (6.5)$$

$$T \ge T_{g} \qquad \sigma_{y}(\dot{\varepsilon}, T) = \sum_{i} \frac{2kT}{v_{i}} \sinh^{-1} \left(\frac{1}{C_{i}T} \frac{\dot{\varepsilon}}{\dot{\varepsilon}_{0,i}} \frac{\exp\left(\frac{E_{i}}{kT}\right)}{\exp\left(\frac{\ln(10) \cdot c_{1}^{g}(T - T_{g})}{c_{2}^{g} + T - T_{g}}\right)} \right)$$
(6.6)

 Table 6.3 Model parameters for Eyring equation

k (J/K)	1.381×10^{-23}
v_{α} (m ³)	$2.119 imes 10^{-27}$
v_{β} (m ³)	5.147×10^{-28}
C_{α} (1/K)	$1.00 imes 10^9$
C_{β} (1/K)	$4.24 imes 10^8$
$\dot{\mathcal{E}}_{0,lpha}$	1.00×10^{3}
$\dot{arepsilon}_{0,eta}$	100
E_{α} (J)	$1.97 imes 10^{-19}$
E_{β} (J)	$1.00 imes10^{-19}$
T_g (°C)	70
C_1^g	17.44
c_2^g (°C)	51.6



Figure 6.11 Yield stress shows bilinear relation with strain rate when plotted on a semi-log scale. Yielding at high strain rates is comprised of both α and β relaxation



Figure 6.12 Strain rate dependent yield stress predictions using Eyring model



Figure 6.13 Temperature dependent yield stress predictions using Eyring model

6.3.2 Prediction of post yield plastic response

Temperature dependent post yield response of the epoxy is predicted by first describing the shape of the curve (Eq. (6.7) - (6.9)) and then adding the corresponding yield stress predicted by Ree-Eyring model (Eq. (6.10)). As mentioned earlier, the initial post-yield softening portion, observed at lower temperature under isothermal condition at quasi-static loading condition, becomes less prominent as the material approaches Tg range (Figure 6.5). The shape of the post yield curves for 25°C to 70°C are essentially the same and are modeled using Eq. (6.7) (Figure 6.14). The behavior then transitions to almost no post yield softening at 80°C, which is described using Eq. (6.8). Fitting parameters for Eq. (6.7) and (6.8) are presented in Table 6.4. To avoid overlapping of the stress strain curves during prediction between 70°C and 80°C, the stress values are linearly interpolated for a given strain using Eq. (6.7) and (6.8). The material becomes completely rubbery at around 110°C as evidenced by the DMA results (Figure 6.4).
Prediction of stress strain response between 80°C and 120°C is done by linearly interpolating the stress values for a given strain as mentioned before.

$$25^{\circ}C < T < 70^{\circ}C \qquad \qquad \sigma_{shp}(\varepsilon_p) = A + \frac{B}{1 + 10^{(C - \varepsilon_p)D}} + E\varepsilon_p^{N} \qquad (6.7)$$

$$80^{\circ}C < T < 120^{\circ}C \qquad \qquad \sigma_{shp}(\varepsilon_p) = a\varepsilon_p^{\ b} \qquad (6.8)$$

$$T \ge 120^{\circ}C \qquad \qquad \sigma_{shp}(\varepsilon_p) = a(1 - e^{b\varepsilon_p}) \tag{6.9}$$

$$\sigma_{p}(\varepsilon, \dot{\varepsilon}, T) = \sigma_{y}(\dot{\varepsilon}, T) + \sigma_{shp}(\varepsilon_{p})$$
(6.10)

Parameters	Temperature	
A (MPa)		-15.33
B (MPa)		16539
С	T < 70°C	-0.5478
D	1 < 70 C	-5.4774
E (MPa)		301.15
N		3.02
a (MPa)	$T = 80^{\circ}C$	151.73
b	1 - 60 C	2.45
a (MPa)	T – 100°C	118.7
b	1 = 100 C	3.657
a (MPa)	$T > 120^{\circ}C$	-1.05
b	$1 \le 120$ C	4.64

 Table 6.4 Curve fitting parameters



Figure 6.14 Curve fitting of post yield plastic flow for temperatures $25^{\circ}C < T < 70^{\circ}C$

6.3.3 Prediction of plastic stress with thermal softening

If adiabatic conditions exist, thermal softening is also taken into consideration by calculating the rise in material temperature using Eq. (6.11), assuming all the plastic work is converted to heat.

$$\Delta T_i = \frac{\beta}{\rho c} \int_{\varepsilon_y}^{\varepsilon_i} \sigma(\varepsilon, \dot{\varepsilon}) \cdot d\varepsilon$$
(6.11)

Where, β is inelastic heat fraction, ρ is density (1150 kg/m³) and *c* is specific heat capacity of the epoxy specimen (1.11 kJ/kg K). The inelastic heat fraction, β can be estimated by determining the specimen temperature through the intersection of the high rate curve exhibiting thermal softening, and isothermal curves for different temperatures at the given strain rate. An example is shown in Figure 6.15, where the experimental curve, true stress versus true plastic strain, obtained for a strain rate of 5000/s has been plotted against isothermal stress strain curves at 25°C, 50°C and 70°C. The high rate isothermal stress strain curves have been predicted by vertically shifting the quasi-static curves based on rate dependent yield stresses. The experimental curve shows strain softening immediately after yielding followed by thermal softening at large strain. There is no rise in specimen temperature until a plastic strain of 12%, where both the isothermal curve and the experimental curve overlap. The specimen temperature increases to 50°C and 70°C when the plastic strain reaches about 26% and 35%, respectively (Figure 6.16). The inelastic heat fraction was then back calculated by inputting temperature increase (ΔT) in Eq. (6.11). The evolution of inelastic heat fraction as a function of plastic strain is presented in Figure 6.17.



Figure 6.15 Estimation of specimen temperature through intersection of experimental curve and high strain rate isothermal curves



Figure 6.16 Solid line showing estimated rise in temperature assuming complete conversion of plastic work into heat. Scattered data points showing temperature of the specimen estimated through intersection of curves



Figure 6.17 Estimated inelastic heat fraction as a function of plastic strain

Figure 6.18 shows an example for the calculation of stresses with thermal softening under adiabatic condition. The dotted line shows the predicted stress and the solid lines represent stress-strain response predicted using Eq. (6.10) under isothermal condition for strain rate of 5000/s at temperatures 25°C to 100°C. It is not possible to simultaneously predict both stress and temperature for a new strain increment. Therefore, to predict the stress value with thermal softening for step *i* (in Figure 6.18), a trial plastic stress ($\sigma_{p,trial}$) is first calculated assuming no change in temperature from the previous step $(\sigma_{n,i-1})$ by following the shape of the isothermal curve for the given strain rate. The estimated rise in temperature due to plastic work during this strain increment is calculated. Then, finally the plastic stress $(\sigma_{p,i})$ is calculated based on the estimated rise in temperature of the material knowing the current strain rate using Eq. (6.12). If the strain increment is kept small enough, the error in the calculation of plastic work is negligible and does not affect the prediction results. Figure 6.19 shows good agreement between the experimental result and model prediction of stress-strain response for DER 353 epoxy resin tested at ambient temperature under a strain rate of 5000/s including thermal softening due to adiabatic heating.

$$\sigma_{p}(\varepsilon_{i},\dot{\varepsilon},T_{0}+\Delta T_{i}) = \sigma_{v}(\dot{\varepsilon},T_{0}+\Delta T_{i}) + \sigma_{shp}(\varepsilon_{i},T_{0}+\Delta T_{i})$$
(6.12)



Figure 6.18 Prediction of stress strain response at high strain rate considering thermal softening. Solid lines represent stress strain response for different temperatures under isothermal condition at 5000/s strain rate



Figure 6.19 Comparison between experimental and model prediction with thermal softening show excellent agreement for stress strain curve at 5000/s

6.3.4 Stress relaxation (strain rate = 0)

6.3.4.1 Stress relaxation tests

Relaxation in a viscoelastic material can be described by two parameters: characteristic relaxation time and equilibrium stress. A series of relaxation tests as a function of strain rates and temperatures were conducted to determine these parameters. Specimens were monotonically loaded at different strain rates (0.001/s, 0.01/s and 0.1/s) and the displacement was held constant for 10 mins at different strain levels (13%, 18% and 31%). At least three replicates were tested for each strain rate. When a viscoelastic material is loaded at a certain strain rate, the resulting stress is always higher than the equilibrium stress. If the strain is kept constant, the material will relax and the stress will decrease and approach the equilibrium stress asymptotically over time.

Figure 6.20a shows stress-strain response for stress relaxation tests conducted at 90°C at different strain rates. When the strain is held constant, stress relaxes to about same equilibrium stress regardless of the applied strain rate. While reloading at a constant strain rate, the stress increases at a slope of the initial elastic modulus until it reaches a maximum point, which appears exactly like the initial yield point. The material then softens and finally merges with the original stress-strain curve which was monotonically loaded without any interruption.

Figure 6.20b shows the relaxation curves for the same tests at 13% strain level. Characteristic relaxation time was determined by fitting the relaxation curves to an analytical solution (Eq. (6.13)) of a standard spring and dashpot solid model (Figure 6.21).

$$\sigma(\dot{\varepsilon}, T, t) = \sigma_e(T) + \sigma_1 \exp\left(-\frac{t}{\tau(\dot{\varepsilon})}\right)$$
(6.13)

Where, σ_e is the equilibrium stress, τ is the characteristic relaxation time. Relaxation time was found to be dependent only on the applied strain rate, which decreased with increasing strain rate.

Stress equilibrium path was also determined at different temperatures (25°C to 90°C) through a series of stress relaxation at several strain levels. Force displacement response to obtain stress equilibrium paths at 50°C is presented in Figure 6.22. The resulting equilibrium stress-strain response was fitted with an appropriate equation, which is presented in next section.



Figure 6.20 (a) Under different strain rates, stress relaxation tests are carried out at different strain levels (dotted lines). Stress strain response at 90°C under monotonic loading (0.001/s strain rate) is shown by solid line for comparison (b) Stress time plot shows strain rate dependent relaxation



Figure 6.21 Characteristic relaxation times are calculated based on analytical solution of a standard solid model. Eq. (6.13) has been used to fit the relaxation curves. Fitting parameters are presented in Table 6.5



Figure 6.22 Raw load displacement response from a series of stress relaxation tests carried out to determine the stress equilibrium path

6.3.4.2 Modeling stress relaxation

Experimental results showed that the characteristic relaxation time for epoxy resin DER 353 is significantly affected by the applied strain rate. The material relaxed quickly (reduced relaxation time) with the increase in applied strain rate. When plotted on a log-log scale, relaxation time and inverse of strain rate have a linear relation (Figure 6.23), which can be used to estimate the relaxation time for higher strain rates (Eq. (6.14)). The stress equilibrium paths (Figure 6.24), which depend on the temperature and strain level to which the material was deformed, was described using Eq. (6.15). The parameters used to fit the relaxation and stress equilibrium curves are presented in Table 6.5.



Figure 6.23 Relaxation time shows linear relation with inverse of strain rate on a log-log plot



Figure 6.24 Curve fitting stress equilibrium path at different temperatures

$$\tau(\dot{\varepsilon}) = 10^{a_e + b_e \log\left(\frac{1}{\dot{\varepsilon}}\right)} \tag{6.14}$$

$$\sigma_e(T) = A_e(T) \tan^{-1} \left(A_e(T) \varepsilon \right) + B_e(T) \left[(C_e(T) \varepsilon) \exp(-D_e(T) \varepsilon) \right]^{M_e(T)} + E_e(T) \varepsilon^{N_e(T)}$$
(6.15)

a_{e}	-0.418	b_{e}	0.695							
	Test Temperature (°C)									
	25°C	50°C	70°C	80°C	90°C	100°C	110°C - 150°C			
A_{e}	30	21.3	14.41	10.34	7.49	4.02	3.63			
B _e	49.78	36.22	34.9	11.17	$2.00 imes 10^{14}$	-1.37×10^{14}	-1.29×10^{15}			
C_{e}	54.1	54.96	53.8	44.62	$7.28 imes 10^{16}$	$2.7 imes 10^{15}$	$4.00 imes 10^{16}$			
D_e	22.64	21.95	26.45	18.96	$4.77 imes 10^{18}$	$5.23 imes 10^{16}$	$4.59 imes 10^{17}$			
E _e	1.246	1.25	1.32	1.65	1.05×10^{25}	6.15×10^{21}	$4.55 imes 10^{21}$			
M _e	183.6	145.92	144.3	120.08	47.33	43.53	36.4			
N _e	3.4	3.4	3.7	3.64	3.29	3.51	3.58			

Table 6.5 Curve fitting parameters for stress equilibrium path

6.3.5 Unloading (strain rate < 0), reloading and change in strain rate

Unloading occurs at a slope comparable to the initial elastic modulus. Consequently, unloading after the material has yielded results in plastic deformation. An example of this can be seen in the unloading portion of the high rate stress strain response (Figure 6.3). In the constitutive model, when the strain rate becomes negative, the slope of the curve is calculated for the unloading strain rate at the given temperature using Eq. (6.16).

Similarly, when reloading or while increasing the strain rate abruptly during loading from any given strain level, the stress does not jump instantly to a higher value corresponding to the new strain rate as would be predicted by standard models such as Johnson-Cook model. Instead, the stress follows the path of the slope of the elastic modulus (Eq. (6.16)) until the curve intersects the stress-strain path for the material which is loaded monotonically. The logic presented in Eq. (6.17) is used for such loading conditions. If the strain rate is decreased compared to the previous time step, the material relaxes (first term in Eq. (6.18)) until the stress values decreases to the ones corresponding to the lower strain rate, after which it follows the path for the new strain rate.

$$E(\dot{\varepsilon},T) = \frac{\sigma(0.003,\dot{\varepsilon},T) - \sigma(0.001,\dot{\varepsilon},T)}{0.003 - 0.001}$$
(6.16)

$$\dot{\varepsilon}_{i} \geq \dot{\varepsilon}_{i-1} \quad \sigma_{i}(\varepsilon_{i}, \dot{\varepsilon}_{i}, T_{i}, t) = \min \begin{pmatrix} \sigma(\varepsilon_{i}, \dot{\varepsilon}_{i}, T_{i}) \\ \sigma_{i-1} + E(\dot{\varepsilon}_{i}, T_{i}) \cdot \dot{\varepsilon}_{i} \Delta t \end{pmatrix} \dots \dots \dots [Eq.6.1 \& 6.10]$$
(6.17)

$$\dot{\varepsilon}_{i} < \dot{\varepsilon}_{i-1} \qquad \sigma_{i}(\varepsilon_{i}, \dot{\varepsilon}_{i}, T_{i}, t) = \max \begin{pmatrix} \sigma(\dot{\varepsilon}_{i}, T_{i}, t) \\ \sigma(\varepsilon_{i}, \dot{\varepsilon}_{i}, T_{i}) \end{pmatrix} \dots \dots \dots \dots [Eq.6.13]$$
(6.18)

6.4 Model Predictions

Model predictions for different loading cases are presented in this section. While comparing the model prediction with the experimental results, only the portion of the experimental curve that were used for the determination of model parameters are shown in the figures. Figure 6.25 shows temperature dependent stress strain prediction for monotonic loading at a strain rate of 0.001/s. Portion of the experimental curves used to obtain model parameters are depicted by hollow dots (°). The initial non-linear stressstrain response up to yield resulting from temperature dependent viscoelastic behavior is accurately predicted by the spring and dashpot models. Prediction of temperature and strain rate dependent yield stress using Eyring equation is critical here as it influences the post yield response and links the elastic and plastic behavior. Figure 6.12 shows good agreement in the prediction of yield stresses and Figure 6.25 shows these yield stresses can be used for the construction of smooth stress strain curves linking elastic and plastic region. Post yield softening is present up to 70°C, which is followed by strain hardening. Appropriate equations (Eq. (6.7) - (6.9)) are employed to ensure the post yield softening begin to vanish at higher temperatures and linear interpolations are used so that the curves do not intersect with each other for different temperatures.

For temperatures above the T_g range (i.e. above 100°C), the yield stress becomes zero when subjected to a strain rate of 0.001/s (Figure 6.6). As the strain rate is increased, the epoxy resin start to exhibit glassy behavior even above 100°C. Modeling of this behavior is presented in Figure 6.26, where the material shows a distinct yield stress at 100°C under 0.1/s strain rate. Comparison between model prediction and experimental results for temperature 110°C under strain rates of 0.001/s and 0.01/s are shown in Figure 6.27 and Figure 6.28. Stress strain prediction for 120°C under 0.001/s strain rate is presented in Figure 6.29. As evidenced from the experiments, the same curve will be used for temperatures up to 150°C at 0.001/s strain rate. For higher strain rates, the curves are shifted vertically depending on the yield stress predicted by Eyring equation (Eq. (6.6)) for the given temperature and strain rate.



Figure 6.25 Model prediction for stress strain response at different temperatures under quasi-static (0.001/s) loading rate. Portions of the experimental curves used to obtain model parameters are shown by hollow dots (\circ)



Figure 6.26 Comparison between experimental results (hollow dots) and model predictions (solid line) for stress strain response at 100°C under 0.001/s and 0.1/s strain rate.



Figure 6.27 Comparison between experimental result (hollow dots) and model prediction (solid line) for stress strain response at 110°C under 0.001/s strain rate



Figure 6.28 Comparison between experimental result (hollow dots) and model prediction (solid line) for stress strain response at 110°C under 0.01/s strain rate



Figure 6.29 Comparison between experimental result (scatter plot) and model prediction (solid line) for stress strain response at 120°C under 0.001/s strain rate

Model prediction for strain rates 0.001/s to 0.1/s at 25°C are shown in Figure 6.30. The overall trend of the post yield response – softening, plastic flow and hardening – is same for all strain rates. For higher strain rates ($\dot{\varepsilon} > 1000/s$), strain hardening is completely absent due to thermal softening caused by adiabatic heating during loading. Softening becomes more prominent when the material approaches the glass transition temperature (T_g), and this point begins to occur progressively at smaller strain level as the strain rate is increased (Figure 6.30b). Comparison between model prediction and experimental results show an excellent agreement at the strain rate of 5000/s (Figure 6.19). Model prediction up to a strain rate of 10^6 /s is presented in Figure 6.30b.



Figure 6.30 Stress strain prediction at strain rates (a) 0.001/s to 0.1/s, (b)10³/s to 10⁶/s shows thermal softening, which becomes more prominent and start to occur at lower strain levels with increasing strain rate

Strain – time input profile for stress relaxation test at 25° C is shown in Figure 6.31a. Applied strain rate is 0.01/s, which is interrupted at different strain levels (0.13, 0.18 and 0.31) with zero strain rate. Model prediction shows stress relaxation

approaching equilibrium stress when the displacement is held constant. While reloading, the stress increases at a slope, E corresponding to the applied strain rate until the curve intersects with the path which would have occurred had the material been loaded monotonically without interruption. Same rule applies during strain rate jumps, as presented in Eq. (6.17). This phenomenon is confirmed by the experimental results where the material is reloaded after stress relaxation (Figure 6.31b). Prediction of stress – time plot for stress relaxation tests at 0.001/s shows decay of stress to the equilibrium point which is in good agreement with the experimental results (Figure 6.32).

A case study for variable strain rate with a sudden jump in strain rate at elastic and plastic region during monotonic loading is presented in Figure 6.33. The strain rate is increased from 0.001/s to 1/s at different strain levels. Immediately following the change in strain rate, the stress increases at a slope, E corresponding to the new strain rate until it crosses path with the monotonically loaded curve as explained earlier. Finally, model prediction for load – unload case at 0.001/s strain rate is presented in Figure 6.34. When unloading occurs, the stress values decrease at a slope, E, regardless of whether the material is in elastic or plastic region.



Figure 6.31 (a) Input strain – time profile for stress relaxation tests at strain rate of 0.01/s, (b) Model prediction with relaxation at 13%, 18% and 31% strain level



Figure 6.32 Model output shows good correlation with stress relaxation experiment for stress time curve



Figure 6.33 (a) Input strain time profile for strain rate jump tests. Strain rate is suddenly increasing from 0.001/s to 0.1/s, (b) Model prediction for strain rate jump tests



Figure 6.34 (a) Input strain time profile for load unload tests, (b) Model prediction for load unload tests at elastic and plastic region

6.5 Discussion on Model Predictions

As mentioned earlier, the accuracy of the constitutive model prediction depends on yield stress predictions as it links the elastic and plastic regimes together. For the prediction of yield stress, Ree-Eyring model parameters were obtained by fitting the experimental yield stress obtained at 25°C over a strain rate range of 0.001/s to 12,000/s. Then, predictions were made for these strain rates up to 90°C. Independent experiments at higher temperatures (50°C, 70°C, 80°C and 90°C) at strain rates of 0.001/s, 0.01/s and 0.1/s were carried out to validate Ree-Eyring model predictions. Then, percentage error in the prediction was calculated by using the following equation:

$$Error = \left| \frac{\sigma_{y}^{\exp} - \sigma_{y}^{\text{mod}el}}{\sigma_{y}^{\exp}} \right| \times 100\%$$
(6.19)

The calculated percentage errors are presented in Table 6.6. The model prediction shows excellent correlation with the experiments up to 70°C with an error below 5%. Although the accuracy of the model start to diminish as the material enters Tg range, the accuracy of the model is still reasonable up to 90°C.

Strain rate Temperature 0.001/s 0.01/s 0.1/s50°C 1.9% 2.1% 3.7% 70°C 2.9% 1.6% 2.6% 80°C 33.8% 6.4% 10.2% 90°C 20.0% 15.0% 8.2%

Table 6.6 Percentage error in Eyring model prediction

Although Ree-Eyring model parameters were obtained from experiments at 25°C, model predictions clearly shows good correlation for yield stresses from 25°C up to 90°C (Figure 6.12). As expected, model prediction shows increased yield stress as the temperature is decreased. However, additional experiments need to be carried out below 25°C to validate the predictions.

The validity of the model at lower strain rate can be checked using the yield stress obtained from the equilibrium tests. The equilibrium yield stress corresponds to zero strain rate, which means the yield stress cannot fall below this value. For 25° C, equilibrium yield stress is about 71 MPa. This value corresponds to Ree-Eyring prediction for strain rate of 10^{-5} /s, which can be considered as the lower limit for strain rate prediction. As for the upper limit for the strain rates, predictions made by molecular dynamics simulation for similar epoxy show a yield stress of about 300 MPa when subjected to a strain rate of 10^{9} /s [145]. This value can be considered a theoretical maximum. Ree-Eyring model predicts a yield stress of this value at a strain rate of 10^{6} /s. Therefore, this strain rate can be marked as the upper limit on model's predictive capability.

6.6 Multiaxial State of Stress

Experimental results from uniaxial tests can be used in FE modeling to account for multiaxial state of stress by employing an equivalent plastic strain increment. Using the equivalent plastic strain, the multiaxial stress state can be reduced to a single scalar quantity called equivalent stress. The equivalent yield stress can be directly compared to the von Mises equivalent stress for the determination of the onset of plastic behavior in the material and subsequent strain hardening. The equivalent plastic strain can be calculated as follows:

$$\varepsilon_{eq}^{p} = \varepsilon^{p}|_{0} + \int_{0}^{t} \sqrt{\frac{2}{3}} \dot{\varepsilon}^{p} \dot{\varepsilon}^{p} dt \qquad (6.20)$$

Where, $\varepsilon^p|_0$ is the initial equivalent plastic strain and $\dot{\varepsilon}^p$ is plastic strain rate. Once the equivalent plastic strain is calculated, the equivalent yield stress can be calculated directly from the constitutive model developed from uniaxial tests as a function of equivalent plastic strain, strain rate and temperature. The yield function then becomes:

$$f = \sigma_{vM} - \sigma_y \left(\varepsilon_{eq}^p, \dot{\varepsilon}_{eq}^p, T \right) = 0$$
(6.21)

Where, $\sigma_{\nu M}$ is von Mises equivalent stress as given by following expression:

$$\sigma_{\nu M} = \sqrt{\frac{3}{2} \boldsymbol{\sigma}' : \boldsymbol{\sigma}'} \tag{6.22}$$

Where, σ' is deviatoric stress tensor.

Due to pressure sensitivity of glassy polymers, the behavior of resin in uniaxial tension and compression tests might be different. Triaxial tension reduces the yield stress and changes the failure mode to cavitation. A pressure-modified von Mises criterion can be applied to account for the change in yielding behavior [146].

Hydrostatic pressure is positive in compression and increases the yield stress. One approach to address this issue is to employ Stassi equation [147], which takes the ratio, R of uniaxial compressive yield stress and uniaxial tensile yield stress:

$$\sigma_{eq} = \frac{(R-1)I_1 + \sqrt{(R-1)^2 I_1^2 + 12RJ_2}}{2R}$$
(6.23)

Where, I_1 is first stress invariant and J_2 is second deviatoric invariant. If compressive and tensile yield stress are equal, then R=1 and the equation reduced to von Mises equivalent stress.

6.7 Test Matrix to Fully Characterize A New Resin System

To fully characterize a new resin system, a series of compression and relaxation tests need to be conducted. Compression tests over a wide range of strain rates and temperatures need to be conducted to obtain a full stress strain response until failure. For the characterization of DER 353 resin system, at least five specimens were tested under compression and at least three specimens were tested for stress relaxation for each test condition. The strain rate range depends on the application of the material. For ballistic applications, the material needs to be tested up to a strain rate of 10⁵/s. The temperature range that needs to be investigated depends on the rise in temperature due to adiabatic heating observed during high strain rate tests. Materials with low Tg tend to be more sensitive to the adiabatic heating and thermal softening, and therefore compression tests will need to be conducted to obtain characteristic relaxation time at different strain levels, strain rates and temperature, and obtain equilibrium stress as a function of temperature. An example of a test matrix for compression and relaxation

Tuble of Test matrix for compression and relaxation experiments for resin							
	Strain Rate						
	0.001/s	0.01/s	0.1/s	1/s	1000/s	5000/s	10,000/s
25°C	CR	C R	CR	С	С	С	С
50°C	C R	C R	C R				
•••••							
Above T _g	CR	C R	CR				

Table 6.7 Test matrix for compression and relaxation experiments for resin

Note: C refers to compression test. R refers to relaxation test

6.8 Conclusions

Constitutive model was developed using an incremental approach to predict stress strain response over a wide range of strain rates $(0.001/s \text{ to } 10^6/s)$ and temperatures ranging from ambient to above glass transition temperature. Stress strain response under monotonic loading is decomposed into elastic and plastic region. For high strain rates, where adiabatic heating occurs, rubbery region follows plastic region if the temperature exceeds T_g . Strain rate and temperature dependent yield stress, which is predicted using Eyring equation, links the two regimes to construct a contiguous stress strain curve. The initial stress strain response and the plastic response are modeled using physically based spring and dashpot models. To determine the model parameters, temperature dependent properties of DER 353 were characterized in uniaxial compression mode under various strain rates. A series of stress relaxation tests were carried out for the determination of characteristic relaxation time and equilibrium stress state. The constitutive model is able to predict stress strain response for monotonic and varying strain rates in loading and unloading scenarios. Thermal softening in the stress strain curve at large strains, which is inevitable at higher strain rates, is also predicted by estimating the rise in temperature of the material during each increment in loading. Moreover, the model can predict relaxation in stress values when the strain rate drops to zero after the material has been loaded to a certain strain level. Model prediction for different loading scenarios show an excellent correlation when compared to the experimental results. This constitutive model is implemented in the next chapter to accurately determine the strain rate dependent cohesive traction laws.

Chapter 7

DETERMINATION OF RATE DEPENDENT TRACTION SEPARATION LAWS FOR COMPOSITE INTERFACE

Based on the experimental force displacement response, an average interfacial shear stress is defined as the failure load divided by the interface shear area $(2\pi r l_e)$. However, finite element simulation [5,11] and analytical models [148] show that a nonuniform shear stress distribution along the interface exists (see Chapter 2) with the highest stress occurring at the loaded end of the drop that decreases to zero at the other end. The interface thickness in glass/epoxy composite has been estimated to be in the range of 10-100 nm. This is very small compared to the fiber diameter (10 μ m or 10,000 nm). In numerical modeling of interfacial failure, it is common to use zero thickness cohesive traction separation laws for computational efficiency. The traction law describes the constitutive behavior of cohesive zone model, which is used to represent the fracture process zone ahead of the crack tip. The procedure for traction law determination can be broadly classified into two categories: direct and iterative methods. In general, direct methods involve J-Integral approaches for materials with large process zones that form at the crack tip (polymers, adhesives, interfaces, etc.). In this case, linear elastic fracture mechanics do not apply. In simple geometries like the double cantilever beam (DCB) for Mode I crack propagation and end notch flexure (ENF) for Mode II crack propagation, analytical expressions for the J-Integral have been derived that incorporate a cohesive zone at the crack tip. An example for strain energy release rate derived for end notched flexure test presented in Figure 7.1 is given by Eq. (7.1).



$$J \approx \frac{9}{16} \frac{P^2 a^2}{EW^2 H^3} + \frac{3}{8} \frac{P \delta_{t_0}}{WH}$$
(7.1)

Figure 7.1 End notch flexure test for the determination of J-integral

These analytical formulations provide the basis for determining the J-Integral as a function of load (*P*), elastic modulus of the beam (*E*), crack length (*a*) and geometry of the beam (width, *W*; height, *H*, length, *L*) as well as additional information about the crack opening displacements at the crack tip (δ_{t_0}) that is measured during these experiments. The traction laws can be calculated from the derivative of the J-Integral with respect to the critical crack tip displacement (Figure 7.2) [13].



Figure 7.2 Determination of traction separation law from J-integral approach

The resulting traction law describes the stress-displacement response of the material at the crack tip. In our study, we have assumed a triangular form for the traction law. The bilinear traction separation law for Mode I is assumed to be the same as Mode II (Figure 7.3). This assumption is later checked by conducting a sensitivity analysis of Mode I properties. The key properties are the peak shear stress (*S*) at which the material within the cohesive zone first softens, then crack opening occurs at the critical displacement δ_c and absorbs energy to propagate the crack. Only two of these parameters are unique as the third can be calculated from any of the two. In this study, we have used the peak stress and absorbed energy parameters.



Figure 7.3 Bilinear traction separation law showing peak stress and critical crack opening displacement [45]

The direct approach becomes increasingly challenging at smaller length scales due to the limitations in the instrumentation required for monitoring the crack tip. In particular, interfaces within composites and our microdroplet specimens are in the 10-100 nm range and are embedded within polymer and cannot be visually monitored. Our CNT sensors were helpful in confirming the load at the onset of interface debonding but do not provide sufficient information for experimental determination of the traction laws. Our collaborators at Purdue University have adapted our test methodology for high rate testing of the interphase with the high-speed synchrotron at Argonne National Laboratories in an attempt to visualize the interface debonding mechanisms through high speed x-ray methods [149]. The spatial (1.5 μ m/pixel) and time (1 frame/ μ s) resolutions have been limited to monitoring dynamic load up to peak load and overall displacement in the microdroplet specimen that includes fiber stretch and machine compliance. However, the spatial resolution was insufficient to measure crack tip displacement information needed for traction law determination. Consequently, we have developed a numerical/experimental iterative method. Such methods involve backing out the parameters by simulating the experiments, and thus require a thorough numerical analysis [11,12,150].

Li et al. [151] estimated the cohesive zone parameters of adhesively bonded polymer composite panels by matching the force-displacement response from a DCB test. Gowrishankar et al. [9] adopted an iterative approach in which the toughness of silicon/epoxy interface was estimated by comparing the crack length in a DCB specimen, and then the peak traction was adjusted to match the experimental results. These parameters were in good agreement with the ones extracted directly. Sockalingam et al. [11,152] used an iterative method to model the quasi-static loading of the microdroplet to determine traction laws but assumed linear elastic material properties for the DER resin. Given the nonlinear behavior of the resin presented in Chapter 6, this approach likely overestimates the energy absorption of the interface. The importance of both resin plasticity and dynamic loading is quantified in this work. Explicit finite element models of the dynamic microdroplet experiments are conducted to generate strain rate dependent Mode II cohesive traction laws for the first time.

Rate dependent traction separation laws reported in the literature [13,153,154] for interfaces in polymer composites suggest that both fracture energy and peak traction could be strain rate dependent. Landis et al. [154] reported strain rate dependent increase in peak traction for a constant critical crack opening displacement for elastic-viscoplastic solids. Corigliano and Ricci [153] formulated rate dependent interface models to simulate delamination in polymer matrix composites. In their model, both peak traction and fracture energy increase with increase in velocity. Non-uniqueness in the determination of traction separation law has been discussed by Kim et al. [155], where the authors have mentioned that the problem is ill conditioned if only one specimen size is considered.

In this study, a methodology to extract rate dependent traction separation law is developed. Explicit FE models of the microdroplet experiments are simulated using an indirect method for each loading rate. Three microdroplet geometries with embedded lengths of 75, 100 and 125 μ m are considered. Unique Mode II traction laws are determined by matching the rate dependent failure loads for each droplet size that exhibits the correct failure mode (i.e. interface failure). Our CNT sensors discussed in Chapter 4, indicate that debonding occurs at the peak load. Traction laws that result in resin failure are eliminated. By considering multiple embedded lengths for a given rate of loading, this approach converges to unique traction law parameters. In the FE model, fiber stretching, strain rate dependent resin properties, residual stress due to mismatch in CTE between fiber and resin and crack growth along the interface have been considered.

Another important factor is that the FE models allow for partitioning of the absorbed energy. Since the rate dependent resin properties are well characterized, it is possible to separate out the energy associated with resin plasticity from the energy absorbed by the interface leading to more accurate interphase traction laws. In the case of quasi-static loading, total energy absorption is measured experimentally and excellent correlation with our simulation results are achieved.

7.1 Preliminary Work

7.1.1 Non-uniqueness in peak traction and fracture toughness

Sockalingam et al. [11] developed an FE model of microdroplet, which can capture the physically observed phenomenon such as interfacial friction, crack growth in the interface and frictional sliding. Zero thickness cohesive elements were used to simulate fiber matrix debonding in the interface. S-2 glass fiber and DER 353 resin properties were assumed to be elastic. A sensitivity study carried out to understand the influence of Mode I and Mode II parameters showed that the loading in the microdroplet is Mode II dominated. Peak loads in the microdroplet experiments were not affected by changes in Mode I properties [11].

Parameters for a bilinear traction separation law were extracted by matching the experimental force response up to complete debonding. Parametric studies [55] demonstrated a non-unique nature of the traction law where there are more than one combinations of peak traction and relative displacement for crack separation that agree with the experimental results. This lack of uniqueness has been reported by others

researchers as well [156]. Figure 7.4 shows two different combinations of peak traction and fracture energy resulting in very similar force displacement response. However, the point at which crack initiation occurs varies. For the traction law with 160 J/m² and 120 MPa peak traction, the crack initiates at around 88% of the peak load, whereas for the one with 200 J/m² and 75 MPa, crack initiation occurs right after reaching the peak load. These parametric studies suggest that additional information such as load at the initiation debonding along the interface is important. Our CNT sensors have provided confidence that the peak load corresponds to the onset of debonding. In our case, where the epoxy yields, it is even more important to define the peak traction stress, which can induce plastic deformation/energy absorption, which would not be an issue if elastic properties are used. Our methodology described above is used to uniquely define the traction separation law.



Figure 7.4 Different combinations of peak traction and fracture energy result in same force-displacement prediction [157]

7.1.2 Role of resin plasticity

Resin plasticity is another factor that needs to be considered while simulating the microdroplet experiments. As discussed in Chapter 2, the previous experimental quasi-static studies [25,26] has attributed the measured energy absorption to the interface. During the experiments, large plastic deformation has been observed at the tip of the droplet where knife edge comes in contact (Figure 7.5). Strain rate dependent properties for epoxy resin DER 353 determined in previous chapters are equally important for dynamic loading and serves as model input.



Figure 7.5 Resin in the microdroplet undergoing large plastic deformation under the knife edge

When only the elastic response of the resin is considered, interface debonding is assumed to be the only energy absorption mechanism. However, when resin yield stress is exceeded additional energy absorption occurs through resin plasticity. In addition, the peak load significantly increases for the same traction law as shown in Figure 7.6b. The peak traction and fracture toughness of the interface had to be reduced to match the experimental peak load (Figure 7.6b). This demonstrates the importance of incorporating resin plasticity for both quasi-static and dynamic loading where we have shown the yield stress and energy absorption are highly strain rate dependent.



Figure 7.6 Force – displacement response from FE simulation for microdroplets with elastic and plastic resin (a) with same traction law (160 J/m² and 120 MPa) showing different peak load, (b) with a different traction law (100 J/m² and 70 MPa) that match the IFSS

7.2 Proposed Methodology for the Determination of Traction Separation Law

A bilinear traction separation law is assumed for the interface under Mode II loading. The key parameters associated with the traction law are the peak shear stress and the energy absorbed for crack separation (the critical displacement is calculated using the other parameters). The initial slope of this curve is chosen to prevent overlapping in contact surfaces between the fiber and resin within the numerical model and has been shown to have negligible effect on predictions of interface debonding.

The first step is to conduct the microdroplet experiments. In our methodology we create specimens with a minimum of three embedded lengths (70-200 μ m). The conditions for a valid test have been covered in Chapter 2. For interface traction law determination, the failure mode of the droplet test must be debonding within the interface. In the case of very strong interfaces and low yield strength resins, it is possible for the drops to shear off the fiber within the resin. This is an unacceptable failure mode for interface characterization. SEM inspection of the failure surface is conducted to ensure interface failure occurs. Our study using CNT sensors indicate that the interface debonding occurs at the maximum load. The IFSS decreases with increasing embedded length. The debond load or IFSS data for each embedded length is used to correlate with the numerical predictions. In the case of quasi-static loading (1 μ m/s), it is possible to load-unload-reload the microdroplet specimens to various load to measure the total energy absorption by the resin and interface. This data is also used to validate the traction law for low rates of loading. Unfortunately, it is not possible to measure this data at high rates of loading.

The iteration process begins by choosing a value for peak traction that is equal or higher than the average interfacial shear strength (recall the gradient in shear stress is high at the loading end and drops to zero at the other end so the actual stress at the initiation at the top of the drop is higher than the average). Since the failure mode was debonding within the interphase, the peak stress should also not significantly exceed the yield stress of the resin (otherwise failure will occur in the resin and not be consistent with interfacial failure). Initial estimates for the critical energy release rate is calculated by using the critical opening displacement from the previous studies by Sockalingam et al. [11] assuming elastic resin.

Simulations with different combinations of peak traction and critical energy release rate within this range are carried out for a 75 μ m droplet. Combinations that cannot reach the maximum load are eliminated. Those combinations that match the peak experimental load are then checked for failure mode (interfacial or resin). Resin failure modes and the associated traction law parameters are also eliminated. This sequence significantly narrows the range. The range of acceptable traction law parameters are then used to predict the IFSS for different droplet sizes (75 μ m and 125 μ m). This sequence is repeated and further narrowing of the range is achieved. Three drop sizes provide convergence of the traction law parameters that provides the correct failure mode and failure loads for all embedded lengths. The simulation results also allow the partitioning of energy absorbing mechanisms (interface and resin plasticity) and prediction of cohesive zone sizes and crack speeds during stable and unstable debonding.

This procedure also works well for droplets tested at higher rates of loading where only the maximum load can be measured accurately (see Chapter 2). The end result of the methodology provides a unique critical stress and energy absorption parameters for the Mode II traction law as a function of loading rate.

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To summarize, following are the steps required for accurate determination of rate dependent traction separation law for composite interface using a microdroplet specimen:

- Develop test methods for accurate determination of rate dependent interface properties
- Test microdroplets over a range of embedded length such that at least three different droplet sizes can be chosen for simulation
- Obtain interfacial properties over a wide range of loading rates spanning over several decades
- Ensure failure occurs along the interface from confocal and scanning electron microscopy
- Develop a test technique to monitor crack growth at the interface during the experiment. Experimental load at the onset of interface debonding is matched with the simulation results to narrow the range of traction laws
- Characterize resin properties over a wide range of strain rates as model input
- Estimate the range of peak stress (IFSS<S<sigma yield) and energy absorption
- Conduct finite element simulation with the experimentally obtained material properties for the composite interface, matrix and fiber, and determine traction separation law by matching the experimental results for each loading rate. Systematically reduce the range of traction law parameters that match the failure load, crack initiation time and failure mode for a minimum of three embedded lengths until convergence of the parameters is achieved. In the case of quasistatic loading validate using the total energy absorbed via load-unload experiments and simulations.

The procedure is demonstrated in the following sections.

7.3 Finite Element Model

A quarter-symmetric FE Model is used to simulate the microdroplet experiment. Glass fiber, steel blade and epoxy resin droplet are modeled using 8-noded linear reduced-integration 3D Brick elements (C3D8R in ABAQUS), with enhanced hourglass control. Reduced-integration elements are chosen since full-integration elements are prone to shear-locking [158] and the resin elements are subjected to large shear strains locally around the interface. The enhanced hourglass control is used to minimize the errors due to hourglassing modes occurring in reduced-integration elements [158]. A one-to-one mapping of nodal coordinates is maintained along the outer circumference of the fiber and the inner surface of the resin droplet and these meshes are connected using zero-thickness 3D cohesive elements (COH3D8). These cohesive elements represent the fiber-matrix interface. The thermal preload during the curing of the droplet is modeled as an initial quasi-static step [11], while the subsequent knife edge loading is simulated as a dynamic explicit load step and solved using the double-precision ABAQUS Explicit solver.

For the high rate loading where the blade velocity is 1 m/s, no mass scaling was applied to the model. The blade velocity of 1 m/s is only 0.11% of the shear wave-speed (886 m/s) of the epoxy material, which is the smallest characteristic wave speed in the FE model. Due to this, the stress wave-propagation effects are negligible even in the high rate model (Kinetic energy is always < 2% of the total internal energy until peak load is reached and droplet debonds dynamically). This simulation involved \sim 21,000 explicit increments per 1 µm displacement of the knife edge. Taking

advantage of this result, fixed mass scaling is applied to the FE models for blade velocities of 1 μ m/s and 100 μ m/s, in order to solve these models with the same number of increments per unit displacement of the knife edge (Table 7.1). This will enable us to solve the FE models for all loading velocities within a reasonable time without affecting the solution accuracy. ABAQUS manual recommends that the ratio of the loading velocity to the characteristic material wave speed should be < 1%, in order to ensure that the dynamic wave-propagation effects (due to artificially reducing the wave-speed in the elements) do not significantly affect the results of the mass-scaled model [158]. The Kinetic Energy is < 2% of the total internal energy for the entire duration of loading until the peak load is attained in all of the simulations, further confirming that the mass-scaling factor (MSCALE) for the different blade velocities are chosen based on Eq. (7.2):

$$MSCALE = 10^{(-2 * \log_{10}(v_{Blade}(in \, um/s))) + 12)}$$
(7.2)

Blade Velocity (v _{Blade})	MSCALE	Shear waves peed (C _{shr-Resin}) in mass-scaled resin elements	$\frac{Blade_vel}{C_{Shr}^{Resin}}$	Time-step (sec)	N _{inc} per 1 um blade displacement
1 um/s	10 ¹²	8.86 x 10 ² um/s	0.0011	4.8 x 10 ⁻⁵ s	2.1 x 10 ⁴
100 um/s	10^{8}	8.86 x 10 ⁴ um/s	0.0011	4.8 x 10 ⁻⁷ s	2.1 x 10 ⁴
10^6 um/s	1	8.86 x 10 ⁸ um/s	0.0011	4.8 x 10 ⁻¹¹ s	2.1 x 10 ⁴

 Table 7.1 Parameters for mass scaling applied to the FE models

The specimen consists of a single S-glass fiber of $10 \,\mu\text{m}$ diameter and a spherical shaped epoxy matrix droplet. A knife edge is used to load the droplet at a distance of 5 μm away from the fiber surface. The fiber is modeled as isotropic linear elastic material. The matrix is modeled isotropic linear elastic up to yield. Rate dependent post yield

behavior of the epoxy resin obtained from compression experiments serves as model input based on Chapter 5. The resin exhibits post yield softening, plastic flow followed by strain hardening at large strain. Element deletion occurs at the failure strain of 70%. After an element is deleted, contact between the elements on either side of the crack is established to avoid interpenetration. Input properties of fiber and matrix are given in Table 7.2. Post yield stress strain curves given by Eq. (6.7) is used for 0.001/s strain rate. For higher strain rates, the entire curve is shifted vertically using the strain rate dependent yield stress predicted by the Ree-Eyring equation (Eq. (6.5)) presented in Chapter 6.

Property	S-glass fiber	Epoxy resin DER 353			
Young's modulus (GPa)	90.0	3.2			
Poisson's ratio	0.17	0.36			
CTE (ppm/°C)	3.4	70.0			

Table 7.2 Properties of fiber and matrix

Boundary conditions applied to the FE model are shown in Figure 7.7. Axes of symmetry in x and y-axis are shown. Nodal displacements are constrained along z-direction at the fiber top. A blade velocity is applied to the knife edge to load the microdroplet. Figure 7.8 shows different components of the model, i.e. fiber, interface and matrix. Meshes on the resin droplets that come in contact with the knife edge were aligned with the meshes on the knife edges to maintain smooth contact between knife edge and droplet during initial phase of loading. An average element size of 2 μ m is used for meshing the knife edge since ABAQUS recommends using coarser mesh for the master surface (bottom surface of the knife edge) with respect to the slave surface

(outer surface of the droplet) in order to improve the accuracy of the contact formulation. Mesh details on the droplet model and knife edge are shown in Figure 7.9.



Figure 7.7 FE model of microdroplet showing boundary conditions



Figure 7.8 FE model of microdroplet showing different components – fiber, interface and resin





Figure 7.9 Close up of FE model showing mesh details for (a), (c) and (e) 1 μm mesh and (b), (d) and (f) 0.5 μm mesh

Due to the mismatch in coefficient of thermal expansion of fiber and matrix, residual stresses are induced resulting from shrinkage as the temperature drops from 150°C to room temperature (25°C) at the end of cure cycle. Compressive forces are induced in the fiber along radial and fiber directions as the matrix contracts during cool down period. After the thermal stresses are applied to the model, the knife edge loads

the droplet at a desired velocity. A Coulomb friction formulation has been used to model the frictional sliding that occurs after complete debonding. A coefficient of friction of 0.54 has been used based on our previous studies [11].

Zero thickness cohesive elements are used to simulate crack growth along the fiber matrix interface. A bilinear traction separation law is assumed where the peak stress represents interfacial shear strength and the area under the curve represents its fracture toughness. Based on the sensitivity studies conducted by Sockalingam et al. [11] on the influence of Mode I and Mode II on the peak loads predicted in microdroplet specimen, Mode I parameters were set equal to Mode II parameters in this study. The initial stiffness of the traction law is chosen to be a sufficiently high value of 1×10^6 GPa/m such that displacement continuity is maintained across the interface until interfacial damage initiates and the interface begins to soften according to the traction law. This stiffness value is also high enough to ensure that there is no interpenetration of the resin nodes into the fiber during the thermal preload. This stiffness value is also low enough to ensure that the global stiffness matrix does not become ill conditioned, which could lead to oscillating singularity of the cohesive tractions.

To check for convergence, three progressively refined meshes with average element size of 1 um, 0.75 um, and 0.5 um (all with aspect ratios close to 1) are employed in the fiber, interphase and the droplet region (except for the region that is outside of the loading edge and hence is not in the load path, where a coarser mesh will suffice). Total numbers of elements in the model for fiber, matrix and interface are presented in Table 7.3.

Mesh size	Fiber elements	Matrix elements	Cohesive elements
0.5 µm	39468	165942	800
0.75 µm	11970	134840	1320
1 µm	4650	58740	2976

Table 7.3 Total number of elements in fiber, matrix and interface

Mesh convergence has been shown in terms of peak load (Figure 7.10), energy dissipated at peak load and after complete debonding, cohesive zone length (Figure 7.11) and size of plastic zone (Figure 7.12) at different load levels. Grid Convergence Index (GCI) is used to estimate the discretization error, which takes the rate of convergence into account. GCI is a measure of the percentage of how much the computed quantity deviates from the asymptotic numerical quantity. Smaller GCI indicates the solution is in the asymptotic range [159]. Using the grid refinement analysis, the observed order of convergence, p is found to be 1.75, which means the solution is approaching a quadratic rate of convergence. The difference in peak load between the 1 μ m (coarsest) and 0.5 μ m (finest) mesh is 3.4% (See Table 7.4), while the GCI is 1.8%. Convergence of 3.1% and 2.3% for mesh sizes 1 μ m and 0.5 μ m, respectively is obtained in terms of damage energy corresponding to peak load. Convergence of 0.8% and 0.013% for mesh sizes 1 μ m and 0.5 μ m, respectively is obtained in terms of damage energy after complete debonding (Table 7.4).

Figure 7.11 and Figure 7.12 show comparison in the evolution of the cohesive zone and plastic zone at 50%, 75% and 100% of peak load for the coarsest (1 μ m) and the finest (0.5 μ m) mesh sizes. Both cohesive zone length and plastic zone are almost identical for the 1 μ m and 0.5 μ m mesh.

Consequently, a mesh size of 1 μ m along the droplet length with an aspect ratio of 1 is used for all the simulations since it is the typical mesh size for FEA of

micromechanical models for similar problems in polymer composites where the traction laws determined from this study will be used as input. Figure 7.13 shows the contribution of hourglass energy is less than 1% of the total internal energy at peak load for 1 μ m mesh size.



Figure 7.10 Convergence study of mesh sizes

100 µm dropiet with different mesh size for conesive ciements				
	Mesh size – cohesive elements			
Parameters	0.5 μm	0.75 μm	1 μm	
Peak load	-	1.5%	3.4%	
Damage energy at peak load	-	2.3%	3.1%	
Damage energy after	-	0.013%	0.80%	
complete debonding				

Table 7.4 Convergence study showing % difference for different parameters for 100 µm droplet with different mesh size for cohesive elements



Figure 7.11 Evolution of cohesive zone length in FE model of microdroplet with 1 μ m mesh at (a) 50%, (c) 75% of peak load and for 0.5 μ m mesh at (b) 50%, (d) 75% of peak load



Figure 7.12 Evolution of plastic zone in FE model of microdroplet with 1 μ m mesh at (a) 50%, (c) 75% and (e) 100% of peak load and for 0.5 μ m mesh at (b) 50%, (d) 75% and (f) 100% of peak load



Figure 7.13 Force and energy versus time plot showing minimal hourglass energy at peak load for 100 µm droplet and 1 µm cohesive elements

7.3.1 Analysis of thermal diffusion in interface during high rate tests

High rate compression tests of epoxy resin showed increase in yield stress as well as the presence of thermal softening of resin at large strain suggesting both strain rate and temperature are coupled. The importance of thermal softening during dynamic loading in the interface of the microdroplet specimen needs to be assessed. Since the measurement of variation in temperature along the interface during high rate microdroplet experiments was not possible, an analytical approach has been employed to classify whether the experiments were carried out under isothermal or adiabatic test conditions by determining the ratio of thermal diffusion time and test time as mentioned in Chapter 5. Thermal diffusion time can be estimated by the following relation [114]:

$$t_d \approx \frac{L^2}{2(k/\rho c)} \tag{7.3}$$

1

Where *L* is the distance from the center of the region along interface and resin that undergoes plastic deformation to the nearest heat sink (glass fiber). *k* is thermal conductivity (2.092 J/(m s K), ρ is density (1150 kg/m³) and *c* is specific heat capacity of the epoxy specimen (1.11 kJ/kg K).

FE simulation show resin plasticity occurring beneath the loading end and across two elements for the rest of the droplet (Figure 7.14). Assuming the nearest heat sink is fiber, the characteristic distance to the fiber is 2 μ m near the loading blade and along the droplet length. The test duration of Hopkinson bar tests that were conducted at 1 m/s was about 100 μ s, whereas the diffusion time (*t*_d) is about 1.2 μ s. Since the test duration is two orders of magnitude longer than the diffusion time, it can be concluded that isothermal test condition exists during high rate microdroplet tests and hence the temperature effects can be neglected. It is assumed that all the heat generated is dissipated into glass fiber, which is a conservative estimate.



Figure 7.14 Resin plasticity in the droplet at peak load for a 100 µm droplet at 1 m/s

7.4 Extraction of Traction Separation Law

7.4.1 High rate loading rate

The first step in determining the traction separation law is the estimation of peak traction, which should be greater than the average interfacial shear strength for the failure to occur along the interface. For high rate loading rate of 1 m/s, the IFSS for a 75 μ m droplet was 88 MPa. So, a peak traction greater than 88 MPa was chosen. A series of parametric studies were conducted for a droplet with 75 μ m embedded length by varying the fracture energy over a wide range to match the peak load from the experiments. A family of IFSS vs. peak traction and fracture energy curves are generated (Figure 7.15). Intercepts of these curves with experimental IFSS are candidates for traction law for this rate. Then the models are checked to see if failure has occurred along the interface. Traction laws with resin failures are eliminated and the remaining combinations of peak traction and fracture energy are then used to predict the IFSS for different droplet sized as part of the procedure. In the FE model, when the equivalent plastic strain reaches a value of 70%, resin failure occurs and the elements are deleted.

For 1 m/s, peak tractions ranging from 110 MPa to 150 MPa match the experimental IFSS. Force time curves for 150 MPa and 150 J/m² and 175 J/m² exhibit crack growth after the peak load has reached (Figure 7.16), which does not match the experimental findings. After reaching the peak load, 110 MPa peak traction and 350 J/m² shows resin failure at the bottom of the droplet (Figure 7.17). Cohesive elements

are still present even after reaching peak load. Based on these observation, these peak tractions (110 MPa and 150 MPa) are eliminated. Traction law range has been narrowed down to 120 MPa to 140 MPa and 250 J/m² – 300 J/m². These results are used next in the simulation of 100 μ m and 125 μ m droplet.



Figure 7.15 Parametric study on peak traction and fracture energy for the determination of traction separation law for 75 µm droplet at 1 m/s loading rate. Traction laws with peak shear stress of 110 MPa and 150 MPa are eliminated



Figure 7.16 Force time curves for 150 MPa peak traction shows crack growth after reaching the peak force for 75 μ m at 1 m/s loading rate



Figure 7.17 FE simulation results for 110 MPa and 350 J/m² showing resin plasticity near loading end and resin element deletion near the non-loading end after reaching peak load for 75 μ m at 1 m/s loading rate

The remaining combinations with peak tractions ranging from 120 MPa and 140 MPa have interfacial failure and the crack growth occurs between 95% to 100% of peak load, which is consistent with the experimental findings. Predicted force time response for 75 μ m with different traction laws (120 MPa to 130 MPa peak traction) are shown in Figure 7.18. These traction laws are further refined by simulating different droplet sizes (100 μ m and 125 μ m).



Figure 7.18 Predicted force time response for different traction laws that closely match the experimental IFSS for 75 µm droplet at 1 m/s

For peak traction higher than 130 MPa, resin failure was observed for 125 μ m droplet. Traction laws (120 MPa-300 J/m² and 130 MPa-270 J/m²) exhibited correct failure modes for both 100 μ m and 125 μ m droplets. Size effects on the interfacial shear strength was also observed from simulation results which is similar to the experiments, where larger droplet sizes showed lower IFSS (Figure 7.19) or conversely the maximum load is plateauing even when the shear area increases for the larger drops. Figure 7.20

shows IFSS data for different droplet sizes from the experiments and a linear fit to these experimental data. Here, we have assumed a linear relation between IFSS and embedded length. As the embedded length goes to infinity, the IFSS plateaus. For the detemination of the traction laws using different droplet sizes, it is essential for the droplets not to fall into the plateau region.



Figure 7.19 Simulation results for the traction law 120 MPa and 300 J/m² showing IFSS vs. time for different droplet sizes (75 μm, 100 μm and 125 μm) subjected to 1 m/s loading rate



Figure 7.20 Average interfacial shear strength from microdroplet experiments and FE model showing size effects for 1 m/s loading rate

Goodness of fit was determined by calculating average absolute relative error between the linear fit of the experimental data and the predicted IFSS using Eq. (7.4). Calculated error for these two traction laws are presented in Table 7.5.

$$Error = \left| \frac{IFSS_{exp} - IFSS_{model}}{IFSS_{exp}} \right| \times 100 \%$$
(7.4)

Table 7.5 Goodness of fit for the predicted IFSS at 1 m/s

Traction law	Error
120 MPa and 300 J/m ²	0.54 %
130 MPa and 270 J/m^2	1.95 %

The traction law 120 MPa - 300 J/m^2 results in a better fit (less error) to the experimental results, hence this combination is chosen as the unique parameters for the loading rate of 1 m/s. Although, we have the methodology to determine unique traction

separation law, the uniqueness is limited by the variability in our experimental data. If the variation in the experimental results are reduced significantly, then we can extract truly unique traction law within the 3.4% convergence error.

7.4.2 Intermediate loading rate

For the intermediate loading rate of 100 μ m/s microdroplet tests, the IFSS was 61 MPa for a nominal 75 μ m droplet. Simulation results on average IFSS from a series of parametric study done with peak traction ranging from 70 MPa to 90 MPa with a wide range of fracture energies are shown in Figure 7.21. For peak traction 70 MPa, resin failure was observed. For peak traction between 75 MPa and 85 MPa, failure occurred along the interface and the traction laws 75 MPa – 120 J/m², 75 MPa – 150 J/m², 80 MPa – 100 J/m², 80 MPa – 120 J/m² and 85 MPa and 90 J/m² predicted IFSS within the experimental error. However, when the peak traction was increased to 90 MPa, crack initiation at the interface occurs after reaching the peak load, which does not match the results from our CNT sensors. Therefore, traction law with 90 MPa peak traction was eliminated.



Figure 7.21 Parametric study on peak traction and fracture energy for the determination of traction separation law for 75 μ m droplet at 100 μ m/s loading rate

For bigger droplets, the traction law with higher peak tractions (above 75 MPa) exhibited resin failure for droplet of 125 μ m and hence these combinations were eliminated. IFSS vs. time prediction for different droplet lengths (75 μ m and 125 μ m) with the traction law 75 MPa – 150 J/m² is shown in Figure 7.22. Simulation results showed interfacial failure for both 75 μ m and 125 μ m droplets. Comparison of the simulation with the experimental results show an excellent correlation including size effect (Figure 7.23) with an average absolute relative error of 5.9% using Eq. (7.4).



Figure 7.22 Simulation results showing IFSS vs. time for different droplet sizes (75 μ m, 100 μ m and 125 μ m) at 100 μ m/s loading rate for the traction law 75 MPa - 150 J/m²



Figure 7.23 Average interfacial shear strength from microdroplet experiments and FE model with traction law 75 MPa - 150 J/m² showing size effects for 100 μ m/s loading rate

7.4.3 Quasi-static loading rates

For quasi-static loading rate of 1 μ m/s, the average IFSS for a 75 μ m droplet was 54 MPa. A peak traction greater than the average IFSS was chosen as a starting point (e.g. 60 MPa) and a series of parametric studies were conducted for a droplet with 75 μ m embedded length by varying the fracture energy to match the peak load from the experiments. Traction laws with peak traction 60 MPa did not reach the experimental IFSS (Figure 7.24). Also, resin failure occurs for this traction law. For the peak traction of 75 MPa, the failure is very brittle and crack initiation occurs after reaching the peak force. So, these peak tractions are eliminated from further study. The ones that matched the experimental IFSS (65 MPa - 100 J/m² and 70 MPa – 80 J/m²) (Figure 7.25) are carried forward and used to predict the IFSS for different droplet sizes as a part of the methodology. These traction laws have a clean interfacial failure and the crack initiation occurs at around 95% of the peak load for these traction laws, which is consistent with the experimental findings obtained with CNT sensors.



Figure 7.24 Parametric study on peak traction and fracture energy for the determination of traction separation law for 75 µm droplet at 1 µm/s loading rate. Traction laws with peak traction 60 MPa and 75 MPa are eliminated from further study



Figure 7.25 Predicted IFSS time response for traction laws 65 MPa – 100 J/m² and 70 MPa – 80 J/m² for 75 μ m droplet at 1 μ m/s

Predicted IFSS vs. time from simulations with different traction laws (65 MPa – 100 J/m² and 70 MPa – 80 J/m²) for 125 μ m droplet are shown in Figure 7.26. Simulations run with 70 MPa traction law exhibited delayed crack growth at the interface for droplet size of 125 μ m and consequently was eliminated from further analysis. Microdroplets with different embedded lengths show size effects similar to the experimental findings (Figure 7.27). The down selected traction law 65 MPa – 100 J/m² show a good fit to the experimental data (Table 7.6). These values are much lower than the ones obtained by Sockalingam et al. [11] considering elastic resin, which was 120 MPa and 160 J/m². This discrepancy arises from the fact that with the elastic resin, all the input energy is absorbed by the interface and hence the values for traction law need to be higher to match the experimental peak load for a given droplet size.

Table 7.6 Goodness of fit for the predicted IFSS at 1 m/s

Traction law	Error
$65 \text{ MPa} \text{ and } 100 \text{ J/m}^2$	2.9 %
70 MPa and 80 J/m^2	5.1 %

Here, the peak traction is 65 MPa whereas the shear yield stress of resin is $85/\sqrt{3}$ MPa or 49 MPa. The resin yields around the interface from top to bottom. However, after yielding, the resin initially softens and then starts to harden. The peak traction is reached in the interface before the failure strain of the resin. This causes the interface to soften and eventually debond before resin failure can occur.



Figure 7.26 Simulation results showing IFSS vs. time at 1 μ m/s for 125 μ m droplet for the traction laws 65 MPa-100 J/m² and 70 MPa-80 J/m²



Figure 7.27 Average interfacial shear strength from microdroplet experiments and FE model with traction law 65 MPa - 100 J/m² showing size effects for 1 μ m/s loading rate

The traction separation law with a peak traction of 65 MPa and fracture energy of 100 J/m^2 was further analyzed to calculate the total energy absorbed by the resin and

interface. A series of load-unload-reload experiments were also carried out at several load levels to determine the total energy absorbed by the constituents (Figure 7.28). The FE models of microdroplet was subjected to load unload cycles (Figure 7.29) and the incremental energy absorption from area under the force displacement load-unload curves was compared to the experimental values. Figure 7.30 shows a good correlation between the experimental and FE simulation results.



Figure 7.28 Load unload curves from microdroplet experiments for a 100 μm droplet at 1 $\mu m/s$



Figure 7.29 Predicted load unload cycles at different load levels from FE simulation for a 100 μ m droplet with the traction law 65 MPa – 100 J/m²



Figure 7.30 Comparison of energy absorbed by the constituents in the microdroplet during load unload tests for 100 μ m droplet at 1 μ m/s

7.5 Partitioning of Absorbed Energy into Resin and Interface

Energy absorption calculation from the experimental load unload curves include the contribution of both resin and interface. Since it was not possible to partition these energies experimentally, FE simulation results were used for this partitioning. The total input energy has been partitioned into strain energy (in resin and fiber), resin plasticity, damage dissipation in interface and kinetic energy. Figure 7.31 - Figure 7.33 indicate that the energy absorption up to the peak load is dominated by resin plasticity and strain energy in fiber and resin. As the load drops after the peak, the stored strain energy in fiber and resin is released to form crack along the interface.

Figure 7.35 - Figure 7.37 show percentage energy absorbed by various mechanisms until the peak load. The total strain energy in the specimen is the highest until the peak. The contribution from resin plasticity to the total energy absorption is higher for lower loading rates (1 μ m/s and 100 μ m/s). However, with increased loading rate, the energy absorption contribution from resin plasticity diminishes. For a 100 μ m droplet at the peak load, the energy absorption due to resin plasticity at 1 m/s loading rate is only 14.5% of total, which is lower compared to 100 μ m/s (36% of total) and 1 μ m/s (40% of total) (See Table 7.7). Since rate dependent resin properties are used in the model, less plasticity and higher strain energy is observed for higher loading rates. The energy dissipated up to the peak load by the interface is small. For 1 μ m/s and 100 μ m/s, the damage dissipation in interface is 10% and 11%, which increases to 22.2% for 1 m/s.

Hourglass energy plus kinetic energy account for less than 1.2% of the total energy at the peak load for all loading rates. There is no energy absorbed due to friction until complete debonding occurs (Figure 7.34). As the crack growth starts along the

interface, contribution of the interface begins to increase (Figure 7.38 - Figure 7.40). At the end of complete debonding, the energy absorbed by interface increases to 73%, 54% and 46% of the total for 1 m/s, 100 μ m/s and 1 μ m/s, respectively. Both kinetic energy and frictional dissipation increases after complete debonding occurs (Figure 7.34).



Figure 7.31 Energy partitioning for 100 µm droplet subjected to 1 m/s loading rate



Figure 7.32 Energy partitioning for 100 µm droplet subjected to 100 µm/s loading rate



Figure 7.33 Energy partitioning for 100 µm droplet subjected to 1 µm/s loading rate



Figure 7.34 Kinetic energy and frictional dissipation for 100 µm droplet subjected to 1 µm/s loading rate



Figure 7.35 Percentage energy dissipation up to peak load for 100 µm droplet subjected to 1 m/s loading rate



Figure 7.36 Percentage energy dissipation up to peak load for 100 µm droplet subjected to 100 µm/s loading rate



Figure 7.37 Percentage energy dissipation up to peak load for 100 µm droplet subjected to 1 µm/s loading rate

	% of total energy					
Loading	Resin	Total	Strain	Strain	Damage	Hourglass
rate	plasticity	strain	energy	energy	dissipation in	and
		energy	in	in	interface	kinetic
			fiber	resin		energy
				- • • •		5 7
1 μm/s	40.2	48.6	29.6	18.9	10.0	1.2
1 μm/s 100 μm/s	40.2 36.0	48.6 52.1	29.6 32.3	18.9 19.8	10.0 11.0	1.2 0.9

Table 7.7 Energy partitioning for a 100 µm droplet at the peak load



Figure 7.38 Percentage energy dissipation during debonding after the peak load for 100 µm droplet subjected to 1 m/s loading rate



Figure 7.39 Percentage energy dissipation during debonding after the peak load for 100 µm droplet subjected to 100 µm/s loading rate



Figure 7.40 Percentage energy dissipation during debonding after the peak load for 100 µm droplet subjected to 1 µm/s loading rate
7.6 Estimation of Strain Rate Along the Interface

Microdroplet experiments were conducted at various loading rates, where the velocity of the knife edge was 1 μ m/s, 100 μ m/s and 1 m/s. However, the actual loading rate at the interface is different from the knife edge velocity. Here, the relative displacement of the nodes in the fiber and resin adjacent to the interface are determined at a location (20 μ m away from the loading end) in the interface shown in Figure 7.41 from the simulation (Figure 7.42 - Figure 7.44) and relative velocity at the interface is calculated. For quasi and intermediate loading rates, the velocity until the maximum load is reached is about 90-100% of the loading velocity (Table 7.8). Whereas, for the high rate loading, the relative nodal velocity is exactly equal to the loading velocity. Shear strain rates determined assuming interface thickness of 10 nm and 100 nm range from 9/s for 1 μ m/s to 10⁸ /s for 1 m/s loading rate (Table 7.9).



Figure 7.41 Nodal displacement and shear strain rates are calculated at the location near the loading end shown by the arrow in the figure



Figure 7.42 Nodal displacements at resin and fiber side of the interface and net relative displacement for loading rate 1 µm/s



Figure 7.43 Nodal displacements at resin and fiber side of the interface and net relative displacement for loading rate 100 µm/s



Figure 7.44 Nodal displacements at resin and fiber side of the interface and net relative displacement for loading rate 1 m/s

	Relative nodal velocity		
Applied loading rate	Before peak load	After peak load	
1 μm/s	0.9 µm/s	21 µm/s	
100 µm/s	90 µm/s	850 μm/s	
1 m/s	1 m/s	36 m/s	

 Table 7.8 Relative nodal velocity before and after peak load obtained from simulation at the location shown in Figure 7.41

 Table 7.9 Estimated shear strain rate for different interface thickness

		Shear strain rate	
Applied loading rate	Before peak	Interface	Interface
	load	thickness: 10 nm	thickness: 100 nm
1 μm/s	0.9 µm/s	90 /s	9 /s
100 µm/s	90 µm/s	9000 /s	900 /s
1 m/s	1 m/s	$1 \ge 10^8 / s$	$1 \ge 10^7 / s$

Immediately after reaching the maximum load, the crack growth becomes unstable. Crack speed is calculated based on the crack front where the cohesive elements are deleted as the relative displacement at the interface exceeds the critical displacement determined by the traction law. Figure 7.45 shows the shear stresses along the interface at an interval of 0.01 µs as the cohesive elements are deleted for a 75 µm droplet. For 1 m/s loading rate, the crack speed after the peak load increases by 3 orders of magnitude and reaches about 3000 m/s during unstable crack growth (Figure 7.46). This wave speed is close to the Rayleigh wave speed of the material [160,161]. As the crack grows, the material starts unloading at much higher speed than the loading velocity. As the traction laws were found to be rate dependent, the traction law will likely change while unloading. Our simulations incorporated strain rate dependent resin properties but the rate dependent traction law was assumed to be constant for a given loading rate.



Figure 7.45 Shear stresses along the interface at an interval of 0.01 μ s showing crack growth (as shear stress approaches zero) at the peak load for a 75 μ m droplet at 1 m/s with traction law 120 MPa – 300 J/m²



Figure 7.46 Crack initiates at the peak load and crack speed increases up to 3000 m/s

7.7 Evolution of Cohesive Zone for Different Loading Rates

Now that accurate tractions laws have been determined, one can investigate the rate dependent debonding process in more detail. Cohesive zone along the interface is the region where the shear stress has exceeded the peak traction and softening has occurred. Evolution of shear stress distribution along the interface at 25%, 50%, 80%, 90% and 100% of the peak load for 100 μ m and 125 μ m droplet subjected to 1 μ m/s are shown in Figure 7.47. Cohesive zone length and cohesive length normalized by the embedded length have been plotted against percentage of failure load in Figure 7.48 for loading rate of 1 μ m/s for 100 μ m, 75 μ m and 125 μ m droplets. Comparison of cohesive zone length show shortening of cohesive zone length as the loading rate is increased from 1 μ m/s to 100 μ m/s and 1 m/s (Figure 7.49).

As the loading rate is increased, the length of the cohesive zone decreases. The most significant difference is between 1 μ m/s and 1 m/s, where the cohesive zone length for a 100 μ m droplet decreases from 84 μ m to 72 μ m at the peak load (Figure 7.49). The trend is similar for different percentage of the peak load, although to varying degrees. The increase in fracture energy from 100 J/m² at 1 μ m/s to 300 J/m² at 1 m/s can be attributed to the decrease in the cohesive zone length.



Figure 7.47 Shear stress distribution along the interface at 25%, 50%, 80%, 90% and 100% of peak load for (a) 100 μm and (b) 125 μm droplet subjected to 1 μm/s loading rate



Figure 7.48 Evolution of (a) cohesive zone length and (b) cohesive zone as % of embedded length as a function % peak load for droplets with different sizes subjected to 1 μ m/s loading rate. Traction law: 65 MPa – 100 J/m²



Figure 7.49 Comparison between cohesive zone length vs. % peak load for different loading rates for a 100 µm droplet show lower cohesive zone length for higher loading rate

7.8 Mode I Sensitivity

Due to the thermal shrinkage that occurs after the curing cycle, majority of the fiber is under radial compression except for the fiber ends, where tensile stresses exist. This can lead to mixed mode crack initiation during the experiment although the microdroplet test is Mode II dominated at the interface. Figure 7.50 shows the evolution of normal stress at two different location along the interface as a function of percentage of peak load, where Mode I equals Mode II has been assumed. Magnitude of normal stresses beneath the loading blade (path 2) are lower compared to the ones along path 1. Mixed mode damage initiation occurs near the ends of the droplet at relatively low

percentage of peak load. To study the effects of Mode I, sensitivity analysis was carried out by varying Mode I parameters. Mode I parameters were reduced by 50%, 30% and 10% corresponding to Mode II parameters. Also, Mode I peak traction was increased by a factor of 1.7 based on molecular dynamics simulation results from the literature [18] for similar S glass/epoxy interface.

Negligible difference in the development of cohesive zone length was observed when the Mode I parameters were reduced by 50% or increased by a factor of 1.7 corresponding to the Mode II parameters (Figure 7.51). The peak load reduced by 5%, 8% and 14% when the Mode I parameters were reduced by 50%, 30% and 10%. Increasing the Mode I parameters by 1.7 times had marginal effects on the peak load (increase by 2%) (Figure 7.52 and Figure 7.53). For Mode I reduced to 10% and 20% of Mode II parameters, damage initiation at the end of the droplet occurs during thermal preload. Since no evidence of damage in the droplet is observed after the curing cycle while preparing the droplets, it can be deduced that the Mode I parameters are higher than 20% of Mode II parameters. With Mode I parameters reduced by 30%, simulation results showed an 8% decrease in peak load, which is within our experimental error.



Figure 7.50 Normal stress distribution along the interface of a 75 μ m droplet at 0%, 25%, 50%, 80%, 90% and 100% of peak load along the path (a & c) away from the loading blade (path 1) and (b & d) beneath the loading blade (path 2) for the case Mode I = Mode II. Traction law: 65 MPa – 100 J/m². Loading rate: 1 μ m/s



Figure 7.51 Cohesive zone length vs. % peak load showing minimal sensitivity to Mode I parameters



Figure 7.52 IFSS – displacement response with various Mode I parameters



Figure 7.53 Percentage difference in IFSS for different ratios of Mode I and Mode II.

7.9 Conclusions

A methodology has been developed to extract the rate dependent traction separation law for composite interface through iterative method by simulating microdroplet experiment. Zero thickness cohesive elements were employed to simulate the crack growth along the interface. Rate dependent large strain resin properties were considered to accurately model the large plastic deformation that occurs under the knife edge. Crack initiation occurs at around peak load, which correlates well with the experimental results obtained from CNT sensors. For quasi-static (1 μ m/s), intermediate (100 μ m/s) and high rate loading (1 m/s), traction separation laws were extracted by simulating the microdroplet experiments with a certain embedded length and using that traction law, predictions were made for a different droplet size as part of the validation.

The simulations showed a general trend where a lower peak traction exhibited resin failure and higher peak traction showed a brittle failure. These failure modes are associated with the crack opening displacements assumed in the traction law. Interfacial traction separation laws (both peak traction and the fracture energy) were found to be dependent on the rate of loading (Figure 7.54 and Table 7.10). Peak traction and fracture energy exhibit a fairly linear relation with shear strain rate when plotted on a semi log scale (Figure 7.55).

Use of accurate rate dependent resin properties in FE model allowed partitioning of energy absorption contribution by the constituents, which was not possible with the elastic resin in the previous studies [11,152]. Up to the peak load, resin plasticity and strain energy in the fiber and resin were found to contribute the most. Energy absorption in interface increases as the damage accumulates with the crack growth.



Figure 7.54 Traction separation law for different loading rates

Loading rate	Relative nodal velocity	Shear strain rate range	Peak traction	Fracture energy	Relative displacement
1 μm/s	0.9 µm/s	9/s - 90/s	65 MPa	100 J/m^2	3.1 µm
100 μm/s	90 µm/s	900/s - 9000/s	75 MPa	150 J/m^2	4.0 µm
1 m/s	1 m/s	$10^7/s - 10^8/s$	120 MPa	300 J/m^2	5.0 µm

Table 7.10 Rate dependent traction separation laws



Figure 7.55 (a) Peak traction and (b) fracture energy as a function of shear strain rate for interface with 10 nm and 100 nm thickness

Chapter 8

CONCLUSIONS AND FUTURE WORK

This research has been carried out to advance the fundamental understanding of deformation and failure mechanisms, and interaction between the constituents and their role in energy absorption capability of composites. This dissertation focuses on the development of novel test methods for the experimental investigation of fiber matrix interface and resin properties at high rate of loading to determine rate dependent traction separation law. The unique contributions that have resulted from this work in the area of polymer composite are summarized in this chapter along with major conclusions and limitations of these studies. Recommendation and future investigation on the research areas relevant to several branches encompassed in this dissertation are presented. Finally, the overall future direction of this research work has been outlined.

8.1 Unique Contributions

The unique contributions resulting from this study with comparison to the stateof-the-art are presented in the table below.

State-ol	f-the-art	
Experiments	Limitations	Dissertation
High rate interface characterization	• Indirectly characterizes interface properties through fragmentation test	 Directly loads interface in microdroplet specimen Direct calculation of interfacial shear

Table 8.1 Current state-of-the-art versus this dissertation

	 Interfacial shear strength is estimated based on critical length using Kelly- Tyson model 	 strength and energy associated with complete debonding Loading rate ranges from 1 μm/s to 1 m/s
Tailoring interfacial properties using CNT coating	 Mostly limited to coating fabrics and show interlaminar shear strength at macro length scale as a measure of interfacial property at micromechanical length scale For coatings on single fiber using EPD, no evidence of control on CNT thickness 	 Uniform CNT coating along the length and around the glass fiber Control of coating thickness down to sub- micron length scale Better understanding on coating mechanisms and on influence of coating thickness on interfacial properties
Crack monitoring along the interface	 Assumes crack initiation based on onset of non-linearity in force-displacement response Uses model interface with modified specimen geometry at larger length scale to optically observe the crack 	 In-situ measurement of crack growth without alteration of specimen geometry Carbon nanotube sensor to form electrically conductive network along the interface
Large strain response at high rate loading	 Long bars for longer duration of loading pulse to achieve large strain Very thin specimen with small cross- sectional area resulting in very small diameter bars and complicated 	 Design of specimen geometry for maximum attainable strain without altering the bar design Maintains uniaxial state of stress in the specimen during the test

	instrumentation techniques	
Rate dependent traction separation law	• For iterative method, traction laws are determined through simulation by matching the experimental load- displacement. More than one combination of peak traction and fracture energy may give the same result	• A unique combination of peak traction and fracture energy has been determined for different loading rates by systematically narrowing the range of traction laws using peak load, information on crack initiation and failure modes for three different specimen sizes

8.2 Major Conclusions

Major conclusions of this dissertation are as follows:

8.2.1 High rate characterization of interface properties

A novel test method to directly characterize interfacial properties in meters per second range was developed by adopting microdroplet specimen and tensile Hopkinson bar. The loading end of the incident bar was modified to load the microdroplet specimen at 1 m/s. Finite element analysis was carried out to study the wave propagation along the gage length and in the droplet during the loading period. Comparison of the evolution of shear stress distribution along the interface from FEA results for quasi-static and high rate loading showed the droplets can be loaded up to a velocity of 10 m/s without invalidating the assumption of dynamic equilibrium. Stress wave propagation

in an S-2 Glass/Epoxy microdroplet specimen was studied with different droplet sizes (100 μ m – 200 μ m) and fiber gage lengths (2 mm – 6 mm). An optimum combination of fiber gage length (2 mm) and droplet size (200 μ m) exhibited the shortest time to reach equilibrium. To demonstrate the feasibility of the newly designed test machine, S-2 glass and epoxy system was tested out at a loading rate of 1 m/s. The interfacial shear strength increased from 49.9 MPa at 1 μ m/s to 80.6 MPa at 1 m/s.

This test method can be employed to a wide variety of high performance fibers and resin systems. However, there are some limitations in terms of specimen preparation and testing. The main prerequisite for a successful test is the formation of microdroplet on a fiber. If the matrix is of extremely low or very high viscosity, there might be issues with the formation of droplets. For such resin systems, a special specimen preparation technique or a modified geometry (disc or quasi-disk) may be necessary [162,163]. For resins exhibiting low modulus and yield stress and very high plastic deformation, probability of resin failure is higher due to large indentation on the droplet where knife edge comes in contact. For such cases, a cylinder specimen [35,164] can be employed where the knife edge comes in contact with the flat portion of the cylinder thereby reducing the deformation due to indentation.

Failure occurs in a microdroplet specimen due to mixed mode crack initiation near the loading end of the specimen. Whereas, the rest of the droplet length is dominated by Mode II loading. However, in real composites, both Mode I and Mode II stress components are present resulting in transverse and longitudinal crack formation. The crack initiation and propagation in real composites occur due to mixed mode state of stress. For the extraction of mixed mode traction separation law, experiments should also be conducted on specimens designed for the study of Mode I opening and combined state of stress, such as a cruciform specimen [165]. The cruciform specimen consists of a single fiber embedded, in a thin film of epoxy resin. The fiber can be placed perpendicular to the loading direction for Mode I dominated crack opening or at different angles for mixed mode loading.

8.2.2 Development of crack monitoring sensor through electrophoretic deposition of carbon nanotubes on glass fibers

Electrophoretic deposition (EPD) method was deposit used to polyethyleneimine (PEI) functionalized multiwall carbon nanotube (CNT) films onto the surface of individual S-2 glass fibers. By varying the processing parameters of EPD following Hamaker's equation, the thickness of CNT film was controlled over a wide range from 200 nm to 2 µm. The films exhibited low electrical resistance, providing evidence of coating uniformity and consolidation. Study on the interrelation between processing parameters showed that decreasing the deposition time is the most efficient way to yield thin and homogeneous CNT coating on glass fiber, which can be used to detect crack initiation at the interface.

Changes in interfacial properties due to the application of CNT coatings onto the fiber surface with and without a CNT-modified matrix were studied. Glass fiber with a 2 μ m thick CNT coating and the unmodified epoxy matrix showed the highest increase (58%) in interfacial shear strength (IFSS) compared to the baseline. The increase in the IFSS was proportional to CNT film thickness and can be attributed to the CNT coating resisting propagation of crack. Untreated fibers with CNT-modified matrix showed a 35% increase in IFSS. Failure analysis of the microdroplet specimens indicated higher IFSS was related to fracture morphologies with higher levels of surface roughness.

This study demonstrated the control of CNT coating thickness onto single glass fibers. However, this deposition method can easily be scaled up for coating CNTs at higher length scale like fabrics. EPD of CNT on glass fiber fabrics has been demonstrated by An et al. [74] that resulted in improved mechanical properties.

Besides glass fibers, which are used as hard armor for vehicles and temporary shelters, EPD method can also be employed to coat CNTs and improve ballistic performance of fibers/fabrics used as flexible body armor in personnel protection applications such as Kevlar. Introduction of CNTs onto Kevlar can improve impact properties by increasing fabric friction without compromising the weight of the material.

8.2.3 Detection of crack initiation in a microdroplet specimen using carbon nanotube sensors

Electrophoretic deposition method enables the thickness of the CNT coating to be adjusted, facilitating control of fiber/matrix interfacial resistivity. The electrical sensitivity was used to detect damage initiation along the interface. By controlling the CNT thickness, a CNT sensor was developed, which does not alter the interfacial shear strength but is still electrically conductive. For S-glass and epoxy system considered in this study, it was found, based on force and electrical resistance measurement, that the crack becomes unstable and complete debonding occurs as soon as the crack reaches the interface. The use of CNT provides a unique opportunity to monitor crack initiation at the interface inside the specimen, which is otherwise difficult to achieve using conventional optical techniques. However, measurement techniques used in the current study does not provide spatial information of the crack tip. For *in-situ* detection of exact location of the crack tip, techniques such as time domain reflectometry [166] can be employed.

Improvements in the mechanical properties of composites due to the incorporation of CNTs coupled with its ability to sense damage has provided a unique opportunity for the creation of truly multifunctional composites. Deposition of CNTs on non-conductive substrates such as glass has enabled sensing damage along fiber matrix interface at submicron length scale. In order to develop a truly non-invasive sensor, individual CNTs can be mixed in the GPS sizing bath to get percolation and use it to coat the glass fibers. This process could potentially eliminate the thick CNT coating.

As mentioned earlier, this deposition method can be easily scaled up to fabric level while still maintaining the control and uniformity of the CNT coating. Such EPD fabrics can be used for real-time strain or damage sensing as well as for structural rehabilitation. In addition, CNT based sensors produced by EPD method show much higher sensitivity to the applied strain compared to foil strain gages. As such, there is a growing interest for the use of these multifunctional sensors in the sector of structural health monitoring.

8.2.4 Time and temperature dependent response of an epoxy resin

Compressive properties of epoxy DER 353 resin was characterized over a wide range of strain rate (0.001/s to 12,000/s) and temperature (ambient to above Tg). To obtain stress strain response up to large strain under high strain rate, a donut shaped specimen was designed through a series of FE simulations. This specimen geometry enables characterization of epoxy resin up to large strain without altering the design of the Hopkinson bar. Stress strain response of DER 353 under high strain rate showed thermal softening due to adiabatic heating. It was estimated that the specimen temperature rises above Tg under high rate of loading, resulting in the epoxy transitioning from glassy to rubbery state. This led to the need for characterization of epoxy resin at different temperatures ranging from ambient to above Tg range.

As the material enters the Tg range, which starts at around 70°C, the yield point in the stress strain curve starts to diminish. As the temperature reaches 100°C, the yield point completely vanishes exhibiting an elastic rubbery behavior. Also, the sensitivity to strain rate decreases as the temperature is increased further above Tg. An Eyring type equation was used for the prediction of strain rate and temperature dependent yield stress.

In this study, rise in specimen temperature at lower strain rates (0.01/s to 1/s) was monitored using an infrared camera. However, this method can only provide information on temperature rise at the surface of the specimen. During the test, thermal gradient exists across the specimen due to differences in the rate of heat generation from

plastic work and dissipation to the surrounding. Information on spatial rise in temperature in the specimen by embedding thermocouples inside could be used in determining strain and strain rate dependent inelastic heat fraction and ultimately in developing more accurate models.

8.2.5 Development of constitutive model for strain rate and temperature dependent large deformation inelastic behavior of an epoxy resin

An incremental approach was adopted to develop time and temperature dependent constitutive model. The model can predict stress strain behavior over a wide range of temperature from ambient temperature, where the material is in glassy state, to above glass transition temperature, where the material is in rubbery state. Thermal softening, which occurs at high strain rates, is also captured in the model through the estimation of temperature rise based on heat generation due to plastic work. Case studies for a wide range of monotonic and varying strain rates and large strains, showing excellent agreement with the experimental findings, were presented to demonstrate the capabilities of the constitutive model.

8.2.6 Extraction of traction separation law and the path forward

Rate dependent traction separation law for composite interface was determined through iterative method by simulating the microdroplet experiments at different loading rates. The microdroplet experiments were accurately simulated by considering the rate dependent resin and interface properties obtained from the experiments, and the information on crack initiation at the interface obtained from the CNT sensors. Both the peak traction and fracture energy in the interfacial traction separation law were found to be dependent on the rate of loading. Partitioning of energy absorption by the constituents showed that the contribution of the interface is small up to the peak load and then increases rapidly as the crack grows along the interface.

The rate dependent traction separation law thus obtained through microdroplet simulation will then feed into models at higher length scale, where more complicated or realistic interactions between multiple fibers and matrix can be studied. Such studies can provide insight into stress redistribution among neighboring fibers after initial fiber break, which ultimately leads to catastrophic failure of composites. Through parametric studies and analysis on energies absorbed by fiber, matrix and interface from FE simulations, an optimum combination of peak traction, yield strength and strain to failure of resin can be obtained for maximum energy absorption.

New epoxy resins based on long chain monoamines in Partially Reacted Substructures (mPRS) are being synthesized at Drexel University that allows one to tailor yield stress, failure strain and energy absorption over a wide range without affecting elastic response [167]. An optimum mPRS epoxy network structure can be identified based on parametric studies conducted using FE simulation to maximize energy absorption for S-2 glass epoxy composite system.

Similarly, interface properties can also be tailored through modification of fiber surface morphology, either by introducing carbon nanotubes as demonstrated in this study or through the application of sizing formulation with different ratios of reactive and non-reactive silanes. Then, experimentally determined strain rate and temperature dependent properties of mPRS resin and interface properties with fiber surface modification will serve as model inputs for validation (Figure 8.1).



Figure 8.1 A framework for design and optimization of composite materials for maximum energy absorption

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