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Durability of FRP-concrete bond and its constituent properties under the influence of moisture conditions

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Abstract:

Strengthening by Fiber Reinforced Polymers (FRPs) is one of the most common solutions to the ageing infrastructures. However, long term durability of such systems under different environment conditions need to be understood properly before widely adopting these methods in the field. This paper presents research outcomes from an experimental program carried out to determine the influence of moisture on the durability of the bond between FRP and concrete along with its constituent materials. Performance was evaluated through single lap shear bond test and various kind of test on the resin samples including water absorption, mechanical characterization and glass transition temperature ($T_g$) analysis. The specimens were exposed to continuous water immersion and wet-dry cycles for a maximum period up to 24 and 18 months respectively.

The results show some deterioration on the material and the bond properties in both exposure conditions. The bond strength decreased up to 32 and 12% for high and normal strength concrete substrate respectively after continuous immersion indicating key role of substrate in the durability of bond. As a result of exposure, failure propagated towards the primer-concrete interface region. The failure mode changed from concrete cohesion to primer-concrete mixed failure for normal strength concrete and from mixed failure to complete adhesion failure in case of high strength concrete. These shifts in failure patterns are mainly due to destruction of adhesion bond caused by water molecules at the interface. However, it is found that the loss of adhesion bond is somehow compensated by the good mechanical interlocking obtained by proper surface roughness condition of the substrate. Finally, the effects of water were also investigated in interfacial bond stress-slip laws and fracture energies.
Keywords: fiber reinforced polymer (FRP); concrete; bond; moisture; interface; continuous immersion; wet-dry cycles
INTRODUCTION

Externally bonded carbon fiber reinforced polymer (FRP) composites are extensively being used in rehabilitation and strengthening of civil infrastructures such as bridge decks, girders, buildings, marine structures etc. The main advantages of this composite include high strength and stiffness, light weight, ease of installation, higher durability against corrosion etc.

Although FRP composites are considered as highly durable, some of the recent studies have reported harmful effects when subjected to long-term environmental exposures such as moisture (Au 2005; Au and Büyüköztürk 2006), temperature (Leone et al. 2009), chemical solutions (Choi et al. 2012), freeze-thaw cycles (Subramaniam et al. 2008), UV (Dolan et al. 2010) etc. In marine environment, moisture is considered as one of the most serious environmental factors which can deteriorate the integrity of bond between FRP and substrate concrete along with its constituent materials. Consequently, durability of composite system is governed by two major factors which are behavior of individual material and bond between these different materials in the system.

In a wet layup system, primary components of FRP-concrete composite are resins, fiber sheet and concrete substrate. The carbon fiber sheets is considered as highly durable material with a very good resistance against harsh environments. Several authors have already reported insignificant effect of moisture and other corrosive solutions on carbon fiber composites (Saadatmanesh et al. 2010; Sciolti et al. 2010). This shifts our attention to the substrate concrete and the resins. In case of concrete, it is generally observed that the mechanical properties degrade with degree of saturation (Bazant and Prat 1988). Reduction in compressive strength was found to be as 30% to 40% (Konvalinka 2002) when cured for 720 days. Therefore, understanding on the mechanical behavior of concrete under moisture conditioning is very important. Another most crucial component of the composite system is
the resin. Thermosetting epoxy resin is the most frequently used adhesive under normal application. Generally, there are 3 different distinct layers of resin in a composite namely primer, saturant/impregnating matrix and putty. These layers are chosen for the composite system based on requirement of the FRP system and manufacturer recommendation. The reported harmful effects of water on the properties of these epoxy resins are plasticization, hydrolysis, cracking and crazing that can directly affect the mechanical properties (Mays and Hutchinson 1992). These effects are often found to be linked with the absorption of water by the resins. Plasticization and hydrolysis of the resins are often caused due to decrease in $T_g$ of the resin whereas cracking and crazing are linked to the swelling of epoxy resins caused by moisture absorption. Wright (1981) found out that above 1% moisture content, there exists a linear relationship between amount of water absorbed and overall volume or thickness change. Table 1 summarizes the results of some previous literatures showing significant effect of water and other exposure conditions on the mechanical and thermal properties of different epoxy resins. It is clear that there are some harmful effects of water on the resin properties. However, the degree of damage caused by such exposures show a big variation among the researchers. Such differences are largely induced by the use of different materials (mainly the epoxy resins) and testing techniques. But in overall, durability of the composite system is not only governed by these resins but also the interaction between different layers.

One of the most important layers in a composite system is the resin-concrete interface, as most of the previous studies have observed failures occur around this region. There are many factors which may affect this interface such as nature of the substrate material, the method of surface preparation, primer and its interaction with substrate, viscosity of the resin, type of FRP system, bond at the interface etc. These all factors make the interface region very complex and difficult to understand the mechanism and durability of the system. Table 2 gives summary of some of the studies conducted on the durability of FRP-concrete bond at
different exposure conditions and durations. As it can be seen that most of the studies have shown large reduction in bond properties and change in failure mode after such exposures. Apart from these, the moisture diffusion information is equally important in FRP strengthened concrete systems. Some of the researchers have tried to find moisture content at the interface and its correlation with the deterioration due to moisture (Au and Büyüköztürk 2006; Ouyang and Wan 2008). Ouyang et al. (2008) have derived the moisture diffusion governing equation for the multilayered systems using the relative humidity which was later used to determine the bond Interface Region Relative Humidity (IRRH) in different relative humidity environment for different durations. This IRRH was correlated with bond fracture energy to propose a bond deterioration model in moist environment (Ouyang and Wan 2009).

Even though there are already many existing studies on this topic, the clear distinct mechanism of moisture effect on the material and the bond behavior is still not clear yet. Great variation in the results and scarce explanations to such behavior prove that more extensive experiments are necessary to investigate several different type of material, exposure conditions, testing approaches etc. Therefore, the present experimental approach aims at giving useful insight in long-term effect of moisture on the shear bond performance of FRP-concrete composite under continuous and wet-dry cycles. As the durability of the bond is highly dependent on the materials, mechanical and thermal test on the resins were also carried out under such exposure conditions so as to determine its effects. This paper also shade light on the effect of primer and substrate concrete strength on the bond failure mechanism at the interface region by observing the failure patterns and degradation at the interface due to moisture.

EXPERIMENTAL PROGRAM
The experimental study is divided into two different parts namely material test and bond test. In the first part, effects of moisture on the mechanical properties of the constituent materials such as primer, saturant and concrete were investigated and in the second part, the FRP-concrete composite bond behavior was examined. Details of the specimen preparation, material description, exposure conditions and experimental instrumentation are presented in this section.

**Materials description**

**Epoxy resin**

Two separate epoxy primers and an epoxy saturant were used in this study which are collectively referred as epoxy resin. All three resins are room temperature curing epoxy adhesives which are referred in the study as Epoxy-E, Epoxy-F and Epoxy-R. Epoxy-E is a two component epoxy primer with base and hardener part mixed in the ratio of 4:1 by weight. The base part is formulation of Bisphenol-A and Bisphenol-F type epoxy resin whereas hardener is combination of polythiol and polyamines. This is a high modulus concrete bonding primer mainly used for anchorage of steel rod in concrete, old-new concrete bonding etc. Epoxy-F and Epoxy-R are also two component resins with base and hardener part mixed in the ratio of 2:1 by weight. The base part is formulation of Bisphenol-A type epoxy resin whereas hardener part consists of blends of polyamines. Epoxy-F is an epoxy primer whereas Epoxy-R is the saturant for carbon fiber sheet supplied by the manufacturer. Higher viscosity and presence of silica components makes it slightly different from Epoxy-F.

**Continuous fiber sheet**
Unidirectional continuous fiber sheet made of carbon fiber is used having design thickness of 0.111 mm and Fiber Areal Weight (FAW) of 200 g/m². The tensile strength and modulus are 3400 N/mm² and 2.45×10⁵ N/mm² respectively.

**Concrete**

Two different range of concrete strength were casted. They are referred as normal and high strength concrete having mean cylindrical compressive strength as 39.4 MPa and 88.6 MPa respectively. ASTM C39 (2004) was followed to obtain compressive strength of cylindrical concrete specimens but the strength was calculated from the mean strength of one specimen tested at different ages (0, 1, 2, 3, 4, 6 months for normal strength and 0, 3, 6 months for high strength). 0 month refers to 28 days after casting and remaining durations were in reference to this time. These concrete cylinders were subjected to environmental exposures only after 2 months together with other specimens.

**Specimen preparation**

**Resin specimens**

Mechanical properties of the epoxy saturant and primers are determined by uniaxial tensile and shear test. The tensile specimens were prepared in accordance with JIS K 7113 (1999) by mixing base and hardener in the specified ratio to form dog-bone shaped specimens. Dimensions of the specimen are shown in Fig. 1. The shear specimens were prepared following JIS K 6850 (1995) by bonding two steel plates with a small quantity of epoxy resins in between as shown in Fig. 2.
In order to investigate bond behavior, single lap shear bond specimens were prepared. The concrete prisms along with cylinders were casted and cured for 28 days under moist condition in the laboratory. The bonding surface of the concrete prism was grinded by disk sander to remove the thin mortar layer and properly cleaned using compressed air to remove the dust particles from the surface. The amount of surface preparation was visually judged and attempt was made to make uniform surface roughness throughout the specimens. A thin uniform layer of primer was applied on the surface and allowed to cure for 24 hours before attaching carbon fiber sheet with necessary saturant as recommended by the manufacturer. Both the resin and bond specimens were cured for more than a month before subjecting to any kind of exposures. In a study conducted by Yang et al. (2008), 90% of the resin was found to be cured in a day and more than 95% in a period of a week. Therefore, it is assumed that a month long curing would be sufficient and the post-curing effect will not be substantial.

The details of the specimen are shown in Fig. 3. The specimen with Epoxy-E and Epoxy-F primers together with Epoxy-R saturant are referred as Type-E and Type-F specimens respectively. The bond length of 200mm was adopted. This bond length was adopted in reference to the previous research by Dai (2003) in which the author found the effective bond length varying from 50 mm to 100mm for the given stiffness value.

Exposure Conditions

All the specimens were subjected to two different environmental exposures apart from the unexposed specimens. First group of specimens were subjected to continuous immersion into a shallow tank containing tap water maintained at a constant temperature of 20 °C. Fig. 4 shows the arrangement of the tank with heaters, pump and temperature sensors to maintain uniform temperature throughout the pool. After the required ageing period, specimens were taken out from the water and tested immediately under wet conditions. The second set of
specimens were subjected to wet-dry cycles for a period of 3, 6, 12 and 18 months. There is no standard for this kind of test so different duration of wet-dry cycles were adopted by past researchers. Taukta et al. (2011) have considered 4 days of drying period and Dai et al. (2010) have taken 4 days wetting and 3 days drying cycles. Similarly, in this study wet-dry cycle include 7 days of immersion in water maintained at 20 °C and 4 days of drying inside temperature control room at 20 °C. The humidity inside the control room was not continuously monitored but initially it was in a range of 50-55%. The authors have considered the specimens as wet and dry when the change in weights were less than 0.15% in a consecutive day. It took 7 days of wetting and 4 days of drying in order to attain that criteria. The remaining sets of unexposed specimens were put in ambient conditions inside the laboratory. These specimens are considered as the control specimens for the study. At least 3 specimens were tested for controlled cases in contrast to 1 specimen for exposure case. The presented results are the mean values of the identical specimens for the controlled case which is referred here as 0 month. Summary of all the parameters along with the number of specimens tested are presented in Table 3.

Test Procedures and Instrumentation

Tensile and shear test of the resin samples were conducted in universal testing machine (UTM) at the loading rate of 2 mm/min and 1 mm/min respectively. The bond test was also carried out in UTM with the arrangement illustrated in Fig. 5. Three long bolts were inserted through the preset plastic pipes inside the concrete specimens and then fixed at the base of the machine. The specimen was adjusted in position to make sure that the FRP-concrete bond line is aligned with the center line of the upper loading grip. Strain gauges were attached on some of the specimens at an interval of 20 mm on the bonded region to record the strain behavior of the FRP sheet and Linear Variable Displacement Transducer (LVDT) was
positioned at the starting point of the bonding zone to measure the loaded end slip between
the concrete and FRP sheet. The loading speed of the upper grip was set as 0.2 mm/min.

The effect of exposures on the glass transition temperature \(T_g\) of the resin was determined
by differential scanning calorimetry (DSC) method following ASTM E1356 (2004). The
temperature range of measurement was -30 to 150 °C at a heating rate of 20 °C/min. \(T_g\) point
was chosen from the midpoint of the tangent between the extrapolated baseline before and
after transition.

RESULTS AND DISCUSSION

Moisture absorption by epoxy resin specimens

Moisture absorption by the epoxy resin is measured in each tensile specimen through
gravimetric means and expressed as the percentage increase in weight. Fig. 6 shows the
amount of moisture absorption by all three epoxy resins until 24 months duration. The
moisture absorbed at the end of 24 months by Epoxy-E, Epoxy-F and Epoxy-R were 1.98%,
2.63% and 2.50% respectively. Epoxy-F and Epoxy-R showed very resembling absorption
trend which could be due to presence of similar chemical components. From the figure, it can
be observed that the moisture diffusion was much quicker at the initial stages of immersion
which became more gradual after 6 months till 18 months. By the time it reaches 24 months,
the absorption curves became steadier suggesting the point of complete saturation. The
saturation time and the maximum amount of moisture absorption by resins are vastly
dependent on the epoxy resin types, its composition, curing period and immersion condition.

Variation of moisture absorption ranging from 0.86% to 4.06% was observed by Karbhari et
al. (2009) after 2 years of immersion in deionized water at 22.8°C when the authors
investigated 10 different resin types. Sciolti et al. (2010) reported even higher absorption of
water by the epoxy resins ranging from 4.7% to 8.2% after 24 weeks at 23±2 °C. This kind of variation in the moisture absorption characteristic makes it too difficult to generalize the behavior of resin based on its moisture absorption property. Further, the nature of moisture diffusion and absorption in the resin samples are different from the phenomenon involved in FRP-concrete composite system as the resin layers are sandwiched between FRP sheet and concrete. This makes diffusion process different and complex than only in case of resin sample. Consequently, this absorption data is only used as a reference purpose to make a comparison between different resins.

Effect of water on mechanical behavior of the resins

Fig. 7 shows the result of mechanical behavior of the three epoxy resins tested after continuous exposure in water at various exposure durations. All the resins show fairly consistent trend in response to immersion in water. Fig. 7(a) shows the response of tensile strength with the exposure duration. The data seems to be scattered a bit thus making it difficult to explain the clear tendency in response to the exposure duration but initial increase in tensile strength can be observed in all three cases. Lau et al. (2009) also found out such increase in tensile strength with the increase in moisture absorption at 23 °C when a commercial two-component concrete bonding epoxy was examined but the reason for this behavior was unknown. May et al. (2002) have explained this initial increase as the effect of the toughening behavior of the resins due to water. Another possibility for such behavior could be due to post-curing effect of the resin, but considering the curing period of more than a month and the temperature of the water being only 20 °C, the post-curing phenomena may not be the case here. It is also evident that the behavior shown by Epoxy-F and Epoxy-R shows a great resemblance similar to the case of moisture absorption. The results indicate a sudden drop of strength for Epoxy-F and Epoxy-R at the 18 month but the recovery of the
strength at the 24 month period suggests that it could only be the experimental scatter rather than the real deterioration. In overall, apart from small insignificant occasional reduction in the tensile strength, all three epoxy resins did not show any serious response to moisture. Among three resins, Epoxy-E seems to be most insensitive to moisture. As seen from the Fig. 7(b), similar to the tensile strength behavior, tensile modulus also showed variation at different durations. Even though there seems to be a small reduction, the variation indicates that there is no strong relationship of tensile modulus with the exposure duration therefore, all the immersion cases are averaged to see the overall response after immersion. In was found that in average, the modulus was reduced by 11, 11 and 4% respectively for Epoxy-E, Epoxy-F and Epoxy-R after exposure. Fig. 7(c) shows variation of shear strength at various exposure durations. The average reduction in shear strength was around 2, 16 and 14% for Epoxy-E, Epoxy-F and Epoxy-R respectively. As the tensile behavior, Epoxy-E seems to be less affected than the remaining other two resins which could possibly due to lower moisture absorption capacity. It is also interesting to observe that despite minimal effect on the tensile strength of the resins, the stress-strain curves changed to ductile nature with reduced stiffness after exposure thus increasing the strain at the failure. This behavior was observed in all three cases in both exposure conditions which are presented in Fig. 8. This increase in fracture strain at the failure is also reported by Petrie (2006) as one of the effects of water on the epoxy resin which can be recovered fully when dried.

Fig. 9 shows the effect of wet-dry cycles on the mechanical properties of the resin at different exposure durations. The overall nature on the mechanical behavior of the resins under wet-dry cycles are similar to the continuous exposure case. There was no reduction in tensile strength until 18 months period whereas slight reduction in tensile modulus was found as 4, 11 and 6% in average for Epoxy-E, Epoxy-F and Epoxy-R respectively. The shear strength was also decreased by 10 and 9% respectively in average for Epoxy-F and Epoxy-R whereas
no reduction for Epoxy-E. Comparison of results to the continuous immersion case does not reveal much significant difference. Therefore, it can be concluded that the drying process does not restore the original properties of the resins.

The above results indicate that there are some harmful effects of moisture on the mechanical properties of resin but the extent of damage is not as severe as observed by few other researchers such as Sciolti et al. (2010) and Yang et al. (2008) while comparing with the similar exposure conditions. There exist a wide range of other previous studies showing similar effects on the resin properties but with big variation in the results. This is mostly due to different composition of the epoxy resins. Usually, the room temperature cured commercial epoxy resins consist of two components namely base part and hardener part which is the curing agent. The base part is mainly composition of Diglycidyl Ether of Bisphenol-A (DGEBA) which is formed by reaction between Bisphenol A and epichlorohydrin but the hardeners are blends of several different components such as amines, amides, sulphide, thiols etc. This blending of different chemicals and addition of various modifiers such as flexibilizers, tougheners, diluents, fillers, thixotropic agents etc. makes each commercial epoxy with the unique characteristics. These modifications on the resin properties are done to improve gel time, increase curing rates and achieve better resistance against heat, chemicals and water. The properties of the resin could be adjusted based on the user-intended application as a result of which durability related studies conducted by using resins from different manufacturers may yield vastly different conclusions. But unfortunately, information on the chemical composition of the resins are scarcely provided. Therefore more specific studies need to be carried out providing such chemical information as well.

Effect of exposure on the glass transition temperature ($T_g$) of the resins
Fig. 10 shows the transition of epoxy resins over a range of temperature. The $T_g$ is measured at the midpoint of the temperature range bounded by the tangents of the two flat regions of the heat flow curve. At the beginning, before subjecting to any sort of exposures, $T_g$ were measured as 71.2, 72.2 and 74.2 °C respectively for Epoxy-E, Epoxy-F and Epoxy-R. To know the changes in $T_g$ for each exposure condition, $T_g$ were measured as a function of exposure duration for each case. The results presented in Fig. 11 clearly indicate that the $T_g$ change is well under 5% over 24 months of exposure which is fairly insignificant. There are some conflicting literatures on the effect of moisture on the $T_g$ of the resin. Abanilla et al. (2006), Wright (1981), Benzarti et al. (2011) all found significant decrease in $T_g$ of the resins caused due to absorption of moisture by the epoxy resins. Wright (1981) even showed the linear relationship between decrease in $T_g$ and the moisture content of the epoxy resin. The author also proposed roughly decrease of $T_g$ by 20 °C for each 1% water absorption. In contrast to that, Choi and Douglas (2010) reported increase in $T_g$ of epoxy-amine thermoset resins after immersion in water at different temperatures. The reason for such behavior is explained by increase in cross-link density due to additional curing at higher temperature. All the above studies were conducted at the presence of moisture in the sample, but in this study, samples were kept at room temperature for more than a month for drying purpose before measuring the $T_g$ to see the permanent effect of water on the resin. This process may have restored the $T_g$ back to the unexposed case.

**Effect of water on compressive strength of concrete**

As can be seen from the Fig. 12, change in compressive strength of the high strength concrete seems to be insignificant over a period of 12 months whereas small reduction is noticeable in case of normal strength for both continuous immersion and wet-dry cycles. It is believed that the mechanical properties of the concrete decreases with increase in the moisture content.
Several previous researchers have studied the effect of moisture in the mechanical properties of the concrete (Bazant and Prat 1988; Konvalinka 2002; Shoukry et al. 2011) and reported decrease in the compressive strength with the degree of saturation. The reason for decrease is due to intensified pore water pressure resulting into generation of micro cracks during application of external forces. Comparatively, wet-dry case showed better performance due to restoration of strength after drying. In case of high strength concrete, similar phenomenon would occur but due to fewer and smaller voids, intensity of pore water pressure is much lower but material resistance properties are much higher causing insignificant effect on the strength.

Effect of water on bond strength for the normal and high strength concrete

Fig. 13 (a) and (b) show the effect of continuous immersion and wet-dry cycles in the bond strength for Type-E and Type-F specimens with normal strength concrete. The bond strength was calculated from the peak load obtained from the test. In response to the continuous exposure, there is a slight different trend for Type-E and Type-F specimens. For Type-E, bond strength along the exposure duration were slightly lower in a range between 5 to 12 % than the non-immersion in most cases expect for the period between 6 to 12 months. However, the increase is only significantly greater for the case of 12 months, which could be the experimental scatter. For the Type-F case, the bond strengths after exposure were either very similar or lesser than the non-immersion case. The reduction in bond strength can be found up to the range of 1 to 12 %. Clearly, no specific trend of change in bond strength with the immersion duration was found. But the observed reduction in bond strength for some cases may be attributed to weakening of adhesion bond at the interface which is explained along with the help of failure patterns at the later part. The results obtained from wet-dry cycles also show reduction in bond strength ranging from 7 to 12 % for Type-E specimen and
1 to 3% for Type-F specimen expect for the case of 12 months as similar to continuous immersion case. In summary, we can see that there are some reductions in bond strength at both exposure conditions but these reductions are not so significant and do not have any clear relation with the exposure duration.

In contrast to the behavior shown by normal strength concrete specimens, both Type-E and Type-F specimens showed greater loss in bond strength with the increase in immersion duration for the high strength specimens. As seen in Fig. 13 (c), the maximum bond strength reduced up to 32% after a year immersion into water. Similar decreasing trend was confirmed for Type-F specimens with reduction of around 30% after a year of water immersion. It is also interesting to note that even with the increase in the concrete strength, there is no significant increase in the bond strength. Despite use of same resins and specimen preparation procedure, the use of different strength concrete affected the bond durability. This brings into focus at the interaction of bond between concrete and epoxy resin. There are two key mechanisms which govern the bond between FRP composite and the concrete substrate. The first is the mechanical bond which is the function of degree of surface roughness, while the other one is the intermolecular forces or chemical bonds formed as a result of reaction between epoxy components (mainly hydroxyl group) with the substrate concrete. Amount of hydroxyl groups is dependent on the epoxy resins so use of same resin on both the surfaces eliminates the possibility of making such difference thus making the mechanical bond as the primary concern. Mechanical bond works by forming interlocking action formed by penetration of resins into the pores, defects and surface roughness in concrete. Numerous articles have been published on the effect of surface preparation on the bond strength (Al-Tamimi et al. 2011; Toutanji and Ortiz 2001). Even though surface roughness is not the only governing parameter, usually surface having higher roughness yields greater strength. High strength concrete consists of closely packed cement grains and reduced amount of pores
compared to normal strength concrete which makes it denser and compact. The bonding area
and surface roughness also becomes lower in high strength concrete due to same reason.
Further, the surface roughness created by disk grinding method may not be sufficient to
create required roughness for the high strength concrete case which is evident by looking at
failure surface. The failure occurred mostly at the interface between concrete and primer in
contrast to the complete concrete cohesion failure in normal strength case suggesting
inadequate surface roughness. These reasons make the mechanical bond comparatively
ineffective than normal strength concrete case thus hindering the full utilization of high
strength concrete substrate. Above explanation can somehow help to understand the reason
for greater reduction in bond strength after exposure to water. Similarly, to the normal
strength concrete, there is a weakening of adhesion bond at the interface by the water but due
to ineffective mechanical bond in case of high strength concrete, the bond cannot be retained
resulting in premature failure thus lowering the bond strength. Here it should be noted that
better surface roughness in case of high strength concrete may yield different result for which
further investigations are required. But for now above presented theory is well supported by
observed failure patterns which are explained below.

Effect of moisture on the failure modes for normal strength concrete

The observation of failure surfaces gives good idea on the propagation of the crack path.
Even without any environmental exposures, there exist slight differences in failure surfaces
for Type-E and Type-F cases. Epoxy-E primer, being specifically used for concrete to
concrete bonding, showed greater adhesion with the concrete than Epoxy-F case. The
comparison of failed FRP sheets subjected to continuous immersion and wet-dry cycles at
different durations are presented in Fig. 14 (a) and (b). Careful observation indicates
difference in failure pattern after exposure in water for both cases. The failure before the
immersion was mostly at the thin concrete layer which later shifted to primer-concrete interface region after immersion. Such shift in failure modes after interaction with water were also observed by other researchers as well (Benzarti et al. 2011; Dai et al. 2010; Tuakta and Büyükoztürk 2011). This kind of phenomenon is observed in both specimen types (Type-E and Type-F) indicating some harmful effects of water on the bond at primer-concrete interface. Although both resins and composite bond properties showed some signs of deterioration under moisture conditions, their correlations between remains unclear since the bond failure was at the interface region and therefore may need further investigations. But in overall interface bond is clearly affected by moisture and shift in failure modes are evident.

The shift of failure to primer-concrete adhesion from concrete cohesion could have two different possibilities. The first could be due to increase in shear strength of the substrate concrete as a result of post-curing of the concrete thus making the adhesion layer more vulnerable to failure. But if we consider the results obtained from the concrete cylinder test as reference, then it clearly indicates that the strength is not further increased despite continuous immersion in water for several months which denies the above hypothesis. This leads to conclusion that the adhesion bond becomes weaker due to interaction of water molecules with the epoxy-concrete bond. To understand more precisely, the bond mechanism at the interface needs to be clarified.

In FRP-concrete bond system, among different layers and interfaces, the weakest interface is often recognized as the resin-concrete interface by many past researchers. In case of wet layup bonding, primer is usually applied on the concrete surface to enhance the bond. This low-viscosity primer penetrates through voids and defects present on the concrete surface and strengthens thin layer of concrete at the top. This layer is referred as the transition zone in this paper which is a sandwiched layer between primer and concrete layer. This layer of concrete
at this transition zone behaves differently than the adjacent concrete which is confirmed by observation of interface by optical microscopy under ultraviolet light illumination as shown in Fig. 15 (Djouani et al. 2011).

At the interface, usually the shear strength of the structural adhesives are very high compared to that of normal strength concrete (Tu and Kruger 1996) and transition zone is already stronger than the adjacent concrete layer due to enhancement of strength by penetration of resin. When adequate surface preparation on the substrate concrete is provided, the adhesion bond at the primer and transition zone interface always remain intact making the concrete adjacent to the transition zone as the weakest layer. Thus as a result, failure occurs at the concrete side when there is no influence of environmental exposures.

When this bonding system is introduced to wet environments, the moisture diffuses through various different ways such as through concrete pores, adhesives, cracks or defects etc. and reaches the interface region. This moisture at the interface could interact with specific hydrophylic functional groups, such as hydroxyl or amine in epoxy resin and disrupt the hydrogen bond (Bellenger et al. 1989). The evidence of such breakage of hydrogen bond due to interaction with water were observed by some researchers (Lefebvre et al. 1991; Zhou and Lucas 1999). Due to high porosity of concrete the moisture easily gains access to the transition zone and the primer-transition zone interface where it combines with some of the epoxy components (hydroxyl groups) thus partially destroying the adhesion bond. Due to destruction of adhesion bond, adhesion strength at the primer-transition zone interface becomes lower than the cohesion strength of concrete and failure tends to propagate along the interface of primer and transition zone but due to presence of mechanical interlocking action induced by surface roughness, the crack propagates towards the transition zone at some locations thus causing mixed mode of failure. The visualization of bond failure mechanism
before and after the exposure is schematically demonstrated in Fig. 16 (a) for the normal
strength concrete. Similar phenomenon can explain the case of wet-dry exposure in which
water molecules destroy the adhesion bond at the primer-transition zone interface which
cannot be restored by the drying process (Tuakta and Büyükoztürk 2011).

Effect of moisture on the failure mode for high strength concrete

The failure observed in high strength concrete is little different from that of normal strength
case which is mainly due to surface condition of substrate and bonding mechanism. As
explained earlier, the dense nature of high strength concrete results in lesser voids due to
which primer does not penetrate deeply inside the concrete thus forming only a thin and week
transition layer as demonstrated in Fig. 16 (b). This reason makes interface between primer
and transition zone the weakest, causing propagation of cracks along the interface region.
However due to effect of thin transition zone, the crack occasionally propagates along the
transition zone creating mixed mode of failure in case of unexposed specimens. After
subjecting the specimens to water, the water molecules destroy the adhesion bond at the
primer-transition zone interface similarly as in case of normal strength case but unlike in
normal strength concrete case, mechanical bond is weaker due to much smoother surface thus
resulting into complete adhesion failure at the interface as shown in Fig. 14 (c).

Effects of moisture on bond stress-slip behavior and fracture energy

Bond stress-slip relation is the most important interface law which determines the overall
performance of the bonded members (Ueda and Dai 2004). The experimental local bond
stress-slip curves were obtained by integrating the strains measured on the surface of the FRP
composites with the interval of 20 mm along the bonded region (Dai 2003). Fig. 17 show
experimentally observed local bond stress-slip curves for normal and high strength concrete
specimens at different stages of exposures. The curves are plotted for the location of 30mm
from the starting point of the bonded end. Like the bond strength behavior, these local bond stress-slip curves do not show clear distinct trend between non-immersion and immersion cases for normal strength concrete for both exposure cases. In contrast to that greater reduction in bond strength for high strength cases are well reflected in the local bond stress-slip behavior. Clearly significant reductions in peak bond stresses and the overall change in the nature of the curve can be observed after 12 months of immersion period.

The area under bond stress-slip curve gives the interfacial fracture energy which is the total amount of energy consumed during the propagation of cracks. This fracture energy usually governs the ultimate bond strength if the sufficient bond length is provided. Therefore, the average fracture energy is calculated from average area of the experimental local bond stress-slip curves at different locations before and after exposure. High strength cases showed significant reductions in average fracture energy than for the normal strength specimens. For the high strength case, the average fracture energy was reduced from 0.98 and 1.25 N/mm to 0.42 and 0.40 N/mm for Type-E and Type-F specimens after 12 months of exposure. These results indicate some degradation of bond properties at the interface mainly caused due to water as explained earlier. Further, significant loss of bond strength in high strength case after the exposure is well supported by observed reduction in fracture energy.

The relationship between average fracture energy and exposure duration for normal strength concrete specimens are shown in Fig. 18. In contrast to the behavior for the high strength concrete, there is no distinct significant loss in average fracture energy at both exposure conditions along the entire period. Initially, the average fracture energy were 0.56 and 0.84 N/mm for Type-E and Type-F specimens respectively which changed insignificantly to 0.52 and 0.82 N/mm after 24 months of continuous exposure. Even after 18 months wet-dry cycles, the values were 0.59 and 0.81 N/mm for Type-E and Type-F respectively.
CONCLUSIONS

Durability of FRP-concrete bond and its constituent properties under moisture conditions are investigated for duration up to 24 months and following conclusions are drawn out:

1. Small reductions in mechanical properties of resins (modulus and shear strength) were observed for both continuous immersion and wet-dry cycle case. However, original properties cannot be fully restored even after drying process signifying permanent damages due to such exposures. The effect of water caused more ductile behavior of resins with increase in elongation at the failure.

2. The use of relative high modulus primer (Epoxy-E) was proved to be good for this FRP composite system. Such epoxy primers can be used as long as it is suitable for concrete applications. However, durability needs to be confirmed before use.

3. Significant reduction on bond strengths was observed for high strength concrete specimens than the normal strength case after exposed to continuous water immersion. The durability of the bond strength was found highly dependent on the substrate concrete and its surface roughness. Higher reduction in bond strength in high strength concrete was attributed to weaker mechanical interlocking action due to relatively smoother surface. Therefore, in case of high strength concrete, it is recommended to use alternative method of surface preparation such as sandblast or water-jet to ensure better bonding surface. However, durability of bond under different methods of surface preparation needs to be further investigated.

4. The failure modes were changed after exposure in water for both normal and high strength case. For the normal strength concrete, it shifted from a complete concrete cohesion failure to a primer-concrete mixed type failure. Whereas in case of high
strength concrete, failure shifted from primer-concrete mixed failure to complete
adhesion failure due to relatively weaker mechanical interlocking action.

5. The effect of water was observed in the local bond stress-slip behavior. The interfacial
fracture energy is calculated before and after exposure to water. Comparison of result
show greater reduction in fracture energy and peak bond stress in the case of high
strength concrete subjected to 12 months of exposure than the normal strength. This
reduction in fracture energy corresponds well with the decrease in the bond strength.

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study was conducted with the financial aid provided by the Grant-in-Aid for Scientific
Research (A) No.22246058.

References

"Investigation of the Effect of Surface Preparation Method and the Degree of Surface Roughness on
CFRP-Concrete Bonding and Substrate Strength." The Built & Human Environment Review, 4(1).
Specimens."
Differential Scanning Calorimetry."
approach." Doctoral dissertation, Massachusetts Institute of Technology.


<table>
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<tr>
<th>Authors</th>
<th>Resin information</th>
<th>Exposure condition/duration</th>
<th>Property Changes</th>
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</thead>
<tbody>
<tr>
<td>Sciolti et al. (2010)</td>
<td>Two-component commercial epoxy primer</td>
<td>23 °C in water/ 27 wks</td>
<td>Reduction by 20 °C</td>
</tr>
<tr>
<td></td>
<td>Two-component commercial adhesive</td>
<td>23 °C in water/ 29 wks</td>
<td>Reduction by 3 °C</td>
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<tr>
<td></td>
<td>Two-component commercial putty</td>
<td>23 °C in water/ 31 wks</td>
<td>Reduction by 18 °C</td>
</tr>
<tr>
<td>Frigione et al. (2006)</td>
<td>Bisphenolic epoxy resin (MW&lt;700)</td>
<td>23±1 °C in water/ 19 wks</td>
<td>Reduction by 3 °C</td>
</tr>
<tr>
<td></td>
<td>Bisphenolic epoxy resin 66% inorganic filler</td>
<td>23±1 °C in water/ 38 wks</td>
<td>Increase by 3 °C</td>
</tr>
<tr>
<td></td>
<td>Bisphenolic epoxy resin 49% of inorganic filler</td>
<td>23±1 °C in water/ 38 wks</td>
<td>Increase by 2 °C</td>
</tr>
<tr>
<td>Benzarti et al. (2011)</td>
<td>Bisphenolic epoxy resin and Polyamide hardener</td>
<td>40°C and 95% RH/ 265d</td>
<td>Reduction by 6-30 °C</td>
</tr>
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<td>Bisphenolic epoxy resin and amine hardener</td>
<td>40°C and 95% RH/ 206 d</td>
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</tr>
<tr>
<td>Yang et al. (2008)</td>
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<td>23°C in deionized water/ 24 m</td>
<td>Reduction by 5%</td>
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<td>37.8°C in deionized water/ 24 m</td>
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<td></td>
<td>60°C in deionized water/ 24 m</td>
<td>Insignificant</td>
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<td>23°C in salt solution/ 24 m</td>
<td>Reduction by 4%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>23°C in alkali solution/ 24 m</td>
<td>Reduction by 5%</td>
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<tr>
<td>Au (2005)</td>
<td>Bisphenolic epoxy resin and amine hardener</td>
<td>23°C in deionized water/ 4 wks</td>
<td>Reduction by 6 °C</td>
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<td></td>
<td></td>
<td>50°C in deionized water/ 4 wks</td>
<td>Reduction by 3 °C</td>
</tr>
<tr>
<td></td>
<td>Two-component epoxy resin and amine hardener</td>
<td>23°C in deionized water/ 8 wks</td>
<td>Reduction by 7 °C</td>
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<td></td>
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<td>50°C in deionized water/ 8 wks</td>
<td>Reduction by 3 °C</td>
</tr>
</tbody>
</table>
Fig. 1 Dumbbell shaped specimen for tensile test
Fig. 2 Adhesively bonded metal specimen for shear test
Fig. 3 Schematic of the bond specimen for single lap shear test
Fig. 4 Exposure tank
Fig. 5 Arrangement for the bond test
Fig. 6 Moisture absorption by epoxy resin specimens
Fig. 7 Mechanical properties of the resin after continuous exposure: (a) Tensile strength; (b) Tensile modulus; and (c) Shear strength
Fig. 8 Stress-strain curves for resins at different exposures: (a) Epoxy-E (Continuous immersion); (b) Epoxy-F (Continuous immersion); (c) Epoxy-R (Continuous immersion); (d) Epoxy-E (Wet-dry cycles); (e) Epoxy-F (Wet-dry cycles); and (f) Epoxy-R (Wet-dry cycles)
Fig. 9 Mechanical properties of the resin after wet-dry cycles: (a) Tensile strength; (b) Tensile modulus; and (c) Shear strength
Fig. 10 Heat flow curves of epoxy resins before exposure
Fig. 11 Effect of continuous exposure on $T_g$ of the resins after drying for a day
Fig. 12 Effects of exposure on concrete compression strength
Fig. 13 Effect of different exposures on bond strength: (a) continuous immersion and normal strength; (b) wet-dry cycles and normal strength; and (c) continuous immersion and high strength
Fig. 14 Comparison of failure surfaces at various exposure conditions (a) continuous immersion for normal strength; (b) wet-dry cycles for normal strength; and (c) continuous immersion for high strength
Fig. 15 Hardened cement paste-epoxy interface image obtained by optical microscopy under UV illumination (Djouani et al. 2011)
Fig. 16 Visualization of bond failure mechanism before and after exposure in (a) Normal strength concrete; and (b) High strength concrete
Fig. 17 Effect of moisture on local bond stress-slip curves at the same location for (a) normal strength concrete and continuous immersion (Type-E); (b) normal strength concrete and continuous immersion (Type-F); (c) normal strength concrete and wet-dry cycles; and (d) high strength concrete and continuous immersion
Fig. 18 Effect of moisture on average fracture energy for normal strength concrete
Table 2  Summary of the existing results for FRP-concrete bond after environmental exposures

<table>
<thead>
<tr>
<th>Authors</th>
<th>FRP system</th>
<th>Exposure conditions/duration</th>
<th>Test</th>
<th>Bond strength</th>
<th>Failure mode</th>
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<tr>
<td>Au (2005)</td>
<td>CFRP plate</td>
<td>23 and 50 °C in deionized water/ 2-8 wks</td>
<td>Peel test</td>
<td>60% decrease in peel fracture toughness</td>
<td>Epoxy/Concrete Interface separation</td>
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<td>Shear test</td>
<td>10, 50% decrease in shear fracture toughness</td>
<td>Epoxy/Concrete Interface separation</td>
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<td>Dai et al. (2010)</td>
<td>CFRP strand sheet with</td>
<td>4 days wet at 60°C seawater and 3 days dry/ 8-24 m</td>
<td>4 point bending</td>
<td>Epoxide-I: No change; Epoxide-II 25% increase in flexural strength; Epoxide-III 20% decrease in flexural strength</td>
<td>Primer/concrete interface separation</td>
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<td>3 different epoxies</td>
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<td>Choi et al. (2012)</td>
<td>CFRP sheet with 3</td>
<td>30, 40, 50, 60 °C Immersion/6-18 m</td>
<td>3 point bending</td>
<td>10-60% decrease in flexural strength for 3 epoxy system; 15% increase in flexural strength for 1 epoxy system</td>
<td>Adhesive failure</td>
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<td>different epoxies</td>
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<td>30, 40, 50, 60% decrease in flexural strength</td>
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<td>CFRP plate</td>
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<td>CFRP sheet and plate</td>
<td>40°C, 95% RH/9-353 d</td>
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<td>CFRP sheet and plate</td>
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<td>Pull-off test</td>
<td>Decrease in pull-off strength up to 60% for plate system; increase in strength up to 25% for sheet system</td>
<td>Concrete cohesive/mixed failure</td>
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<td>Toutanji et al. (1997)</td>
<td>CFRP sheet with 3</td>
<td>300 WD cycles (4 hrs wet and 2 hrs dry)</td>
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<td>Decrease in flexural strength 5-30%</td>
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Table 3 Summary of parameters along with number of specimens tested for the study

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<tr>
<th>Exposure duration (months)</th>
<th>Resin (Epoxy-E/F/R)</th>
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