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MULTISCALE ANALYSIS OF ADHESIVE INTERFACE BETWEEN CEMENT PASTE AND EPOXY

By

Jovan Tatar

August 2016

Chair: H. R. Hamilton
Major: Civil Engineering

Externally bonded fiber reinforced polymer (FRP) composites represent a viable alternative to traditional repair methods in deteriorated concrete structures. The main disadvantage of FRP is vulnerability of their bond to concrete when subjected to moisture. Previous work concentrated on macroscale investigations of bond behavior and durability, which does not provide evidence concerning the exact mechanisms behind bond formation and degradation.

It is recognized, in this study, that adhesive bond between epoxy and cement paste transcends multiple length scales; the conducted work focused on nano-microscale phenomena: (1) formation of distinct chemo-mechanical transition region between epoxy and cement paste termed interphase, and (2) chemical bonding between the adherents. Raman spectroscopy and nanoindentation investigation of the region near the interface revealed the existence of interphase which was found to be a consequence of permeation of epoxy adhesive through the porous structure of cement paste substrate. Interphase in epoxy resulted from increased crosslinking between epoxy monomers due to higher concentrations of aminated hardener near the interface (owing to its preferential adsorption by the substrate). Evaluation of nanomechanical data by
means of continuum micromechanics revealed a strong correlation between mechanical properties of interphase and the amount of epoxy-filled porosity.

Finite element analyses were performed to determine the effects of interphase and epoxy adhesive properties (thickness and elastic modulus) on available energy for crack growth along the interface (interfacial energy release rate). It was found that increased elastic modulus of adhesive and interphase, and decrease in adhesive layer thickness result in reduction of interfacial energy release rate. Effects of interphase on energy release rate dissipate with increasing crack size relative to interphase thickness.

Mechanical testing was conducted to assess the fracture energy and durability of interface between cement paste and epoxy governed by chemical bonding, which was accomplished through minimizing the mechanical bond component by polishing. Extreme degradation of interface had occurred following conditioning in water; a group of samples that were treated with silanes to modify the type of chemical bonding at the interface exhibited an improvement in interfacial fracture energy and durability.
CHAPTER 1
INTRODUCTION

Research Motivation

Aging infrastructure in the US, bridges in particular, is in need of reliable, economical, and fast repair method—National Academy of Engineering named “restoration and improvement of urban infrastructure” as one of the grand challenges for engineering (National Academy of Engineering 2015) which placed infrastructure problems in the same category with other problems of global importance, such as engineering better medicine or providing access to clean water.

Eleven percent of bridges in 2012 were classified as structurally deficient, and 24.9% were found to be functionally obsolete (ASCE Report Card 2013); the total cost to repair deficient bridges in the US is estimated at $76 billion. Externally bonded fiber reinforced polymer (FRP) wraps can be used to effectively increase the strength and stiffness of decayed bridge superstructures while mitigating the corrosion processes by slowing down the diffusion of chlorides into concrete. Their ability to extend the lifetime of a structure makes them a uniquely sustainable solution—compared to a complete replacement of the structure, a relatively small amount of FRP is required which makes it a viable alternative in terms of cost, energy consumption and carbon footprint. Short-term performance and behavior of FRP-repaired concrete systems has been extensively studied; however, since use of FRP composite reinforcement in concrete structures is a relatively novel repair method information on long-term performance of these systems is scarce. Research is, therefore, required on problems that may arise due to exposure of FRP-concrete systems to highly aggressive environments.

Carbon reinforced fiber polymers (CFRP) are most commonly employed in bridges, due to the fibers’ resistance to harsh environmental conditions typically experienced in such
applications. Extensive studies have been performed at University of Florida on durability of FRP-concrete bonded systems, and it was confirmed that the most prominent flaw of these systems is the durability of their bond to concrete: when exposed to moisture the adhesive bond becomes inefficient (Tatar and Hamilton 2015; Dolan et al., 2009; Douglas et al. 2014).

**Conceptual Bond Model**

In this work it is recognized that adhesive bond between FRP and concrete is a phenomenon that transcends across multiple length scales: the conceptual bond formation model is presented in Figure 1-1. At macro scale three-distinct phases are observed in the bonded system: FRP, epoxy adhesive, and the concrete substrate. Bond between FRP and concrete is formed by means of epoxy adhesive that transfers load between the composite and substrate. Owing to the complexity of the adhesive bond at epoxy-concrete interface, such treatment of the bond is only valid when “perfect” adhesion between epoxy and the substrate exists; however, this assumption is often not true, particularly when considering the effects of bond degradation on the overall bond behavior. This is mainly due to the nature of bonding mechanism between epoxy and concrete at smaller length scales, where both mechanical interlock and chemical bonding contribute to the overall bond performance (Tatar et al., 2013); degradation of each bond formation mechanism can occur and contribute to the macroscale bond properties. Relative contribution and degradation of each of the bonding mechanisms is not clear from a macroscale prospective, which hinders a more intelligent design of FRP-concrete adhesive joints.

Mechanical interlock is established primarily at micro-macro scale (Figure 1-1) by flow of epoxy into the holes, crevices and pores of concrete substrate. After it cures, epoxy locks in mechanically to the surface. However, due to plasticization effects in epoxy, caused by its exposure to water, mechanical bond may be weakened. Plasticization is a change in the thermal and mechanical properties of a given polymer which involves: (a) lowering of rigidity at room
temperature; (b) lowering of temperature, at which substantial deformations can be effected with not too large forces; (c) increase of the elongation to break at room temperature; (d) increase of the toughness (impact strength) down to the lowest temperature of serviceability (Immergut and Mark 1965).

At nano-microscale, the main bond-forming mechanisms are interphase formation and hydrogen bonding between the adhesive joint constituents. Interphase represents a transition region between the properties of neat epoxy adhesive and those of the substrate (concrete/cement paste) and is believed to be formed by permeation and adsorption of adhesive into the substrate. Hydrogen bond forms as a result of polarization of molecules or groups of atoms and represents a dipole interaction: it is formed between a negatively charged atom like oxygen (O) or nitrogen (N) and hydrogen (H). In general, hydrogen bond is a type of van der Walls interaction termed Keesom force. These bonds are relatively weak when compared to covalent and metallic bonds. In case of concrete, hydrogen bonds are believed to be established through O atoms on concrete surface and H atoms of epoxy hydroxyl groups, or epoxy hardener N atoms. When bond is exposed to moisture, hydrogen bonds can get displaced by water molecules (Lefebvre, 2000) causing chemical bond to degrade. The effects of interphase in degradation of the adhesive joint at nano-micro are not clear.

Furthermore, epoxy structure is affected by temperatures higher than $T_g$, which causes epoxy to lose stiffness due to increased chain mobility. $T_g$ (glass transition temperature) is the approximate midpoint of the temperature range over which reversible change in an amorphous polymer, or in amorphous regions of a partially crystalline polymer, to a rubbery or viscous condition from a glassy or hard condition (ISO 22768:2006).
Figure 1-1. Conceptual FRP-concrete bond model.

**Research Objectives**

The conducted work focused on nano-microscale which is characterized by (1) formation of distinct chemo-mechanical transition region between epoxy and cement paste termed *interphase*, and (2) chemical bonding between the adherents. Better understanding of the two mechanisms is thought to form the basis for intelligent adhesive interface design. Surface roughness effects and mechanical bond mechanisms, characteristic for micro-macroscale, were not taken into consideration as they are not thought to govern the behavior of bond at nano-microscale; these effects were reduced through vigorous polishing of the substrate surface, which
was believed to minimize the coupling between nano-microscale and micro-macroscale phenomena.

In the context of this work, *interface* is defined as a surface of physical separation between epoxy and cement paste; on either side of interface lay *cement paste interphase* and *epoxy interphase* (Figure 1-2). Research approach is graphically outlined in Figure 1-2 and was aimed at achieving the following objectives:

- **Objective 1:** Perform nanomechanical and spectroscopic characterization adjacent to cement paste-epoxy interface to establish evidence of interphase existence, its formation mechanisms and mechanical properties. Raman spectroscopy and nanoindentation were utilized to accomplish the objective.

- **Objective 2:** Numerically evaluate the effects of interphase and adhesive properties on interfacial energy release rates to identify the most prominent parameters affecting the energy available for interfacial crack growth (interfacial energy release rate).

- **Objective 3:** Determine the effects of moisture exposure on interfacial fracture parameters governed by chemical bonding between the adherents (while mechanical bond component is minimized). This was accomplished through development of a novel adhesion test method that utilizes a sharp precrack at the interface between the adherents to initiate the crack growth. Effects of mechanical bond were minimized by vigorous polishing of bonding surfaces. Cement paste surface functionalization by silane coupling agents was also explored as a method of enhancing strength and durability of chemical bonds between cement paste and epoxy. Quantitative data and fractographic evidence were discussed in regards to results from **Objective 1** and **Objective 2**.
Figure 1-2. Research agenda to examine two bond formation mechanisms at nano-microscale: interphase formation and chemical bonding.
CHAPTER 2
BACKGROUND ON EXPERIMENTAL METHODS

Advanced experimental characterization methods were utilized to study the interphase region between cement paste and epoxy: Raman spectroscopy and nanoindentation. This chapter provides a concise overview of the experimental techniques.

**Raman Spectroscopy**

When light interacts with a molecule photons can be scattered (Figure 2-1). Most of the scattering is elastic (no change in energy between incident and scattered photons) and is called Rayleigh scattering. Only a very small portion of all photons (approximately 1 in every $10^7$) experiences an increase (anti-Stokes) or decrease (Stokes) in wavelength due to the interaction with a molecule or a group of atoms—these process is referred to as inelastic scattering or Raman scattering. Inelastic scattering is due to activation of vibrational, rotational, and stretching modes within the molecule when interacting with incident photons. The corresponding change in energy of a proton due to an inelastic scattering event contains information about the molecule deformation mode, and its characteristics. Theoretical details surrounding involved mechanisms of interaction between photons and molecules/atoms can be found elsewhere (Ingle and Crouch 1988).

The change in energy in inelastically scattered protons can be used to characterize materials and forms the basis of an experimental characterization technique called micro Raman spectroscopy. The typical experimental setup is shown in Figure 2-2. A monochromatic light beam (laser) is generated at the excitation source and focused to a desired location on the sample through the optical microscope objective lens. The inelastically scattered photons are then directed to detector through a set of filters and mirrors where the photons of the same wavelength are counted. The output signal, therefore, contains the wavelength of inelastically scattered
photons and their corresponding counts. The signal that can interfere with Raman scattering
signal is called fluorescence (Figure 2-1); this occurs when electrons return from exited (higher
energy) electronic state to their ground energy which results in emission of a photon.

Change in energy/wavelength of a proton is often described in terms of Raman shift that
represents the difference in wavelength between incident and scattered photon and is expressed
in cm\(^{-1}\):

\[
\bar{\nu} = \nu_0 - \nu_v = \frac{1}{\lambda_0} - \frac{1}{\lambda_v}
\]  

(2-1)

where \(\nu_0\) and \(\nu_v\) are respectively frequencies of incident and scattered photon; \(\lambda_0\) and \(\lambda_v\) are
wavelengths of incident and scattered photon, respectively. The associated change in energy of a
photon can be calculated as:

\[
\Delta E = h\bar{\nu}
\]  

(2-2)

where \(h\) is Planck’s constant.

Types of scattering events (Stokes and anti-Stokes) are graphically represented in Figure
2-3 and Figure 2-4. *Raman lines* or *Raman peaks* are indicative of distinct deformational modes
within the molecules in the sample. The relative intensity between the peaks is related to the
relative number of occurrences of each of the deformational modes, and therefore can be related
to the concentration of different species within the material.
Figure 2-1. Scattering of photons after interaction with the sample. (Butler et al. 2016)

Figure 2-2. Typical Raman Spectroscopy instrumentation setup. (Butler et al. 2016)
Figure 2-3. The possible events in scattered photons: (a) Rayleigh scattering (no change in energy between incident and scattered photon); (b) Stokes scattering (energy from incident photon is absorbed, and scattered photon has lower energy level); (c) anti-Stokes scattering (following interaction with incident photon, molecule/atom releases energy, thus energy of scattered photon is higher).


Figure 2-4. Raman signal represented in terms of counts, and energy levels (expressed as frequency of scattered photons).
Nanoindentation

Indentation, an experimental technique used to assess hardness of engineering materials, has existed for a very long time. Technological progress and introduction of sophisticated displacement control and load sensing hardware have resulted in development of nanoindentation—technique that allows access to nanoscale mechanical properties of materials (hardness and elastic modulus) by accurately measuring load and displacement during loading and unloading of the sample. The technique gained its wide acceptance and recognition following the work of Oliver and Pharr (1992), which set the basis of modern experimental nanomechanics.

Nanoindentation Equipment

The nanoindentation experiments, in this study, were conducted on an Asylum Research MFP-3D SA Nanoindenter (Figure 2-5). The equipment utilizes the optical lever system of the MFP-3D atomic force microscope, combined with a vertical nanoindentation probe. The gold coated silicon chip on the back of the nanoindentation fixture reflects the laser light back through a collimating lens to a mirror that sends it to a photodetector. Depending on the position of the laser light relative to the four quadrants of the photodetector, the lateral and vertical deflection of the indenter tip are determined. Given the vertical setup of the nanoindentation system, the lateral component is negligible.

To assure accurate acquisition of nanoindentation data and minimize measurement error, multiple calibrations are performed on the system prior to any experiments:

1. Virtual deflection calibration is done by performing an indent away from the surface of the specimen, in air. Any registered change in load is due to the opto-mechanical artifacts and is accounted for by subtracting the slope of load-displacement curve from actual indentation experiments.

2. Optical lever sensitivity calibration is needed to establish a correlation between the movement of laser light on the photodetector that is expressed in Volts to the actual
The deflection of the indenter tip (in nm). The deflection of flexure ($z_{LVDT}$) is governed by a piezo actuator. The calibration is performed by conducting a series of indents with a sapphire ball probe of a flat sapphire sample. Since both probe and sample are extremely hard, it can be assumed that negligible deformation occurs in the sample and indenter and most of the registered displacement is due to the deflection of the flexure. The constant that correlates photodetector signal ($V$) to the movement of indenter flexure (nm) is determined from the slope of the deflection signal ($V$) vs. the displacement of piezo ($z_{LVDT}$ in nm). Establishing the relationship between the two allows the force acting on the sample to be calculated from the stiffness constant of the spring attached to the indenter tip ($k$).

![Figure 2-5. Nanoindentation test setup scheme on Asylum Research MFP-3D. (MFP-3D Manual)](image)

**Oliver and Pharr Method**

The most common purpose of nanoindentation experiments is to obtain elastic modulus and hardness of the tested sample. This is done by penetrating the indenter tip into the sample and analyzing the resulting indentation load-displacement response; a typical plot is given in Figure 2-6a. The first part of the curve (from 0 to $P_{max}$) corresponds to loading phase. In this phase, elastic and eventually plastic zone in the test specimen is developed beneath the indenter tip. Once the plastic zone is sufficiently large, so that there is no additional increase in load, the specimen is unloaded. During the unloading phase, elastic energy stored in the material surrounding the plastic zone recovers a portion of its maximum deformation, but it is unable to return the indentation point to the original shape due to developed residual deformation. The
schematic representation of indented surface during loading and unloading is shown in Figure 2-6b.

Figure 2-6. (a) Load-displacement curve; (b) schematic of section through indenter surface during loading and unloading: $P_{\text{max}}$ is the maximum load, $h_e$ is the elastic recovery displacement, $h_r$ is the depth of residual impression, $h_{\text{max}}$ is maximum depth of penetration corresponding to maximum load ($P_{\text{max}}$), $h_c$ is contact depth, $h_a$ is displacement of the surface at the contact perimeter, $\alpha$ is indenter tip angle. (Fischer-Cripps 2011)

Most common types of indenter geometries are: conical, Berkovich (three-sided pyramid), Knoop (elongated diamond), and cube-corner (Figure 2-7). One common characteristic in all indenters is the property of geometric similitude: projected area of indent scales with the penetration depth, which allows for load, depth and plastic zone to scale at the same rate. The Berkovich indenter was used for all nanoindentation experiments performed in this study.
Elastic modulus can be obtained by considering a physical quantity representing a combination of elastic moduli of the tip and sample, referred to as reduced modulus:

\[
\frac{1}{E_r} = \frac{(1 - \nu^2)}{E} + \frac{(1 - \nu_i^2)}{E_i}
\]  

(2-3)

where \(E\) and \(\nu\) are respectively elastic modulus and Poisson’s ratio of the sample; and \(E_i\) and \(\nu_i\) are elastic modulus and Poisson’s ratio of the indenter, respectively.

When nanoindentation experiments are performed using an indenter tip made of material with an elastic modulus (e.g. diamond—\(E_{diamond} = 1140 \text{ GPa}; \ \nu = 0.07\)) that is much larger than the elastic modulus of sample (\(E_i \gg E\)), the second term in eq. (2-3) becomes negligible.

The elastic modulus of sample can then be determined as:

\[
E = (1 - \nu^2)E_r
\]  

(2-4)

According to Oliver and Pharr (1992), the slope of upper portion of the unloading curve can be correlated to reduced modulus according to the following equation:

\[
E_r = \frac{\sqrt{\pi} \ S}{2 \ \sqrt{A}}
\]  

(2-5)

where \(A\) is the contact area at maximum load; \(S\) is the measured stiffness of the sample—slope of unloading portion of P-h curve in Figure 2-6a \((dP/dh)\). The contact area at maximum load is a function of the indenter geometry and the depth of Figure 2-6b. While the relationship between the contact area and tip geometry can be determined from Table 2-1 by assuming perfect
indenter geometries (Figure 2-7), the actual contact areas often deviate from analytically derived values due to fabrication defects and wear of the indenter tip; the function correlating contact area to a range of contact depths is, therefore, determined experimentally prior to data analysis. Stiffness of the unloading portion of the curve is determined by fitting the following relation:

\[ P = A(h_{\text{max}} - h_r)^m \]  \hspace{1cm} (2-6)

where \( A, h_r \) and \( m \) are determined from a least squares fit.

The main challenge, however, is determining the contact depth from experimental data. According to Oliver and Pharr (1992), contact displacement can be expressed as:

\[ h_c = h_{\text{max}} - h_a \]  \hspace{1cm} (2-7)

While the value of \( h_{\text{max}} \) can be easily obtained from the P-h graph, determining the value of \( h_a \) is more difficult. Based on analytical expressions for shape of indented surface outside of the contact area (Sneddon 1965) for conical indenter geometry, Oliver and Pharr (1992) demonstrated that:

\[ h_a = \frac{\pi - 2}{\pi} (h_{\text{max}} - h_r) \]  \hspace{1cm} (2-8)

By substituting term \( (h_{\text{max}} - h_r) \) in eq. (2-8) with the following relationship by Sneddon (1965):

\[ (h_{\text{max}} - h_r) = 2 \frac{P_{\text{max}}}{S} \]  \hspace{1cm} (2-9)

it can be shown that:

\[ h_a = \varepsilon \frac{P_{\text{max}}}{S} \]  \hspace{1cm} (2-10)

where \( \varepsilon = 2(\pi - 2)/\pi \) for conical indenter; for Berkovich indenter geometry parameter \( \varepsilon \) takes the value of 0.75.
In addition to reduced modulus, hardness can be also determined from the nanoindentation data:

\[ H = \frac{P_{\text{max}}}{A} \]  \hspace{1cm} (2-11)

where \( A \) is projected area of the indenter tip.

### Table 2-1. Projected area for sharp indenter geometries.

<table>
<thead>
<tr>
<th>Indenter type</th>
<th>Projected Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>Berkovich</td>
<td>( 24.5h_c^2 )</td>
</tr>
<tr>
<td>Cube Corner</td>
<td>( 2.60h_c^2 )</td>
</tr>
<tr>
<td>Knoop</td>
<td>( 108.21h_c^2 )</td>
</tr>
</tbody>
</table>

### Tip-Area Calibration

As already discussed, contact area of Berkovich indenter can be determined according to the following relation:

\[ A = 24.5h_c^2 \] \hspace{1cm} (2-12)

which assumes three-sided pyramid geometry with a 142.3° angle. The assumption of a perfectly sharp tip (radius of curvature at the tip approaching 0), however, is not valid. Due to manufacturing defects and wear due to use every probe will have a finite curvature at the very tip, which makes eq. (2-12) invalid for very small contact depths. To account for realistic tip geometry, Oliver and Pharr (1992) suggested the following relationship between the contact area and contact depth:

\[
A(h_c) = C_0h_c^2 + C_1h_c^1 + C_2h_c^{1/2} + C_3h_c^{1/4} + \cdots + C_8h_c^{1/128}
\] \hspace{1cm} (2-13)

where \( C_0 \) through \( C_1 \) are constants calibrated to a realistic Berkovich tip; for a perfect Berkovich indenter geometry \( C_0 = 24.5 \) and \( C_1 = C_2 = C_3 = \cdots = C_8 = 0 \). The coefficients are determined by conducting a series of indents at varying contact depths on a sample of known reduced modulus.
modulus and hardness, such as quartz ($E_r = 69.6\text{GPa}; H = 9.25\text{GPa}$). The coefficients are obtained by iterative fitting so that the contact area function results in values of reduced modulus/hardness that are constant over a range of contact depths, and are in agreement with that of the calibration sample. The described calibration procedure was performed prior to all experiments reported in this study.

**Possible Sources of Error**

Given the extreme sensitivity of nanoindentation sensing equipment, multiple sources of error can affect the validity of test results. One of the main concerns is the effect of external vibrations on the acquired data; vibration damping equipment was utilized to minimize these effects in Asylum MFP-3D. Additionally, specimen surface geometry (primarily roughness and tilt angle) poses a risk of introducing a significant measurement error due to their effect on the actual contact area. Finally, thermal drift can have an effect on test results: changes in displacement due to unstable temperature in the chamber atmosphere while the force remains constant can introduce a significant error, particularly when conducting creep and long-term measurements. To minimize these effects the chamber Asylum Research MFP-3D was housed in was kept closed for approximately an hour to allow the environment to stabilize. Moreover, effects of thermal drift were corrected for by the analysis software.
CHAPTER 3
BACKGROUND ON CONCRETE-EPOXY BOND

This chapter covers background material on constituents of bond between epoxy and cement paste. In subsequent experiments cement paste was chosen over concrete due to its simplicity in chemical composition and pore structure when compared to concrete. The novelty of employed experimental approach in this work necessitated this simplification.

Epoxy Adhesives

Structural epoxies used with FRP composites are available in two forms: *clear epoxy*, and more viscous *paste epoxy*. The difference in viscosity between the two products comes from additives (such as silica particles) that are not included in clear epoxies. Epoxy adhesives used in construction are generally based on bisphenol A molecules hosting an epoxide functional group at both ends, forming the monomer in the epoxy structure (Stewart, 2012)—Bisphenol A diglycidyl ether or DGEBA (Figure 3-1). Epoxy hardener is composed of amines that react with the epoxide groups to form covalent bonds. The amines bond the monomers together in a linear fashion to form polymer chains. They also allow for cross-linking between the polymer chains to form additional covalent bonds. The described process is termed “curing of epoxy”; with subsequent cross-linking a non-crystalline hardened molecular structure is formed (Douglas, 2013). At “full-cure” no additional cross-linking between the polymer chains is possible; at this point epoxy has reached its full mechanical properties. The cross-linking density is usually described in terms of conversion that takes values from 0 to 1.0, where a value of 1.0 signifies a fully-cured epoxy (Choi, 2011).
The bond between epoxy and concrete is established through chemical interactions and mechanical bonding (Tatar et al., 2013). While the exact nature of the chemical bond is not known, it is thought to consist of mostly hydrogen bonding between the surface molecules of concrete and epoxy (Djouani et al., 2011). Integrity of epoxy-concrete bond is considered to be primarily due to mechanical interlocking (Djouani et al., 2011; Kim et al., 2010; Stewart, 2011; Tatar et al., 2013). The stiffness of the epoxy, and consequently the integrity of its mechanical bond, can be compromised by two main degradation mechanisms: its transition to rubbery state at temperatures higher than the $T_g$, and plasticization of epoxy matrix.

Once the $T_g$ is exceeded, the covalent bonds between the polymer chains are capable of rotating, but remain intact. Therefore, the general shape of the epoxy structure in glassy state is maintained, but its stiffness and strength are reduced. The value of $T_g$ is dependent on polymer chain mobility. The lower the cross-linking density of the epoxy molecular structure, the less thermal energy is required for transition from a glassy state to a rubbery state (Douglas, 2013; Frigione, 2006). Amounts of free volume and cross-linking (measured by conversion) affect polymer chain mobility and consequently change the epoxy $T_g$. At room temperature conditions for two or more weeks, the conversion of most commercially available structural epoxies ranges from 0.8 to 1.0, which means that 80 to 100% of possible covalent bonds are formed (Blackburn, 2013). Exposure to temperatures above those experienced during initial curing will cause

Figure 3-1. Chemical structure of DGEBA.
additional cross-linking (Choi, 2011). Cross-linking restrains polymer chain mobility by interconnecting individual chains; therefore, the higher the cross-linking density (more covalent bonds), the less chain mobility and the higher $T_g$.

Chain mobility is also affected by the amount of free volume in the polymer structure. Free volume is the available space within the polymer chain network on a microscopic level (Douglas 2013; Frigione 2006). With increase in free volume, the mobility of polymer chains increases as there is more available space for their movement; hence, less thermal energy is required to convert the epoxy into a rubbery state. Water absorption can lead to increases in free volume in the epoxy. Epoxy curing results in the formation of hydroxyl groups in the network. Upon exposure to water, the water molecules flow into the epoxy and interact with the hydroxyl groups via hydrogen bonding (Frigione, 2006; Choi, 2011). This hydrogen bonding creates more space between the cross-linked polymer chains, thereby enlarging the free volume available. Water absorption into the epoxy is referred to as plasticization (Immergut, 1965), and will cause a decrease in $T_g$ (Frigione, 2006; Stewart, 2012; Choi, 2011). Complicating this issue further, exposing epoxy to water at temperatures above the $T_g$ can cause an increase in the rate of water absorption due to the greater chain mobility at those temperatures.

According to Zhou and Lucas (2011), two types of water bonding may exist in an epoxy matrix. One type of bonding is responsible for plasticization by breaking the inter-chain Van der Waals forces, while the other water bonding type is deemed to allow for secondary cross-linking (pseudo cross-linking) by forming hydrogen bonds between two polymer chains. The former is associated with lower desorption activation energy (approximately 10 kcal/mol), and water sorption process that takes place in low-temperature hygrothermal conditions; the other type of water bonding in such conditions is considerably less. On the other hand, presence of the latter
type of water bonding is associated with hygrothermal conditioning at higher temperatures and longer exposure times, and approximate desorption activation energy of 15 kcal/mol.

Multiple researchers examined the effects of hygrothermal conditioning on construction epoxies. Moussa et al. (2011) showed that strength and $T_g$ of epoxy strongly depends on curing temperature as well as the duration of curing. They also found that decreasing the testing temperature increased epoxy stiffness. Changes in $T_g$, conversion and water absorption of two construction exposures, during the 0 to 28-day hygrothermal conditioning, were reported by Choi (2011). It was found that effects of plasticization and additional cross-linking during exposure were in competition with each other causing changes in $T_g$ throughout the exposure. In all test groups, by 28 days of conditioning, increase in $T_g$ ranged from 1 to 14 °C. Stewart (2012) found that both modulus and strength of ambient-cured epoxies decreased due to hygrothermal conditioning, mostly due to plasticization. Similar findings were reported by Quan et al. (2008), Benzarti et al. (2011), and Latteri and Frigione (2012).

**Chemical, Morphological, and Mechanical Properties of Cement Paste**

Anhydrous cement powder has four main compounds: tricalcium silicate (C$_3$S), dicalcium silicate (C$_2$S), tricalcium aluminate (C$_3$A), and tetracalcium aluminoferrite (C$_4$AF). Reaction with water of anhydrous cement powder yields four main hydration products: calcium silicate hydrate (C-S-H), calcium hydroxide (CH), ettringite (AFt), and monosulfate (AFm). In addition to the main hydration products, hydrated cement pastes also contain varying amounts of unhydrated cement clinker (depends mostly on water-to-cement ratio and the degree of hydration).

Cement paste is inherently a multiscale material; different chemo-morphological species exist at distinct length scales. In a multiscale model of concrete, discussed by Ulm et al. (2004),
three distinct length scales associated with cement paste were identified (Figure 3-2—Levels ‘0’ through “II”). Goal of nanoindentation experiments in cement paste is to provide a better understanding of its macroscale mechanical properties, behavior, and durability.

![Figure 3-2. Distinct length scales in concrete. (Ulm et al. 2004)](image)

### Atomic Scale

At atomic scale, the exact stoichiometry of the main hydration product, C-S-H, is still an unknown. It has been confirmed, however, that the properties and structure of C-S-H are strongly affected by mass ratio of Ca to Si (Richardson and Groves 1992). A model of C-S-H, allowing for realistic Ca/Si ratios, was proposed by Pellenq et al. (2009) and, in its basal configuration (Ca/Si=1), resembles a tobomorite with an interlayer space of 11 Å with two CaO layers and eight silicate chains; the interlayer Ca$^{2+}$ ions balance out the negative charge of the configuration. To obtain a more realistic structure of C-S-H, in agreement with spectroscopic analyses results, neutral SiO$_2$ groups of silica tetrahedral are removed; this process results in “defective” C-S-H structures allowing to represent a range of realistic Ca/Si ratios. Based on this model, Qomi et al. (2014) conducted a combinatorial study to determine the relationship between C-S-H structure (defined by Ca/Si ratio) and elastic modulus; they found that elastic modulus is inversely proportional to
increasing Ca/Si ratio—high Ca/Si ratios result in C-S-H structure with more defects (Figure 3-4).

Figure 3-3. Layered structure of toboromite (top), and realistic atomic model of C-S-H (bottom). (Pellenq et al. 2009)

Figure 3-4. TEM image of C-S-H corresponding to Ca/Si ratio of 0.86 (top), and Ca/Si ratio of 1.70 (bottom). (Qomi et al. 2014)
**Level ‘0’**

Level ‘0’ represents the most fundamental length scale where a separation between the atomic and continuum phenomena occurs. This scale is represented by formation of C-S-H solid by hydration of C₃S and C₂S, which was found to have an approximate size of 5.6 nm (Figure 3-5). Many studies have concentrated on investigations at Level ‘0’, including Powers and Brownyard (1948), Feldman and Sereda (1968), and Jennings (2000). A mutual agreement is that C-S-H solid has colloid properties, meaning that it is sensitive to changes in its moisture contents. According to Jennings, the structure of C-S-H at Level ‘0’ can be regarded as a collection of globular structures with intra-globular nanoporosity of approximately 18%. Structure of the “basic building blocks” of globules is assumed to be layered; the spaces between the “basic building blocks” represent nanoporosity which carries structural water.

**Level I**

At Level I, gel porosity defines the properties of the C-S-H matrix; based on porosity two structurally distinct types of C-S-H exist: (1) a more porous low-density C-S-H (LD C-S-H); and (2) more densely packed high-density C-S-H (HD C-S-H). In addition, Chen et al. (2010) showed that a nanocomposite of calcium hydroxide (CH) and C-S-H exists at this length scale, commonly referred to as ultra-high-density C-S-H (UHD C-S-H). Hydrated aluminates, ettringite (AFt) and monosulfate (AFm), intrinsically occur within C-S-H matrix. It should be noted that gel porosity is on the length order of magnitude of about 5 nm and can contain non-structural water, and therefore participates in the fluid flow through the cement paste. Characteristic length scale of Level I is in the range 0.1-1 μm.
At a range of length scales from 1 to 100 μm, cement paste can be considered a composite consisting of C-S-H matrix with unhydrated cement clinker (C\textsubscript{3}S, C\textsubscript{2}S, C\textsubscript{3}A, C\textsubscript{4}AF), macroporosity, and large CH crystals, with a characteristic size on the order of 1 μm, representing inclusions. Transport phenomena at this lengths scale are governed primarily by a network of capillary porosity, which is mainly a result of excess water in the mixture. Amount of capillary porosity is, therefore, strongly dependent on the water-to-cement ratio (w/c).

**Nanoindentation in Cement Paste**

The purpose of nanoindentation experiments in cementitious materials is to provide access to mechanical properties of the constituent material phases existing in cement paste. Indentation elastic properties (reduced modulus and hardness) will primarily depend on the size and depth of the indent, which dictates the length scale of testing. Given the multiscale nature of cement paste, it is therefore necessary to define the range of indentation interaction volumes that will allow access to the specific lengths scale. Level I (0.1-1 μm) is, presently, the smallest material length scale of cement paste that is accessible for nanomechanical characterization by
nanoindentation; therefore, nanoindentation can provide access to mechanical properties of LD C-S-H, HD C-S-H, UHD C-S-H and unhydrated clinker. Multiple researchers have used nanoindentation to study the properties of cement hydrates existing at Level I; the indentation loads and maximum depths are summarized in Table 3-1. It should be noted that a wide range of maximum depths is due to variation in stiffness of different constituents of cement paste.

Example of load-displacement curves from literature is given in Figure 3-6.

The maximum loads in literature were selected to allow access to the individual nanomechanical properties of the three major hydration products and clinker phases existing in cement paste at Level 1 (LD C-S-H, HD C-S-H, and UHD C-S-H) whose size is on the order of magnitude between 0.1-1 μm. The radius of interaction volume in cement paste was found to be about 3 to 4 times the maximum indentation depth (Constantinides and Ulm 2004), meaning that the indentation load should be selected so that the maximum indentation depth does not exceed 500 nm. Higher loads result in larger interaction volumes and therefore provide “homogenized” (bulk) response of the material containing nanomechanical information of multiple material phases; example of the concept is shown in Figure 3-7.

Table 3-1. Summary of nanoindentation maximum loads and maximum depths from literature.

<table>
<thead>
<tr>
<th>Study</th>
<th>Max Load Range (μN)</th>
<th>Range of max depths (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Barbhuiya et al. (2014)</td>
<td>n/a</td>
<td>300-400</td>
</tr>
<tr>
<td>Chen et al. (2010)</td>
<td>4,000</td>
<td>310 (mean)</td>
</tr>
<tr>
<td>Davydov (2011)</td>
<td>1,000-5,000</td>
<td>150-600</td>
</tr>
<tr>
<td>(recommended 4,000)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Howind et al. (2011)</td>
<td>n/a</td>
<td>200</td>
</tr>
<tr>
<td>Li et al. (2015)</td>
<td>1200</td>
<td>50-800 (figure)</td>
</tr>
<tr>
<td>Miller et al. (2008)</td>
<td>2,000</td>
<td>100-400</td>
</tr>
<tr>
<td>Mondal (2008)</td>
<td>500-1,000</td>
<td>150-350</td>
</tr>
<tr>
<td>Nemecek (2012)</td>
<td>n/a</td>
<td>100-400</td>
</tr>
<tr>
<td>Zhu et al. (2007)</td>
<td>N/a</td>
<td>300-400</td>
</tr>
<tr>
<td>Zhu et al. (2009)</td>
<td>5,000</td>
<td>100-300</td>
</tr>
</tbody>
</table>
Table 3-2. Ranges of indentation mechanical properties for the three C-S-H phases based on analysis of large population of different OPC samples by Vandamme (2007), as cited in Vanzo (2009).

<table>
<thead>
<tr>
<th>Material phase</th>
<th>Reduced modulus</th>
<th>Hardness</th>
</tr>
</thead>
<tbody>
<tr>
<td>LD C-S-H</td>
<td>16-26</td>
<td>0.27-0.88</td>
</tr>
<tr>
<td>HD C-S-H</td>
<td>27-40</td>
<td>0.74-1.45</td>
</tr>
<tr>
<td>UHD C-S-H</td>
<td>36-54</td>
<td>1.15-2.35</td>
</tr>
</tbody>
</table>

Figure 3-6. Example of load-depth curves from Li et al. (2015).
Figure 3-7. Principle of statistical indentation in cement paste: relatively large indentation depths encompassing multiple constituents result in homogenized response of material; whereas indent size that is much smaller than the size of the smallest material phase provides access to individual response of material constituents. (Constantinides and Ulm 2004)

**Statistical Deconvolution of Nanoindentation Data**

A complete set of nanoindentation test results is inherently a multivariate distribution representing a mixture of mechanical properties corresponding to different material phases found in the indented sample (Figure 2-6). Following the assumption that mechanical properties of the material constituents are each normally distributed, the mechanical properties of individual constituents can be determined by fitting a number of Gaussian distributions to the experimental distribution of data; in that case the number of fitted Gaussian distributions corresponds to number of material phases with distinct mechanical properties.

An example of raw reduced modulus and hardness data obtained by nanoindentation, from literature (Krakowiak et al 2015), is given in Figure 3-8a. To determine the number of distinct material phases (Gaussian distributions), based on the contrast between the measured
material properties, Bayesian Information Criterion (BIC) was employed. BIC (Schwartz, 1978) evaluates the goodness-of-fit for a multimodal Gaussian distribution by introducing a penalty score for overfitting (excessive number of Gaussian distributions). Minimum BIC score corresponds to the optimal number of Gaussian distributions existing within a multimodal distribution.

Number of Gaussian distribution, corresponding to a minimum BIC (five in case of Figure 3-8b), was fitted to the experimental distribution by employing Gaussian mixtures model. This revealed indentation properties associated with each of the five identified material phases of distinct mechanical properties. The iterative procedure fits a desired number of Gaussian distributions to multivariate data, using maximum likelihood via the expectation maximization algorithm.

Krakowiak et al. (2015) demonstrated that the number of distinct material phases determined from nanoindentation data by analytical means, through BIC, exhibited a satisfying correlation with independent chemical analyses conducted via energy dispersive spectroscopy (EDS), shown in Figure 3-9. Deconvolution of mechanical data did not, however, differentiate between CSH and hydrated aluminates (AFt and AFm) which are an intrinsic component of C-S-H matrix (Figure 3-9). Additionally, spectroscopic analyses revealed presence of C$_4$AF crystals within the CH dominated family (Figure 3-9).

**Gaussian Mixtures Model**

Let us define a Gaussian mixture as:

$$ p(X) = \sum_{k=1}^{K} f_k N(X|\mu_k, \Sigma_k) $$

(3-1)

where $f_k$ is mixing proportion of $k$-th cluster, and $N(X|\mu_k, \Sigma_k)$ is k-th Gaussian distribution with mean $\mu_k$ and covariance $\Sigma_k$. It should be noted that the following is true:
\[ \sum_{k=1}^{K} f_k = 1 \]  \hspace{1cm} (3-2)

which means that each mixing coefficient correspond to an area occupied by a corresponding material phase. For composites with a random distribution of material phases contained within a unit volume, mixing coefficients are equal to volume fractions of the corresponding material phases.

To fit a Gaussian mixture to multimodal distribution, expectation maximization algorithm is utilized. The algorithm is initialized by dividing data into \( k \) clusters, and calculating their means. For each cluster, covariances and mixing coefficients are determined. Then, at each point in the analyzed population, an assignment score is calculated:

\[
\gamma(z_{nk}) = \frac{f_k N(x_n | \mu_k, \Sigma_k)}{\sum_{j=1}^{K} f_j N(x_n | \mu_j, \Sigma_j)} \hspace{1cm} (3-3)
\]

Assignment score \( \gamma(z_{nk}) \) is often termed “responsibility” as it quantitatively describes how much Gaussian \( k \) is “responsible” for evaluated point \( x_n \). Assignment score for each cluster is defined as:

\[
N_k = \sum_{n=1}^{N} \gamma(z_{nk}) \hspace{1cm} (3-4)
\]

To find the best match for the calculated assignment scores the initial means, covariances and mixing proportions are updated, as follows:

\[
\mu_k^{new} = \frac{1}{N_k} \sum_{n=1}^{N} \gamma(z_{nk}) x_n
\]

\[
\Sigma_k^{new} = \frac{1}{N_k} \sum_{n=1}^{N} \gamma(z_{nk}) (x_n - \mu_k^{new}) (x_n - \mu_k^{new})^T \hspace{1cm} (3-5)
\]

\[
f_k^{new} = \frac{N_k}{N}
\]

Finally log likelihood is calculated:
\[
\ln p(X|\mu, \Sigma, f) = \sum_{n=1}^{N} \sum_{k=1}^{K} \ln f(x_n | \mu_k, \Sigma_k)
\]

Log likelihood score can be interpreted as a goodness of fit of the assumed Gaussian mixture; maximum log likelihood score corresponds to a theoretically best fit, or lowest error. The iterative procedure is terminated when the likelihood function has converged.

This approach can be used for a single or multiple (correlated) multivariate Gaussian distributions. Since both modulus and hardness are the outcomes of a single indentation experiment it is prudent to assume that the two values are correlated; in other words, each modulus and hardness value can correspond to one and only one material phase (or a composite phase).

Figure 3-8. Reduced modulus and hardness data from nanoindentation on class G cement: (a) raw data with reference data for CH crystals, unhydrated clinker, and quartz from literature; (b) data after Gaussian mixtures deconvolution. (Krakowiak et al. 2015).
Review of State-of-the-Art on Epoxy-Cement Paste/Concrete Interfaces

As discussed previously, bond between FRP and concrete is formed by means of epoxy adhesives. In such an adhesive joint, multiple failure modes are possible in FRP-concrete joints (Figure 3-10). The most common failure mode that is inherent to dry ambient condition is cohesive failure mode in concrete substrate (Figure 3-10). Due to exposure to moisture, failure mode shifts to the interface between concrete substrate and adhesive (Figure 3-10). This failure mode is termed adhesive failure mode. Failure modes corresponding to adhesive decohesion or adhesive failure between FRP and adhesive are typically not experienced (Figure 3-10). FRP decohesion (Figure 3-10) is usually not of concern and may occur in underreinforced members, due to development of high interlaminar stresses, or due to exposure to aggressive environments.
While macro scale tests on FRP-concrete bond have been widely explored (comprehensive review provided in Tatar 2013), literature related to analyses of epoxy-concrete bonded joints at microscale and nanoscale is scarce. In this section, the current state-of-the-art on the subject is briefly presented, to the best of author’s knowledge.

Djouani et al. (2011) studied the adhesive properties between epoxy (Bisphenol A diglycidyl ether - DGEBA) and cement paste by multiple techniques: x-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FTIR), inverse gas chromatography (IGC), and differential scanning calorimetry (DSC). The main findings from this research were as follows:

1. Interphase zone measuring about 200 μm was confirmed from XPS scans across the interface. This finding established that permeation of epoxy into cement paste occurs, confirming the efficient wetting of the substrate. Mechanisms behind this behavior were not discussed.

2. Hydrogen bonding was confirmed by FTIR between the hardener (diethylenetriamine - DTETA) and cement paste. Interactions between DGEBA and cement paste were deemed low in comparison to the sensitivity of the instrumentation; interactions between the hydroxyl groups (OH) of the DGEBA and calcium hydroxide (hydration product) were noted.

3. As a consequence of a very strong interaction between cement paste and hardener, the $T_g$ of epoxy in interphase region is higher due to an increase in crosslinking density.

Molecular dynamics approach was taken by Lau et al. (2012) to determine the adhesion strength between epoxy on silica substrate, analogous to bond between epoxy and aggregate.
found in concrete. Authors found the adhesion strength of 134 pN for a single molecule of epoxy. Authors then developed a multiscale approach to apply their findings from molecular dynamics simulation to a continuum model of FRP-concrete shear lap specimen; disagreement between the behavior observed in an actual experiment and the model was accredited to a variety of factors that could have caused the discrepancies. The same group of authors (Buyukozturk et al., 2011) also found from the atomistic simulations (Figure 3-11) that the adhesion strength of a single epoxy molecule on silica substrate decreased by 15% (in both direct shear and peel conditions) in the presence of water.

Figure 3-11. Molecular dynamics model by Buyukozturk et al. (2011): (a) dry conditions; and (b) wet conditions.

Lau et al. (2014) also performed an experimental study on epoxy-silica bimaterial specimens. Interfacial fracture energy was estimated based on results from superlayer adhesion test method. The test method is based on depositing the Cr superlayer on bilayer specimen with a precrack. Residual stresses from the deposited Cr superlayer create compressive stresses at the top surface of the coating causing bending of the coating. Once the critical thickness of the superlayer is reached the debonding will occur. Interfacial fracture energy is determined from the
curvature of the debonded coating (Figure 3-12a), based on linear elastic fracture mechanics (LEFM). Presence of hair-like structures was observed near the crack tip in debonded specimens in higher resolution SEM images (Figure 3-12b); according to the authors this observations is an evidence that debonding of epoxy from silica is introduced by detachment of epoxy chains from the silica surface. Authors found that wet ambient conditions can lower the critical fracture energy of the interface by as much as 50%.

![Figure 3-12. (a) Interfacial debonding in wet sample with 1 μm Cr superlayer; and (b) presence of hair-like structures near the crack tip (Lau et al., 2014).](image)

Stewart (2012) conducted a study on epoxy-cement paste samples to determine the type of interaction occurring between the adherents. Weak interactions were observed in solid state nuclear magnetic resonance (SSNMR) and two-dimensional nuclear magnetic resonance (2D NMR), but the type of interactions was not discerned.

**Effect of Silane Coupling Agents on the Adhesive Bond**

Hydrogen bonding between cement paste hydration products and epoxy is thought to be established between nitrogen atoms of the adhesive and hydroxyl groups of the substrate (O−H···:N), and/or between oxygen and hydrogen atoms in the adhesive and substrate (O−H···:O). The energy required to break these bonds is on the order of 30-50 kJ/mol (Callister and Rethwisch 2008), which is very small compared to energy required to break covalent bonds
(on the order of 450-700 kJ/mol—Callister and Rethwisch 2008). Additionally, due to the polar nature of hydrogen bonds they can be easily disrupted by water molecules; this is thought to be a contributing mechanism to overall degradation of epoxy-cement paste interfaces (Lefebvre et al. 2000). On the other hand the lack of dependence on polarity is believed to make covalent bonds less vulnerable to the effects of aqueous environments.

To improve chemical bonding between epoxy and concrete multiple researchers employed silane coupling agents. Silanes consist of Si molecule that hosts two functional groups, one that can establish covalent bonds with organic materials and the other one that bonds covalently with an inorganic material, which allows to indirectly form covalent bonds between the adhesive and substrate. Ye et al (1997) used silane treatment to examine its effects on global fracture energy of bond between CFRP and concrete, and found that silane had improved the bond fracture energy in specimens with improper surface preparation. They, however, did not report significant improvement in bond strength in the samples with properly prepared substrate, likely because the failure mode shifts from adhesive to cohesive. Choi et al. (2013) tested the durability of bond between epoxy and silane-treated concrete to water, using slant shear test method. To functionalize the concrete surface prior to bonding an epoxy functional silane (3-glycidoxypropyltrimethoxysilane) was used. While the control groups (dry conditions) showed no statistically significant difference between the silane-treated and non-treated cement substrate, the silane-treated group presented better resistance to deleterious effects of water on bond properties. Amidi and Wang (2016) examined the effect of concrete surface functionalization with γ-glyci-doxypropyltrimethoxysilane (γ-GPS) on sub-critical crack growth along the interface between CFRP and concrete in dry and humid environments. The study reported improvement in bond durability in specimens that were treated with silane.
Subsequent work by Stewart et al. (2013) examined the change in contact angle, and XPS spectra of cement paste surfaces treated with three different silanes: Aminopropyltriethoxy silane (APTES), 3-glycidyloxypropyltrimethoxy silane (GPTMS), and methoxy terminated polydimethyl siloxane (PDMS). While APTES decreased the contact angle, an increase was observed in PDMS-treated samples. This was explained by the hydrophilicity and hydrophobicity of the free functional groups in respective silanes. GPTMS presented no significant change in contact angle most likely due to its functional groups not presenting neither hydrophilic nor hydrophobic preference. XPS spectra showed successful formation of covalent bonds between three of the silanes and cement paste which provided additional evidence explaining the mechanism behind the positive effect silanes have on durability of adhesive bonds between concrete and epoxy reported in the literature.
CHAPTER 4
LITERATURE REVIEW OF CONTINUUM MICROMECHANICS

Cement paste, like many other infrastructure materials, is a multiscale material; depending on the length scale of observation, the material structure changes. The aim of continuum micromechanics lies in bridging different material scales in order to deduct the material’s effective (homogenized) behavior (e.g. stiffness, strength, thermal properties, etc.) by “linking” the length scales that are separated by orders of magnitude. This can be accomplished by considering the individual physical properties of constituting material phases, morphology, and their interaction. Establishing upscaling relationships (bottom-up approach) opens up opportunities for optimized design of engineering materials, including cement and concrete, through modifications in the materials’ microstructure. In the development of upscaling schemes, continuum mechanics framework is employed; in case of atomic and sub-atomic length scales, where material properties are dominated by quantum effects, these theories do not apply.

Initial attempt to establish the relationship between materials microstructure and their macroscopic properties was by Voigt (1887) and Reuss (1929), what is commonly referred to as Voigt-Reuss bounds or Rule of Mixtures. Voigt-Reuss bounds are respectively based on the uniform strain and uniform stress assumption, and represent the absolute upper and lower effective material property estimates, when the Poisson’s ratios are the same between the different material phases. Similar methods to Voigt and Reuss bounds exist that can provide more accurate estimates of materials’ effective properties.

Micromechanical theories of elastic homogenization, based on evaluation of representative elementary volume (REV), are herein explored. The purpose of the micromechanics analyses is to establish the general understanding of macroscopic elastic
modulus distribution in the cement paste interphase. Some of the micromechanical methods summarized in this chapter will be used sand recalled in subsequent chapters.

**Representative Elementary Volume (REV)**

Micromechanical homogenization requires the knowledge of distinct length scales in the evaluated material. For example, in microfiber-polymer particulate composite the two main length scales exist: (1) the length scale of the microfiber, defined by the length of the individual fibers \(d\); and (2) the composite length scale \(\mathcal{D}\). To evaluate the homogenized properties of the composite, the requirement of scale separability has to be met \((\mathcal{D} \gg d)\). If macro fibers are added to the mix, three distinct length scales (levels) exist as shown in Figure 4-1: (1) length scale at which microfibers and macrofibers exist is defined by the length of individual microfibers \(d_1\), (2) length scale of macrofibers defined by their length \(d_2\) embedded in a homogenized composite matrix of the polymer and microfibers; and (3) length scale of the composite \(\mathcal{D} (\mathcal{D} \gg d_2)\). At length scale \(\mathcal{D}\), in both cases, heterogeneous materials can be regarded as homogeneous.

Characteristic dimension \(\mathcal{D}\) defines what is commonly referred to as representative elementary volume (REV), the smallest volume of heterogeneous material for which properties do not change from one REV to another. The effective elastic properties of REV, therefore, correspond to the effective elastic properties of the entire material.

Figure 4-1. Schematic representation of scale separability for two different cases: two-phase and three-phase composite.
Multiple micromechanics methods for estimation of effective elastic properties of REV will be discussed, as reviewed by Qu and Cherkaoui (2006). All methods consider a heterogeneous material that consists of inhomogeneities under domain $\Omega_i (i = 1, 2, ..., N)$ and stiffness tensor $C_{ijkl}^i (i = 1, 2, ..., n)$ embedded in a matrix having domain $\Omega_m$ and stiffness tensor $C_{ijkl}^m$. Volume fraction of inhomogeneities over the entire domain $\Omega$ is defined as:

$$f_i = \frac{\Omega_i}{\Omega} \quad (4-1)$$

In case where stiffness tensors of inhomogeneities are same as those of matrix ($C_{ijkl}^m = C_{ijkl}^1 = C_{ijkl}^2 = \cdots = C_{ijkl}^n$) the stress and strain fields do not vary across the entire composite; in other words, when no inhomogeneities are present in the matrix, matrix stress and strain ($\sigma_{ij}^m$ and $\varepsilon_{ij}^m$) are constant throughout the domain $\Omega$. It should be noted that, when inhomogeneities have stiffness matrices different than those of the matrix they will introduce strain perturbations across the domain $\Omega$ (Figure 4-2). Considering a single n-th inhomogeneity surrounded by matrix it can be inferred that the strain in matrix is no longer constant ($\varepsilon_{ij}^m$) but it rather changes due to perturbation caused by n-th inhomogeneity and those in its vicinity (Figure 4-2b). To simplify the problem, it will be assumed that matrix was subjected to strain $\varepsilon_{ij}^m$ prior to embedding the n-th inhomogeneity. The influence of other inhomogeneities will be accounted for by assuming that n-th inhomogeneity is embedded in a fictitious material matrix that has a stiffness tensor $\hat{C}_{ijkl}^m$. The stated assumptions form the basis of micromechanical methods estimates of effective properties of REV. All presented methods are mean-field methods, which by definition, assume that stress and strain fields across each of the domains, are adequately represented by their volume-averaged values. Homogenized elastic properties will be expressed
in terms of effective stiffness tensor—\( \bar{C}_{ijkl} \); review of methods of property homogenization are based on Qu and Cherkaoui (2006).

![Diagram of inhomogeneities in the composite and n-th inhomogeneity in matrix of homogeneous stiffness \( \hat{C}_{ijkl} \) that was subjected to uniform strain \( \hat{\varepsilon}_{ij} \) prior to embedding the inhomogeneity.](image)

**Eshelby Method**

Eshelby method for estimation of effective elastic properties of REV is based on Eshelby’s solution (Eshelby 1961) for ellipsoidal inclusion in an infinite homogeneous isotropic elastic medium subjected to surface traction at the boundaries of the entire domain. The solution was derived by combining the principle of superposition and Green function (Eshelby 1961). It is initially assumed that the material has undergone a permanent inelastic deformation; therefore uniform strain is assumed and zero stress (eigenstrain \( \varepsilon_{ij}^* \)). In Eshelby’s solution, the inclusion is first removed from the matrix; at this step the inclusion will be under uniform strain and zero stress (eigenstrain). Then, surface traction is applied to inclusion to return it to its initial shape (eigenstrain equals zero, and average stress equals the applied surface traction). The inclusion,
with surface traction acting on it, is returned into the matrix. Finally, the surface traction is removed from the inclusion. Strain inside the inclusion (\( \varepsilon_{ij} \)) is related to prescribed eigenstrain (\( \varepsilon^*_{ij} \)) by Eshelby tensor (\( S_{ijkl} \)):

\[
\varepsilon_{ij} = S_{ijkl} \varepsilon^*_{kl}
\]

Eshelby tensor is a function of material elastic constants and the inclusion geometry; closed-form solutions for ellipsoidal and spherical inclusions are available; for anisotropic materials Eshelby tensor can be evaluated numerically.

It should be noted that Eshelby tensor satisfies the following:

\[
S_{ijkl} = S_{jikl} = S_{ijlk}
\]

but it does not possess the diagonal symmetry (i.e. \( S_{ijkl} \neq S_{klij} \)).

With the knowledge of Eshelby tensor, a relationship between the strain in inhomogeneous inclusion and any arbitrary strain tensor. Eshelby method utilizes this finding to estimate the effective elastic properties of composite material consisting of inhomogeneities that are embedded in a matrix. The method considers n-th inhomogeneity embedded in a matrix of original stiffness tensor (\( \hat{C}_{ijkl}^m = C_{ijkl}^m \)) that was subjected to uniform strain \( \varepsilon^m_{ij} \) before the inhomogeneity was embedded. Due to the assumption that neither stiffness tensor nor the matrix strain are modified by the presence of other inhomogeneities, Eshelby method provides accurate estimates for effective stiffness tensor only for dilute concentrations of inhomogeneities that are well-distanced apart. Detailed derivation of Eshelby solution for effective stiffness matrix is provided in Qu and Cherkaoui (2006); the solution for a two-phase composite with spherical isotropic material inhomogeneities embedded in an isotropic material matrix (Qu and Cherkaoui 2006). In this case the complete effective stiffness tensor (\( \tilde{C}_{ijkl} \)) is defined by effective bulk
modulus ($\bar{K}$) and effective shear modulus ($\bar{G}$) (subscripts 0 and 1 correspond to matrix and inclusion respectively):

$$\bar{K} = K_m + \frac{f_1(K_1 - K_m)(3K_m + 4G_m)}{3K_1 + 4G_m}$$

(4-4)

$$\bar{G} = G_m + \frac{5f_1G_m(G_1 - G_m)(3K_m + 4G_m)}{3K_m(3G_m + 2G_1) + 4G_m(2G_m + 3G_1)}$$

(4-5)

Bulk modulus and shear modulus are related to modulus of elasticity ($E$) and Poisson’s ratio ($\nu$) as follows:

$$E = 3K(1 - 2\nu)$$

(4-6)

$$\nu = \frac{3K - 2G}{2(3K - G)}$$

(4-7)

---

Figure 4-3. (a) Inhomogeneities in the composite; (b) n-th inhomogeneity in matrix of homogeneous stiffness tensor $C_{ijkl}^m$ that was subjected to uniform strain $\varepsilon_{ij}^m$ prior to embedding the inhomogeneity.
Mori-Tanaka Method

Mori-Tanaka method addressed the inaccuracy of Eshelby method for large concentrations of inhomogeneities by accounting for the effect that inhomogeneities have on the strain field of the matrix. This was done by considering the volume averaged strain in matrix, defined as:

$$\bar{\varepsilon}_{ij}^m = \frac{1}{\Omega_m} \int_{\Omega_m} \varepsilon_{ij}^m dV$$

(4-8)

Even though strain will vary from one point to another in a matrix, the average strain represents a good approximation of the effects of inhomogeneities on strain distribution in the matrix. To estimate the effective stiffness tensor, Mori-Tanaka assumed that matrix of original stiffness tensor was subjected to uniform average matrix strain $\bar{\varepsilon}_{ij}^m$ prior to embedding the n-th homogeneity into the matrix (Figure 4-4). Detailed derivation of effective stiffness matrix according to Mori-Tanaka homogenization method is presented in Qu and Cherkaoui (2006); solution for a two-phase composite consisting of spherical isotropic material inhomogeneities embedded in an isotropic material matrix is herein presented. Effective bulk and shear moduli are:

$$K = K_m + \frac{f_1(K_1 - K_m)(3K_m + 4G_m)}{3K_1 + 4G_m + 3(1 - f_1)(K_1 - K_m)}$$

(4-9)

$$G = G_m + \frac{5f_1G_m(G_1 - G_m)(3K_m + 4G_m)}{5G_m(3K_m + 4G_m) + 6(1 - f_1)(G_1 - G_m)(K_m + 2G_m)}$$

(4-10)

It should be noted that when modeling porous martials that do not necessarily have a matrix-inclusion morphology in which matrix represents the porosity (such as in REV consisting of closely packed spheres) is not possible with Mori-Tanaka method. This is because the method is based on the assumption strain in matrix is equal the average matrix strain, which is physically
not admissible when $K_m = G_m = 0$; in a case where matrix represents the porosity, it can be easily shown that $\bar{K} = \bar{G} = 0$ which is not a correct estimate of elastic properties associated with such composite.

Figure 4-4. (a) Inhomogeneities in the composite; (b) n-th inhomogeneity in matrix of homogeneous stiffness tensor $C_{ijkl}^m$ that was subjected to uniform strain $\varepsilon_{ij}^m$ prior to embedding the inhomogeneity.

**Self-Consistent Method**

Self-consistent method (Hill 1965) estimates effective stiffness tensor by assuming that n-th inhomogeneity is embedded in a matrix of effective stiffness tensor $\bar{C}_{ijkl}$ (that is yet to be determined) and subjected to uniform average matrix strain $\bar{\varepsilon}_{ij}^m$ prior to placing the n-th homogeneity into the matrix (Figure 4-5). The effect of interaction between the inhomogeneities on matrix are here accounted through the stiffness tensor the n-th inhomogeneity is embedded in. Relationships used to obtain effective bulk and shear moduli is given by eq. (4-11). The solutions assumes spherical morphology of inhomogeneities made of isotropic material that are embedded
in an isotropic matrix. It should be noted that both side of equation contain the effective moduli; self-consistent method results in a set of nonlinear equations that can be solved numerically.

\[
\bar{K} = K_m + \frac{f_1(K_1 - K_m)(3\bar{K} + 4\bar{G})}{3K_1 + 4\bar{G}}
\]

\[
\bar{G} = G_m + \frac{5f_1G_m(G_1 - G_m)(3\bar{K} + 4\bar{G})}{3K(3\bar{G} + 2G_1) + 4\bar{G}(2\bar{G} + 3G_1)}
\]

Figure 4-5. (a) Inhomogeneities in the composite; (b) n-th inhomogeneity in matrix of effective stiffness tensor \(\bar{C}_{ijkl}\) that was subjected to uniform strain \(\bar{\varepsilon}_{ij}\) prior to embedding the inhomogeneity.

The self-consistent method was additionally extended to evaluate the materials which do not necessarily have a matrix-inclusion morphology, such as polycrystalline materials and rocks. The method assumes that each grain of material is an inhomogeneity of distinct properties forming an N-phase composite. The effective elastic properties can be obtained according to self-consistent micromechanical homogenization scheme, defined by the following system of equations (Berryman 1980 and Berryman 1995, as cited in Mavko et al. 2009):
\[ \sum_{i=1}^{N} f_i(K_i - \bar{K})P_i^* = 0 \]  
\[ \sum_{i=1}^{N} f_i(G_i - \bar{G})Q_i^* = 0 \]

where \( f_i \) is volume fraction of \( i \)-th phase; \( K_i \) and \( \bar{K} \) are respectively bulk modulus of \( i \)-th phase and effective bulk modulus; and \( G_i \) and \( \bar{G} \) are respectively shear modulus of \( i \)-th phase and effective shear modulus. \( P_i^* \) and \( Q_i^* \) are factors that depend on the geometry of the \( i \)-th phase. For spherical geometry of phases in the \( N \)-phase composite:

\[ P_i^* = \frac{3K_{\text{eff}} + 4G_{\text{eff}}}{3K_i + 4G_{\text{eff}}} \]  
\[ Q_i^* = \frac{5G_{\text{eff}}(3K_{\text{eff}} + 4G_{\text{eff}})}{6G_i(K_{\text{eff}} + 2G_{\text{eff}}) + G_{\text{eff}}(9K_{\text{eff}} + 8G_{\text{eff}})} \]

Similarly to Hill’s self-consistent method (Hill 1965), it is assumed that each inclusion is embedded in an effective medium which properties are yet to be determined; therefore, the method results in a set of implicit equations for the effective medium (eq. (4-13) and (4-14)). The solution is determined iteratively, starting with some initial guess for the effective medium bulk and shear moduli.

Self-consistent method for polycrystalline materials, unlike Mori-Tanaka, may be used to model porosity that is represented through matrix phase. This is mainly because of the assumption that the \( n \)-th inhomogeneity is embedded in a matrix that has effective stiffness tensor of the entire REV, meaning that the assumption of average matrix strain is admissible. The method, however, possesses a “percolation threshold” depending on the geometry of the inhomogeneities. For spherical inhomogeneities, this percolation threshold is 0.50, meaning that porosity represented by a volume fraction higher than 50% is not possible. This is in accordance
with physics of the stress-strain transfer through the material; to enable continuity of strain through the REV all inclusions have to be in contact, which is physically not possible (in case of spherical inclusions) when porosity occupies more than 50% of the REV volume.

**Application of Continuum Micromechanics to Cement Paste**

Works of multiple researchers have concentrated on micromechanical modeling of cement paste at Level I in an attempt to establish a relationship between nanoindentation measurements and macroscopic/effective material properties (Nemecek 2012; Randal et al. 2011; Davydov et al. 2011; Constantinides and Ulm 2004). By assuming each nanoindentation experiment represents a single phase in the cement paste with spherical geometry, Randall et al. (2011) and Davydov et al (2011) successfully obtained effective elastic modulus of cement paste that matched the macroscopic elastic modulus obtained by other measurement methods (ultrasonic pulse velocity, and instrumented microindentation). Both studies assumed a virtual N-phase composite with spherical morphology (Figure 4-6) where N is the total number of indentation experiments, and therefore, each indentation experiments represents a single phase in the composite; effective elastic properties of the virtual composite were determined from eq. (4-13) and (4-14).

![Grid of indents](image1.png)

![Assumed virtual N-phase composite](image2.png)

Figure 4-6. (a) Grid of indents; (b) assumed virtual N-phase composite, where N is the total number of indents (Randal et al. 2011).
The goal of the above-described approach was upscaling of elastic properties obtained from nanoindatation—elastic constants corresponding to length scale of Level I were used to compute effective properties of Level II. Constantinides and Ulm (2007) employed a reverse approach—from nanoindentation data corresponding to LD and HD C-S-H (Level I), with aid of continuum micromechanics, they back-calculated properties of C-S-H solid (Level ‘0’). The procedure was based on Jenning’s model of C-S-H (Jenning 2000) that represent LD and HD C-S-H by loosely and densely packed granules, respectively (Figure 4-7). By assuming spherical morphology of C-S-H, the researchers used polycrystalline self-consistent micromechanical model formulation to extrapolate the packing density of each of the phases and determine the elastic modulus of C-S-H building blocks from nanoindentation data. Packing density of C-S-H was defined as:

\[ \eta = \frac{V_e}{V_t} \]  

(4-17)

where \( V_e \) is volume of C-S-H solid within the total volume \( V_t \) of REV. Figure 4-8 shows that results of employed analytical procedure were in a perfect agreement with independently experimentally obtained packing densities of LD and HD C-S-H of 0.63 and 0.76 by Jennings (2000), respectively. The method also provided an estimate of reduced modulus of a single globule (C-S-H solid—Level ‘0’) of approximately 65 GPa. Up to date, no direct measurements of the elastic properties of C-S-H solid have been reported. This is mainly due to the inability of available nanomechanical characterization instrumentation to access the length scale of a realistic C-S-H solid. The elastic properties of C-S-H solid, however, have been quantified via atomistic simulations (Pellenq et al. 2009); the obtained reduced modulus from a computational atomistic model of C-S-H (66-68 GPa) compared well with that extrapolated from nanoindentation data (65 GPa).
In the work of Constantinides and Ulm (2007) it was shown that Mori-Tanaka homogenization scheme does not provide as accurate values of porosity and C-S-H solid elastic modulus (Figure 4-8); this is mainly because in Mori-Tanaka method an underlying assumption is that C-S-H solid is the matrix phase while the porosity represents inhomogeneities which is not correct. Inability of Mori-Tanaka to provide correct estimates of C-S-H solid reduced modulus further backs up the assumption of nanogranular morphology of C-S-H solid, with no distinct matrix phase; the stress is transferred through contact interaction between C-S-H globules.

Figure 4-7. Nanogranular structure of: (a) LD C-S-H; and (b) HD C-S-H. (Jennings 2000).
Figure 4-8. Reduced (indentation) modulus as a function of packing density. Packing densities of LD C-S-H and HD C-S-H were back-calculated from nanoindentation data assuming self-consistent (SC) arrangement of C-S-H globules (markers) and according to Mori-Tanaka (MT) scheme. Solid red line represents relationship between indentation modulus and packing density based on self-consistent micromechanical model that assumes spherical morphology of C-S-H globules. Dotted line represents relationship between reduced modulus and packing density based on Mori-Tanaka method. (Constantinides and Ulm 2007)
Interfacial Cracks and Elastic Mismatch

Stress field associated with the crack tip of cracks located at the interface between two dissimilar materials (Figure 5-1) follows the singularity described by (solution by Williams, 1959):

\[ \sigma_{rr}, \sigma_{\theta\theta}, \sigma_{r\theta} \sim r^{-1/2 + i\epsilon} \]  \hspace{1cm} (5-1)

where \( \sigma_{rr}, \sigma_{\theta\theta}, \sigma_{r\theta} \) are radial, tangential and shear stress at distance \( r \) from the crack tip in polar coordinates; \( \epsilon \) is bimaterial constant (oscillation index). The extent of elastic mismatch between the adherents can be quantified through Dundurs parameters (Dundurs, 1969):

\[ \alpha = \frac{G_1(\kappa_2 + 1) - G_2(\kappa_1 + 1)}{G_1(\kappa_2 + 1) - G_2(\kappa_1 + 1)} \]  \hspace{1cm} (5-2)

\[ \beta = \frac{G_1(\kappa_2 - 1) - G_2(\kappa_1 - 1)}{G_1(\kappa_2 + 1) - G_2(\kappa_1 + 1)} \]  \hspace{1cm} (5-3)

where \( G_i \) is shear modulus of material material \( i \); and \( \kappa_i = 3 - 4\nu_i \) (plane strain) or \( \kappa_i = (3 - \nu_i)/(1 + \nu_i) \) (plane stress) for material \( i \); \( \nu_i \) is Poisson’s ratio of material \( i \). It should be noted that \( \alpha \) represents mismatch in elastic moduli, and \( \beta \) defines the mismatch in bulk moduli between the two adjoining materials (for \( \alpha = \beta = 0 \) there is no material mismatch). In general \( |\alpha| \leq 1; \alpha \) will approach \( \pm 1 \) when one of the layers has relatively very high stiffness. The other parameter is within the limits -0.5 to +0.5 (\( |\beta| \leq 0.5 \)). For typical values of elastic constants associated with concrete (\( E_1 = 35 \text{ GPa}, \nu_1 = 0.24 \)) and epoxy (\( E_1 = 3.55 \text{ GPa}, \nu_1 = 0.40 \)), Dundur’s coefficients point out a significant mismatch between the adherents (\( \alpha = 0.8, \beta = 0.1 \)), which means that the elastic mismatch of the bimaterial interface should not be neglected.
Dundur’s parameters were found to have a linear correlation which can be explicitly expressed as follows (Schmauder and Meyer 1992):

\[
\beta = \frac{1}{4} \left[ \left( \frac{1 - 2\nu_1}{1 - \nu_1} + \frac{1 - 2\nu_2}{1 - \nu_2} \right) \alpha + \left( \frac{1 - 2\nu_1}{1 - \nu_1} - \frac{1 - 2\nu_2}{1 - \nu_2} \right) \right] (plane \ strain)
\] (5-4)

\[
\beta = \frac{1}{4} \left[ (2 - \nu_1 - \nu_2) \alpha + (\nu_2 - \nu_1) \right] (plane \ stress)
\] (5-5)

When Dundur’s parameter \( \beta \neq 0 \), stress oscillating region exists ahead of crack tip which can be characterized by oscillation index:

\[
\epsilon = \frac{1}{2\pi} \ln \frac{1-\beta}{1+\beta}
\] (5-6)

The implication of \( r^{-\frac{1}{2}+i\epsilon} \) singularity is that stresses change in an oscillating manner as the crack tip is approached; the stresses change sign indefinitely; stress singularity infers interpenetration of two crack faces, which is physically not possible. The crack faces must come in contact at the crack tip (England, 1965). While significant in the context of interfacial crack stress analysis, this oscillatory field was found to be present in a very small region near the crack tip.
tip. It should be noted that this oscillatory behavior exists in Mode I and Mode II, and is not present for Mode III loading condition (Sun and Jin 2012).

Most analytical solutions for stress intensity factor related to the problem of interfacial cracks in Mode I and Mode II loading conditions are based on implementation of complex function method (method of Kolosov-Muskhelishvili), normally used to solve problems specific to homogeneous materials (Muskhelishvili, 1953). Using this approach Rice and Sih (1965) derived a complex stress intensity factor that has a general form of:

\[
k_1 + i k_2 = 2 \sqrt{2} e^{\pi \epsilon} \lim_{z \to 0} z^{1+ie} \psi_1'(z)\]

(5-7)

where \( k_1 \) and \( k_2 \) are local mode I and mode II stress intensity factors, \( z = x + iy = 0 \) represents the crack tip (Figure 5-1), and \( \psi_1'(z) \) is the first derivative of analytic function of a complex argument \( z = x + iy \) (Goursat function). Utilizing the complex stress intensity factor by Rice and Sih (1965), stress ahead of the crack tip is defined as (in polar coordinates—Figure 5-1):

\[
(\sigma_{yy} + i \sigma_{xy})_{\theta=0^\circ} = \frac{k_1 - ik_2}{\sqrt{2r}} r^{ie} \cosh(\pi \epsilon)
\]

(5-8)

For an example problem of crack lying at the bimaterial interface in an infinite plate the solution for stress intensity factors is as follows:

\[
k_1 = \frac{\sqrt{a}}{\cosh(\pi \epsilon)} \left( \sigma_{yy}^{\infty} \left[ \cos(\epsilon \ln(2a)) + 2\epsilon \sin(\epsilon \ln(2a)) \right] + \sigma_{xy}^{\infty} \left[ \sin(\epsilon \ln(2a)) - 2\epsilon \cos(\epsilon \ln(2a)) \right] \right) + \sigma_{xy}^{\infty} \left[ \cos(\epsilon \ln(2a)) + 2\epsilon \sin(\epsilon \ln(2a)) \right] \]

\[
k_2 = \frac{\sqrt{a}}{\cosh(\pi \epsilon)} \left( \sigma_{xy}^{\infty} \left[ \cos(\epsilon \ln(2a)) + 2\epsilon \sin(\epsilon \ln(2a)) \right] + \sigma_{yy}^{\infty} \left[ \sin(\epsilon \ln(2a)) - 2\epsilon \cos(\epsilon \ln(2a)) \right] \right) + \sigma_{xy}^{\infty} \left[ \cos(\epsilon \ln(2a)) + 2\epsilon \sin(\epsilon \ln(2a)) \right]
\]

(5-9)
A difficulty with implementation of stress intensity factor by Rice and Sih (eq. (5-9)) is that it contains \( \ln(a) \) term, which defines the stress intensity factor a function of the measuring unit of the crack length (Sun and Jih, 1987). To eliminate this impracticality, Sun and Jih (1987) proposed a similar stress intensity factor \( K = K_1 + iK_2 \) where:

\[
\begin{align*}
K_1 &= \frac{\sqrt{\pi a}}{\cosh(\pi \varepsilon)} \left( \sigma_{yy}^\infty - 2\varepsilon \sigma_{xy}^\infty \right) \\
K_2 &= \frac{\sqrt{\pi a}}{\cosh(\pi \varepsilon)} \left( \sigma_{xy}^\infty - 2\varepsilon \sigma_{yy}^\infty \right)
\end{align*}
\]  

(5-10)

Stresses ahead of crack tip, in polar coordinates (Figure 5-1), are then defined as:

\[
(\sigma_{yy} + i\sigma_{xy})_{\theta=0^\circ} = \frac{K}{\sqrt{2}\pi r} \left( \frac{r}{2\alpha} \right)^\varepsilon \cosh(\pi \varepsilon) 
\]  

(5-11)

The relationship between stress intensity factors in eq. (5-10) and total energy release rate is defined by:

\[
G = \frac{1}{16} \left( \frac{K_1 + 1}{G_1} + \frac{K_2 + 1}{G_2} \right) (K_1^2 + K_2^2) 
\]  

(5-12)

The above solutions point out an important characteristic related to interfacial cracks: localized mode I and mode II stress intensity factors are coupled independently of the loading condition, thus, pure Mode I or Mode II stress intensity factors cannot be unambiguously defined. For that reason, fracture criterion need to be given as total critical energy release rate (fracture energy) and mode mixity parameter defined as:

\[
\psi = \tan^{-1}(K_2/K_1).
\]  

(5-13)

which is a function of both global loading mode and elastic mismatch at the crack tip. An example of this behavior is shown in Figure 5-2 as a deformed finite element analysis (FEA)
model mesh of epoxy-concrete joint loaded in pure tension (Mode I). Due to elastic mismatch between the adherents, a significant component of shear (mode II) deformation is apparent near the crack tip, even though no shear loading was applied.

![Figure 5-2. Example of deformed FEA mesh of epoxy-concrete joint loaded in pure tension. Note the deformation of circular mesh around crack tip—deformation in horizontal direction in epoxy is due to local (mode II) shear component of stress caused by elastic mismatch between adherents.](image)

**Numerical Evaluation of Energy Release Rate**

Representations of interfacial complex stress intensity factors, similar to those obtained by Rice and Sih (1965) and Sun and Jih (1987), were derived by Hutchinson et al. (1987) and Malysev and Salganik (1965). The available analytical solutions are not applicable to majority of practical loading conditions experienced by cracks in bimaterial media; however, there exist numerical methods that are can estimate the total energy release rates, such as J-integral (Rice, 1968), crack closure method (per Irwin, 1957) and virtual crack closure technique (Rybicki and Kanninen, 1977).
J-integral, as derived by Rice (1968), has the following form:

\[ J = \int_{\Gamma} \left(W dy - T_i \frac{\partial u_i}{\partial x} n_j ds\right) \]  

where \( W = \int_0^{\varepsilon_{ij}} \sigma_{ij} d\varepsilon_{ij} \) (\( W = \frac{1}{2} \sigma_{ij} \varepsilon_{ij} \) for linear elastic material) is strain energy density; \( T_i = \sigma_{ij} n_j \) is traction vector acting on \( \Gamma \); and \( u_i \) is the displacement on an element along arc \( s \).

Under the framework of linear elastic fracture mechanics, J-integral equals energy release rate. It can be proven that J-integral is completely path independent; the integrating contour can be arbitrarily chosen, but the path should begin at the crack lower face and end at the crack upper face (Figure 5-3). The contour is to be evaluated in the counter clockwise direction (Figure 5-3). The benefit of using J-integral, over other numerical methods, is that it is implemented in the most major commercial FEA programs. The biggest difficulty with J-integral method, however, is the special mesh requirements that may be challenging to accommodate in certain geometries.

Figure 5-3. J-integral around a sharp crack.

Crack closure technique is based on crack closure integral by Irwin (1957). The method is based on the principle of work required to close a unit area of crack. This work was found to
equal the work of stress ahead of the crack tip of closed crack (crack length \(a\)) on closing the crack extension \(\Delta a\) of propagated crack (crack length \(a + \Delta a\)). This principle can be implemented in FEA (Figure 5-4). The procedure consists of two steps (e.g. mesh in Figure 5-4):

Step 1: the crack is closed and forces acting on node i are recorded.

Step 2: node i is released, and relative displacements due to crack extension are noted.

Energy release rates associated with mode I and mode II, can then be determined as follows:

\[
G_I = \frac{1}{2\Delta a} Y_{1i} \Delta w_{2i}; \quad G_{II} = \frac{1}{2\Delta a} X_{1i} \Delta u_{2i}
\]  
(5-15)

Virtual crack closure technique (VCCT) is based on the same principles as crack closure technique; however, this method does not require two problems to be solved. Instead, since \(\Delta a/a\) is very small it can be assumed that displacements of node i of extended crack can be approximated by relative displacements of node h behind the crack tip. Therefore, based on VCCT, energy release rates can be determined from one FEA (Figure 5-4a) model as:

\[
G_I = \frac{1}{2\Delta a} Y_{1i} \Delta w_{2h}; \quad G_{II} = \frac{1}{2\Delta a} X_{1i} \Delta u_{2h}
\]  
(5-16)

Using VCCT multiple crack extension lengths (\(\Delta a\)) can be evaluated, by considering the forces and displacement at nodes further away from the crack tip (\(2\Delta a, 3\Delta a, 4\Delta a, etc\.). In addition, it should be noted that same principles apply to a three-dimensional case (Mode I, Mode II, and Mode III), and quadratic element formulations. A review of VCCT procedures for different element formulations is given by Krueger (2004).
Figure 5-4. Crack closure method: step 1: crack closed; step 2: crack extended by releasing node $i$ (modified from Krueger, 2004).

VCCT can be also applied to the problem of a crack at bimaterial interface to determine the total energy release rate; determining interfacial mode I and mode II components of total energy release rate is not a trivial task. Mode I and mode II components change with the chosen crack extension size ($\Delta a$) due to the existence of crack oscillation zone. Multiple researchers found that while the mode I and mode II energy release rate components do not converge and
vary with the chosen crack extension length, the total energy release rate stays constant over a range of crack extension length values.

Methods to compute distinct mode I and mode II stress intensity factors from VCCT were developed by multiple researchers (Sun and Qian 1997; Agrawal and Karlsson 2006). The approach has proven to give accurate results for stress intensity factors under the recommendations proposed by the authors; comparisons to known analytical solutions yielded errors of less than 1%.

**Fracture Criterion for Interfacial Cracks**

The previous discussions have focused on how to quantify the energy available for crack growth—energy release rate. Once this energy release rate reaches its critical value, termed interfacial fracture energy, the conditions have been satisfied for a crack to extend along the interface:

\[ G = \Gamma_i \quad (5-17) \]

In adhesive interfaces fracture energy has two components (Andrews and Kinloch 1973a): (1) the intrinsic adhesion energy \( \Gamma_0 \) and (2) an order of magnitude larger component that is due to energy dissipation mechanisms \( \zeta \):

\[ \Gamma_c = \Gamma_0 + \zeta \quad (5-18) \]

In a flat surface without chemical/mechanical pretreatment, the intrinsic adhesion energy was found to be in good agreement with thermodynamic work of adhesion \( W_A \) (Andrews and Kinloch 1973a); and therefore, it is clearly representative of secondary bonds formed between the adherents. Thermodynamic work of adhesion is defined by Dupre equation:
\[ \Gamma_C = W_A = \gamma_s + \gamma_a - \gamma_{sa} \quad (5-19) \]

where \( \gamma_s \) and \( \gamma_a \) are surface free energies of substrate and adhesive, respectively; and \( \gamma_{sa} \) is interfacial free energy between the substrate and adhesive.

In a realistic interface, however, multiple mechanisms would be engaged during crack growth; clean interfacial failure is only possible under special conditions. In surfaces that were subjected to silane treatment and etching, Andrews and Kinloch (1973a) found that intrinsic work of adhesion was much larger than the corresponding work of adhesion. They accredited this to a different failure mode that occurred in these samples. In a general case, according to Andrews and Kinloch (1973b), the intrinsic fracture energy can be represented as:

\[ \Gamma_C = i\Gamma_i + s\Gamma_s + a\Gamma_a \quad (5-20) \]

where \( i, s, \) and \( a \) are area fractions of interfacial failure, substrate failure and adhesive cohesion failure, respectively; and \( \Gamma_i, \Gamma_s \) and \( \Gamma_a \) are respectively interfacial adhesion energy, substrate cohesive fracture energy and adhesive cohesive fracture energy.

The second term, \( \zeta \), is normally orders of magnitude larger than the intrinsic adhesion energy, and is a result of viscoelastic energy dissipation, heat generation, and friction. While mostly dependent on the adhesive material properties, \( \zeta \) was found to scale with the intrinsic adhesion energy (Andrews and Kinloch 1973a), which means that both components are important in the total interface fracture energy \( \Gamma_C \).
Along the line of joining between the adhesive and cement paste substrate exists a transition region of distinct chemo-mechanical properties, termed \textit{interphase}. Given the porosity of cement paste and characteristics of chemical interactions between cement paste and epoxy (Djouani et al. 2011) it was initially assumed that interphase is a result of: (1) chemical adsorption of adhesive into the substrate; (2) permeation of adhesive into the substrate; or (3) a combination of the two. In the context of discussions presented in this chapter the following definitions should be noted (Figure 6-1):

1. Interface—surface that clearly separates the two adherents;
2. Cement paste interphase—transition region in cement paste;
3. Epoxy interphase—transition region in epoxy.

Chemo-mechanical characterization of the interphase region that was conducted using Raman spectroscopy, and site-specific nanoindentation, is presented and discussed. Spatial orientation of the corresponding material phases, in all plots, follow the one shown in Figure 6-1.

Figure 6-1. Schematic representation of interface region between epoxy and cement paste on an optical microscope image of an actual interface region.
Specimen Preparation

For the purpose of this study epoxy-cement paste bonded specimens were made. The cement paste samples with w/c ratio of 0.40 were prepared by mixing in a high shear mixer; type I/II cement by Cemex was used. High shear mixing was chosen over traditional paddle mixing to produce a more uniform mixture; this mixing method is deemed to break down the clunks of cement clinker during mixing and provide optimal wetting the cement powder, which results in a more homogeneous mixture when compared to traditional mixing methods. Cement paste samples were cast in brass molds to make 5-cm cubes (Figure 6-1). Following the initial cure, after 24 hours, cement paste samples were placed in lime solution for 6 months, and air-dried for a minimum of 3 months prior to sample preparation.

![Figure 6-2. Pouring cement paste into brass mold.](image)

Samples were then cut in a slow-speed diamond saw (Allied TechCut 4) into 1 cm cubes (Figure 6-3). The bonding surfaces on each of the cubes were flattened with a 240 grit silicon carbide polishing disc. Polishing was then performed in multiple steps with silicon carbide polishing paper, and finished with a 1 μm diamond suspension in polyethylene glycol (PEG) on a silk cloth. Polished surfaces were cleaned with acetone between the polishing steps. The polishing procedure resulted in smooth appearance without glossy finish with root mean square
surface roughness ($R_{RMS}$) on the order of 300-400 nm on 50x50 μm area, as measured on Asylum Research MFP-3D atomic force microscope (AFM); $R_{RMS}$ is defined as:

$$R_{RMS} = \sqrt{\frac{1}{n} \sum_{i=1}^{n} y_i^2}$$

(6-1)

where $y_i$ is distance of point $i$ from mean surface roughness ($\frac{1}{n} \sum_{i=1}^{n} y_i$); and $n$ is the total number of measurement points. Lack of glossy finish was believed to be important to alleviate the effects of extremely low surface tortuosity on reduction in surface free energy, which could affect the wetting ability of the adhesive.

Figure 6-3. Cement paste cutting with low-speed diamond saw.

Epoxy-cement paste “sandwich” specimen procedures are summarized in Figure 6-4. Two cement paste cubes were placed approximately 2-3 mm apart and wrapped with a PTFE tape. Epoxy adhesive consisting of diglycidyl ether of bisphenol A (DGEBA, Hexion® EPON 826) resin with epoxide equivalent weight of 178 to 186 g/eq, and poly(oxypropylene) diamine (POPDA, Huntsman ® Jeffamine D-230) hardener with an average molecular weight of 230 g/mol was mixed in a weight ratio of 100:32.9 which corresponds to stoichiometric equivalence between the functional groups. Chemical structure of DGEBA and POPDA are given in Figure
3-1 and Figure 6-5, respectively. Vigorously mixed epoxy was slowly injected into the gap between the cement paste cubes a syringe. The bonded samples were cured for 7 days, before proceeding with polishing of the top surface intended for characterization.

**Figure 6-4.** Specimen preparation procedures.

**Step 1:** Cement paste cubes placed 2-3 mm apart

**Step 2:** Cubes wrapped with PTFE tape

**Step 3:** Epoxy injected into the gap with syringe.

**Step 4:** PTFE tape removed after epoxy cured

**Figure 6-5.** Chemical structure of POPDA.

\[ \text{H}_2\text{N-} \quad \begin{array}{c} \quad \text{O} \quad \end{array} \quad \text{NH}_2 \quad \text{x} \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{x} \approx 2.5 \]
Multiple polishing procedures were explored, however, it was found that the successive polishing with silicon carbide sand paper in the following order 320, 600, 800, 1200, 4000, followed by 2-3 minutes on 1 μm diamond solution in PEG on Buehler TexMet P polishing pad smoothest surface in terms of $R_{RMS}$.

Polishing on each of the silicon carbide grits was done until the scratch marks from the previous grit were imperceptible under the optical microscope. Diamond solution polishing did not appear to reduce the surface roughness following 4000 carbide grit polishing, however, it was performed for a short period of time to remove sporadic scratches on the sample surface from 4000 grit polishing. Samples were cleaned with 99% isopropanol between the polishing steps. Isopropanol was chosen over more potent solvents to avoid possible degradation of epoxy cross-link network. Final surface had a mirror finish (Figure 6-6) with $R_{RMS}$ in 200-300 nm range on 50x50 μm area (Figure 6-7; Figure 6-8); measured surface roughness was well within the range of the lower bound of intrinsic surface roughness of cement paste determined by Trtik et al. (2008). Any decrease in roughness beyond that limit is believed to be due to polishing artifacts and surface damage. AFM images (z-axis aspect ratio of 1:1) of the interface and neat cement paste are shown in Figure 6-8.
Figure 6-6. Light reflecting off of surface of cement paste-epoxy sandwich sample.

Figure 6-7. AFM topographic image of epoxy-cement paste interface.
Raman Spectroscopy Characterization

To determine the presence of epoxy and cement paste interphases spectroscopic characterization was conducted to determine the transport mechanism of epoxy into the cement paste matrix along with possible interactions between the two adherents in the interphase region. Multiple spectroscopic techniques were examined as potential candidates: Wavelength Dispersive Spectroscopy (WDS), X-Ray Photoelectron Spectroscopy, and Raman spectroscopy. WDS was initially disqualified due to its low sensitivity to nitrogen, a characteristic elemental marker for epoxy. While XPS has a significantly improved sensitivity to elements with low atomic numbers (such as nitrogen), even when found in low concentrations, the relatively large spot size of the available equipment does not permit to access small volumes of material located adjacent to the interface and, thus, high resolution spectroscopic mapping which is thought to reveal the details about transport phenomena between epoxy and cement paste was not possible. Raman spectroscopy was, hence, selected due to its ease of use (no need for vacuum or special specimen preparation), high sensitivity to organic materials such as epoxy, and the relatively
small spot size (approximately 1μm in diameter) which allowed to chemically characterize the regions near interface with high spatial resolution (Figure 6-9).

Figure 6-9. Epoxy-cement paste specimen under Raman microscope objective lens with a laser beam.

**Line Scans**

Raman spectra were collected on Renishaw InVia® Raman spectrometer with a 532 nm Si laser with approximately 1 μm diameter spot size as the excitation source. Spectra were acquired through a 50x or 100x objective lenses in reflection mode with the 5% laser power through an optically connected Leica® microscope with a motorized XYZ stage. Extended Raman scans were collected with a 10 s exposure time. Spectroscopic data were analyzed in Matlab. Baseline correction was performed by utilizing a “backcor” function in Matlab that minimizes an asymmetric Huber function with a threshold of 0.01 for a 3rd order polynomial fit (Mazet et al. 2005). Data was then smoothed with a Savitzky-Golay filter (Orfanidis 1996) to reduce the noise. Example of post-processed data is shown in Figure 6-10.
Initial scans on neat cement paste and epoxy were performed in a spectral range of 100-4000 cm\(^{-1}\) to identify strong characteristic peaks in each material. Peak found at 3618 cm\(^{-1}\) (Figure 6-11) characteristic for stretching of O-H bonds of CH was chosen as a representative peak for cement paste. Raman shift of 3069 cm\(^{-1}\) (Figure 6-11), characteristic for phenyl C-H stretch of DGEBA (Colthup et al. 1990; Lin-Vien, D. et al., 1991), was chosen as a characteristic peak for the epoxy. Later scans were performed in the spectral range of 2700-3800 cm\(^{-1}\) to minimize the time required for data acquisition.

Multiple line scans were performed across the interface to determine the depth of permeation of epoxy. Data from an exemplary scan (Figure 6-12) are given in Figure 6-13—results have shown that the cement paste interphase extends up to approximately 80 \(\mu\)m away from the interface. The epoxy peak intensities beyond 80 \(\mu\)m were determined to be within the 5% fractile of noise that was measured at the same peak location far away from the interface (where no epoxy would be present), and were considered not statistically significant. It should be noted that due to the large spatial variations in CH concentrations the scatter of cement peak
intensity with the distance from the interface is significant. Nonetheless, the cement paste peak intensity clearly revealed location of the interface (Figure 6-13).

Figure 6-11. Raman spectra for different locations away from the interface in cement paste. Characteristic peak for epoxy was at 3069 cm$^{-1}$, and the characteristic peak for cement paste was 3618 cm$^{-1}$.

Figure 6-12. Optical microscope image and line scan location.
Relationship between Porosity and Depth of Epoxy Permeation

To evaluate the effect of porosity on the epoxy permeation, additional two cement paste-epoxy samples were fabricated with a w/c ratio of 0.4 and 0.5 using a conventional paddle mixer to achieve higher levels of porosity. Porosity measurements were taken on cement paste with mercury intrusive porosimetry (MIP). Quantification of pore size distribution by MIP is a well-established method that has been utilized by many researchers to study porosity of hardened cement paste (Winslow and Diamond 1970; Alford et al. 1981; Midgley and Illston 1983; Cook and Hover 1999).

Cement paste specimens used in this study were cut out from 5-cm cement paste cubes (Figure 6-1), which was followed by sonication for 10 minutes in 99.9% ethanol. Three samples per cement paste mix were prepared, making a total of nine samples. Bulk volumes of each sample was taken by measuring the ethanol displacement in a graduated cylinder when cement paste sample was submerged; total volumes of samples were in 0.4-0.7 cm$^3$ range. Prior to testing, all samples were placed in an air-tight container with silicon-based desiccant for approximately 3 days. Porosity measurements were conducted using a Quantachrome...
PoreMaster 60, a mercury porosimetry analyzer. Each sample was first placed in a low-pressure chamber where it was initially evacuated to 2 Pa, and then injected with mercury up to a pressure of 350 kPa. The sample was then moved inside the high pressure chamber where mercury was incrementally injected to a maximum pressure of 420 MPa. The applied pressures were automatically corrected by the software to account for effects of atmospheric pressure and pressure of the mercury column on the sample. Washburn’s equation (Washburn 1921) was used to convert corrected pressures to equivalent pore widths:

\[ d = \frac{-\phi \gamma \cos \theta}{P} (0.145) \]  

(6-2)

where \( d \) is equivalent pore width; \( \phi \) is a pore shape factor; \( \gamma_\infty \) is the surface tension of mercury (erg/cm\(^2\)); \( \theta \) is the contact angle between mercury and the pore wall; \( P \) is the corrected pressure; 0.145 is a unit conversion factor; \( \phi, \gamma_\infty, \) and \( \theta \) were respectively assumed to take the values of 4, 480 erg/cm\(^2\), and 140° (Cook and Hoover 1999).

Equivalent pore size distribution data from all three groups of specimens is given in Figure 6-14. Total porosities, as measured by MIP, can be divided into three distinct groups. Samples with w/c ratio of 0.5 had the highest porosity, and those mixed in high shear mixer with w/c ratio of 0.4 had the lowest values; average total porosities from MIP are given in Table 6-1. In addition to differences in porosity, equivalent pore size widths were skewed toward higher values for the two sample groups prepared in paddle mixer, when compared to samples prepared with a high shear mixer.
Raman line scan data were then collected on all cement paste samples at varying distances from the interface. Data were collected from multiple 60-μm lines parallel with the interface with 20-30 data points in each line. Line scan data are plotted in Figure 6-15a. As expected, due to the higher inherent porosity, and larger pore sizes, the epoxy peak intensities were the most prominent in the sample with 0.5 w/c ratio.

While it is understood that permeation of epoxy through cement paste is a complex process that is dependent on many factors amongst which are: viscosity of the adhesive, interconnectivity of the pore network, surface tension effects, pore size distribution, degree of saturation of substrate with water, etc., a simplified approach is taken here to evaluate the depth of permeation of epoxy into each of the different cement paste samples. Based on Raman spectroscopy measurements in Figure 6-15a, power law of the following form was fit to average values of epoxy concentration from each of the line scans:

\[ y(x) = ax^b \]  \hspace{1cm} (6-3)
where \( a \) and \( b \) are the fitting parameters. Exponential and Gaussian error function fits, commonly used to model diffusion phenomena, did not provide adequate fits for Raman intensity data.

Based on the characteristics of the power law fit, \textit{representative permeation depth} was then defined as the point on the power function where the rate of change of slope (first derivative—\( dy/dx \)) was at its maximum; that point corresponds to transition between the dominating part of the curve (asymptotic to \( y \)-axis) and its “long tail” (asymptotic to the \( x \)-axis). Representative permeation depth was not an actual permeation depth, but rather a normalized value that allowed for relative comparison of epoxy permeation depths between different groups; this value was determined by evaluating the curvature of the first derivative of fitted power function as follows:

\[
\kappa_{dy/dx} = \frac{|d^3 y|}{|dx^3|} 
\left( 1 + \frac{d^2 y}{dx^2} \right)^{3/2}
\]

Maximum of curvature of the first derivative function of power law fit is the location that corresponds to a maximum rate of change in slope of the fitting function. Variation of \( \kappa_{dy/dx} \) with respect to distance form interface is shown in Figure 6-16; representative permeation depths, corresponding to maxima of plots in Figure 6-16, are summarized in Table 6-1.

Plotting the representative permeation depths with respect to total porosity of the corresponding cement paste substrates revealed an excellent positive correlation between the two independent experimental measurements (Figure 6-17) confirming that porosity of substrate has a strong influence on the ability of epoxy to permeate through the cement paste pore network. Given the variability of porosity in an actual concrete substrate due to different w/c ratios,
aggregate gradations, admixtures, and deterioration, it can be concluded that the amount of penetrated epoxy and size of interphase can vary widely among different cases.

Table 6-1. Summary of representative permeation depths and MIP porosity measurements.

<table>
<thead>
<tr>
<th>Group</th>
<th>Representative Permeation Depth (μm)</th>
<th>Total Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>w/c=0.5 (paddle mixer)</td>
<td>38</td>
<td>22.5</td>
</tr>
<tr>
<td>w/c=0.4 (paddle mixer)</td>
<td>29</td>
<td>15.0</td>
</tr>
<tr>
<td>w/c=0.4 (high shear mixer)</td>
<td>23</td>
<td>9.1</td>
</tr>
</tbody>
</table>

Figure 6-15. (a) Epoxy peak intensity as a function of distance from the interface (after 5% fractile data for cement paste was subtracted); (b) power law fits for each test group.

Figure 6-16. Curvature of first derivative for each of the power law fits.
Figure 6-17. Relationship between total porosity measured by MIP and representative permeation depth obtained via Raman spectroscopy.

**Cement Paste Interphase**

The permeation of liquid through the cement paste is affected by interconnectivity of porosity near the surface of the cement paste. In cement paste, capillary porosity (10 nm-100 μm per Young 1988) system is thought to be the most important factor affecting its transport properties (Sant et al. 2011). Capillary pores (medium: 10-50 nm and large 50-100 μm) in cement paste are grouped into clusters; with decreasing w/c ratios, the clusters reduce in size and the mutual interconnectivity becomes more and more limited. Therefore, the permeation through cement paste starting from the surface would be limited by the amount of “entry” clusters, and the interconnectivity of capillary pores at the surface. Gel pores (0.5-10 nm), however, are considered internal pores of the C-S-H and are believed to have a secondary participation in the mass transport through the cement paste structure (Liu et al. 2009); to contribute these pores need to be accessible to the capillary pore network. Additionally, due to their size, particularly...
the lower bound on the length range, some of the gel pores may be inaccessible to a liquid depending on the viscosity and molecule size.

Limited research on permeation of epoxy into the cement paste and/or concrete substrates is available in the literature. Johansen and Thaulow (1996) showed the correlation between the w/c ratio of concrete substrate and depth of permeation of low-viscosity epoxy into its structure. Authors explained that with higher w/c ratio capillary pore network of cement paste is more developed, thus allowing epoxy to penetrate deeper into the substrate. Similar images (Figure 6-20) were obtained by Chen et al. (2002) by pressure-impregnation of cement paste and mortar samples with epoxy; the permeation depth is clearly increasing with the impregnation pressure indicating that porosity of cement paste/mortar plays key role in the mass flow of epoxy through the material. Additionally, Djouani et al. (2011) showed that epoxy adhesive can penetrate the porous structure of cement paste, under atmospheric conditions, between 100 and 200 μm depending on the substrate’s porosity, water saturation, and epoxy’s viscosity (Figure 6-21).

To provide evidence supporting the potential mechanism for epoxy permeation into cement paste, Raman map scan was collected to study the spatial distribution of epoxy in cement paste. The scans were performed using a 100x objective lens. Data were collected in a 40x40 μm area adjacent to the epoxy/cement paste interface, with a spatial resolution of 1 μm; data from a total of 1600 scans was collected. Intensities of epoxy peaks as a function of x and y coordinates are plotted in Figure 6-22.

As previously discussed, the permeability of cement paste matrix to liquids is mainly attributed to the interconnectivity of capillary porosity. Moreover, porous hydration phases (primarily LD C-S-H) are deemed to contribute to the mass flow processes, too (Baron and Van Damme 1988, as cited in Bentz et al. 2000). Analysis of spatial distribution of epoxy peak
intensities are thought to support these hypotheses. Figure 6-22 clearly shows multiple “wells” with relatively high concentrations of epoxy around which the intensity of Raman peaks dissipates. The “wells” are likely larger capillary pores or clusters of capillary pores filled with epoxy, while the area around them with dissipated peak intensities is indicative of epoxy penetrated into the smaller pores within the porous hydration products. Interestingly, the areas with very low epoxy peak intensities (less than 10% of maximum epoxy peak intensity) generally correspond to areas with high concentrations of CH (greater than 25% of maximum peak intensity). CH is mainly found as crystals of varying size or as a part of densely packed C-S-H/CH nanocomposite (also known as UHD C-S-H), both of which would not significantly contribute to the capillary flow of mass through the cement paste matrix. According to the presented data (Figure 6-22 and Figure 6-23), areas with neither CH nor strong epoxy peaks are thought to correspond to clinker phases and portion of C-S-H matrix that was inaccessible to epoxy.

Based on the herein presented experimental results, it was concluded that the mechanism of cement paste interphase formation is by permeation of epoxy through the cement paste matrix driven by the interconnectivity of the cement paste porosity. As shown in the previous discussions, the depth of permeation is dependent on the interconnectivity of the capillary pore network and the availability of the entry pores on the bonding surface of cement paste. Furthermore, this finding suggests that proper wetting of cement/concrete substrate in the field would be strongly dependent on the porosity of the substrate, meaning that required amount of epoxy to achieve proper wetting could widely vary. The specified coverage areas by manufacturers could, therefore, be erroneous.
Figure 6-18. “Class A concrete, w/c=0.35-0.40. Thin section (16x). Penetration of fluorescent epoxy from surface and into the interior of the concrete. The maximum penetration is 1.5 mm.” (Johansen and Thaulow, 1996).

Figure 6-19. “Façade element concrete with w/c=0.50. Thin section at 16x magnification. Penetration of florescent epoxy from the surface into the interior of the concrete. The maximum penetration is 3.5 mm.” (Johansen and Thaulow, 1996).
Figure 6-20. “Cross-section of 0.3 w/c paste and mortar samples viewed under UV light.” (Chen et al. 2002).

Figure 6-21. “Hardened cement paste–epoxy adhesive interface image obtained by optical microscopy under UV light illumination.” (Djouani et al. 2011).
Epoxy Interphase

In the presence of aminated hardener epoxide groups undergo a crosslinking reaction, hence the relative number of reacted epoxide groups can be used to estimate the degree of conversion (cure) of the epoxy crosslinking network. This can be done by tracking the change in the number of available epoxide groups to that of a reference structure within epoxy (which does
not change in number during the curing reaction), such as phenyl groups. A few studies have used this approach to study the rate of curing reaction in epoxy (Vaskova and Kresalek 2011, Aust et al. 1996). In this work, a novel approach is presented, utilizing Raman spectroscopy, that provides insight into how interactions between epoxy matrix and cement paste affect the degree of conversion of epoxy adhesive.

In a comprehensive study on chemical interactions between epoxy and cement paste, Djouani et al. (2011), indeed, noted that epoxy film that was bonded to cement hydrates (C-S-H and CH) had increased $T_g$ by as much as 14%. They explained this phenomenon by chemisorption of aminated hardener into cement hydrates governed by a preferential reaction between the two, which ultimately resulted in higher cross-linking density at the epoxy/cement paste interface. The increase in $T_g$ is indicative of an increase in rigidity of the cross-link network of epoxy, and thus a higher relative degree of conversion of the polymer; it is not clear from the study by Djouani et al (2011) if the same condition would apply to an actual cement paste-epoxy interface, given that the study considered “artificially” synthesized model cement paste hydration products.

To verify the validity of the epoxy/cement paste interface model presented by Djouani et al (2011) in an actual epoxy-cement paste interface, Raman peak intensities corresponding to epoxide group peak found at 1230 cm$^{-1}$ (Vaskova and Kresalek 2011) were analyzed in reference to the interface. Raman peak found at 1608 cm$^{-1}$, corresponding to phenyl ring stretch, was chosen as a reference peak as its intensity does not change during the curing reaction (Vaskova and Kresalek 2011). Relative degree of conversion was then evaluated in terms of a ratio of intensity of epoxide peak ($I_{1230}$) to that of phenyl peak ($I_{1608}$) — $I_{1230}/I_{1608}$; the more epoxide groups have reacted, the lower the ratio of intensities of the two peaks, and thus higher the
relative degree of conversion. Relative degree of conversion does not correspond numerically to the actual degree of conversion of the epoxy, but it is rather indicative of the relative spatial change in the degree of conversion relative to the interface.

Raman spectra were collected in a 14x30 μm area traversing the interface (Figure 6-26a) in a wavelength range from 1000 to 1700 cm⁻¹; epoxide (1230) and phenyl group peak intensities are plotted in Figure 6-25. \( I_{1230}/I_{1608} \) ratio was represented in the form of a color map plot (Figure 6-26). By observing the change of the ratio when approaching the interface it is apparent that the relative degree of conversion is increasing. Values of \( I_{1230}/I_{1608} \) greater than 0.50, found mostly in inside of cement paste interphase, correspond to the locations with very low intensities the reference peak (Figure 6-26b). The peak intensities at those locations were within the noise range of the acquired data, therefore the calculated \( I_{1230}/I_{1608} \) ratio extremely high values. To identify and eliminate the erroneous data from the maps the noise was evaluated in terms of root mean square (RMS) deviation on a linear portion of a typical Raman spectrum, as follows:

\[
RMS = \sqrt{\frac{\sum_{i=1}^{n}(\hat{I} - I)^2}{n}}
\]  

(6-5)

where \( I \) and \( \hat{I} \) are the actual signal intensity and the signal intensity of the linear fit at the same wavelength, respectively; \( n \) is the number of evaluated data points.

The data points in the map scan (Figure 6-26a) that corresponded to \( I_{1608} \) values equal or smaller than three times the RMS were marked with a grey square with diagonal line (Figure 6-26b). Using this approach, the figure shows an increase in relative degree of conversion as traversing from neat epoxy into the cement paste; \( I_{1230}/I_{1608} \) ratio is decreasing. This finding not only shows that chemical interaction between cement paste substrate and epoxy undeniably
exists, but also, that it may be a part of the driving mechanism for the permeation of epoxy into the cement paste.

Figure 6-24. Map scan location relative to the interface.

Figure 6-25. Epoxy peak intensities: (a) Intensity of epoxide peak (1230 cm⁻¹); and (b) Intensity of phenyl peak (1608 cm⁻¹).
Figure 6-26. Relative degree of conversion: (a) Color map plot of $I_{1230}/I_{1608}$ ratio; (b) color map plot of $I_{1230}/I_{1608}$ ratio with erroneous values marked with grey squares with diagonal line.

Nanoindentation

Test Procedures

Nanoindentation experiments were conducted in the interphase region of the epoxy-cement paste specimen (Figure 6-6). All indentations were performed with a maximum load of 2 mN; the loading function is shown in Figure 6-28. The specimen placed in the test apparatus is shown in Figure 6-27. Load-controlled indentations resulted in maximum indentation depths between approximately 200-400 nm.

Indentation experiments were performed in 5 parallel lines along the interface; each indentation area was 90x90 μm and contained a total of 50 indents (Figure 6-29). To obtain a substantial dataset for statistical analysis, the experiment was repeated on 30 areas, to generate a total of 300 indents per each line parallel to the interface. First line was located approximately 10 μm from the interface, in the epoxy; the spacing between the lines of indents was 22.50 μm.
Location of the interface was determined using the imaging mode of the indenter at each indentation location (Figure 6-29).

Figure 6-27. Test specimen in nanoindentation test apparatus.

Figure 6-28. Indentation loading function.
Figure 6-29. Locations of indents relative to the interface shown in AFM images.

Data Analysis and Discussion of Findings

Exemplary nanoindentation load-displacement curves for epoxy, C-S-H, and cement clinker are shown in Figure 6-30; a significant difference in the slope of unloading portion (stiffness) between the curves is apparent, resulting from dissimilarity in stiffness between the corresponding material phases.

Gaussian mixtures deconvolution algorithm was utilized to identify clusters of data with distinct mechanical properties within the experimental data (Figure 6-31); the process was completely automated through a Matlab function. The validity of the approach was verified on an artificially generated multivariate distribution with multiple Gaussian distribution component of known parameters. An example of clustered indentation data corresponding to one of the indentation lines within the interphase is graphically shown in Figure 6-31a, for 4 material phases (as determined by BIC). Example of deconvoluted reduced moduli data (eq. (2-3)) of portion of data dominated by cement hydrates ($E_r < 65$ GPa) is shown in Figure 6-31b as a probability density function.
Deconvolution algorithm was applied to each line of indents in the cement paste sample, in addition to a control location that was located far away from the interface. Results of deconvolution procedure for reduced modulus ($E_r$) and hardness ($H$) at control location are summarized in Table 6-2; graphical representation of clustered nanoindentation data, and reduced moduli data in a form of probability density function (PDF) are given in Figure 6-31a and Figure 6-31b, respectively. The four identified material phases at control location correspond to: LD C-S-H, HD C-S-H, UHD C-S-H and unhydrated clinker grains based on the available literature (Table 3-2).

As discussed in the literature review section, morphologically, LD C-S-H can be considered an equivalent of randomly packed spheres (C-S-H globules), while the HD C-S-H is an equivalent of more orderly packing of spheres (Constantinides and Ulm 2004). UHD C-S-H was found to be a nanocomposite of HD C-S-H and calcium hydroxide (CH) present in the gel pores of C-S-H (Chen et al. 2010). ‘Clinker’ phase is mostly composed of unhydrated clinker grains (Nemecek 2012); given that unhydrated cement particles are large solid crystals with no porosity, they are not deemed to contribute significantly to transport of epoxy in cement paste. Focus of the analysis will be primarily on the most porous phases—LD C-S-H and HD C-S-H. The data is very scattered for clinker phase due to varying size of clinker crystals—if the crystal size is smaller than the indentation interaction volume the response will contain composite mechanical properties of the crystal and surrounding material. UHD C-S-H also has a significant scatter in data due to varying size of CH crystals within its structure in addition to possible occurrence of $C_4AF$ crystals. LD and HD C-S-H have a relatively low variation in mechanical properties which is mostly due to them occupying the majority of the material volume.
The naming of four phases in the interphase region was adjusted to reflect the fact that this region was modified by the presence of epoxy; consequently, the phases were named: ‘LD Phase’, ‘HD Phase’, ‘UHD Phase’, and unhydrated ‘clinker’. Summary of Gaussian mixtures deconvolution on interphase data is presented in Table 6-3 and Table 6-4. Example of nanoindentation data and Gaussian mixtures deconvolution results from nanoindentation ‘Line 2’ (Figure 6-29) are graphically presented in Figure 6-39.

Reduced modulus of bulk epoxy was determined to be 4.40 GPa with a standard deviation of 0.39 (COV=0.09), from a population of 100 indents. Measured reduced modulus corresponds to an elastic modulus of 3.70 GPa (assuming Poisson’s ratio of 0.4, per Holmann and Hahn 1989), which compares well to the value determined from tensile tests on 165 mm long coupons (Type I coupon—ASTM D638) of 3.45 GPa (Burton et al. 2005). Average hardness of epoxy was 0.18 GPa with a standard deviation of 0.02 (COV=0.12).

<table>
<thead>
<tr>
<th>Location [um]</th>
<th>LD Phase</th>
<th>HD Phase</th>
<th>UHD Phase</th>
<th>Clinker</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( f_k )</td>
<td>( \mu_k \pm \sigma_k ) [GPa]</td>
<td>( f_k )</td>
<td>( \mu_k \pm \sigma_k ) [GPa]</td>
</tr>
<tr>
<td>10</td>
<td>0.15</td>
<td>18.8±3.1</td>
<td>0.59</td>
<td>29.4±5.9</td>
</tr>
<tr>
<td>32.5</td>
<td>0.25</td>
<td>20.1±4.1</td>
<td>0.43</td>
<td>30.2±5.6</td>
</tr>
<tr>
<td>55</td>
<td>0.41</td>
<td>25.9±5.4</td>
<td>0.39</td>
<td>37.6±8.7</td>
</tr>
<tr>
<td>77.5</td>
<td>0.35</td>
<td>24.9±5.4</td>
<td>0.44</td>
<td>34.9±9.9</td>
</tr>
</tbody>
</table>
Table 6-4. Summary of hardness within interphase.

<table>
<thead>
<tr>
<th>Location [um]</th>
<th>LD Phase $f_k$</th>
<th>$\mu_k \pm \sigma_k$ [GPa]</th>
<th>HD Phase $f_k$</th>
<th>$\mu_k \pm \sigma_k$ [GPa]</th>
<th>UHD Phase $f_k$</th>
<th>$\mu_k \pm \sigma_k$ [GPa]</th>
<th>Clinker $f_k$</th>
<th>$\mu_k \pm \sigma_k$ [GPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.15</td>
<td>0.43±0.13</td>
<td>0.59</td>
<td>0.66±0.20</td>
<td>0.19</td>
<td>1.41±0.62</td>
<td>0.07</td>
<td>4.29±2.01</td>
</tr>
<tr>
<td>32.5</td>
<td>0.25</td>
<td>0.44±0.11</td>
<td>0.43</td>
<td>0.73±0.18</td>
<td>0.22</td>
<td>1.17±0.42</td>
<td>0.10</td>
<td>4.44±2.99</td>
</tr>
<tr>
<td>55</td>
<td>0.41</td>
<td>0.57±0.15</td>
<td>0.39</td>
<td>0.92±0.29</td>
<td>0.09</td>
<td>1.83±0.74</td>
<td>0.10</td>
<td>5.07±2.35</td>
</tr>
<tr>
<td>77.5</td>
<td>0.35</td>
<td>0.58±0.15</td>
<td>0.44</td>
<td>0.86±0.22</td>
<td>0.19</td>
<td>2.32±1.06</td>
<td>0.03</td>
<td>6.05±3.64</td>
</tr>
</tbody>
</table>

Figure 6-30. Example load vs. displacement plots for epoxy, C-S-H and clinker.
Figure 6-31. Nanoindentation test results for control location: (a) Gaussian mixtures deconvolution of reduced modulus and hardness data represented by cluster allocation; (b) deconvoluted reduced modulus data for range of moduli corresponding to cement hydrates (<65 GPa).

Figure 6-32. Nanoindentation test results for interphase Line 2: (a) Gaussian mixtures deconvolution of reduced modulus and hardness data represented by cluster allocation; (b) deconvoluted reduced modulus data for range of moduli corresponding to cement hydrates (<65 GPa).

Decrease of reduced modulus

Figure 6-33 shows the spatial evolution of average values of reduced moduli for LD Phase and HD Phase (respectively corresponding to LD C-S-H and HD C-S-H in neat cement paste). Lower reduced moduli of C-S-H phases near the interface are a result of their chemical
reaction with the epoxy hardener (POPDA). Epoxy hardener can generate a localized increase in pH, which results in partial ionization of silanol sites in C-S-H structure, causing dissolution of C-S-H (Djouani et al., 2013). As explained by Djouani et al. (2013), in low pH the C-S-H is charged negatively due to the silanol sites supported by the silicon tetrahedra (Figure 6-34a). At higher pH the negative charge is carried by the non-bridged silicate tetrahedra; the Ca$^{2+}$ ions balance out this negative charge. The consequence of adsorption of hardener into the C-S-H is, therefore, a higher Ca/Si ratio of C-S-H crystals in chemical analyses. The transition from low to high Ca/Si ratios results in transition of C-S-H structure from layered to a more amorphous arrangement, which was shown (experimentally and through atomistic simulations) to result in a decrease of the reduced modulus of C-S-H (Pelisser et al. 2012; Qomi et al. 2014). Additionally, ettringite, which is intrinsically a component of C-S-H structure was found to be similarly affected by the amine-rich hardener; the same effect is was well-pronounced in isolated CH crystals (Djouani et al., 2012), too.

Effect of dissolution of hydrates due their interaction with epoxy on their nanomechanical properties, according to herein presented experimental results, are most emphasized close to the interface. By distancing from the interface, the effect dissipates, which results in the stiffening effect of epoxy matrix on the measured moduli of the C-S-H phases. HD Phase (corresponding to HD C-S-H in neat cement paste), particularly, has higher values of reduced modulus at 55 and 77.5 μm away from the interface than control which suggests that softening effect of epoxy hardener is likely dependent on its concentration.
Figure 6-33. Change in mean reduced modulus as a function of distance from interface.

Figure 6-34. Structure of C-S-H at proposed by Vallis-Terrisse (2000), as cited in Djouani et al. (2013).: (a) pH=10 (corresponding to Ca/Si ratio of 0.66); and (b) pH=12.5 (corresponding to Ca/Si ratio of 1.5). (Djouani et al. 2013)

To determine the extent of influence of epoxy hardener on the nanomechanical properties of LD and HD C-S-H, a two sample unpaired t-test statistical analysis was conducted. The goal of the analysis was to determine if a statistically significant difference in means exist between two groups of data that are being compared. Unpaired t-test was chosen because it does not assume equality of variance nor equal sample sizes. All tests were performed for a significance level of 0.05. Given the likelihood of exhibiting a rare event (Type I error) when conducting multiple comparisons, the Bonferroni correction was applied by dividing the desired significance
level of 0.05 by the number of comparisons (10), yielding a significance level of 0.005. When the calculated P-value is greater than the set significance level, then the difference in means is not considered statistically significant.

The results of unpaired t-test for LD Phase reduced moduli are shown in Table 6-5. It appears that no statistically significant difference exists between means at 10 and 32.5 μm away from the interface, while both populations are significantly different from the control value. On the other hand, means at 55 and 77.5 μm away from the interface are considered statistically equal; both means are equal to the control value, too. For HD Phase (Table 6-6), again, no statistically significant difference between means at 10 and 32.5 μm away from the interface exist; however, only the mean at 77.5 μm from the interface is deemed statistically equal to that measured in a control set of indents.

Based on the analysis of data, it is clear that there is a difference between means observed at 10 and 32.5 μm, and those observed at 55 and 77.5 μm away from the interface. This confirms that effects of hardener on the reduced modulus are dependent on its concentration which explains why the degradation of the reduced modulus of LD and HD C-S-H is more statistically significant closer to the interface (10 and 32.5 μm).

Table 6-5. P-values for two-sample unpaired t-test on reduced moduli of LD Phase; bolded font signifies P>0.005.

<table>
<thead>
<tr>
<th>Distance from interface (μm)</th>
<th>10</th>
<th>32.5</th>
<th>55</th>
<th>77.5</th>
<th>Control</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
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<td>0.069</td>
<td>0.0001</td>
<td>0.0001</td>
<td>0.0001</td>
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<tr>
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<td>0.0001</td>
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<tr>
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<td>1</td>
<td>0.165</td>
<td>0.334</td>
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<tr>
<td>77.5</td>
<td></td>
<td>1</td>
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</tr>
<tr>
<td>Control</td>
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</tbody>
</table>
Table 6-6. P-values for two-sample unpaired t-test on reduced moduli of HD Phase; bolded font signifies P>0.005.

<table>
<thead>
<tr>
<th>Distance from interface (μm)</th>
<th>10</th>
<th>32.5</th>
<th>55</th>
<th>77.5</th>
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</tr>
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<td>1</td>
<td>0.194</td>
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</tr>
<tr>
<td>Control</td>
<td></td>
<td></td>
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<td>1</td>
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</tbody>
</table>

**Volume fractions of interphase constituents**

When considering chemo-morphology of material phases in the cement paste interphase, it should be noted that the structure of C-S-H would have been modified by the presence of epoxy. Volume fractions for each of the four material phases, at the corresponding indentation locations (Figure 6-35), indicate a significant difference in the distribution of volume fractions with respect to distance from interface. Particularly, the ratio of volume fraction of LD Phase to that of HD Phase is changing with the distance from the interface; the amount of LD Phase is increasing on the account of HD Phase.

Based on the experimental findings from Figure 6-35, it is herein postulated that LD Phase corresponds to LD C-S-H that has not been accessible to the epoxy penetrating the cement paste matrix; this portion LD C-S-H was, however, involved in adsorption of epoxy hardener close to the interface which resulted in degraded reduced moduli of this phase (at 10 and 32.5 μm away from the interface). HD Phase represents a composite consisting of: (1) HD C-S-H; and (2) composite of LD C-S-H and epoxy. Existence of composite of HD C-S-H and epoxy is believed to be unlikely mainly due to the size of gel pores characteristic for HD C-S-H (which were found to be so small as to be inaccessible to nitrogen molecules by Jennings (2000)). Based on the above-postulated modifications of cement paste microstructure in presence of epoxy, it can be deduced that the distribution of nanomechanical material properties of material phases (reduced moduli and hardness values) of cement paste-epoxy nanocomposite would be dissimilar from
that of neat cement paste. Hypothesis that ratio of volume fractions of LD Phase to that of HD Phase is due to the stiffening of LD C-S-H when saturated with epoxy is supported by continuum mechanics principles presented in the following section.

**Figure 6-35.** Volume fractions of material phases as a function of distance from interface. Note that in “Control” group, material phases (top to bottom) correspond to LD C-S-H, HD C-S-H, UHD C-S-H and clinker.

**Continuum micromechanics evaluation of C-S-H/epoxy composite**

As shown in the literature review, at Level I, C-S-H can be modeled using a polycrystalline self-consistent micromechanics model that assumes spherical morphology of the C-S-H solid (Constantinides and Ulm 2007) to estimate the effective elastic modulus of C-S-H phases. Self-consistent relationship between reduced modulus and packing density of C-S-H, per Constantinides and Ulm (2007), is given by a dashed line in Figure 6-36 with data points for LD and HD C-S-H from this study. As discussed in the background section, the lower bound on packing density of 0.50 represents a minimum percolation threshold and corresponds to a perfectly disordered arrangement of spheres; values of packing density lower than 0.50 are not
physically admissible for spherical inhomogeneity geometry. The packing density of 1.0 assumes that entire REV is occupied by a C-S-H solid with a reduced modulus of 65 GPa, as determined by Constantinides and Ulm (2007) and Pellenq et al. (2009).

At length scale of Level I, the amount of gel porosity (defined by packing density—eq. (4-17)) is a function of multiple variables (hydration degree, cement composition, cement particle size distribution, etc.). Packing density ranges, based on an extensive nanoindentation experimental program by Vandamme (2007), are listed in Table 6-7. Based on the reduced modulus-packing density relationship established by self-consistent micromechanics formulation (Figure 6-36), LD C-S-H and HD C-S-H of the studied cement paste were found to have the average packing densities of 0.69 and 0.76, respectively; both values were well within the range of packing densities specified in Table 4.

When epoxy fills the pore space within LD C-S-H, it can be regarded as a matrix phase with the C-S-H globules representing inhomogeneities within the matrix. In this configuration, Mori-Tanaka micromechanical model is a more suitable choice for estimation of the effective modulus (eqs. (4-9) and (4-10)). Even at high concentrations of isotropic spherical inclusions, which would be typical for range of packing densities associated with LD C-S-H, Mori-Tanaka homogenization scheme was proven to be valid (Ferrari, 1991). Mori-Tanaka method also overcomes the inaccuracies associated with self-consistent model for matrix-inclusion morphology (eqs. (4-11) and (4-12)) when inhomogeneities are relatively rigid compared to the matrix phase (Qu and Cherakoui 2006). By assuming spherical morphology of C-S-H globules, effective reduced modulus of C-S-H/epoxy composite per Mori-Tanaka homogenization scheme was plotted with a solid line in Figure 6-36 for a range of packing densities. In this case packing density represents relative volumetric ratio of C-S-H solid to epoxy matrix. Per Mori-Tanaka
micromechanical model, composite of LD C-S-H and epoxy has an effective reduced modulus of 37.4±2.5 GPa for packing density in 0.69±0.03 range (Figure 6-36), which is significantly greater than the reduced modulus of HD C-S-H of 33.2±6.2 GPa. The micromechanics evaluation of C-S-H/epoxy composite, thus, explains the increase in average reduced modulus of HD Phase of in the interphase region at 55 and 77.5 μm away from the interface.

The results of herein presented micromechanical analysis are also in agreement with the postulated composition of HD Phase in the interphase region (LD CSH/epoxy composite and HD C-S-H). Obtained effective modulus of LD C-S-H and epoxy composite, per Mori-Tanaka method, provides an adequate explanation for the changing ratio of LD Phase to HD Phase with respect to distance from the interface. Continuum micromechanics analysis also confirmed the important effect of cement paste porosity on mechanical properties within the interphase region; based on the results it can be expected that interphase properties could widely vary between substrates of dissimilar porosity. Effective reduced modulus estimate of LD C-S-H/epoxy composite, based on Mori-Tanaka method, represents the upper bound on the effective reduced modulus value for C-S-H/epoxy composite since the analytical procedure assumes that all porosity within C-S-H is filled with epoxy.
Figure 6-36. Reduced moduli of C-S-H and C-S-H/epoxy composite based on self-consistent and Mori-Tanaka micromechanical schemes.

Table 6-7. Ranges of packing densities for the three C-S-H phases based on extrapolation analysis of nanoindentation data from a large population of different OPC samples by Vandamme (2007), as cited in Vanzo (2009).

<table>
<thead>
<tr>
<th>Material phase</th>
<th>Packing density</th>
</tr>
</thead>
<tbody>
<tr>
<td>LD C-S-H</td>
<td>0.62-0.88</td>
</tr>
<tr>
<td>HD C-S-H</td>
<td>0.69-0.82</td>
</tr>
<tr>
<td>UHD C-S-H</td>
<td>0.78-0.90</td>
</tr>
</tbody>
</table>

**Effect of accelerated conditioning on reduced modulus**

The same sample that was used for previously discussed nanoindentation experiments was subjected to environmental conditioning by water immersion in 30°C tap water bath for 4 weeks to determine the effects of conditioning in water on the nanomechanical properties of the epoxy and the interphase. The same test procedures described for the “dry” specimen were followed. Data was also analyzed in a same manner: number of distinct material phases was determined per BIC, and according to it nanoindentation data was deconvoluted using Gaussian mixtures model. Reduced moduli and hardness from 600 indents conducted at a control location
are summarized in Table 6-8. Graphical representation of deconvolution on control nanoindentation data is given in Figure 6-37.

Results of deconvolution procedure for reduced moduli and hardness within the interphase region are summarized in Table 6-9 and Table 6-10, respectively. Graphical representation of deconvolution on nanoindentation data is given in Figure 6-38. It should be noted that for each of the indentation locations, three distinct material phases were observed, with LD Phase and HD Phase occupying over 90% of the material volume. This is thought to be due to dissolution of calcium and previously unhydrated clinker from the cement paste, a process more commonly referred to as calcium leaching. Calcium leaching begins with dissolution of CH in water, which increases the porosity of cement paste and initiates progressive dissolution of C-S-H gel with low Ca/Si ratios, ultimately having a deleterious effect on the mechanical properties of the material (Constantinides and Ulm 2004). In the control location of conditioned sample, therefore, the two phases occupying over 90% of volume are leached LD C-S-H and HD C-S-H (Constantinides and Ulm 2004); the third phase is thought to be composite of remaining unleashed UHD C-S-H and smaller clinker crystals. The relative ratio of volume fractions of LD C-S-H and HD C-S-H, at control locations, was the same in conditioned and ‘dry’ sample.

Complete calcium leaching of cement paste is a process that develops over a long period of time, and in laboratory conditions can be accelerated by adjusting the pH value of the conditioning environment. In case of the present study, the cement paste was partially leached, which is apparent by a significant decrease in volume fractions of Phases #3 and #4, corresponding respectively to UHD C-S-H and unhydrated clinker grains when compared to those observed in the sample that was kept in dry conditions. Additionally, reduced moduli of
LD C-S-H and HD C-S-H decreased by 37 and 25.3%, respectively, when compared to control location on the dry specimen.

Comparison of reduced moduli of interphase to those of control show that LD Phase modulus is statistically significantly higher than that of the control (Table 6-11). Once again, this is a confirmation that low-density C-S-H is contributing to flow of epoxy in cement paste; following decalcification of the C-S-H, the penetrated epoxy matrix contributes to the effective reduced modulus of the LD C-S-H. HD Phase (corresponding to HD C-S-H in control), as previously discussed, is not thought be permeable to polymer macromolecules, which is confirmed by the herein presented results—no statistically significant difference exists between the interphase and control locations (Table 6-12).

Besides degradation of the cement paste, degradation of epoxy was also observed in nanoindentation experiments. The measured reduced modulus of epoxy was 3.65 GPa with a standard deviation of 0.34 GPa (COV=0.09) based on a population of 100 indents. The measured reduced modulus corresponds to an elastic modulus of 3.07 GPa (assuming a Poisson’s ratio of 0.4, per Holmann and Hahn 1989) which represents a reduction of 17% when compared to the elastic modulus of epoxy from the dry sample (3.70 GPa). Average hardness was found to be 0.16 with a standard deviation of 0.02 (COV=0.12), which represents a 11% reduction when compared to control sample.
Table 6-8. Summary of nanoindentation mechanical properties at control location (far away from interface).

<table>
<thead>
<tr>
<th>Property</th>
<th>LD C-S-H</th>
<th>HD C-S-H</th>
<th>UHD C-S-H</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_r$</td>
<td>0.70</td>
<td>15.7±3.3</td>
<td>0.26</td>
</tr>
<tr>
<td>$H$</td>
<td>0.70</td>
<td>0.23±0.07</td>
<td>0.26</td>
</tr>
</tbody>
</table>

Table 6-9. Summary of reduced moduli within interphase.

<table>
<thead>
<tr>
<th>Location [μm]</th>
<th>LD Phase</th>
<th>HD Phase</th>
<th>UHD Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>$f_k$</td>
<td>$\mu_k \pm \sigma_k$ [GPa]</td>
<td>$f_k$</td>
<td>$\mu_k \pm \sigma_k$ [GPa]</td>
</tr>
<tr>
<td>10</td>
<td>0.78</td>
<td>17.2±3.3</td>
<td>0.20</td>
</tr>
<tr>
<td>32.5</td>
<td>0.74</td>
<td>16.7±3.6</td>
<td>0.20</td>
</tr>
<tr>
<td>55</td>
<td>0.68</td>
<td>17.4±3.1</td>
<td>0.25</td>
</tr>
<tr>
<td>77.5</td>
<td>0.73</td>
<td>18.0±3.4</td>
<td>0.24</td>
</tr>
</tbody>
</table>

Table 6-10. Summary of hardness within interphase.

<table>
<thead>
<tr>
<th>Location [μm]</th>
<th>LD Phase</th>
<th>HD Phase</th>
<th>UHD Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>$f_k$</td>
<td>$\mu_k \pm \sigma_k$ [GPa]</td>
<td>$f_k$</td>
<td>$\mu_k \pm \sigma_k$ [GPa]</td>
</tr>
<tr>
<td>10</td>
<td>0.78</td>
<td>0.25±0.06</td>
<td>0.20</td>
</tr>
<tr>
<td>32.5</td>
<td>0.74</td>
<td>0.24±0.05</td>
<td>0.20</td>
</tr>
<tr>
<td>55</td>
<td>0.68</td>
<td>0.26±0.05</td>
<td>0.25</td>
</tr>
<tr>
<td>77.5</td>
<td>0.73</td>
<td>0.26±0.06</td>
<td>0.24</td>
</tr>
</tbody>
</table>

Table 6-11. P-values for two-sample unpaired t-test on reduced moduli of LD Phase; bolded font signifies $P>0.005$—no significant difference in means exist between compared groups.

<table>
<thead>
<tr>
<th>Distance from interface [μm]</th>
<th>10</th>
<th>32.5</th>
<th>55</th>
<th>77.5</th>
<th>Control</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>1</td>
<td></td>
<td></td>
<td>0.1240</td>
<td>0.5155</td>
</tr>
<tr>
<td>32.5</td>
<td>1</td>
<td>0.0114</td>
<td></td>
<td>0.0001</td>
<td>0.0029</td>
</tr>
<tr>
<td>55</td>
<td>1</td>
<td>0.0333</td>
<td>0.0001</td>
<td>0.0501</td>
<td>0.0001</td>
</tr>
<tr>
<td>77.5</td>
<td>1</td>
<td></td>
<td>0.0001</td>
<td>0.2373</td>
<td>1</td>
</tr>
</tbody>
</table>

Table 6-12. P-values for two-sample unpaired t-test on reduced moduli of HD Phase; bolded font signifies $P>0.005$—no significant difference in means exist between compared groups.

<table>
<thead>
<tr>
<th>Distance from interface [μm]</th>
<th>10</th>
<th>32.5</th>
<th>55</th>
<th>77.5</th>
<th>Control</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>1</td>
<td></td>
<td></td>
<td>0.5248</td>
<td>0.7536</td>
</tr>
<tr>
<td>32.5</td>
<td>1</td>
<td>0.0123</td>
<td></td>
<td>0.0601</td>
<td>0.0001</td>
</tr>
<tr>
<td>55</td>
<td>1</td>
<td>0.0327</td>
<td>0.0036</td>
<td>0.1786</td>
<td>0.0341</td>
</tr>
<tr>
<td>77.5</td>
<td>1</td>
<td></td>
<td>0.0036</td>
<td>0.2373</td>
<td>1</td>
</tr>
</tbody>
</table>
Figure 6-37. Nanoindentation test results for control location: (a) Gaussian mixtures deconvolution of reduced modulus and hardness data represented by cluster allocation; (b) deconvoluted reduced modulus data for range of moduli corresponding to cement hydrates (<65 GPa).

Figure 6-38. Nanoindentation test results for interphase: (a) Gaussian mixtures deconvolution of reduced modulus and hardness data represented by cluster allocation; (b) deconvoluted reduced modulus data for range of moduli corresponding to cement hydrates (<65 GPa).

**Evaluation of effective elastic modulus of interphase**

To obtain effective elastic modulus for each indentation location, each line of indents was regarded as an N-phase composite, where N is the number of nanoindentation locations in that line; thus, each indentation experiment represents a single phase of the composite and is defined by its reduced modulus.
The solutions for effective reduced moduli, based on eq. (4-13) and (4-14), for both dry and conditioned sample are summarized in Table 6-13. Similar trend in variation of elastic modulus is observed between the two groups (Figure 6-39). In both cases stiffening effect of the epoxy matrix on the effective elastic modulus are most pronounced at 55 and 77.5 µm away from the interface. The elastic modulus at 10 and 32.5 µm appears to be very close to that of the bulk cement paste; this is likely due to the negative effect of C-S-H dissolution on reduced modulus in presence of epoxy hardener that cancels out the stiffening effect of epoxy on cement paste. The stiffening effect of epoxy is thought to be more pronounced in the ‘dry’ sample mainly due to higher elastic modulus of epoxy in dry conditions, and lower porosity. Conditioning in water not only did affect the elastic properties of the adhesive, but it also introduced additional porosity which both had deleterious effect on the interphase modulus.

Table 6-13. Summary of effective reduced moduli in dry and conditioned specimens.

<table>
<thead>
<tr>
<th>Line</th>
<th>Distance from Interface [µm]</th>
<th>Dry</th>
<th>Conditioned in Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10</td>
<td>30.40</td>
<td>17.15</td>
</tr>
<tr>
<td>2</td>
<td>32.5</td>
<td>30.71</td>
<td>17.39</td>
</tr>
<tr>
<td>3</td>
<td>55</td>
<td>34.56</td>
<td>18.17</td>
</tr>
<tr>
<td>4</td>
<td>77.5</td>
<td>33.35</td>
<td>18.39</td>
</tr>
<tr>
<td>n/a</td>
<td>Control</td>
<td>30.85</td>
<td>16.76</td>
</tr>
</tbody>
</table>
Figure 6-39. Variation in effective reduced modulus with distance from interface.

**Chapter Summary**

Raman spectroscopy and nanoindentation characterization of the interphase region between epoxy and cement paste were performed to provide evidence of interphase existence, its formation mechanisms and nanomechanical properties. Analysis of Raman shift intensities in the interphase region, combined with independent porosity measurements of cement paste substrate with MIP confirmed that porosity is a major contributing factor to depth of permeation of epoxy into the cement paste substrate and can, consequently, have a significant influence on the characteristics of the cement paste interphase. Additional evidence from Raman map scans showed that the mechanism of epoxy permeation into the substrate is likely permeation through the network of capillary and gel pores.

Evaluation of relative degree of conversion by Raman spectroscopy in the interphase region revealed the existence of epoxy interphase adjacent to the interface. Based on the experimental data, it appears that higher number of epoxides have reacted with amine-rich hardener very close to the interface. This was explained by a higher concentration of epoxy
hardener available for curing reaction near the interface due to its preferential adsorption by C-S-H (Djouani et al. 2011).

Nanoindentation in the interphase region was conducted on both ‘dry’ and environmentally conditioned sample (by immersion in 30°C water for 4 weeks). In dry sample, four mechanically distinct material phases were identified in the interphase region: LD Phase, HD Phase, UHD Phase and clinker that respectively correspond to LD C-S-H, HD C-S-H, UHD C-S-H and clinker in neat cement paste. Based on the experimental results, adjacent to the interface LD and HD Phase experienced degradation of reduced modulus and hardness, probably due to dissolution effect of epoxy hardener on hydration products within cement paste (Djouani et al. 2013). Stiffening of cement paste within the interphase region occurred at 55 and 77.5 μm away from the interface, and reflected mainly in the increase of reduced modulus of HD Phase. Analysis of volume fraction of the interphase material phases showed gradual increase in LD Phase on the account of HD Phase. Continuum micromechanics methods were used to show that this behavior is due to formation of LD C-S-H and epoxy composite. Mori-Tanaka homogenization scheme explained the observed change in volume fractions with distance form interface—epoxy was found to have the ability of increasing the effective reduced modulus of LD C-S-H by as much as 50%.

In conditioned sample degradation of mechanical properties of epoxy, interphase and cement paste had occurred. Hardness and elastic modulus of epoxy had degraded by 11 and 17%, respectively. Probably due to calcium leaching, effective elastic modulus of neat cement paste was reduced by 46%; hardness of corresponding material phases within cement paste was reduced too. Exposure to water also had a negative impact on reduced moduli and hardness within interphase. Most likely due to increased pore space from calcium leaching, the effects of
epoxy on nanomechanical properties of interphase was not as pronounced as it was in the dry sample.
CHAPTER 7
ANALYTICAL EVALUATION OF INTERFACE

As it was shown in the previous chapter, interphase, with distinct chemo-mechanical properties exists between the epoxy and cement paste; similar scenario is expected in case of concrete substrate. Changed elastic properties of substrate, in the interphase region, are expected to affect the stress state ahead of the interfacial crack. In this section the effects of interphase mechanical properties on the interfacial cracks are quantitatively evaluated in terms of total interfacial energy release rate of the epoxy-substrate interface.

It should be noted that in case of interfacial cracks in FRP-concrete bonded joints, for the same crack size, local energy release rates are expected to change depending on the relative thickness of the adhesive layer, and interphase. This is mainly due to the size and shape of the region dominated by stress singularity, K-dominance zone, ahead of the crack tip with respect to other geometrical features of the interface (Figure 7-2). The postulated dependency of interfacial energy release rate was examined and quantified via finite element analysis (FEA) and virtual crack closure technique (VCCT), the basis of which was covered in a previous chapter.

To the best of authors’ knowledge, there is no currently available information on optimizing the design of adhesive interface between epoxy and cement paste/concrete or FRP and concrete. As a result of this study some of the design parameters affecting interfacial energy release rate were identified and their effect with respect to field applications is discussed.
**FEA Model—Verification against Analytical Solution**

To verify the FEA numerical procedure utilizing VCCT to calculate the total interfacial energy release rate, the results of FEA analyses were first compared to an analytical solution for an infinite plate with a crack lying at the interface between two adjoined material (Sih and Rice 1965) (Figure 7-3). Uneven stresses that were found to be generated in the x-direction are due to the elastic mismatch between the adherents and were mathematically quantified by Rice and Sih.
Expressions for local stress intensity factors is given by eq. (5-10). Total energy release rate can then be calculated according to eq. (5-12).

\[ \sigma_{yy} \]

\[ \tau_{xy} \]

\[ \sigma_x \]

\[ \sigma_y \]

\[ \tau_w \]

\[ 2a \]

Figure 7-3. Bimaterial plate loaded in tension.

FEA model of the crack lying at the interface between epoxy and cement paste was created in the generalized FEA software Abaqus®; schematic representation of the model is shown in Figure 7-4. To simplify the model and reduce the computational time, symmetry and antisymmetry boundary conditions were utilized. A far-field unit pressure load and unit surface traction were applied at the boundaries to simulate pure Mode I and Mode II loading conditions, respectively. The edge perpendicular to the interface (opposite from symmetry boundary condition) of the FEA model loaded in Mode I (Figure 7-4a) was constrained to account for the uneven stress state described by Rice (1965). The substrate was assigned an elastic modulus of 29 GPa and Poisson’s ratio of 0.24 characteristic for a cementitious material substrate. Epoxy was assigned the elastic modulus of 3.7 GPa, as determined from nanoindentation, and Poisson’s ratio of 0.40. The combination of materials introduces a significant elastic mismatch characterized by Dundur’s parameters of \( \alpha = 0.75 \) and \( \beta = 0.10 \).
The model was built using quadrilateral elements with plane strain formulation. Area surrounding the crack tip was meshed in a structured manner (Figure 7-5). The regions outside the crack tip were assigned quadrilateral-dominated free-form mesh, with element size progressively increasing with the distance from the crack to optimize the computational time (Figure 7-5). To further reduce the model size, symmetry boundary condition was assigned along the symmetry plane for Mode I loading condition. In Mode II loading antisymmetry boundary condition was applied along the plane of antisymmetry.

Post processing of data, to determine the interfacial energy release rates, was performed according to general VCCT procedures. Multiple crack extension lengths were evaluated to assure that the total energy release rate had converged, and did not change with the chosen crack.
extension. To calculate Mode I and Mode II components of the total energy release rate for a unit crack extension, equivalent to the size of one element located adjacent to the crack, eq. (5-16) was used. For crack extension lengths encompassing multiple elements, the following equations were used (Figure 7-6):

\[ G_I = \frac{1}{2k\Delta a} \sum_{i=1}^{k} Y_i \Delta w_{i-k}, \quad G_{II} = \frac{1}{2k\Delta a} \sum_{i=1}^{k} X_i \Delta u_{i-k} \]  (7-1)

Figure 7-5. (a) FEA model mesh shown in deformed shape to emphasize the crack location; (b) structured mesh around the crack tip; (c) close-up image of mesh around crack tip.
To determine the optimal element size \((m)\) in the crack tip region, a mesh convergence study was performed by varying the \(m/a\) ratio. For each element size increment, defined by \(m/a\) ratio, an error from analytical solution by Rice and Sih (1965) was noted (Figure 7-7) as:

\[
Error = \left| \frac{G_{FEM} - G_a}{G_a} \right| \cdot 100(\%) \tag{7-2}
\]

where \(G_{FEM}\) and \(G_a\) are total interfacial energy release rates determined from FEA model and analytically, respectively. \(G_a\) was calculated from complex stress intensity factor (eq. (5-10)) by Sun and Jih (1987) using the eq. (5-12). From Figure 7-7 it is apparent that error reduces with decreasing element size \((m/a\) ratio); element size corresponding to the point of convergence of error to 0% was used in all other analyses performed as a part of the study (Figure 7-7).

Depending on the geometry, to satisfy the fine mesh requirement in the crack tip region, the total number of elements in the generated models ranged from approximately 100,000 to over 500,000.

As mentioned in the background section, the convergence of independent mode I and mode II components of the total energy release rate is not achievable in FEA analyses, and is
dependent on the selected crack extension size. The total energy release rate, however, is independent of the chosen crack extension length; this was shown for the benchmark case in Figure 7-8. Therefore, while FEA analyses can provide an accurate total interfacial energy release rate, the exact mode mixity parameter $\psi$ (eq. (5-13)) remains an unknown.

Figure 7-7. Convergence of FEA analysis solution.

Figure 7-8. Energy release rate as a function of crack extension size for: (a) Mode I; and (b) Mode II loading conditions.
Parametric Study on FEA Model with Interphase

Once the bimaterial plate FEA model was verified against the analytical solution, the next step in the analysis was to incorporate the interphase region into the model to determine the effect of interphase stiffness on interfacial energy release rate at different conditions. Parametric study was designed to examine the influence of multiple variables on the total interfacial energy release rate. Cracks located at the interface between substrate and epoxy adhesive were considered for two distinct cases: (1) adhesive layer thickness that is very large compared to the crack size (Figure 7-9a); and (2) adhesive layer thickness that is on the order of magnitude of crack size (Figure 7-9b). While the geometry of the model was varied, the crack size was kept constant, which allowed for direct comparison between interfacial energy release rates corresponding to the two cases. The effect of following variables on interfacial energy release rate was investigated:

1. loading mode (Mode I vs. Mode II)
2. interphase thickness ($t_{int}$)
3. mismatch between elastic properties of epoxy and interphase by varying the interphase modulus ($E_{int}$)
4. Mismatch between elastic properties of epoxy and interphase by varying the elastic modulus of epoxy ($E_{adh}$)
5. Thickness of epoxy layer relative to crack size ($a/t_{adh}$).

Since the focus of this work is mostly small-scale cracking, the crack size was assumed to be very small compared to the thickness of bonded FRP composite. The underlying assumption in all models was that the external force acts on the surface of the FRP composite, which has a thickness that is at least an order of magnitude larger than the thickness of the adhesive layer; therefore, following Saint Venant’s principle the actual loading acting on the composite can be reduced to uniform far-field stress acting on the boundaries of each model, similar to Figure 7-4.
The comparison between different cases of the performed parametric study are reasonable only under the assumption that fracture energy (failure criterion) of the interface remains constant between different cases. Such an assumption would be difficult to prove experimentally, given the difficulty with controlling the parameters. The purpose of this study, however, is to identify possible parameters that would inform a more optimized design of FRP-concrete and epoxy-concrete adhesive joints. The practical implications of theoretical findings would, however, have to be confirmed experimentally.

![Diagram of adhesive layers](image)

**Figure 7-9.** (a) Three-layer model (thickness of adhesive layer very large compared to crack length); and (b) four-layer model (thickness of adhesive on the order of magnitude of crack length).

**Parametric Study of Interphase on Total Energy Release Rate for Very Large Adhesive Layer Thickness**

To implement the interphase region in the FEA model of infinite bimaterial plate, the region adjacent to the interface was assigned dissimilar elastic properties from those associated with the substrate (Figure 7-10). It should be noted that three-layer model (Figure 7-10) represents the case where thickness of the adhesive ($t_{adh}$) is very large when compared to the crack size ($t_{adh} \gg a$); therefore, no contribution from the FRP composite is considered.
The effects of interphase elastic properties on the interfacial energy release rate were evaluated as a function of ratio of crack size to interphase thickness ($\alpha/t_{int}$) and mismatch between adhesive and interphase ($\alpha$) which was accomplished by varying the elastic modulus of the interphase ($E_{int}$). The values of $E_{int}$ were selected relative to the elastic modulus of substrate ($E_{sub} = 29$ GPa); $E_{int}/E_{sub}$ ratios that were considered were 0.5, 0.75, 1, 1.25, 1.5, which correspond to elastic mismatch between epoxy and interphase expressed as Dundurs’ parameter $\alpha$ of 0.55, 0.68, 0.75, 0.79, 0.82, respectively. Epoxy and cement paste were assigned Poisson’s ratios of 0.40 and 0.24, respectively; interphase was assumed to maintain the same Poisson’s ratio as cement paste. Sensitivity of interfacial energy release rate with respect to Poisson’s ratio of interphase was examined parametrically by varying the value of Poisson’s ratio of the substrate in analytical model by Rice and Sih (1965) from 0.05 to 0.4 for a bimaterial plate loaded in tension with a unit crack size in plane strain condition. The selected case was thought to correspond to the most conservative estimate of effects of Poisson’s ratio on interfacial energy release rate (very large interphase in comparison to the crack size). It was found that changing Poisson’s ratio had a minor effect on the total interfacial energy release rate (Figure 7-11); the total interfacial energy release rates at 0.05 and 0.4 Poisson’s were within 2% of the interfacial energy release rate corresponding to Poisson’s ratio of 0.24. Epoxy and substrate were respectively assigned elastic moduli of 3.70 GPa and 29 GPa that were obtained from nanoindentation experiments, but also are representative of actual epoxy-concrete adhesive joints.

Parameter used to quantify the effects of elastic mismatch between the adhesive and interphase on the interfacial energy release rate is defined as the ratio of interfacial energy release rate when the interphase is present ($G_{int}$) to interfacial energy release rate when no
interphase is present ($G_{t_{int}=0}$) — $G_{int}/G_{t_{int}=0}$. Results of the numerical simulations for pure tension (Mode I) and pure shear (Mode II) loading conditions are presented in Figure 7-12a and Figure 7-12b, respectively.

By inspecting the plots it becomes immediately apparent that the interfacial energy release rate increases in case of a relatively flexible interphase and decreases for a relatively stiff interphase; effects of flexible interphase on the change in the interfacial energy release rate are also more pronounced. For example, for $a/t_{int}$=0.1 interfacial energy release rate for soft interphase ($E_{int}/E_{sub}$=0.50) increases by 17% when compared to the case with no interphase. The decrease in interfacial energy release rate for stiff interphase ($E_{int}/E_{sub}$=1.5), however, is approximately 5%, when compared to the case with no interphase. On the other hand, when considering the relationship between $G_{int}/G_{t_{int}=0}$ and $\alpha$, for the selected interphase elastic modulus range, there appears to exist a negative linear correlation between the two, which is particularly evident in Mode II loading (Figure 7-12); by increasing the elastic modulus of interphase, therefore, interfacial energy release rate is reduced. The rate of change of interfacial energy release rate is not proportional to the elastic modulus of interphase, but rather the introduced elastic mismatch between the adhesive and interphase.

Important to note is the effect of $a/t_{int}$ ratio on the change in interfacial energy release rate. While the effects of interphase diminish for crack sizes that are large compared to the interphase thickness ($a/t_{int} = 16$), for both loading modes, significant differences between the Mode I and Mode II loading exist. Namely, when the crack is subjected to Mode II loading, for crack interphase thickness that is on the order of magnitude of crack length ($a/t_{int}=2$) or very large compared to the interphase thickness ($a/t_{int} = 16$), change in interfacial energy release rate from the control case ($\alpha = 0.75$) due to changing interphase stiffness is more drastic than for
Mode II loading. This is mainly due to the shape of K-dominance zone which was evaluated by examining the von Mises stress distributions for Mode I and Mode II (Figure 7-13). Mode I K-dominance zone is wider in the direction perpendicular to the interface, while for Mode II the K-dominance zone is wider in the direction parallel to the interface; therefore, the strain energies associated with Mode II would be affected more by the elastic properties of the interphase—larger volume of crack process zone is within the interphase.

Effects of elastic modulus of the epoxy adhesive on interfacial energy release rate, when no interphase is present, can be shown by considering the analytical solution for interfacial crack lying at the interface. Figure 7-14 shows a positive correlation between the interfacial energy release rate and the elastic mismatch parameter $\alpha$. As elastic modulus of epoxy increases, its magnitude starts to approach that of the elastic modulus of substrate material; consequently, the elastic mismatch parameter $\alpha$ decreases, and the total interfacial energy release rate converges to the homogeneous case (corresponding to $\alpha=0$) in which contribution of localized mode II stress vanishes while the energy release rate decreases due to the overall higher elastic modulus.

To better understand the effect of increased/decreased elastic modulus of epoxy when interphase is present, FEA analyses were conducted for the two boundary cases for ratios of $\alpha/t_{int}$ of 0.1 and 2:

1. Soft adhesive—soft interphase: $E_{adh}=1.85$ GPa and $E_{int}/E_{sub}=0.5$ ($\alpha = 0.75$);
2. Stiff adhesive—stiff interphase: $E_{adh}=5.55$ GPa and $E_{int}/E_{sub}=1.5$ ($\alpha = 0.75$).

Results are presented in Figure 7-15. It is clear that in case of soft adhesive and interface the energy release rate nearly doubles when compared to the control case; on the contrary, for stiff interphase and adhesive the energy release rate decreases by up to 33% from the control situation. On the contrary from the case where only interphase elastic modulus is being modified
(Figure 7-12), in this analysis there appears to exist no significant difference between Mode I and Mode II response. This is likely due to the large thickness of adhesive layer relative to the crack size \( t_{adh} \gg a \) governing the change in interfacial energy release rate. In relationship to the reduced elastic modulus of substrate and adhesive, following exposure, that were revealed by nanoindentation experiments (Table 6-13), it would be expected that in conditioned specimen under the same loading interfacial energy release rate would be increased when compared to the specimen kept in dry conditions. Additionally, the increase in interfacial energy release rate combined with degradation of the interfacial bonds between the adherents would result in a lower required load to initiate fracture along the interface. This concept is further discussed in the following chapter.
Figure 7-10. Three-layer model of crack lying at adhesive interface in: (a) Mode I; and (b) Mode II loading.
Figure 7-11. Sensitivity of interfacial energy release rate to Poisson’s ratio based on Rice and Sih (1965) solution for a unit load, unit crack size, and plane strain condition. Elastic moduli of epoxy and substrate were assigned from values determined from nanoindentation experiments (3.70 and 29 GPa, respectively).

$$\frac{G_{int}}{G_{tint}} = 0$$

$0.55 \ 0.65 \ 0.75 \ 0.82 \ 0.9 \ 0.95 \ 1 \ 1.05 \ 1.1 \ 1.15 \ 1.2$

$a/t_{int} = 0.1$

$a/t_{int} = 2$

$a/t_{int} = 16$

Figure 7-12. Change in interfacial energy release rate as a function of elastic mismatch between epoxy and interphase introduced by varying the interphase elastic modulus: (a) Mode I; and (b) Mode II loading conditions.
Figure 7-13. Example Von-Mises stress distribution at the crack tip lying at the interface for: (1) Mode I; and (b) Mode II loading condition.

Mode I/Mode II

\[ \frac{G_a}{G_a(\alpha=0.75)} \]

Figure 7-14. Effect of elastic modulus of adhesive on interfacial energy release rate, for case without interface; \( G_a \) is calculated according to analytical solution.
**Parametric Study of Interphase on Total Energy Release Rate for Small Adhesive Layer Thickness**

While maintaining the same crack size, the geometry of previously discussed three-layer model was modified to incorporate the FRP and introduce the effects of adhesive layer thickness, resulting in formation of a four-layer model (Figure 7-16). The analysis similar to the one in previous section was conducted, where effects of multiple values of $E_{int}/E_{sub}$ and $a/t_{int}$ on interfacial energy release rate were examined in addition to those of the $a/t_{adh}$ ratio. FRP composite was modeled as transversely isotropic material with the following compliance matrix:
\[ C_{FRP} = \begin{pmatrix} \frac{1}{E_1} & -\frac{v_{12}}{E_2} & -\frac{v_{13}}{E_3} \\ -\frac{v_{12}}{E_2} & \frac{1}{E_1} & -\frac{v_{23}}{E_3} \\ -\frac{v_{13}}{E_3} & -\frac{v_{23}}{E_3} & \frac{1}{E_3} \\ \end{pmatrix} \begin{pmatrix} 1 \\ \frac{1}{G_{23}} \\ \frac{1}{G_{31}} \\ \frac{1}{G_{12}} \end{pmatrix} \]  

(7-3)

where subscripts 1-2-3 correspond to material coordinates, as defined in Figure 7-17. The following material properties \( E_1 = 68.83 \) GPa, \( E_2 = E_3 = 4.866 \) GPa, and \( G_{12} = G_{13} = 2.5 \) GPa were assigned according to experimental data for a commercially available unidirectional carbon FRP (CFRP), as reported by the manufacturer. Measurements of Poisson’s ratio were not available—all values were assumed to be \( v_{12} = v_{13} = v_{23} = 0.2 \). Shear modulus in the transverse plane was estimated as \( G_{23} = \frac{E_2}{2(1 + v_{23})} = 2.025 \) GPa. Material coordinates 1-2-3 correspond with global coordinates x-y-z of the model (Figure 7-16), respectively.

Initially the sensitivity of interfacial energy release rate to adhesive thickness was evaluated. Figure 7-18 shows the change in interfacial energy release rate is as a function of thickness of the adhesive layer while the crack size is kept constant. A significant decrease was observed for both Mode I and Mode II loading condition; Mode II, however, experienced a more marked reduction in interfacial energy release rate. This is mainly a result of FRP material properties; in Mode I loading condition, transverse modulus of FRP is utilized, which is very close to that of the epoxy adhesive; therefore, no significant change in energy release rate was observed between \( a/t_{adh} \) ratios of 2 and 10. Mode II loading makes use of the longitudinal modulus of FRP which is an order of magnitude larger than its transverse elastic modulus;
therefore, interfacial energy release rate of the interfacial crack is more sensitive to changing thickness of the adhesive layer.

Increase in failure load of the adhesive joint between two dissimilar solids with decreasing thickness of adhesive layer that experienced interfacial failure mode was experimentally confirmed in a study by Afendi et al. (2011). Similar studies were performed on FRP-concrete joints (Lopez-Gonzalez et al. 2012), but they resulted in an opposite finding—with increase in adhesive layer thickness the stress of the adhesive joint decreased. This is mainly due to the fact that cohesive (concrete) failure modes were experienced in majority of experiments; therefore, the findings do not purport to a purely interfacial failure mode. The reason for a positive correlation between adhesive layer thickness and failure load is due to a better redistribution of stress for thicker adhesive layer, which also results in an increase in the size of the softening zone and ultimately the higher fracture energy (Chen and Qiao 2009). The discrepancy between optimal adhesive layer thicknesses for two different failure modes indicates that selection of adhesive layer thickness, when practical, is an important parameter to consider. While it may be advantageous for sound bond to have a thicker adhesive, the same may not be true in case where the bond has degraded and interfacial failure mode is to be expected, or for a very substrate that is relatively very tough when compared to the interface. A parametric optimization study to determine the most appropriate adhesive layer thickness for any given case would be beneficial.

Effects of adhesive layer thickness were also examined with regards to the changing elastic modulus of interphase for $a/t_{int}=2$ and $a/t_{adh}$ values of 0, 2, and 10. The energy release rates were all normalized to the respective control case ($E_{int}/E_{int} = 1$) for each geometry. From Figure 7-19 it is obvious that thickness of the adhesive plays a more important role for Mode II
loading when compared to Mode I loading condition. While results from all three cases approximately overlap in case of Mode I loading condition, Mode II loading shows significant sensitivity to the adhesive layer thickness. Specifically, for $a/t_{adh}=2$ the effects of elastic mismatch between epoxy and interphase are most pronounced in Mode II loading. Again, direction-dependent properties of FRP combined with K-dominance zone shape effects are deemed to govern this behavior.

Finally, effects of changing adhesive layer thickness and its elastic modulus on the interfacial energy release rate were examined (Figure 7-20). It should be noted that results for $a/t_{adh}=0$ were determined from analytical solution for a crack lying at the bimaterial interface; the interfacial energy release rates are equal between Mode I and Mode II loading modes, thus, the two lines overlap. Numerical results show, again, a positive correlation between change in interfacial energy release rate, and elastic mismatch between the substrate and epoxy. Similarly to the previous discussions, the effects of varying epoxy elastic modulus are more significant in Mode II loading when compared to Mode I loading condition; the disparity, however, is not significant as that caused by changing elastic modulus of interphase layer observed in Figure 7-19.
Figure 7-16. Four-layer model of crack lying at adhesive interface in: (a) Mode I; and (b) Mode II loading.

Figure 7-17. Material coordinates for FRP.
Figure 7-18. Change in interfacial energy release rate with decreasing adhesive thickness for when no interphase is present.

Figure 7-19. Change in interfacial energy release rate as a function of elastic mismatch between epoxy and interphase introduced by varying the modulus of interphase for \(a/t_{int} = 2\).
Summary and Comments on Practical Applications of Presented Numerical Results

Raman spectroscopy and nanoindentation provided evidence of interphase existence at the interface between epoxy and cement paste. Similar scenario is expected for concrete substrate. Given that change in modulus of examined cement paste-epoxy interface corresponds to a very specific case, a theoretical study was conducted considering a range of possible elastic moduli within the interphase.

The presented FEA investigation showed sensitivity of interfacial energy release rate to changing elastic modulus of interphase, epoxy, and thickness of the adhesive layer. As discussed earlier, the results of parametric study can be practically evaluated under the assumption that interfacial fracture energy is constant between different cases which would have to be shown experimentally; thus, experimental investigation of the discussed implications of the FEA analysis is recommended.
When considering adhesive-interface couple where the substrate has a greater fracture toughness than the interface between the two materials, it may be more prudent to select a thin bond line to reduce energy release rate along the interface. On the other hand, based on the experimental findings from the available literature (Lopez-Gonzalez et al. 2012), when substrate has lower toughness than that of interface a thicker bond line may be beneficial to redistribute the stress within the substrate.

In many practical applications of externally bonded FRP, a considerable amount of degradation may have occurred within the substrate (such as calcium leaching, alkali-silica reaction, sulfate attack, etc.). Given the increase in interfacial energy release rate with the degradation of substrate elastic modulus (Figure 7-12, Figure 7-19), it would be beneficial to improve the condition of substrate material both from the perspectives of cohesive and adhesive failure modes. For damaged substrate with toughness that is lower than that of interface failure at low loads would be expected due to the low intrinsic toughness of substrate. On the other hand, if the substrate stiffness/strength/toughness were to be improved (e.g. pressure injecting with epoxy) not only would the available energy for crack growth along the interface be reduced (due to increase in substrate elastic modulus), but the toughness of the underlying substrate would be likely improved (e.g. due to reduction in porosity).

Based on the numerical investigations increase in elastic modulus of epoxy adhesive has a desirable effect on interfacial energy release rate. Decreasing elastic modulus of epoxy, for example due to plasticization effects in epoxy when exposed to water, will result in an increase of available energy for crack growth along the interface. Based on these findings, future work should concentrate on development of adhesives with improved stiffness and resistance to moisture.
CHAPTER 8
EXPERIMENTAL CHARACTERIZATION OF INTERFACE

Work in the previous sections provided characterization of the interphase region between cement paste and epoxy. Effects of interphase and adhesive properties on interfacial energy release rates were further discussed by employing FEA analysis. This section aims at quantifying the fracture parameters and durability of chemical bonding between epoxy and cement paste. Discussions of results in this chapter consolidate findings from nanomechanical characterization of interphase and those from FEA model to explain their respective effects on failure mechanisms and degradation phenomena governed by the chemical bond component.

As described in the literature review section, bond between epoxy and concrete transfers applied loads through a combination of chemical (hydrogen bonding) and mechanical bonding (mechanical interlock) mechanisms. While in cohesive failure modes (crack extension through substrate), energy required to form new surfaces corresponds almost entirely to fracture energy of the substrate/interphase, in interfacial failure modes the total fracture energy represents a combination of contributions from chemical bond, and bonding surface tortuosity (mechanical bond) components:

\[ \Gamma_{total} = \Gamma_{chemical} + \Gamma_{mechanical} \]  \hspace{1cm} (8-1)

Previous work on the topic (overview given in Tatar 2013) has concentrated on evaluation of overall change in fracture energy during accelerated conditioning, without considering the effects harsh environments on each of the two bond components. While the results from tests quantifying an overall effect on bond provide useful information for design of FRP-concrete bonded joints, they do not offer insight into the exact mechanisms behind bond degradation. Work presented in this chapter provides characterization of fracture energy associated with chemical bonding primarily \((\Gamma_{total} = \Gamma_{chemical})\), which is accomplished by
minimizing the tortuosity of the bonding surface \( (\Gamma_{\text{mechanical}} \approx 0) \). Use of silane coupling agents to functionalize the cement paste surface and improve the chemical bond component were also explored. The previous studies on silane functionalization have not examined the effects of silane surface treatment in a case where mechanical bonding is minimized, and therefore, it is difficult to ascertain whether surface tortuosity has an influence on the effectiveness of silane functionalization; the presented work addressed this concern. Two main hypotheses were tested:

1. Chemical bond component \( (\Gamma_{\text{chemical}}) \) between cement paste and epoxy is severely degraded when the interface is saturated with water.
2. Silane coupling agent surface treatment can improve the durability of chemical bond component \( (\Gamma_{\text{chemical}}) \) between epoxy and cement paste.

**Test Method**

For the purpose of quantification of chemical bonding between epoxy and cement paste three-point bending test, shown in Figure 8-1, was designed. The test specimen consists of two cement paste bars bonded together with epoxy. A notch (precrack) is incorporated into the specimen between epoxy and cement paste to initiate a crack at the interface. This failure mode, as discussed earlier, allows quantification of the fracture energy associated with the chemical bond component; effects of surface tortuosity on the test results are minimized by polishing with increasingly fine abrasives until the bonding cement paste surface is as smooth as possible.

A three-point bending test setup was selected over a more commonly utilized four-point bending test due to the rigidity of the test fixture of the four-point bending test, and small deflections at fracture load. The main concern with using four-point bending test was that one of the loading points would not come in contact with the test specimen (due to artifacts introduced by imperfections in specimen preparation, and those in test fixture) under very low expected deflections at fracture. This would have resulted in changed shape of moment diagram, and shear loading at the location of the notch.
Test Matrix and Accelerated Conditioning Protocol

Specimens were divided into four test groups, as shown in Table 8-1. Two control groups were created: one with silane treatment (S-C), and one without (NS-C); both control groups were held in standard laboratory conditions prior to testing. The remaining two groups of specimens were also one silane-treated (S-4), and one without silane treatment (NS-4); both groups were conditioned by water immersion at 30°C for 4 weeks, following one week of curing in standard laboratory conditions. Exposure was conducted in tap water in a 36-gallon water tank with a circulating pump and a heating element. Water temperature was continuously monitored throughout the exposure with a thermocouple; temperature readings were taken on an Omega HH314A humidity and temperature meter, and were in the 30.5±0.2°C range. All four groups were tested sequentially on the same day within the first two hours after being removed from the exposure tank.
Table 8-1. Test matrix.

<table>
<thead>
<tr>
<th>Group</th>
<th>Surface Treatment</th>
<th>Exposure Condition</th>
<th>Number of Samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>NS-C</td>
<td>None</td>
<td>SLC</td>
<td>8</td>
</tr>
<tr>
<td>S-C</td>
<td>Silane</td>
<td>SLC</td>
<td>8</td>
</tr>
<tr>
<td>NS-4</td>
<td>None</td>
<td>30°C water immersion</td>
<td>6</td>
</tr>
<tr>
<td>S-4</td>
<td>Silane</td>
<td>30°C water immersion</td>
<td>7</td>
</tr>
</tbody>
</table>

**Specimen Preparation Procedures**

Ordinary Portland cement (OPC) paste cubes (Cemex Type I/II), measuring 5 cm, with w/c ratio of 0.40 were prepared by mixing in a high shear mixer and pouring into brass molds (Figure 6-2). High shear mixing was chosen over standard paddle mixing to produce a more uniform mixture with low porosity, given that the main goal of the test was to study the chemical bonding between the adherents. Fresh cement paste was covered with a Teflon sheet to minimize moisture loss, and allowed to harden for 24 hours. The cubes were then transferred to a tank with lime solution in tap water for 6 months. Following cure, the samples were stored in standard laboratory conditions for an additional 6 months. Cement paste bars, measuring 5 cm in length and approximately 0.5x0.5 cm in cross-sectional dimensions, were cut from 10-cm cubes with a low-speed diamond saw (Allied TechCut 4) (Figure 6-3). One end of each bar was then polished to a mirror finish using the same polishing procedures that were described in the previous chapter.

**Silane Surface Treatment**

Following polishing, all bars were thoroughly cleaned with acetone and separated into two groups: (1) silane-treated; and (2) group without surface treatment. An epoxy-functional silane, 3-glycidoxypropyltrimethoxysilane (GPTMS), was selected for functionalization of silane-treated group. The silane solution was prepared by mixing 1 wt% of the GPTMS in 90:10 wt% ethanol and deionized water solution. A few drops of acetic acid were added to bring the pH of the solution to approximately 5. The mixture was then stirred for 60 minutes in a magnetic stirrer to
allow for complete hydrolysis of the silane. Prepared solution was pipetted on the polished surfaces of cement paste bars, and allowed 10 minutes to absorb into the surface before placing the samples in an oven for 80 minutes at 60°C. This surface functionalization procedure was found to result in formation of covalent bonds between the silane molecule and cement paste substrate (Stewart et al. 2013).

**Beam Specimen Preparation**

Beam specimen assembly procedures are outlined in Figure 8-2. PTFE tape was applied to one of the bonding faces of a cement paste bar to prevent adhesion between the epoxy and cement paste at that location, and simulate the notch (Figure 8-2—Step 1). Two cement paste bars were then placed 1 mm apart, and PTFE tape was applied to the sides and bottom of the specimen (Figure 8-2—Step 2).

Epoxy adhesive consisting of diglycidyl ether of bisphenol A (DGEBA, Momentive® EPON 826) resin and poly(oxypropylene) diamine (POPDA, Huntsman ® Jeffamine D-230) was mixed in a weight ratio of 100:32.9 which corresponds to stoichiometric equivalence between the functional groups. The 1 mm gap between the two cement paste bars was slowly filled with epoxy using a syringe to ensure no air was trapped (Figure 8-2—Step 3); 1 mm gap was chosen as it is on the similar order of magnitude as the actual adhesive layer thickness in FRP-concrete bonded joints, and it also allowed to efficiently introduce a notch at the interface in the later steps of specimen preparation.
To create a sharp notch, following approximately 20 hours of curing in standard laboratory conditions (temperature 23±3°C and relative humidity 50±10%), the PTFE tape was removed from the interface and a 0.22 mm thick razor blade was inserted at the interface at a slight angle. Epoxy was cured at standard laboratory conditions for additional 48 hours before removing the razor blades. The notch created in such manner was additionally sharpened with a 0.10 mm thick razor blade in a sawing motion; to increase the friction and removal of material razor blades were coated with 6 μm diamond suspension prior to sawing. Fresh blades were used for each sample to maintain the consistency between the specimens. SEM images of a typical notch resulting from above-described procedure are shown in Figure 8-3. The radius of crack tip at the interface was approximately 1.2 μm (Figure 8-3c) which is very small compared to the total precrack length (1-2 mm). Even though a perfectly sharp crack has a tip which radius of
curvature is on the order of magnitude of Å, it is expected that sawing process would have introduced additional damage ahead of the physical crack tip which would justify the assumption of a perfectly sharp crack under the framework of linear elastic fracture mechanics principles.

After notching, all specimens were subjected to gradual polishing to 1200 grit to remove the surface flaws (Figure 8-4). Control beam preparation included coating the cement paste bars (away from the interface) with a thin layer of epoxy to reduce the probability of surface flaws causing failure in cement paste, away from the notched interface. Exposure group was not coated with epoxy, as interfacial failure mode was expected due to degradation of the adhesive bonds.
Figure 8-3. Backscatter image of notch at interface at: (a) 100x; (b) 640x; and (c) 9300x magnification.
Test Procedures

All specimens were tested in an Instron universal testing machine (Figure 8-5). Special care was taken to align the tip of the loading point with the interface to isolate the interface from the effects of shear stress. Load was applied at a constant displacement rate of 0.005 mm/sec; data was acquired with a 50-kN load cell affixed to the testing machine with a noise range of approximately ±0.5 N. Displacement data were collected from the movement of testing machine cross-head.

Load at fracture and failure mode are reported in Table 8-2 for all tested specimens. Three typical failure modes were observed: (1) along the notched interface; (2) away from notch and in cement paste; and (3) along the interface opposite from the notch. All conditioned specimens without silane treatment experienced interfacial failure during handling post-exposure without any significant load being applied to them; the assumed failure load of the NS-4 group was, therefore, 0 N for all specimens. Typical load vs. displacement plots are shown in Figure 8-6; all specimens that achieved the desired failure mode (along notched interface) experienced unstable crack growth indicating brittle nature of the interface.
Table 8-2. Summary of test results.

<table>
<thead>
<tr>
<th>Test Group</th>
<th>Specimen #</th>
<th>Fracture Load (N)</th>
<th>Failure Location</th>
</tr>
</thead>
<tbody>
<tr>
<td>NS-C</td>
<td>1</td>
<td>66.09</td>
<td>Notched Interface</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>90.71</td>
<td>Notched Interface</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>65.11</td>
<td>Notched Interface</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>N/A</td>
<td>Notched Interface</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>129.68</td>
<td>Opposite Interface</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>78.53</td>
<td>Notched Interface</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>78.89</td>
<td>Notched Interface</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>104.04</td>
<td>Notched Interface</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>97.41</td>
<td>Notched Interface</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>46.88</td>
<td>Notched Interface</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>90.91</td>
<td>Cement Bar</td>
</tr>
<tr>
<td>S-C</td>
<td>4</td>
<td>87.11</td>
<td>Notched Interface</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>79.22</td>
<td>Cement Bar</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>115.83</td>
<td>Notched Interface</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>91.9</td>
<td>Notched Interface</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>46.38</td>
<td>Cement Bar</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>0*</td>
<td>Notched Interface</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0*</td>
<td>Notched Interface</td>
</tr>
<tr>
<td>NS-4</td>
<td>3</td>
<td>45.88</td>
<td>Notched Interface</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>20.85</td>
<td>Notched Interface</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>26.39</td>
<td>Notched Interface</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>28.27</td>
<td>Notched Interface</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>17.88</td>
<td>Notched Interface</td>
</tr>
</tbody>
</table>

N/A: the load was not recorded due to loss of connection between testing machine and computer
*: Specimens fractured along notched interface during handling, prior to being tested.
Figure 8-5. Beam test specimen in three-point bending fixture.

Figure 8-6. Typical load vs. displacement plots from three-point bending test.

**Data Analysis**

Data analysis was performed under the framework of interfacial fracture mechanics principles associated with interfacial crack in a “sandwich”. Considering the principle of energy conservation, it can be shown that local (at the crack tip) and global energy release rates are equal (Hutchinson and Suo, 1989); therefore, there exists a relationship between the local stress
intensity factors, and those calculated for a crack in an equivalent homogeneous specimen, when thickness of the adhesive layer is small compared to all other in-plane dimensions. Interfacial fracture energies were evaluated according to Hutchinson and Suo (1989); the following equation was used:

\[ \Gamma_i = \frac{K_{IC}^2}{E^*} \]  

(8-2)

where \( K_{IC} \) is stress intensity factor at fracture load calculated for an equivalent homogeneous specimen; \( E^* = E/(1 - \nu^2) \) for plane strain condition and \( E^* = E \) for plane stress condition; \( E \) and \( \nu \) are modulus of elasticity and Poisson’s ratios of the bulk material (cement paste in this case). Plane strain conditions were assumed in further calculations.

Stress intensity factor in an equivalent homogeneous sample was determined using an equation by Bar-On et al. (1996); the relationship was developed from extensive numerical analyses on cracked beam specimens subjected to three-point bending loading:

\[ K_{IC} = \frac{1.5P_{max}S\alpha^{1/2}}{BW^{3/2}(1 - \alpha)^{3/2}} f(\alpha) \]  

(8-3)

where \( P_{max} \) is maximum load; \( B \) and \( W \) are respectively width and height of the test specimen; \( S \) is span length (6 cm); \( \alpha = a/W \) where \( a \) is crack length The value of \( f(\alpha) \) is defined by a 5th order polynomial:

\[ f(\alpha) = A_0 + A_1\alpha + A_2\alpha^2 + A_3\alpha^3 + A_4\alpha^4 + A_5\alpha^5 \]  

(8-4)

where coefficients \( A_0 \) through \( A_5 \) are given by Bar-On et al. (1996).

The tabulated values of \( A_0 \) through \( A_5 \) (Bar-On et al. 1996) allow \( f(\alpha) \) to be computed for values of \( S/W \) of 4, 5, 6, 7, 8, and 10. Since the \( S/W \) ratio of the tested specimens varied from 5.45 to 7.02, to account for the variation in \( S/W \) ratio, the \( f(\alpha) \) values corresponding to the actual \( S/W \) ratios were interpolated by a 3rd order polynomial (Figure 8-7).
Discussion of Interfacial Fracture Energy Results

Interfacial fracture energies corresponding to fracture along the notched interface were calculated for all specimens per Eq. (8-2); moduli of elasticity for control and conditioned group of 29 GPa and 16.8 GPa were used based on the nanoindentation data, respectively. Results from specimens with other failure modes were not considered. Outliers were identified according to ASTM E178, based on the tabulated values for one-sided 5% significance level. Test results for each test group are summarized in Table 8-3 and Figure 8-8.

Table 8-3. Summary of fracture energy results.

<table>
<thead>
<tr>
<th>Test Group</th>
<th>Mean±Standard Deviation (J/m²)</th>
<th>COV</th>
</tr>
</thead>
<tbody>
<tr>
<td>NS-C</td>
<td>18.87±3.21</td>
<td>0.17</td>
</tr>
<tr>
<td>S-C</td>
<td>31.66±2.03</td>
<td>0.06</td>
</tr>
<tr>
<td>NS-4</td>
<td>0±0</td>
<td>0</td>
</tr>
<tr>
<td>S-4</td>
<td>2.94±1.31</td>
<td>0.45</td>
</tr>
</tbody>
</table>
Figure 8-8. Interfacial fracture energies from three-point bending test on beam specimens.

It is apparent that fracture energies in silane treated samples are higher than those of the corresponding non-treated groups (Figure 8-8), indicating the effectiveness of surface functionalization on the interfacial fracture energies. While silanes proved to increase the resistance of the adhesive bond to the effects of water, a reduction in fracture energy of 91% from control silane group was noted. This could be due to low cohesive strength of the deposited layer of the coupling agent combined with inadequate stability of formed interfacial bonds (Schmidt and Bell 2005). Another possibility is that dissimilar chemical interactions occur between silane and different material phases within the cement paste; additional research is required to characterize the interactions between silanes and different material phases in the cement paste under the influence of moisture.

All non-treated conditioned specimens (NS-4) failed during handling when being removed from the conditioning tank. While this is thought to be mostly due to the vulnerability
of hydrogen bonds between epoxy and cement paste to lubricating effect of water molecules at the interface, another potential mechanism that would be disruptive to integrity of hydrogen bonds was identified: swelling of the adhesive layer. This phenomenon has been observed by Amidi and Wang (2016); no strong evidence, however, was provided in support of it. Epoxy adhesives undergo a significant volumetric change due to water sorption, which could introduce stress along the faces of the adhesive that are constrained from free expansion.

Epoxy adhesives possess a property termed birefringence; their refractive index depends on the polarization and direction of the light passing through the sample. When birefringent isotropic material (such as epoxy) is subjected to mechanical stress and placed between two polarizers oriented in 0-90° direction, a fringe color pattern can be observed. The spacing and number of fringes can be directly correlated to difference in principal stresses ($\sigma_1 - \sigma_2$) by using the principles of experimental technique called photoelasticity; review of the photoelasticity technique can be found elsewhere (Sciammarella and Sciammarella 2012). Given the birefringence property of the epoxy adhesive, photoelasticity was identified as a potential technique to evaluate the effect of swelling of epoxy on interface. Following conditioning, a beam specimen was polished to a thickness of approximately 2 mm, to be able to pass the light through the epoxy adhesive layer, and placed between two linear polarizers with a relative orientation of 90° (Figure 8-9). The specimen was then examined with an optical microscope. The resulting fringe pattern, shown in Figure 8-10, suggests that stresses have developed during the exposure of beams to water; the parallel fringes near the two interfaces indicate that some difference in two principal stresses occurs, while no stress is present in the middle of epoxy adhesive layer (Figure 8-10b). Although the quantification and a more rigorous analysis of the swelling stresses is outside the scope of this work and will be conducted in the future, it should
be noted that besides degradation of hydrogen bonds at the interface between epoxy and cement paste, swelling stresses were at least a contributing factor to decrease in measured interfacial fracture energies following exposure in water.

Additionally, regarding the FEA analyses presented in the previous chapter, degradation of mechanical properties of epoxy and cement paste during conditioning would have contributed to an increase in interfacial energy release rate which would result in the specimen failing at a lower applied load. It appears that in NS-4 group the effects of swelling stress, and epoxy and cement paste degradation were significant enough to cause fracture along already degraded interface without substantial external stimulus.

Figure 8-9. Photoelasticity test setup.
In conditioned silane group (S-4), similarly, in addition to the possible low cohesive strength of the silane layer and instability of silane bonds, the significant decrease (91%) from control (S-C) fracture toughness can be also attributed to development of swelling stress across the interface. The existence of interfacial stress due to swelling of epoxy combined with increased interfacial energy release rate due to decay of mechanical properties of epoxy and cement paste indicates that degradation of the interface is a combination of chemical and mechanical phenomena. The test results from three-point bending test of S-4 group specimens are, therefore, apparent interfacial fracture energies; the actual fracture energies associated with this group are likely to be significantly higher.

To statistically evaluate the data, null-hypothesis that means between the two control and two conditioned groups are equal were tested using unpaired t-test; the main underlying assumption was that interfacial fracture energies in each group were normally distributed.
Corresponding P-values are shown in Table 8-4; for both cases the null-hypothesis was rejected, confirming that statistically significant difference in interfacial fracture energies exist between the non-treated and silane-treated groups, confirming the effectiveness of epoxy-functional silane in increasing the interfacial fracture energy and improving the durability of the adhesive interface.

**Table 8-4. Summary of p-values from unpaired t-test.**

<table>
<thead>
<tr>
<th>Group 1</th>
<th>Group 2</th>
<th>P-value</th>
<th>Reject Null-hypothesis?</th>
</tr>
</thead>
<tbody>
<tr>
<td>NS-C</td>
<td>S-C</td>
<td>0.0002</td>
<td>Yes.</td>
</tr>
<tr>
<td>NS-4</td>
<td>S-4</td>
<td>0.0004</td>
<td>Yes.</td>
</tr>
</tbody>
</table>

**Fractographic Analyses of Failed Surfaces**

Following three-point bending test fractured interfaces were examined under optical microscope and SEM to determine the characteristics of the fractured surfaces; both epoxy and cement paste sides of the failed interface were inspected (Figure 8-11). Backscatter electron images in the vicinity of notch (Figure 8-12), on the epoxy side of failed interface, clearly revealed that the crack growth occurs along a significant length of the notch, instead of initiating from a single point. Smooth epoxy surface is indicative of stable crack growth along the notch. Acceleration of crack growth is reflected by irregularities in fractured surface geometry; transition to unstable crack growth is apparent from hackle pattern pointed out by white arrows in Figure 8-12. The fact that crack extension occurred along the notch tip is important in a sense that it supports the underlying assumptions behind eq. (8-3).

Optical microscope photographs of typical failed interfaces in each of the four groups are shown in Figure 8-13; a special light filter was used to intensify the reflection from the surfaces and exaggerate the contrast between the areas of different roughness. From the reflection of light in images it is apparent that specimens in all groups, except for S-C, have experienced fracture along the adhesive interface. Examination of reflective regions in SEM provided additional
evidence that these areas had experienced a clean interfacial failure mode. Secondary electron image (Figure 8-14) of failed cement paste surface shows striations caused by polishing, which signifies that no damage had occurred in the substrate; similar markings were observed on the epoxy side (Figure 8-14b), too. On the other hand, all control specimens that were treated with silane (S-C group) experienced a mixed failure mode—within the cement paste substrate (cohesive) and along the interface. Secondary electron and backscatter images taken on cement paste and epoxy side of failed interface (Figure 8-15a and Figure 8-15b, respectively), of areas marked with ‘1b’ in Figure 8-13, show that the crack had bounced between interface and substrate/interphase resulting in a mixed failure mode; it was shown through FEA simulations by Xuefu and Aoki (1992) that for interfaces loaded in Mode I, where interface strength is sufficient, the crack meanders through the weaker material along the interface.

Dark areas on exposed specimens (NS-4 and S-4 test groups), labeled as ‘2a’ in Figure 8-13, are locations that experienced deposition of salts resulting from dissolution of cement paste minerals, as it was confirmed from SEM micrographs (Figure 8-16)—growth of needle-like crystals was observed. This is not surprising since it was confirmed by nanoindentation that leaching of cement paste matrix occurred during conditioning in water.

Figure 8-11. Failed beam specimen. Fracture surfaces on both epoxy and cement paste side of each specimen were examined.
Figure 8-12. Stitched backscatter electron images showing crack growth along the notch tip.
Figure 8-13. Optical microscope photographs of typical failed interfaces showing cement paste and epoxy adhesive side.

Figure 8-14. Images corresponding to NS-C, NS-4, and S-4 test groups: (a) Secondary electron image of typical post-mortem cement paste surface showing no damage to the substrate following three-point bending test; (b) backscatter electron image of epoxy surface showing polishing marks with no pulled off cement paste particles (lack of contrast).
Figure 8-15. Images corresponding to S-C group: (a) Secondary electron image of typical post-mortem cement paste surface showing significant changes in topography (smooth and rough regions) indicating a combination of interfacial and cohesive failure modes; (b) backscatter image of typical post-mortem epoxy surface of the interface on showing significant changes in contrast corresponding to distinct failure modes (dark areas indicate epoxy surface and interfacial failure mode, and bright area correspond to pulled off cement paste grain and cohesive failure mode).

Figure 8-16. Deposited salt crystals on exposed samples at two magnifications (backscatter electron signal).
Evaluation of Kink Criterion in Relationship to the Experimental Results

As it was shown in the previous section dissimilar failure modes were observed between the two control groups (NS-C and S-C). While interfacial failure mode generally indicates that the substrate was tougher than the interface, the opposite is true for a cohesive failure mode. To further examine the relationship between observed failure modes and measured fracture energies associated each group of samples, an analytical model considering the kinking of crack out of a bimaterial interface was considered (Figure 8-17). He and Hutchinson (1989) demonstrated that a crack will kink out of interface inside Material 2 when the following criterion is satisfied:

\[
\frac{\Gamma_i}{\Gamma_s} \geq \frac{G_i}{G_{\omega}^{\text{max}}}
\]

(8-5)

where \(\Gamma_i\) is fracture energy of the interface, \(\Gamma_s\) is fracture energy of substrate; \(G_i\) is energy release rate available for crack growth along the interface; \(G_{\omega}\) is energy release rate associated with the kinked crack path inside Material 2; \(G_{\omega}^{\text{max}}\) represents maximum energy release rate associated with the kinked crack path inside Material 2. When \(\Gamma_i/\Gamma_s < G_i/G_{\omega}^{\text{max}}\) crack extends along the interface. The transitioning case is, therefore, \(\Gamma_i/\Gamma_s = G_i/G_{\omega}^{\text{max}}\).

Relationship between \(G_i/G_{\omega}\) and \(\omega\) for cement paste-epoxy interface, according to He and Hutchinson (1989), is given in Figure 8-18a for varying mode mixity parameters \(\psi\). Variation of \(G_i/G_{\omega}^{\text{max}}\) with respect to mode mixity parameter \(\psi\) was obtained by plotting the minima from each of the curves from Figure 8-18a, and is presented in Figure 8-18b. Figure 8-18b defines the range of \(\Gamma_i/\Gamma_s\) values that will result in crack kinking out of interface for a given mode mixity parameter \(\psi\). Figure 8-19 plots the crack kink angles \(\omega\) at which \(G_i/G_{\omega}^{\text{max}}\) occur; the plots shows that crack kinks out of interface at an angle that is in 0 and 40º, depending on the mode mixity parameter \(\psi\). All plots were computed for elastic mismatch representative of epoxy-cement paste interface characterized by \(\alpha = -0.75\). Dundur’s parameter representing...
mismatch in shear moduli, $\beta$, was assumed to equal zero. Even though in an actual epoxy-cement paste interface $\beta = -0.1$, implementing the actual value of $\beta$ necessitates consideration of stress oscillating region ahead of the crack tip (eq. (5-6)), which introduces computational difficulties. It was shown by Hutchinson and He (1989) that implementation of actual $\beta$ value does not have a significant effect on $G_t/G_\omega$ allowing for simplification introduced by choice of $\beta = 0$.

![Figure 8-17. Graphical representation of crack kinking out of interface (modified from Suo and Hutchinson 1989).](image_url)
Figure 8-18. Crack kink criterion: (a) Relationship between $G_i/G_\omega$ and kink angle $\omega$ for different values of mode mixity parameter $\psi$; (b) relationship between $G_i/G_\omega$ and mode mixity parameter $\psi$. Both graphs are for a bimaterial couple with $\alpha = -0.75$ and $\beta = 0$.

Figure 8-19. Relationship between $G_i/G_\omega^{\text{max}}$ and $\omega$ for varying values of mode mixity parameter $\psi$.

In a homogeneous isotropic material, for pure Mode I loading, no mode mixity is present ($\psi = 0^\circ$); however, in this analysis the entire range of loading modes is considered due to a mode mixity introduced by the mismatch in materials properties, and possibility of those due to imperfections in specimen geometry combined with microscale defects on the surface introduced
by polishing. As demonstrated in Figure 8-18b, to satisfy the crack kink criterion, in the worst case scenario, \( \Gamma_i/\Gamma_s \) would have to be greater than 0.88. By comparing the measured interfacial fracture energy of NS-C group (18.87 \( J/m^2 \)) to those of cement paste found in the literature (Table 8-5) it becomes apparent that the kink criterion would have been satisfied \( (\Gamma_i > \Gamma_s) \) which is different than the experimental observation; however, it should be noted that for a crack to kink out of interface into the substrate, it would first have to overcome the fracture energy of the interphase. As shown by Raman spectroscopy and nanoindentation, interphase region represents a composite of cement paste and epoxy, with epoxy occupying the porosity. Given that the main fracture-inducing flaws in cement paste are pores, which volume fraction is reduced by permeated epoxy, and also considering the fracture energy of epoxy that is an order of magnitude higher than that of cement paste (Table 8-5), it can be inferred that interphase, indeed, is likely to be characterized with a higher fracture energy than neat cement paste. Roughly speaking, as S-C group specimens failed within a thin region of substrate it can be assumed that the measured fracture energies correspond to that of interphase. Taking fracture energy corresponding to S-C group into consideration, when analyzing the kink criterion in reference to NS-C group, it can be easily shown that \( \Gamma_i/\Gamma_s = 18.87/31.66 = 0.60 \), which means that kink criterion as defined by eq. (8-5) is not satisfied in case of epoxy-interphase interface (Figure 8-18) for a full range of mode mixities.

Considering the same criterion in S-C- group, it can be inferred that the minimum interfacial energy release rate \( \Gamma_i = 0.88 \times 31.66 J/m^2 = 27.86 J/m^2 \) is associated with the epoxy-cement paste interface, which is still significantly higher than interfacial energy release rate associated with the NS-C group (18.87 \( J/m^2 \)). This proves, again, the significant
improvement in interfacial bonding between epoxy and cement paste following functionalization of cement paste surface with GPTMS.

Table 8-5. Cement paste fracture toughness values from literature.

<table>
<thead>
<tr>
<th>Material</th>
<th>Reference</th>
<th>Fracture Toughness ($K_c$)</th>
<th>Fracture energy ($\Gamma_c$)</th>
<th>Test method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cement paste</td>
<td>Akono et al. (2011)</td>
<td>$0.66 \text{MPa}\sqrt{\text{m}}$</td>
<td>$14.1 \text{J/m}^2$*</td>
<td>Micro-scratch test</td>
</tr>
<tr>
<td>Cement paste</td>
<td>Higgins and Bailey (1976)</td>
<td>$0.65 \text{MPa}\sqrt{\text{m}}$</td>
<td>$13.7 \text{J/m}^2$*</td>
<td>Notched three-point bending test</td>
</tr>
<tr>
<td>Cement paste</td>
<td>Cotterell and Mai (1987)</td>
<td>$0.62 \text{MPa}\sqrt{\text{m}}$</td>
<td>$12.5 \text{J/m}^2$*</td>
<td>Notched three-point bending test</td>
</tr>
<tr>
<td>DGEBA+Jeffamine D-230a</td>
<td>Ma et al. (2008)</td>
<td>$0.73 \text{MPa}\sqrt{\text{m}}$</td>
<td>$180 \text{J/m}^2$</td>
<td>Compact tension (CT)</td>
</tr>
<tr>
<td>DGEBA+Peperidineb</td>
<td>Dittanet and Pearson (2012)</td>
<td>$1.11 \text{MPa}\sqrt{\text{m}}$</td>
<td>$300 \text{J/m}^2$</td>
<td>Single-edge notch bend (SENB)</td>
</tr>
</tbody>
</table>

*calculated based on elastic modulus from nanoindentation experiments

a Huntsman®

b Sigma-Aldrich®

Chapter Summary

Mechanical testing was conducted to assess the interfacial fracture energy associated with chemical bonding between epoxy and cement paste in dry conditions, and following conditioning by immersion in 30 °C water for 4 weeks. Additionally, influence of substrate functionalization with an epoxy-functional silane (GPTMS) on fracture energy associated with chemical bond, and interface durability was examined. Interfacial fracture energies were measured with a novel adhesive bond test method that utilizes a beam specimen with sharp notch in three-point bending to introduce crack growth along at the interface. Effects of mechanical bond due to tortuosity of the substrate were minimized by vigorous polishing of the bonding surfaces.

Test results indicated that chemical bond in non-treated group was severely affected by conditioning in water—all conditioned samples failed without any significant external stimulus. This was explained by a combined influence of: (1) hydrogen bond displacement with water...
molecules; (2) development of swelling stress in epoxy adjacent to the interface; (3) degradation of epoxy matrix and cement paste substrate that is deemed to increase interfacial energy release rates (as shown by FEA). Silane-treated group, on the other hand, exhibited a significant improvement in interfacial fracture energy in both control and conditioned group. Conditioned samples, however, exhibited a degradation of interfacial fracture energy of approximately 91% from control, most likely due to similar effects that occurred in conditioned non-treated group. Additionally, is it possible that observed degradation in silane-treated group was also due to low cohesive strength of silane layer combined with instability of bond between silane and substrate and/or silane and epoxy in aqueous environment.

Fractographic analyses revealed that all specimens, besides silane-treated control group, failed along the interface which confirms that the measured fracture energies were governed by chemical bonding. Silane-treated control group had experienced crack growth within a thin layer of substrate—measured fracture energy corresponds to the interphase and represents a lower bound on fracture energy of the interface. Finally, failure modes were evaluated with respect to the analytical kink criterion (He and Hutchinson 1989) which showed that interphase may have higher fracture energy than neat cement paste substrate.
CHAPTER 9
SUMMARY AND CONCLUSIONS

Externally bonded fiber reinforced polymer (FRP) composites can be used to strengthen and repair the decayed infrastructure; however, the adhesive bond between FRP and concrete, formed by means of epoxy adhesives, was found to be susceptible to environmental degradation, particularly in highly moist environments. The majority of research on the topic had concentrated on bond behavior and degradation phenomena at the macroscale, hence these studies fail to explain the exact mechanisms behind bond formation and degradation. The intent of this research was to clarify the phenomena occurring at smaller length scales that would have an effect on the macroscale behavior of the bonded joints. Such treatment of the topic is deemed to form the basis for systematic bottom-up adhesive interface design in concrete structures.

Multiscale characteristics of the adhesive bond between epoxy and cement paste were recognized; subsequent experimental and analytical procedures were focused primarily on two phenomena at the nano-microscale: (1) formation of distinct chemo-mechanical transition region between epoxy and cement paste termed *interphase*, and (2) chemical bonding between the adherents along the *interface* (the surface of separation between the adhesive and substrate). The research agenda employed Raman spectroscopy, nanoindentation, continuum micromechanics, finite element analysis and mechanical testing to examine the epoxy-cement paste interface region. Based on the presented evidence and discussions, a set of conclusions were drawn:

1. Cement paste interphase was confirmed to exist by Raman spectroscopy and nanoindentation. The main contributing factor to its thickness is the porosity of the underlying cement paste substrate. Contributing mechanism to cement paste interphase formation, based on the Raman spectroscopy characterization, was shown to be permeation through the network of capillary and gel pores of the cement paste.

2. Raman spectroscopy analysis of relative degree of conversion in interphase region revealed the existence of epoxy interphase. More reacted epoxide groups were registered near the interface; this was due to a higher concentration of epoxy hardener near interface (owing to
its preferential adsorption by cement hydrates) which allowed for additional cross-linking opportunities.

3. Nanoindentation experiments revealed softening of cement paste hydrates’ phases in cement paste interphase adjacent to the interface.

4. Statistical analysis of nanoindentation data showed a changing ratio of LD and HD Phase within interphase, which was explained by the stiffening effect of epoxy matrix on LD C-S-H porous structure. Continuum micromechanics approach based on Mori-Tanaka method showed that the existence of LD C-S-H/epoxy composite would be responsible for the observed evolution of volume fractions of material phases with distance from interface; the analytical procedure also indicated a possible significant effect of epoxy-filled pores on effective mechanical properties of the interphase.

5. Based on the parametric finite element analysis of crack located at the interface between cement paste and epoxy, it was shown that increasing the elastic modulus of adhesive and/or interphase can decrease interfacial energy release rates. The same was true when reducing the thickness of the adhesive layer. On the other hand, flexible adhesive and/or interphase, and thick adhesive layer result in increased available energy for crack growth. Effects of interphase on the interfacial energy release rate dissipate with increasing crack size relative to interphase thickness. The presented findings from FEA are valid only under the assumption that fracture energy of the interface remains constant between different cases of the parametric study.

6. Mechanical testing showed that water conditioning has a deleterious effect on fracture energy of chemical bonding between epoxy and cement paste, which is thought to be mainly due to the displacement of hydrogen bonds between the adherents with water molecules.

7. Silane functionalization of cement paste substrate increased interfacial fracture energies in both dry and conditioned specimens when compared to the non-treated group. Effectiveness of silane surface treatment in increasing the chemical bond capacity of the interface was, therefore, confirmed.

8. Adhesive swelling stress and plasticization, combined with degradation of cement paste substrate, were found to contribute to degradation of apparent fracture energy of the adhesive interface following conditioning in water. Presence of stress along the epoxy-cement paste interface, following conditioning, was confirmed by a well-developed photoelastic fringe pattern.

9. Analysis of observed failure modes in mechanical testing with respect to analytical crack kink criterion indicated that interphase is tougher than neat cement paste.
CHAPTER 10
FUTURE WORK

This study identified parameters that affect the fracture properties and durability of cement paste-epoxy interfaces at nano-microscale: elastic moduli of adhesive and interphase, thickness of epoxy adhesive, and nature of chemical bonding between the adherents. It is recommended that future work concentrates on bridging nano-microscale and macroscale behavior by conducting the proof-of-concept experiments and confirming the effect of discussed parameters on the behavior of realistic FRP-concrete bonded interfaces. Based on the obtained experimental data, a parametric optimization study is recommended to identify the most appropriate set of parameters at nano-microscale affecting bond behavior at macroscale. Future work should also consider the effects of surface roughness on the macroscale bond behavior and its implementation in the bottom-up design of adhesive interfaces encountered in concrete structures.
LIST OF REFERENCES


BIOGRAPHICAL SKETCH

Jovan Tatar was born in Sarajevo, Bosnia and Herzegovina in 1988, and was raised in Kotor, Montenegro. He obtained his BS in civil engineering in 2011 from the University of Montenegro. During his undergraduate studies author attended the University of Wyoming and Vienna University of Technology where he gained exposure to academic research and developed interest in application of composite materials in construction. These experiences motivated him to seek graduate education at the University of Florida where his research focused on a broad range of topics related to the durability of fiber reinforced polymer (FRP) composite repairs in civil infrastructure. He obtained MS degree in 2013, and enrolled in the Ph.D. program immediately thereafter. Following graduation, the author will be joining the Department of Civil Engineering at the University of Louisiana at Lafayette as an assistant professor.