



DEVELOPMENT OF BONDING AGENT USED IN FRP STRENGTHENING SYSTEM

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Abstract: Fiber Reinforced Polymer (FRP) composite is an attractive material for strengthening various civil infrastructures. The strengthening system that based on FRP composites consists of many elements. These are: strengthening material (FRP), strengthened element (concrete, steel, wood, etc) and bonding agent. The latter is the most important elements which affect the performance of the whole strengthening system. Different types of bonding agent are used based on service conditions. Epoxy-based adhesive (EBA) is the most commonly used to strengthen concrete or steel structures. Due to the limitations of the application of EBA, cement-based adhesive (CBA) is utilized as an alternative bonding agent. The CBA have been developed by modifying its properties. The modification was conducted using different powder-state materials or by magnetic water treatment. The development of bonding agent that used in FRP strengthening system is addressed in this paper in order to highlight the most modern bonding agent which consider as a promising material to employ in the actual outdoor structures.

Keywords: *FRP, Bonding agent, Strengthening, Service conditions.*

1. Introduction

Retrofitting and strengthening of existing structures are one of the most needed processes in civil engineering applications. Various factors are responsible for such need such as increment in the service loads, retrogradation of some structures due to the exposure to severe service conditions, human mistakes in primary design process and required updates for code regulations [1]. Fibre Reinforced Polymer (FRP) is the promising candidate material for strengthening over other materials such as steel plate [2]. The is due to the key-advantages of FRP such as low density, high stiffness, high strength-to-weight ratio, chemical and corrosion resistances, suitable for new and old structures, low coefficient of thermal expansion and available in different forms and shapes to suit the strengthening of structures of different geometries [3]. Different types of FRP are used for strengthening and the most commonly used are Carbon Fibre Reinforced Polymer (CFRP), Glass Fibre Reinforced Polymer (GFRP) and Aramid

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Fibre Reinforced polymer (AFRP). The CFRP is the most used FRP for strengthening since it provides high strength and modulus, low strain, excellent resistance to environments, creep and fatigue. The E-glass provides high strength and strain, low modulus and more sensitive to environments, creep and fatigue [4]. Depending on the shape of the strengthened element as well as the design requirements for strengthening, FRP may be used with different forms such as fabrics, laminates, rods and textile.

The FRP strengthening system consists of FRP material, strengthened structural element and bonding agent. The adherent (strengthening element) varies in types of structures such as masonry [5-7], concrete [8,9], timber [10,11] and steel [12-14]. In terms of bonding agent, it plays an effective role in achieving the desired goals of strengthening with FRP. This agent transfers loads to and between the fibers. The most commonly used adhesive that is used to bond FRP to structural member is polymer-based adhesive. Different polymers are available but thermoset-based polymer such as epoxy resin is the commonly used in strengthening system [4]. Many techniques are available for strengthening and the most commonly used are externally strengthening FRP system and Near-surface mounted (NSM) FRP strengthening system [15].

Service conditions are one of the factors that affect the performance of FRP strengthening system. When epoxy resin is used for bonding FRP to structural member, service conditions limit the usage of such material (resin). If the service temperature approaches or exceeds the glass transition temperature (T_g) of the adhesive that is used in FRP strengthening system, then the properties of the adhesive deteriorate dramatically which results in losing the bond between FRP and strengthened structure. According to ACI 440 [1], T_g of most epoxy adhesives used in FRP strengthening systems is within the limits (60-82°C). Thermo-mechanical properties of epoxy-based adhesives are affected negatively as the service temperatures are greater than (or even close to) T_g of the adhesive. The latter lose its capacity to transfer stresses from fibers to strengthened structural member. Due to such limitation of the epoxy resin to use as bonding agent, the need to develop bonding agent became an urgent need to overcome the drawbacks of epoxy resin and use more environmental-friendly adhesive in FRP strengthening system. Extensive work by researchers to modify the bonding agent has been conducted and reported in literatures. The objective of the present paper is to overview such work to highlight the most modern adhesives that are used in FRP strengthening systems for actual application of such adhesive in outdoor structures.

2. Background on FRP strengthening system

2.1 Components

FRP is a type of advanced composite materials which comprise of two elements (materials) (Figure 1). One of these materials (reinforcing phase) may be in the form of fibers, sheets, or particles. Such fibers are embedded in the other materials (matrix phase). The reinforcing material and the matrix material are made from different types of materials such as metal, ceramic, or polymer. In structural composites, the function of the fibers is to carry the load in addition to provide stiffness, strength and thermal

stability to the composite. The main role of the matrix in the composites is to bind and protect the fibres as well as transfer the load to fibres [16, 17]. In case of polymeric matrix which is commonly used in FRP application, thermoset and thermoplastic polymers are usually used. The thermoplastic polymers [18] are not commonly used for FRP strengthening system due to the behavior of such thermoplastic polymers represented by softening and hardening reversibly on change in temperature. Therefore, thermosetting polymers present the preferable matrix for FRP applications in infrastructures due to irreversible change from soluble products into highly cross-linked resins [19]. In terms of reinforcing phase in FRP, fibres are available in different types such as carbon, glass and aramid. The most widely used are carbon and glass fibres [16].

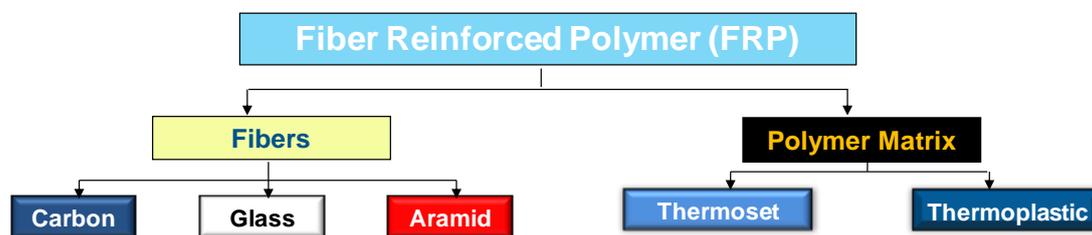


Figure.1: Compositions of FRP composites

Despite their high cost, FRP composites have been globally preferred to be used to repair and rehabilitate different civil infrastructures (bridges, buildings, offshore platforms, etc) since such advanced composites have attractive properties that suit the purpose of strengthening with FRP over the traditional materials such as steel plates. Coupling with the properties, FRP availability in different shapes and forms encourage the employing of FRP for various strengthening of structures such as strengthening in shear [20,21], flexural [22,23], torsion [24,25], fatigue resistance [26,27] and corrosion resistance [28].

The main components of FRP strengthening system are strengthening materials; strengthened substrates and bonding adhesive (refer to section 1). Different forms and shapes are available of FRP to be used for strengthening (Figure 2). Depending of the installation technique as well as the way of delivery in the site, many FRP composite systems are available. According to ACI 440.2R-02 [1], the common FRP system forms suitable for the strengthening of structural are: wet-lay up, pre-cured, pre-preg systems and other forms. In *wet lay up method*, a layer of dry flexible sheets or fabric of raw fibres are saturated with an epoxy adhesive resin and placed on the concrete structure. The epoxy resin acts as the adhesive, as well as the FRP matrix. The saturation and curing of this wet-lay up system is carried out onsite. In the *Pre-cured Systems* cured rigid strips or plates, shells, jackets or angles, and manufactured off-site and installed on-site using epoxy adhesives. Different pre-cured system is available such as pre-cured unidirectional laminate sheets, pre-cured multidirectional grids, and pre-cured shells. In terms of *Pre-preg Systems*, unidirectional or multidirectional fibre sheets are glued to

the existing concrete structure with or without the application of additional resin. After they are pre-impregnated with a resin during manufacture, the FRP system is saturated off-site and cured on-site in similar way like wet-lay up system. Different types of pre-preg FRP systems may used and these are: Pre-impregnated unidirectional fiber sheets, Pre-impregnated multidirectional fiber sheets or fabrics, and Pre-impregnated fiber tows [29].

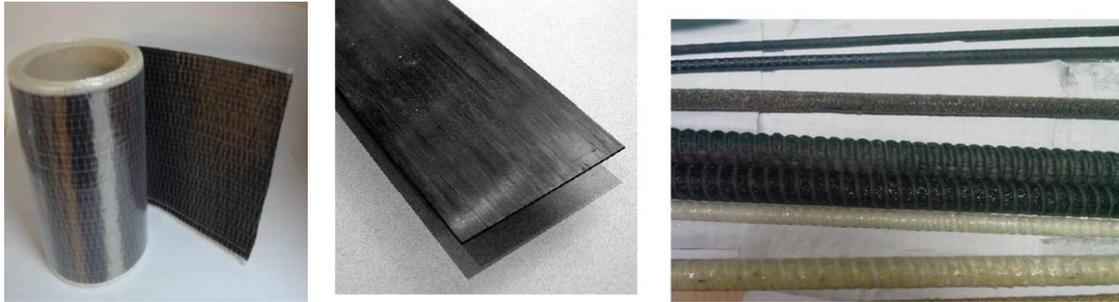


Figure. 2: Different forms of FRP composites for strengthening: sheets (*left*), laminate (*middle*); and bars (*right*)

2.2 Installation Techniques

Various installation techniques are available nowadays for strengthening with FRP. The most widely used is externally strengthening (ES) and Near-surface Mounted (NSM) strengthening systems. The externally strengthening system (Figure 3) [30] is based on the use of either pre-cured laminated FRP plates or FRP sheets (fabrics) which applied using wet-lay up method. In terms of NSM technique (Figure 4) [31], it is commonly used for strengthening concrete structures in which a groove is needed to be cut on the surface of the structural member with specific dimensions to be filled later with high strength structural adhesive to bond FRP. The latter is used in NSM with various forms such as pre-cured FRP laminate plate and bars.

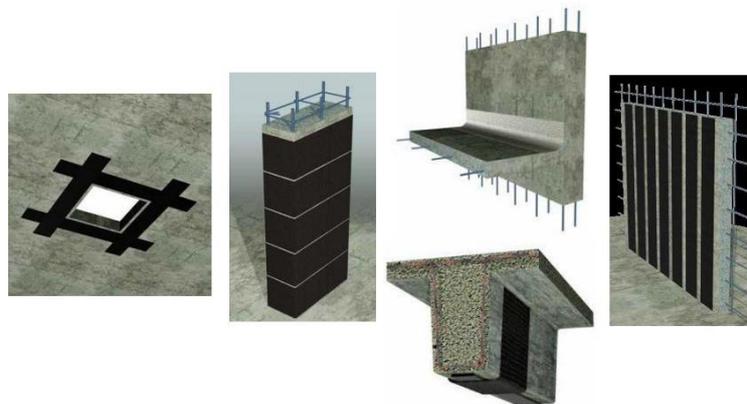


Figure.3: Externally strengthening with CFRP [30]

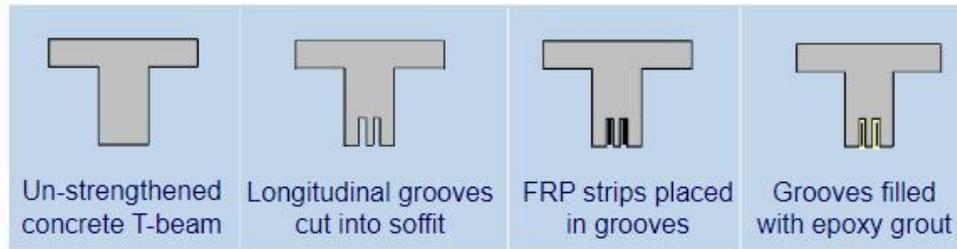


Figure.4: Application of Near-Surface Mounted (NSM) FRP strengthening technique on T-section of concrete structure [31]

The requirements of FRP ES involve proper surface preparation to bond FRP to the structural element while NSM technique needs no surface preparation. High-pressure water jet and sand blasting are the most commonly used methods to prepare the surface. The utilization of NSM provides more protection for FRP material from the service conditions which affect the thermo-mechanical properties of not only FRP material but the bonding agent. Therefore, less degradation in the performance of the whole strengthening system is expected when NSM is applied. However, more specific shapes of the structural member are compatible with the application of NSM. ES technique, particularly the wet-lay-up method, offers the chances to strengthen structural elements with various geometries [32].

2.3 Performance of strengthened system

Many factors may affect the performance of FRP strengthening system and particularly on the bond between FRP and the adherent (structural member). Some of these factors are type of FRP, interfaces between FRP and structural element, surface preparation, temperature and moisture [33]. Reported work in literatures [34-37] showed that severe environmental conditions (temperature, humidity, combined effect of temperature and humidity) have greatest potential effects on the behavior of FRP strengthening systems when such conditions approach or exceeded T_g of adhesive that used for bonding. Performance (short and long terms) of FRP strengthening of concrete members in flexural was conducted at various exposure temperatures (40-120°C) [38] using different bonding agents with and without post-curing. Different types of CFRP were used for strengthening and these were CFRP sheets (unidirectional woven fabrics) and CFRP laminates. The adhesives were commercially available as Sikadur[®]30, Epolam 2025/2035 and Macroplast EP 9177 with T_g of 62°C (after ad hoc post-curing), 130°C (after ad hoc post-curing) and 100°C (without post-curing) respectively. The CFRP/concrete system were three different systems and they were CFRP plates with Sikadur[®]30 epoxy adhesive, CFRP fabrics with Epolam 2025/2035 adhesive and CFRP fabrics with Macroplast adhesive. The first system (CFRP laminate and Sikadur[®]30) showed good bond efficiency for exposure temperatures up to 85°C. The second strengthening system was affected by the cyclic temperatures as the latter affected negatively on the bond interface between CFRP and concrete which led to lose the

bond. The adhesive that was used in the third strengthening system was with high viscosity that unable its usage of FRP applications for strengthening.

Another reduction in the performance of FRP/concrete system was reported [39] as the strengthened system was exposed to elevated temperatures using bonding agent (SikaDur 30) and FRP was CFRP (SIKA CarboDur S512). The bond performance was achieved by means of double-lap shear tests at elevated temperatures (20, 50, 65 and 75°C). The failure load was increase as the exposure temperature reaches 40°C and 50°C. However, reduction in the failure load was observed as the temperature reached 65°C. The latter was exceeding T_g of the adhesive (62°C) and the stiffness of adhesive and the failure pattern was in the interface between adhesive and concrete.

The influence of combined effect of temperature and humidity on bond efficiency of CFRP strengthening system was reported by others [40]. Loaded single-lap shear samples of CFRP/concrete system were exposed to different exposure regimes based on cyclic temperature and humidity as well as cyclic humidity and temperatures. The CFRP was normal modulus sheets, which was used to externally strengthened concrete blocks using commercially available adhesive as MBrace[®] Saturant to bond CF-fabrics to concrete. The T_g of the adhesive was 58°C measured by dynamic mechanical thermal analysis (DMTA). The exposure regimes were: (1) cyclic temperature (20°C-50°C) and constant humidity (30%, 60% and 90%) for 95 days. (2) constant temperature (40°C, 45°C and 50°C) and ramped humidity for 21 days. After the end of exposure, the residual strength was measured via single-lap shear test at ambient conditions. Some samples that exposed to regime (1) did not survived under the exposure conditions of humidity more than 60% but other samples survived under the exposure conditions and the measured residual strength were reduced. Concrete rupture and interface failure was the common failure mode of all tested survived samples at ambient conditions. Regarding samples that exposed to exposure system (2), samples were survived only for 3 days at exposure temperatures of 50°C and constant humidity.

3. Developed Bonding agents

The most commonly used adhesive to bond FRP to concrete is epoxy-based adhesive (EBA). Alternative adhesive; namely cement-based adhesive (CBA) is used instead of EBA due to limitations of using EBA at specific service conditions such as temperatures that exceeded T_g of epoxy. The following sections address the reported work in the literatures to develop bonding agent that suits the application of FRP at various harsh environmental conditions.

4. Epoxy-based adhesives

4.1 General

The commonly used bonding agent to glue FRP composites to structural elements (concrete, steel, wood, etc) is thermosetting polymer which consists of two parts (Part A and Part B) epoxy system of room temperature curing. Part A is the monomer (epoxy resin) while part B is the hardener (curing agent). Excessive attempts were made to

enhance the thermo-mechanical properties of epoxy adhesive which affects the performance of the whole strengthening system that based on FRP and structural members at various service conditions. Most commonly used commercially available structural adhesives are MBrace[®] Saturant MBrace, Araldite[®] 420 and Sikadur[®]-30.

4.2 Commercially available structural adhesives

4.2.1 MBrace[®] Saturant epoxy adhesive

This type of adhesive (Figure 5) is one of the commonly used epoxy-based adhesives in civil engineering applications to bond FRP sheets or fabrics to concrete structures. The MBrace[®] Saturant or as it is known recently with MasterBrace[®] 4500 is a low viscosity two-part epoxy system: part A (the monomer) and part B (the hardener). Around 60% only of part A is mainly based on pure bisphenol- epoxy resin (known in the literatures as DGEBA-based epoxy resin) and 10-30% of the monomer contains other commercially chemicals known alkyl glycidyl ether. In terms of part B, Isophoronediamine is forming more than 60% of the hardener as provided by the manufacturer and less than 30% of part B contains of salicylic acid. As provided by the manufacturer (BASF construction chemicals Pty Ltd), this epoxy adhesive is of ambient temperature curing for 7 days. The modulus of this adhesive is more than 3 GPa and 50 MPa of tensile strength as provided by the manufacturer [41]. The glass transition temperature (T_g) of this adhesive is 70°C measured by Dynamic Mechanical Thermal Analysis (DMTA) [42] or 60°C measured by Differential Scanning Calorimetry (DSC) [43].

Such adhesive is suitable for bonding various types of FRP sheets such CFRP, GFRP and AFRP to concrete. The application of MBrace[®] Saturant epoxy adhesive requires previous preparation of concrete surface using high pressure water jet or sand blasting to roughen the surface. A commercially available primer MBrace[®] Primer (known as Master[®] MP3500) is used to enhance the adhesion properties of the concrete surface is applied firstly as one thin layer on the area that want be strengthened with FRP sheets as recommended by the manufacturer. The primer is a two-part epoxy system of room temperature curing. Following 45 mins of the primer application, FRP sheets are bond to the concrete by wet-lay up method (refer to section 2).



Figure.5: MBrace[®] Saturant epoxy adhesive to bond FRP sheets to concrete [44]

When this type of adhesive was used to glue normal modulus CFRP sheets to concrete at expose to various elevated temperatures, the bond strength was reduced as the exposure temperature was increased. The mode of failure was concrete rupture at temperatures up to 36°C and adhesive failure for concrete exposed to (50-70°C) with peeling-off of CF-fabrics. The latter failure pattern was achieved since exposure temperatures were approaching and exceeding T_g of the adhesive that used for bonding. Therefore, such adhesive needs to be modified to overcome such lose of bond in FRP strengthening system [45].

4.2.2 MBrace[®] Laminate adhesive

It is a two-part epoxy-based adhesive that used to glue FRP laminate (peel ply) to concrete and steel structures. Its mixing ratio is (3:2) of (part A; part B) by weigh. As provided by the manufacturer (BAF construction chemical) , this red colored adhesive is with bonding strength to concrete of > 3.5 MPa and > 5 MPa for steel. The flexural strength is >30 MPa while its compressive strength is > 60 MPa. Recently, the manufacturer produced such adhesive under a commercially available name as MasterBrace[®] ADH 4000 [46]. The requirements of surface preparation of concrete or other structural member is similar to MBrace[®] Saturant adhesive as well as the application of MBrace[®] laminate adhesive to concrete (refer to section 4.2.1).

4.2.2 Araldite[®] 420 adhesive

This type of epoxy-based adhesive (Figure 6) [47] is used commonly to bond FRP sheets to steel structures [36]. In addition to metal surfaces, such adhesive is used to glue several materials such as wood, rubber, etc which make it suitable for different applications such as aerospace applications. The Araldite[®] 420 is a high viscosity epoxy-based adhesive consists of two parts (part A and part B). As provided by the manufacturer (Huntsman Duxford, Europe), part A (yellow colour) and part B (blue colour) are mixed with (100:40) mixing ratio by weight and cured at ambient conditions for 7 days to produce homogenous mixture of the adhesive (dark-green) [48].



Figure 6: Araldite[®] 420 adhesive to bond FRP to metals [47].

The tensile properties and T_g of this adhesive was conducted by group of researchers [49]. An extracted sample from dog-bone shape adhesive samples of 44 mm in length was placed in Dynamic mechanical thermal analysis (DMTA) technique to obtain various experimental values (T_o , T_{II} , T_{II} and T_g). These T_o and T_{II} present the onset point of the stiffness decrease of the dynamic modulus E' and peak of the viscous modulus E'' respectively. The T_i is related to inflection point of the (E' -T) curve while T_g presents the peak of the loss factor = E''/E' .

The sample is exposed to a range of temperature (-45°C to 110°C) with 2°C/min of ramping rate. The amplitude of static strain was 0.2% with 0.01% of superimposed dynamic amplitude. The frequency of 10 Hz was applied. In terms of tensile strength and modulus, an average of six dog-bone specimens were prepared in accordance to ISO 527-2:2012. These samples were 185×10×5 mm in dimensions for length, width and thickness respectively. After casting, some samples were left for 7 days at room conditions to cure while other samples were accelerated cured. The latter samples were placed inside an oven for at 95°C for 60 mins. The tensile test was performed at ambient conditions through the application of load with 1 mm/min loading rate. The strain measurements were conducted via extensometer with a gauge length of 50 mm. The extensometer was placed at the middle of each specimen. The obtained T_g was in the range of 40°C. It was concluded that high tensile strength was reported for Araldite® 420 adhesive with ductile behavior. T_g of this adhesive was in the range of 40°C, therefore, the application of this adhesive is recommended to bond FRP to steel structures but only for service temperatures less than T_g (40°C). Alternative adhesives or modified adhesives need to be considered for service temperatures high than 40°C.

4.2.3 Sikadur®-30 adhesive

It is a commercially available epoxy based adhesive (Figure 7) that used to bond FRP to different structures such as concrete and steel [50]. This adhesive is thixotropic adhesive of room temperature curing. The thixotropic means two-part epoxy resins with special filler. The mixing ratio is (3: 1) of (part A: part B) by weight with light grey color with T_g of 62 °C. The elastic modulus of this adhesive is 12800 MPa. The bonding strength on concrete is > 4 MPa while it is > 33 MPa on steel. All the above values are as provided of the manufacturer (Sika, Co.) [51].



Figure 6: Sikadur®-30 adhesive to bond FRP to various structures [50]

The properties of this type of adhesive were conducted as well by researchers in the literatures. The T_g measured by DMTA was within the range of (40-50°C) which was less than T_g mentioned in the data sheet of the product. The measured T_g was obtained through scanning sample of the adhesive from 20°C to 150°C using heating rate of 0.5°C/min using DMTA technique [52]. The tensile properties were conducted by others via tension test which was performed in accordance to ASTM D638. The reported young modulus and tensile strength were 12049 MPa and 30 MPa respectively and these values were close to those provided by the data sheet of the manufacturer [53].

4.3 Non-commercial epoxy resins

Many epoxy-based resins are used in materials and aerospace applications and are rare to be used in civil engineering. Such resins are more pure than commercially adhesives in which the latter contain in their ingredients some commercially additives. One of the pure epoxy-based resins is high-functionality-based resin (DGOA) (Figure 8) which is also known in some literatures as TGAP or DGGOA. Its chemical component is N,N-diglycidyl-4-glycidyoxyaniline produced by Sigma-Aldrich. As provided by the manufacturer, this resin is a clear liquid (light yellow in color) with low viscosity at ambient condition. Its density is 1.22 g/cm³ at 25°C and its molecular weight is 277.32 g/mol [54].



Figure 8: High-functionality based resin (DGOA) [54]

Due to its chemical structure, DGOA was used by some researchers in civil engineering application in which such high-functionality resin was employed as part A to produce epoxy adhesive with enhanced properties. Such properties are needed to improve the performance of FRP/concrete system at sever service conditions in which the commercially available epoxy adhesive (MBrace[®] Saturant) was not able to withstand such harsh environment which causes insufficient strengthening system. DGOA was used to replace the part A of MBrace[®] Saturant partially or completely [55]. Many trial mixes were carried out in this regard. These mixes were varies in percentages of DGOA that replaced partially part A of MBrace[®] Saturant as well as various mixing ratio of (DGOA+ part A) with the hardener (part B) of MBrace[®] Saturant. In terms of complete replacement of part A, various mixing ratios of (DGOA:

part B) were used. The mix with highest T_g was used to bond CFRP sheets to concrete substrates. T_g was enhanced by 11°C (measured by DMTA) when DGOA was replacing completely part A with mixing ratio of (100:50) by weight in comparison with control adhesive (part A: part B of MBrace[®] Saturant).

An improvement of 5°C in T_g (measured by DMTA) was achieved when DGOA was partially replaced part A with 40wt % with mixing ratio of (100:40): 40 by weight for (part A:DGOA): part B). Regarding tensile strength test at ambient condition, the complete replacement of part A with DGOA led to higher tensile strength (47.58 MPa) when compared with control samples (without replacement (part A: part B) in which the tensile strength of the latter was 34.57 MPa. Similarly, an increment of 42.26% was reported for adhesives samples of complete replacement of part A with DGOA in comparison with control samples. Tests at elevated temperatures showed as well improvement of 8.81% and 43% for in the tensile strength and tensile modulus respectively was noted for samples of DGOA when replaced completely part A of MBrace[®] Saturant in compared with control specimens when tested at 40°C . When test temperature was 60°C , highest increment of 8.57 MPa in tensile strength and 54% of the tensile modulus was reported for adhesive samples with complete replacement of part A with DGOA. The increment in the tensile properties as well as T_g was referred to highly-cross link density due to the chemical structural of DGOA which contains three epoxy groups.

The usage of DGOA with (100:50) mixing ratio for (DGOA: part B) in bonding CFRP to concrete showed good bond efficiency for CFRP/concrete system when exposed to combined effect of temperature and humidity. The strengthened system composes of concrete samples of $75 \times 75 \times 250$ mm in dimension and strengthened externally with one layer of CFRP sheets using bonding adhesive of (DGOA :part B) with mixing ratio (100:50). Other samples were fabricated using control adhesive (MBrace[®] Saturant). All samples were loaded (30 and 40% of the ultimate load) and then exposed to two accelerated durability tests (A1 and A2) for various periods (21 days and 44 days) respectively inside an environmental chamber. A1 involves the exposure of CFRP/concrete system to constant temperature (50°C) and ramped humidity (30% to 90%). Cyclic temperature of ($20\text{--}50^\circ\text{C}$) and constant humidity (90%) were the exposure conditions of A2. No sample was failed inside the chamber during the whole exposure time when DGOA was used for bonding and no reduction in the residue strength was reported for these samples when single-lap shear test was performed after the exposure to harsh conditions. Control samples failed after only 24 hrs of starting the expose to severe conditions of combined effect of temperature and humidity.

4.4 Modified Epoxy-based adhesive

4.4.1 Modification with Nanomaterials

Due to their attractive properties, nano-scale materials have been used as a reinforcement of epoxy-based matrix. Numerous studies were conducted to explore

thermo-mechanical properties of polymers that modified with various types of nanomaterials. Some of these studies are presented in the following paragraphs.

4.4.1.1 Modification with Carbon Nanotubes (CNTs)

An experimental investigation was carried out to reinforce epoxy-based adhesives with CNTs. The adhesive is used to glue steel members with CFRP plates [56]. The CNT was multi-walled carbon nanotubes (MWCNTs) with properties of 110-170 nm in diameter and length of 5-9 μm as provided by the manufacturer (Sigma-Aldrich Co.). Different concentrations (0,1, 2 and 3wt%) of MWCNTs were different added to two types of epoxy adhesive of room temperature curing. These epoxies are commercially available as Araldite[®]420 and Sikadur[®]-30. Each of these epoxies system comprises of part A (monomer) and part B (hardener). Ultrasonic probe mixer was used to mix MWCNTs into part A. Prior to mixing, pure Ethanol was added to the desired concentrations of NWCNTs and placed inside a vacuum chamber for 2 days in order to facilitate the dispersion of MWCNT into the monomer. After 2 days, MWCNTs were added to part A and mixed first manually then ultrasonic waves were applied via ultrasonic probe with 55% energy density. The mixing was carried out for 50 mins in which the application of ultrasonic waves was for 30 sec and out of every 50 sec. The temperature of the mixture was kept below 55°C by surrounding the beaker that contain the mixture with ice and monitor the temperature of the mix via another probe during the mixing process. Later, the hardener was added manually to the whole mixture (MWCNTs+monomer) for 4 mins. The tensile samples of modified adhesive with MWCNT were prepared in accordance to ASTM: D 3039 and left for 7 days at ambient conditions for curing as recommended by the manufacturer [56].

4.4.1.2 Modification with Silicon Carbide nanopowder (SiC)

An attempt was conducted to explore the effect of reinforcing two types of epoxy-based adhesives with nanomaterials on tensile properties and glass transition temperature [57]. In their study, different concentrations (0%, 1 wt%, 2 wt% and 3wt%) of two different nano-based materials (multi-walled carbon nanotubes (MWCNTs) and Silicon Carbide nanopowder (SiC)) were added to two different epoxy adhesives (Araldite-420 and Sikadur-30). Both nanomaterials were provided by Sigma-Aldrich. As provided by the manufacturer, the diameter of MWCNTs was 110–170 nm while nano-SiC was with particle size less than 100 nm. The length of MWCNTs was 5–9 μm with purity of more than 90%. The dispersion of nanomaterials into epoxy resin was carried out following the same procedure by the authors in their previous study [56]. The preparation of control samples (without nanomaterials) was conducted by two mixing methods of Part A and Part B and for each type of epoxy adhesive. These methods were manual and mechanical mixing.

In terms of samples that reinforced with MWCNTs, the addition of 1 wt% of MWCNTs was found to increase the tensile strength (27.9 MPa) of Araldite-420 in comparison of the strength of control sample of manual mixing (26.4 MPa) as well as

mechanical mixing samples (26.7 MPa). The strength was increased with the increment in MWCNTs to 2 wt% in which the latter showed tensile strength of 30.9 MPa. Further increment in MWCNTs (up to 3 wt%) led to reduction in the strength. Regarding the addition of MWCNTs to Sikadur-30, an increment (3.07%) in the tensile strength was reported for 1 wt% samples in comparison with control samples of mechanical mixing. However, strength was reduced with further addition of MWCNTs (2 wt%). The effect of nanomaterials on tensile elastic modulus of the adhesive was more effective than tensile strength. All added concentrations of MWCNTs to Araldite[®] 420 showed increment in the elastic modulus of epoxy adhesive. Highest elastic modulus (2.13 MPa) was reported for 2 wt% samples in comparison with control specimens (1.87 MPa). In terms of Sikadur[®]-30, the addition of 1 wt% and 2 wt% results in an increment of elastic modulus of the adhesive in comparison with control samples of manual mixing. The highest tensile modulus (12.37 MPa) was achieved for 1 wt% samples of MWCNTs.

As nano-SiC was added to Araldite[®] 420 and Sikadur[®]-30, the tensile strength was increased with the addition nano-SiC (up to 1 wt%) in comparison with the control samples. The increment in the strength was 5.68% and 13.6% for Araldite[®]420 and Sikadur[®]-30 respectively when reinforced with 1 wt%. When more concentrations of nano-SiC were added (2 wt% and 3 wt%), reduction of tensile strength was reported. Same behavior was reported for the modulus. It was slightly increased with the addition of 1 wt% of nano-SiC in comparison with control samples for Araldite[®]420 only. An increment in the modulus was reported for all samples of Sikadur[®]-30 when reinforced with various concentrations of nano-SiC (1 wt%, 2 wt% and 3 wt%). The highest modulus (11.63 MPa) was for samples with 1wt% SiC. The enhancement in the modulus was referred to the irregular shape of the SiC which restrict the movement of the epoxy bundles which results in reduction in the strain and hence increment in the modulus. Regarding T_g , no effect was reported with the addition of nanomaterials to the adhesive due to restriction of nanomaterials to the chemical reaction between the monomer and the hardener of the adhesive which led to lower the cross-linked density of the adhesive.

4.4.1.2 Modification with nanoclay (NC)

Layered silicate nanoclay (NC) was used to modify thermoset epoxy adhesive system that use to bond CF-fabrics to concrete [58]. In their study, tests on modified adhesive samples were conducted as well as bond performance of CFRP/concrete system using modified adhesive as bonding agent. A commercially available nanoclay as Nanomer I.30E (provided by Nanocor, USA) was added to commercially available epoxy adhesive as MBrace Saturant (provided by BASF, Australia). The latter is a two parts epoxy adhesive system (part A and part B) of room temperature curing and it is commonly used in civil engineering applications. NC was layered silicate of clays with

platelets of 1 nm. These layered silicates was added with various percentages (0, 1, 2.5, 5 and 7.5 wt%) of epoxy resin. Mechanical stirrer was utilized to mix NC with part A of MBrace Saturant. The mixing procedure involves the usage of heat to facilitate the dispersion of NC into part A. The required amount of part A was placed in a beaker. After the addition of dried NC to part A, the temperature of the whole mixture was raised up to 80°C by placing the beaker on hot plate. Then mechanical stirrer was used for mixing for 1 hr at 500 rpm. Part B (hardener) was added later to the mixture (NC+ Part A) after it was cooled to room temperature. The microstructure of adhesive samples (with and without NC) was evaluated using different techniques such as Differential Scanning Calorimetry (DSC), Transmission Electron Microscopy (TEM) and X-ray diffraction (XRD). The effect of NC on glass transition temperature (T_g) of adhesive was measured via DSC. Tensile strength of the adhesive at elevated temperatures (40°C and 60°C) was obtained as well in which the tensile test was conducted in accordance to ASTM D 638-03. The bond loss temperature was conducted by means of adhesion –pull out test at elevated temperatures for CFRP/concrete samples. They were 75×75×75 mm in dimensions. A constant load (20% of the ultimate load) was applied to pull- out an Aluminum disc attached to CFRP/concrete sample. The load was applied till the disc was de-attached.

The T_g of all adhesive samples was found to be decreases with the addition of NC except for 2.5 wt% when compared with unmodified adhesive (control). The reduction in the crosslink density of epoxy coupled with plasticisation due to the existence of unreacted resin, might led to such reduction in T_g . Results of tensile test at 40°C showed that adhesive samples with NC showed lower tensile strengths (21, 20, 19 and 16 MPa) for 1%, 2.5%, 5% and 7.5% of NC respectively in comparison 27 MPa for control sample. Similarly, tests at 60°C showed reduction in the tensile strength when NC was used for modification epoxy adhesive. However, higher tensile modulus was reported for NC-modified adhesive samples when tested in tension at 40°C and 60°C. The highest tensile modulus (2722 MPa) was for 2.5% NC samples in comparison with other NC-modified samples (2315, 2287 and 2200 MPa) for samples with 1 %, 5% and 7.5% of NC respectively when tested at 40°C. As a comparison with control samples, higher tensile modulus was found for all NC-modified adhesive and the highest enhancement (24%) was for adhesive samples with 1% NC when tested at 60°C. The samples with 5% NC showed highest ductility when compared with other NC-modified adhesive samples tested at 40°C as well as at 60°C. In terms of the microstructure, the usage of mechanical stirrer to mix NC with part A results in obtain a combination of intercalated and exfoliated structure of NC in the epoxy matrix. This structure was detected by XRD and TEM. The XRD measurement of d -spacing was found to be 2.9 nm for NC- modified adhesive while it was 2.11 nm for NC alone. In terms of adhesion pull-out test at elevated temperatures, samples with NC were found to lose their bond between CFRP and concrete at temperatures less than that for control samples and the failure was detected at the adhesive line.

4.4.1.3 Modification with Vapour Grown Carbon nanofibre (VGCF)

The epoxy adhesive that used to bond CF-fabrics to concrete was reinforced with VGCF [59]. The VGCF was a commercially-available carbon nanofibre, PR-24 XT-LHT (Pyrograf®-III, Applied Sciences, Inc., USA) with 100 nm average fiber diameter and 43 m²/g as surface area. Various percentages of VGCF (0.5, 1, 1.5 and 2 wt%) were added to the monomer of commercially available epoxy adhesive as MBrase[®] Saturant. Speed mixer was used to disperse VGCF into the monomer with mixing period of 15 mins at 2000 rpm. The hardener was later added to the mixture (VGCF + monomer) and mixed manually at ambient conditions. DSC technique was utilized to measure T_g of the adhesive (with and without modification). Regarding DSC measurements, small sample of adhesive was exposed firstly to heat from 20°C to 120°C at 10°C/min ramping rate. The temperature was kept at 120°C for 1 min then the sample was cooled to 20°C using the same ramping rate. Following the cooling process, the sample was heated again from 20°C to 120°C in order to obtain the optimum properties of the adhesive. No significant effect of VGCF on the cross-linked epoxy adhesive which causes no change or slight decrease in T_g. The microstructure of VGCF-modified adhesive was conducted using TEM technique using various magnifications. Agglomeration of VGCF was observed in the epoxy matrix and the orientation of fibres was random distributed.

The short term durability of concrete samples that strengthened externally with CF-fabrics using VGCF-modified adhesives was conducted through the exposure of strengthening system to different accelerated durability tests (A1 and A2) that based on combined effect of temperature and humidity. The adhesive was modified with (1wt% and 2 wt%) of VGCF. The A1 involves the application of constant temperature (50°C) and ramping humidity (30-90%) for 21 days while A2 includes the application of constant humidity (90%) and cyclic temperatures (20-50°C) for 44 days. During the exposure to accelerated durability tests, CFRP/concrete samples were loaded (40% of the ultimate load). Various failure modes were reported for CFRP/concrete samples after the exposure to A1. It was primer/adhesive interface for samples of 1 wt% while it was combination of primer interface with the adhesive and concrete for samples with 2wt%. All CFRP/concrete samples that exposed to A2 showed the same failure pattern (combination of primer interfaces with the concrete and adhesive) for 1wt% and 2wt% VGCF samples [59].

4.4.2 Modification with fine aggregate

A study was conducted to improve the properties of epoxy- based adhesive used in strengthening concrete with CF-fabrics using fine aggregate (sand) [60]. A commercially available adhesive as Sikadur[®]-330 was used to be modified with sand. The adhesive is a two parts thermosetting epoxy system of 1.31 kg/L density with mixing ratio of 1:4 (part A: part B) by weight as recommended by the manufacturer. The tensile strength, flexural strength and tensile modulus of the adhesive after 7 days curing were 30 MPa, 3800 MPa and 4500 MPa respectively as provided by the supplier. The modification of the adhesive was carried out via the addition of sand to either part A or part B. The added dried granular sand have particle size passing sieve 300 µm and

retained on sieve 75 μm . Other properties of sand were 2.41, 2.13 0.045% for specific gravity, absorption and sulfate content after washing with water respectively. Various sand-to-epoxy mixing ratios (0, 0.25, 0.5, 1, 1.5 % by weight) were used.

The consistency of the adhesive with and without modification with sand was obtained in accordance to ASTM C230 as well as ASTM C1437 in which initial and final percentages of flow were measured. The effect of sand addition to the adhesive on thermal properties was evaluated via monitoring the temperature of interaction for samples with and without sand, shrinkage test and measurements of coefficient of thermal conductivity. The mechanical properties of adhesive with and without sand were obtained by testing cubic adhesive samples with (40 \times 40 \times 40mm) in dimension in compression and prismatic samples with (40 \times 40 \times 160mm) in dimension in flexural for various curing periods (3, 7, 14 and 18 days). These tests were conducted in accordance to ASTM C109 and ASTM C348 for compression strength and modulus of rupture respectively.

It was found that as the addition ratio of sand increases, the flowability of adhesive was reduced and the optimum sand/epoxy ratio was 1 which shows good workability in comparison with other mixing ratios. The heat of reaction of mixing part A and part B was reduced with the addition of sand. The reported reduction in the maximum temperature of reaction was 20%, 36% and 44% for sand-to-epoxy ratios of 0.25, 0.5 and 1% respectively. A significant reduction in the shrinkage of adhesive was recorded for samples of sand-modified adhesive. The initial ultimate shrinkage was reduced by 96.4%, 97.3% and 98.2% for adhesive mixes of 0.25, 0.5 and 1% by weight of sand/epoxy ratios respectively. Consequently, the final ultimate shrinkage was decreased by 72%, 79.01% and 86.3% for samples of sand/epoxy ratio of 0.25, 0.5 and 1% respectively. The coefficient of linear expansion and thermal conductivity was decreases with the addition of sand. In terms of mechanical properties, an enhancement in compressive strength as well as modulus of rupture was obtained for adhesive samples with sand addition. The enhancement increase with the increase in the sand percentage and the highest improvement was reported for samples of sand/epoxy ratio =1. It was also concluded that the addition of sand to adhesive reduces the cost of the adhesive that needs to be used in CFRP strengthening system.

The influence of high temperatures on mechanical properties of sand-modified adhesive was explored by others [61]. Cubic and prismatic samples of sand-modified adhesives were prepared according to the procedure in [60]. These samples were exposed to various cyclic temperatures (20-150 $^{\circ}\text{C}$, 20-250 $^{\circ}\text{C}$, 20-350 $^{\circ}\text{C}$ and 20-400 $^{\circ}\text{C}$). The temperature was ramped from 20 $^{\circ}\text{C}$ to the desired temperature at 10 $^{\circ}\text{C}/\text{min}$. As soon as the desired temperature was reached, the heating was kept for 1 hr at that temperature. The residual strength of samples was tested at the end of the exposure period by means of compression and flexural tests. It was concluded that the addition of sand increases the resistance of adhesive to high temperatures. As the temperature was increased (less than 300 $^{\circ}\text{C}$), compressive strength was increased. A reduction in compressive strength was obtained due to the carbonation of the adhesive when the temperature was 300 $^{\circ}\text{C}$. In terms of testing the performance of the whole strengthening system using sand-modified adhesive, six reinforced concrete beams were fabricated.

These have a cross section of (150×150mm) with length of 1000 mm. The reinforcement at top were 2Ø6 mm and 3Ø6mm at the bottom with Ø6mm@75 mm for shear. All six beams were tested in flexural with one point load. Two beams were prepared without any strengthening (control) (FR1). Four beams were strengthened with CFRP. Two of them were strengthened with CFRP using unmodified adhesive (SF1). Other two beams were fabricated using sand-modified adhesive for bonding CFRP to reinforced concrete beams (SF2). The latter showed increment (10%) in the ultimate load carrying capacity. Additionally, SF2 beams showed highest ductility, stiffness and toughness in comparison with SF1 and RF1. The failure mode of SF1 was interfacial de-bonding while it was separation of concrete cover for SF2 [60].

5. Cement-based adhesives

5.1 Modification with minerals and additives

A study was carried out to modify cement based bonding agent that used to bond various forms of CFRP [62]. The modification was based on enhance the properties of cement mortar with the addition of mineral additives or polymeric material. Four mortar mixes were prepared and these were OC, OS, OL and MS. The OC is cement-based mortar without additives and consists of Ordinary Portland cement, water, Silica-based filler, fine aggregate and superplasticizer (commercially available as Viscocrete[®] 5-500). The cement-to- sand (C:S) ratio was 1:0.85 by weight with water-to-cement (w/c) ratio of 0.48 by weight. The addition of the superplasticizer was added by 1% of the weight of cement. In terms of cement mortar (OS), the same ingredients of OC were used but with the addition of silica-fume by 10% by weight of cement. The dosage of the superplasticizer was 5% by weight of cement which is higher than that used in OC. The third type of mortar is the polymer-modified cement mortar (OL). Its contain the same components of OS but Latex SBR, commercially available as Bara Emulsion 157, was added by 0.25 by weight of cement with 0.5% by weight of cement for the superplasticizer addition. The fourth cement mortar (MS), is the micro-cement mortar which consists of same compositions of OS mortar with the addition of micro-cement by 0.25 by weight of cement.

The mechanical properties (compression and modulus of rupture) of four mortar mixes (OC, OS, OL and MS) were obtained in accordance to AS 1012.9 and 1012.11 respectively. The highest properties were reported for MS mortar with 65 MPa in compression and 5.6 MPa for the modulus of rupture. The OS mortar showed the second highest properties with 60 MPa and 5.1 MPa for the compressive strength and modulus of rupture respectively. Lowest properties (46 MPa and 4.1 MPa) were obtained when a polymeric material was introduced to the cement-based mortar (OL).

The MS mortar was used as bonding adhesive between CFRP and concrete by the same authors in another study [63]. In their work, bond properties of CFRP/concrete samples using MS mortar as a bonding agent was evaluated. The single-lap shear samples were 245×75×75mm in dimensions. Sand blasting method was used on concrete samples in order to prepare the surface for bonding with CFRP. Different

series of test were performed to explore the effect of CFRP form, bonding length and availability of anchorage at the end of the sample. Two types of CFRP were utilized (fabric and textile). The application of CFRP was on 20 mm in the MS mortar overlay. The width of CFRP was 50 mm with 0.175 mm depth. Various bonding lengths (100mm and 180 mm) were used. The CFRP was extended 100mm out of the concrete samples in which two Aluminum plates were placed at both sides of free end of CFRP for load applications. Some CFRP/concrete samples were anchored with CFRP sheets. A groove with dimensions of 30×20 mm was installed in the concrete specimen to obtain the anchorage. Stain gauges were placed along the bonded length in order to obtain the strain values in the CFRP. It was concluded that MS mortar showed efficient performance as bonding glue between CFRP and concrete elements. An increase in the load failure capacity of 25% was reported for CF-fabrics/concrete samples with 100 mm bonding length and with in comparison with CF-fabrics/concrete samples with the same bonding length and without anchorage. Such enhancement was attributed to the contribution of the anchorage. When the bonding length was 180 mm, the ultimate failure load was 1080 kN and 940 kN for concrete samples hat strengthened with CF-fabrics with anchorage and without anchorages respectively. It was reported that concrete samples that strengthened with CFRP textile with 180 mm bonding length showed higher failure loads (1250 kN) when compared with CF-fabric samples for the same bonding length. The penetration of MS mortar through the CFRP textile was better than CF-fabric which led too such enhancement in the ultimate failure load of CFRP textile/ concrete system.

Al-Abdwais and Al-Mahaidi [64] investigated the modification of cement based-adhesive (CBA) used in Near-Surface Mounted (NSM) CFRP strengthening system. The CBA consists of Ordinary Portland cement, silica fume, silica filler (Silica 200G), micro-cement, water, MBrace primer (two-part epoxy adhesive) and superplasticizer (provided by Sika, Co.). Various mixes of CBA (mix1, mix2, mix3 and mix4) were prepared using same above ingredients with the same mixing ratios except for MBrace primer and superplasticizer. These two compositions were added to each mix with different ratios. Compressive and tensile strengths were conducted in accordance to AS 1012.9 and AS 1012.10 respectively using cylindrical samples with 50×100 mm in dimension. Highest compressive strength (86 MPa) was reported for mix4 in comparison with other mixes. Their compressive strengths were 68.5 MPa, 84.6 MPa and 85.5 MPa for mixes m1, m2 and m3 respectively. The obtained tensile strength were 5.2, 6.0, 6.2 and 6.2 MPa for mix1, mix2, mix3 and mix4 respectively. The modulus of elasticity was 24000 MPa and 24800 MPa for mix1 and mix2 respectively. Mix 3 and mix4 showed the same modulus of elasticity (25000 MPa).

In terms of performance of NSM CFRP strengthening system, single-lap shear samples were fabricated using the above four mixes as bonding agents between concrete and CFRP textile. Concrete specimens with 75×75×250mm in dimensions were cast and cured for 28 days. A groove was made of the concrete surface with width of 4mm and depth of 18 mm. The CFRP textile, with 1450 MPa tensile strength and 135000 MPa modulus of elasticity, was inserted in the concrete groove and extended out of the sample for 50 mm. The cross section of CFRP textile was 1.5×2.33 mm. Four mixes of

CBA were utilized as bonding agent between CFRP and concrete with different mix age (5,10, 20 and 30 mins). Two Aluminum plates of 40×50mm in dimensions were placed on both sides of free end of CFRP textile using epoxy adhesive Araldite 420. CFRP/concrete samples were left to cure for 21 days at ambient conditions. It was found that the CFRP/concrete specimens with mix4 showed the highest ultimate failure load in comparison with other CFRP/concrete samples using other mixes (mix1, mix2, mix4) as bonding agent.

5.2 Modification with fibres

High strength mortar (HSM) was developed by researchers to use for bonding concrete members with Basalt fibres (BFRP) sheets [65]. In their work, 18 mixes of HSM were designed and only three with the highest properties were used for glue BFRP sheets to concrete beams. Each mix consists of cement (CEM I 52.5 N) supplied by Aalborg cement, sand with maximum size of 2mm from Germany, undensified silica fume (USF) supplied by Elkem, superplastizer (SP) (commercially available as Procon SPC 25), Acryl as an admixture to enhance the workability, adhesion as well as tensile strength, and two types of synthetic macro-fibres (commercially available STRUX 90/40 and STRUX BT50). The properties of STRUX 90/40 as provided by the supplier are 620 MPa, 9.2 GPa and 0.92 for tensile strength, modulus of elasticity and specific gravity respectively. In terms of STRUX BT50, the tensile strength, modulus of elasticity and specific gravity are 550 MPa, 7 GPa and 0.91 respectively.

The 18 mixes of cement –based bonding material consists of control mixes and other modified mixes. The control mix comprises of cement, sand, water and SP. Other mixes involve the addition of different concentrations of USF, SP, micro-fibres and Acryl. The three mixes (Mix1, Mix2 and Mix3) of cement-based bonding material that gave the best properties were chosen to fabricate BFRP/concrete samples. Mix 1 composes of cement, sand, USF, and SP. The latter was added with 1.3% while the USF was added by 0.1% by weight of cement. Mix2 contains the same mixes of Mix1 but with the addition of fibres (0.75% of STRUX BT50). In terms of the Mix3, same mix components of mix1 were used with the addition of 11% of Acryl. The sand-to-cement (S:C) ratio of all three mixes were kept constant and it was 1.8. The water-to-binder (w/b) ratio was the same for Mix1 and Mix 2 (w/b= 0.27) while it was 0.3 for Mix 3.

Two sets of tests were conducted: (1) tests for cement-based bonding materials only and (2) tests on BFRP/concrete samples using cement-based bonding material. The first set was performed to obtain flexural strength of the above cement-based bonding material via cast prisms of this material with dimensions of 100×40 ×40 mm which were de-molded after 24 hrs at ambient conditions then cured in plastic for 2 days at 20°C. The second set of tests was carried out on two stages: small-scale samples and large-scale specimens. Small-scale samples were fabricated from normal strength concrete with dimensions of 100×100×360 mm. One of these beams was cast as control samples (without strengthening with BFRP). Another beam was strengthened with BFRP sheet that laid in Acryl. Other six beams of the eight beams were prepared using three types of cement-based adhesive with highest properties among the 18 mixes that

mentioned in the previous paragraph. Two types of BFRP sheets were used. These are BAS BI450 and BAS UNI 600. Both types of BFRP has the same ultimate tensile strain, elastic modulus and tensile strength (3.15 %, 84 GPa and 2500 MPa respectively). However, BAS BI 450 are with 0.45 mm thickness and surface weight of 464 g/m². The thickness and surface weight of BAS UNI 600 are 0.65 mm and 657 g/m² respectively.

Regarding large-scale samples (BF1-BF8), eight samples were fabricated in which two of them were control beams (without strengthening with BFRP) while other 6 samples were for strengthened samples using cement-based bonding material for BFRP. The dimensions of concrete beams were 2.5m, 3m, 15m and 25m for span length, total length, width and depth respectively. After the application of BFRP on concrete using cement-based bonding material, the concrete/BFRP samples were cured at ambient conditions for 14 days. Results of testing small-scale beams showed that an increment in the strength (26% up to 54%) when cement-based bonding material to glue one layer of BFRP. In terms of large-scale specimens, an increment in the flexural bearing capacity was obtained when BFRP sheet was glued to concrete using different mixes of cement-based bonding materials. The observed failure mode was rupture of the longitudinal fibres. Highest load capacity of concrete was recorded for samples that prepared using cement-based bonding material that containing micro-fibres in their compositions.

5.3 Modification with magnetic water

Magnetic water treatment was employed to develop cement-based adhesive (CBA) to use as bonding agent in CFRP laminate with concrete in near-surface mounted (NSM) strengthening system. In their study [66], two types of CBA (CBA-A and CBA-B) were modified. The compositions of each CBA are Ordinary Portland Cement (OPC), Micro-cement (MC), Silica filler (Silica 200G), silica fume, Superplasticizer (Viscocrete 5-500) and water. Only CBA-A contains another component which is Polymer (MBrace Primer). The water that used for mixing CBA was magnetized via two magnetic devices (MD-I and MD-II) with different magnetic strengths (9000 and 6000 Gauss) respectively. The effect of water flow rate through the magnetic devices on the properties of CBA was investigated. Three flow rates (0.1, 0.2 and 0.4 m²/ hr) for various periods (15, 30 and 60 mins) were explored. The mechanical properties of the magnetized and non-magnetized CBA were obtained by means of compression and tension tests. These tests were conducted by testing cylindrical samples with 100×200 mm dimensions in both compression and splitting tensile strength tests at various curing periods (3,7,14,21 and 28 days). Additionally, predication of compressive and tensile strengths was conducted in their study using genetic programming. Higher mechanical properties were reported for samples with magnetized water (MCBA) when compared with non-magnetized CBA (control) for the same magnetic time (T=15 MINS). The highest improvements in the mechanical properties were for MCBA-A in comparison with MCBA-B. Samples that prepared with magnetized water using magnetic device MD-I showed higher compressive and splitting tensile strengths when compared with

samples that prepared using magnetic device (MD-II) for magnetization of water and for different flow rates of water (0.1 and 0.2 m³/hr) at the same circulation time of water inside the magnetic device. Results showed that the effect of circulation time of water (T) in the magnetic device on compressive strength was less than that on indirect tensile strength. The latter was increased by 23.55% for MCB-A samples at 7 days when T was increased from 15 mins to 30 mins using MD-I when compared with control samples. The increment in the tensile strength of about 29.91% was reported for MCB-A samples when T_g was increased from 30 mins to 1 hr. In terms of the effect of flow rate of water (F) on mechanical properties of CBA, samples of MCBA showed highest compressive strength than CBA (control) when F was low (0.1 m³/hr) using MD-I. The highest enhancement (22.46% and 1.11%) of the compressive strength was achieved for MCB-A and MCB-B specimens respectively at 28 days. Higher percentage of enhancement in splitting tensile strength (56.25% and 27.56%) was reported for MCB-A and MCB-B samples respectively when F was 0.1 m³/hr using MD-I for curing period of 3 day. It was also concluded that the models that predicted using genetic programming showed good correlation of strength with the obtained results from the experimental program with some limitations.

5.4 Modification with graphene oxide

High-strength cement-based adhesive was developed via the utilization of graphene oxide (OG) [67]. The composition of cement-based adhesive was the same that obtained by others [64] with the addition of OG to the mix. Various test series were conducted to evaluate the properties of the new developed cement-based adhesive to suit FRP applications. Flow table test was carried out in accordance to ASTM C1437, setting time was obtained according to ASTM C191, pore structure was performed by means of nitrogen adsorption test, adhesion tests via pull-off test in accordance with ASTM C1583 and mechanical tests via compression and splitting tensile strength tests. The modified cement-based adhesive with OG showed adequate workability and setting time. The adhesive that modified with OG showed life up to 120 min with a flow of 7.5%. Also, higher strengths 13.8 MPa, 101 MPa and 1.2 MPa were obtained for tensile, compression and pull-off strengths respectively.

6. Geopolymer-based adhesive

Metakaolin-based geopolymer mortar (MBGM) was developed to bond Carbon Fibre Reinforced Polymer (CFRP) fabrics to concrete members [68]. The MBGM comprised from metakaolin, sand, calcium hydroxide and alkaline silicate solution. Various mixes of MBGM were prepared using various sand-to-binder ratios (0.3, 0.6 and 0.9) by weight. Three different concentrations (12M, 14M and 16M) of calcium hydroxide were used with calcium hydroxide of about (0.05% and 0.1%) by weight of metakolin. The mixing ratio of the alkaline activator (sodium hydroxide and sodium silicate solution) was 1:2.5. This activator was prepared previously by dissolve the flakes of the sodium hydroxide into distilled water. In terms of the metakolin, it was exposed to high

temperature (650°C) for few seconds prior to mixing with other compositions of MBGM. Regarding the sand that used in the mix, its specific gravity and absorption were 2.6 1.2% respectively. The preparation of MBGM involves dry mixing of metakolin with sand and calcium hydroxide prior to the addition of the alkaline activator.

The MBGM was used to bond CFRP to concrete samples (slabs and beams). These specimens were fabricated using normal strength concrete of 300 ×200 ×50 mm in dimensions for slabs and 850× 100×80 mm for beams. After 28 days of curing, concrete surface of these samples were prepared for bonding with CFRP sheets through the usage of MBGM as bonding agent. The MBGM was applied followed by placing CFRP sheets then another layer of MBGM was introduced. The CFRP was commercially available as MBrace CF130 with thickness of 0.176 mm, tensile modulus of 4900 MPa and elastic modulus of 230 GPa.

Tests were carried out on MBGM as well as on the whole strengthened system (CFRP/concrete samples). Compressive and flexural strength of MBGM were obtained through testing prismatic samples of 160× 40× 40 mm and the test was conducted in accordance to EN 1015-11. The flexural strength test of CFRP/concrete beams was carried out in accordance to NP EN 12390-5. In terms of adhesion strength test, the pull-out test was conducted in accordance to EN 1015-12. A compressive strength of 30 MPa was recorded for all MBGM mixes that cured after 7 days. It was attributed to the positive effect of sodium hydroxide concentrations on compressive strength. Regarding the adhesion strength, lower values were reported for samples of MBGM mix of sand/binder ratio of 0.6. This may related to the negative effect of lower sand/binder ratio which causes high shrinkage behaviour that due to the surface of the specimens with a lower sand content which results of high level of micro-cracks. In terms of pull-off test, the recorded strength was below 0.2 MPa due to the shrinkage behaviour of the MBGM in addition to MBGM was not optimized. It was pointed that the type of CFRP as sheets is not recommended with MBGM as bonding agent and further work needs to be conducted in this regard.

7. Conclusions

The bonding agent in FRP strengthening system plays a significant role to achieve the required performance of such applications at various service conditions. Proper selection of the bonding adhesive is based on the exposure conditions on FRP strengthening system. Excessive work was performed to develop bonding agents with specific properties that enable adequate bond between FRP and structural member at severe service conditions such as temperature and humidity. Epoxy-based adhesive is recommended for FRP applications at service temperature less than the T_g of the adhesive. Some modifications may utilize to extend slightly the usage of epoxy-based adhesive at temperatures approach or exceeded T_g of the adhesive with considerable care. Alternatively, cement-based adhesives are recommended for FRP applications at service conditions that limit the utilization of epoxy-based adhesives.

8. References

1. ACI 440, 2R-08 (2008). "Guide for the Design and Construction of Externally Bonded FRP Systems for Strengthening Concrete Structures". (Farmington Hills, MI: American Concrete Institute).
2. Jumaat, M.Z. and Alam, M.A.. (2006). "Problems Associated with Plate Bonding Methods of Strengthening Reinforced Concrete Beams". Journal of Applied Sciences Research, Vol.2, No. 10, pp. 703-708.
3. Alkhrdaji, T. (2015) "Strengthening of Concrete Structures Using FRP Composites". Structural magazine , available from : <https://www.structuremag.org/?p=8643>
4. fib TG9-3 (2007). "FRP reinforcement in RC structures." Technical Report: PP. 2-1, 2-2.
5. Bradley., J. Christensen., Jeremy Gilstrap and Dolan, Charles W. (1996). "Composite Materials Reinforcement of Existing Masonry Walls." Architectural Engineering June: pp. 63-70.
6. Saadatmanesh, H. (1997). "Extending Service Life of Concrete and Masonry Structures with Fibre Composites". Construction and Building Materials, Vol.1, No.5, pp. 327- 335.
7. Neale, KW (2000). "FRPs for structural rehabilitation: a survey of recent progress." Prog. Struct. Engng. Mater 2: pp. 135.
8. Gamage, J.C.P.H., Al-Mahaidi, R. and Wong, M.B. (2006). "Bond characteristics of CFRP plated concrete members under elevated temperatures." Composite Structures. Vol. 75, pp. 199-205.
9. Kalfat, R., and Al-Mahaidi, R. (2010). "Investigation into bond behaviour of a new CFRP anchorage system for concrete utilising a mechanically strengthened substrate." Composite Structures , Vol. 92, No.11, pp. 2738-2746.
10. Davalos, Julio F. (2005). "Characterization of Bonded Interfaces for Wood- Fibre Reinforced Polymer Composites." Abstracts of the Proceedings of 3rd International Conference on Advanced Engineered Wood Composites , Bar Harbor, ME, USA: 3 pp.
11. Ganda, A.K., Yeboahb, D., Khoramia,M., Olubanwoa, A.O., and Lumorc, R. (2018). "Behaviour of strengthened timber beams using near surface mounted Basalt Fibre Reinforced Polymer (BFRP) rebars", Engineering Solid Mechanics, Vol. 6, No.4, pp. 341-352.
12. Suzuki,H. (2005) "First application of carbon Fiber reinforced polymer strips to an existing steel bridge in Japan," Fifth Conference on Advanced Materials for Construction of Bridges, Buildings, and Other Structures, Maui, HI, Aug. 14-19, 2005, Engineering Conferences International, Brooklyn, NY.
13. Fawzia, S., Al-Madhaidi, R., Zhao, X.L. and Rizkalla, S. (2007). "Strengthening of circular hollow steel tubular sections using high modulus CFRP sheets." Construction and Building Materilas, Vol. 21, pp. 839-845.
14. Al-Mosawe, A., and Al-Mahaidi, R. (2014). "Bond characteristics between steel and CFRP laminate under impact loads ", 23rd Australasian Conference on the

- Mechanics of Structures and Materials (ACMSM23) Byron Bay, Australia, 9-12 December 2014, S.T. Smith (Ed.), pp. 489-494.
15. Lang, K. and Schumacher, A. (2010). " *Strengthening of masonry & metallic structures* ". The international Handbook of FRP composites in Civil Engineering , CRS Press, Taylor & Francis Group, LLC (2010), edited by Mannochehr Zoghi, Page 294.
 16. Martin Alberto Masuelli M.A. (2013). " *Introduction of Fibre-Reinforced Polymers – Polymers and Composites: Concepts, Properties and Processes*", Fiber Reinforced Polymers - The Technology Applied for Concrete Repair, DOI: 10.5772/54629. Available from: <https://www.intechopen.com/books/fiber-reinforced-polymers-the-technology-applied-for-concrete-repair/introduction-of-fibre-reinforced-polymers-polymers-and-composites-concepts-properties-and-processes>.
 17. The Fundamentals for Fiber-Reinforced Polymer (FRP) Strengthening. Available from:https://www.roadsbridges.com/sites/rb/files/MIS_3127%20RenewWrap%20Wihite%20Paper-WEB.PDF
 18. Chanda, M. (2006). " *Introduction to Polymer Science and Chemistry, A Problem Solving Approach*." (CRC Press, Taylor & Francis Group): p. 24.
 19. Cowie, J.M.G and Arrighi, Valeria (2008). Polymers: " *Chemistry and Physics of Modern Materials* ", Taylor & Francis Group.
 20. Lee, T. K. and Al-Mahaidi, R.(2008). " *An experimental investigation on shear behaviour of RC T-beams strengthened with CFRP using photogrammetry*." Composite Structures, Vol. 82, No. 2, pp. 185-193.
 21. Alzate, A., Arteaga, A., de Diego, A., Cisneros, D., Perera. R. (2013) " *Shear strengthening of reinforced concrete members with CFRP sheets*" Mater. Construcc., Vol. 63, No.310, pp. 251-265.
 22. Huy, Ph. and Al-Mahaidi, R. (2006). " *Experimental investigation into flexural retrofitting of reinforced concrete bridge beams using FRP composites*." Composite Structures, Vol. 66, No. 1-4, pp. 617-625.
 23. Yang, J., , Haghani, R. , Al-Emrani, M. (2018). " *Flexural FRP Strengthening of Concrete Bridges Using an Innovative Concept*". 9th International Conference on Bridge Maintenance, Safety and Management (IABMAS 2018), Melbourne, Aistralia, 7 pages.
 24. Hii , Adrian and Al-Mahaidi, R. (2006). " *Experimental Investigation on Torsion Behavior of Solid and Box- Section RC Beams Strengthened with CFRP Photogrammetry*." Composites for Construction, Vol. 10, No.4, pp. 321-329.
 25. Al-Bayati, G., Al-Mahadi, R. and Kalfat, R. (2017). " *Torsional strengthening of RC Beams using NSM FRP technique with CFRP Rope and mortar*". APFIS2017 - 6th Asia-Pacific Conference on FRP in Structures Singapore, 19-21st July 2017, 6 pages.
 26. Yost, J.R., Gross, Sh.P., Deitch, M.J. (2007). " *Fatigue Behavior of concrete beams strengthened in flexural with Near surface mounted CFRP*". FRPRCS-8 University of Patras, Patras, Greece, July 16-18, 2007, 8 pages.

27. Vůjtěch, J., Ryjáček, P., and Vovesný, M. (2017). "Application of carbon FRP for fatigue strengthening of old steel structures", IOP Conference Series: Materials Science and Engineering, Vol.175 , 6 pages.
28. Gadve, S., Mukherjee, A., and S. N. Malhotra, S.N. (2010). "Corrosion Protection of Fiber-Reinforced Polymer-Wrapped Reinforced Concrete". ACI Materials Journal/July-August 2010,NO.4, Vol.107, pp. 349-356.
29. Bisby, L.A. (2004). "An Introduction to FRP Strengthening of Concrete Structures." ISIS Educational Module No.4: pp.4.
30. Fiber-Reinforced Polymer (FRP) Simpson -Composite Strengthening Systems , available:<http://www.foundationperformance.org/pastpresentations/BohrenPres-Slides-11Oct17.pdf>
31. Presentation on theme: "An Introduction to FRP-Strengthening of Concrete Structures", (2010), ISIS Educational Module 4: An Introduction to FRP-Strengthening of Concrete Structures, ISIS Canada ISIS EC Module 4, available online <https://slideplayer.com/slide/232965/>
32. FRP Structural Strengthening-NSM & Externally Bonded, available online on: <http://www.aslanfrp.com/StructuralStrengthening/>
33. Ueda, T., and Dai, J. (2005). "Interface bond between FRP sheets and concrete substrate: properties, numerical modeling and roles in member behaviour." Progress in Structural Engineering Materials banner,. Vol.7, No.1, pp. 27-43.
34. Myers, J.J., Murthy, S.S. and Micelli, F. (2001). "Effect of combined environmental cycles on the bond of FRP sheets to concrete." Proceedings of the International conference on composites in construction, Portugal: 55-59.
35. Nigro, E., Manfredi, G., Cosenza, E. and Zappoli, M. (2006). "Effects of High Temperature on the Performances of RC Bridge Decks Strengthened with Externally Bonded FRP Reinforcement". *Proceedings of the 2nd International Congress: Session 12 – Response of concrete structures to high temperatures and fire*. Naples, Italy: 1- 12.
36. Al-Shawaf, A. (2010), Characterization of bonding behavior between wet lay-up carbon fibre reinforced polymer and steel plates in double-strap joints under extreme environmental temperatures, PhD thesis, Department of Civil Engineering, Monash University, Melbourne, Australia.
37. Savvilotidou, M., Vassilopoulos, A.P., Frigione, M., Keller, T. (2017) "Development of physical and mechanical properties of a cold-curing structural adhesive in a wet bridge environment". *Construction and Building Materials*, Vol. 144, pp.115–124.
38. Camata, G., Pasquini, F., and Spacone, E. (2007). "High Temperature Flexural Strengthening with Externally bonded FRP reinforcement." FRPRCS-8 University of Patras, Greece, pp. 1-10.
39. Klamer, Ir. E.L. (2006). "The influence of temperature on concrete structures strengthened with externally bonded CFRP." Report : O-2006 (rev. 1) (Unit Structural Design & Construction Technology -SDCT (TU/e)):1-98.

40. Gamage, K.. (2009). "*Cyclic Temperature and Humidity Effects on Bond Between CFRP and Concrete*". PhD thesis, Department of Civil Engineering, Monash University, Melbourne, Australia.
41. BASF Construction Chemicals , Australia. Pty Ltd "*MBrace Saturant*." Technical data sheet, BASF Construction Chemicals,7 Kingston Town Close, Oakleigh, Australia.
42. Al-Safy R., Al-Mahaidi R., Simon G. (2009). "*Bond performance of CFRP strengthening of concrete members using nanoclay modified adhesives*". In: Proceedings of 09 PCI annual convention/exhibition & national bridge conference, San Antonio, TX, USA; 2009.
43. Al-Safy, R., Al-Mahaidi, R., and Simon G. P., and Habsuda J. (2012). "*Experimental investigation on the thermal and mechanical properties of nanoclay-modified adhesives used for bonding CFRP to concrete substrates*". Construction and Building Materials, Vol. 28, No.1, pp. 769-778.
44. Al-Safy, R. (2012), "*Development of Modified Adhesives for Bond between CFRP and Concrete subjected to Harsh Environmental Conditions*", PhD thesis, Department of Civil Engineering, Monash University, Melbourne, Australia, page 71.
45. Gamage, J.C.P.H, Wong, M.B. and Al-Mahaidi, R. (2005). "*Performance of CFRP strengthened concrete members under elevated temperatures*". Proceeding of the International Symposium on Bond Behaviour of FRP in Structures (BBFS), pp.113-118.
46. Materials properties of MasterBrace[®] ADH4000, available from :
<https://assets.master-builders-solutions.basf.com/en-mne/basf-masterbrace-adh-4000-tds.pdf>
47. Products data: <https://www.mouldlife.net/araldite-420-ab-14kg-kit-2841-p.asp>
48. Materials properties for Araldite[®] 420, available from
<http://www.chemcenters.com/images/suppliers/169257/Araldite%20420.pdf>
49. Hosseini, A., Barbezat, M., Michels, J., Ghafoori, E., Motavalli, M., and Terrasi G. (2018). "*Glass transition evaluation of commercially available epoxy adhesives for strengthening of steel structures with bonded CFRP plates*". 9th International Conference on Fibre-Reinforced Polymer (FRP) Composites in Civil Engineering (CICE 2018), Paris 17-19 July 2018.
50. Structural strengthening with products of Sika, available from:
<https://www.sika-distributor.com/sika-structural-strengthening.php>
51. Products data , available from :
https://scdcs.com.au/documents/ST_SE_Sikadur30_tds.pdf
52. Michels,J; Windmann,R.; Czaderski,C.; Allahvirdizadeh R.; Motavalli, M. (2015). "*Glass transition evaluation of commercially available epoxy resins used for civil engineering applications*". Composites Part B , Vol. 77, pp. 484-493.
53. Hernandez, D.A., and Orlandi, M.O. (2016). "*Mechanical Properties of composites materials Sikaarbondur512, SikaDur30 and SikaDur330*" .22^o CBECiMat - Congresso Brasileiro de Engenharia e Ciência dos Materiais 06 a 10 de Novembro de 2016, Natal, RN, Brasil, pp.3504-3515.

54. Al-Safy, R., Al-Mahaidi, R., Simon, G.P. (2013). "A study of the use of high functionality-based resin for bonding between CFRP and concrete under harsh environmental conditions". *Composite Structures*, Vol. 95, pp. 295–306.
55. Al-Safy, R. (2012). "Development of Modified Adhesives for Bond between CFRP and Concrete subjected to Harsh Environmental Conditions". PhD thesis, Department of Civil Engineering, Monash University, Melbourne, Australia, page 74.
56. Faleh, H., Shen, L., and Al-Mahaidi, R. (2010). "Fabrication and Mechanical Characterization of Carbon Nanotubes-Enhanced Epoxy". *Advanced Materials Research*, Vols. 168-170, pp 1102-1106.
57. Faleh, H., Al-Mahaidi, R., Shen, L. (2012). "Fabrication and characterization of nano-particles-enhanced epoxy". *Composites: Part B*, Vol. 43, pp. 3076–3080.
58. Al-Safy, R., Al-Mahaidi, R., Simon, G.P., Habsuda, J. (2012). "Experimental investigation on the thermal and mechanical properties of nanoclay-modified adhesives used for bonding CFRP to concrete substrates". *Construction and Building Materials*, Vol. 28, pp. 769–778.
59. Al-Safy, R.A., Al-Mahaidi, R., Simon, G.P., and Habsuda, J. (2014). "Thermo-Mechanical Characterization of VGCF Modified Adhesive for Bond between CFRP and Concrete Subjected to Combined Effect of Concrete Subjected to Combined Effect of Temperature and Humidity". *Advances in Structural Engineering*, Vol. 17 No. 12, pp. 1817-1823.
60. Abdulla, A.I. (2016). "Thermal properties of sand modified resins used for bonding CFRP to concrete substrates". *International Journal of Sustainable Built Environment* No.1, Vol. 5 , pp. 176–182.
61. Abdulla, A.I., Abdul Razak, H., Salih, Y.A., Ali, M.I. (2016). "Mechanical properties of sand modified resins used for bonding CFRP to concrete substrates". *International Journal of Sustainable Built Environment* , Vol. 5, pp. 517–525.
62. Hashemi S, Al-Mahaidi R. (2009). "Cement based bonding material for FRP strengthening of concrete structures". *Proceedings of the International Symposium on Fibre Reinforced Polymer Reinforcement for Concrete Structures (FRPRCS-9)*, Sydney, Australia, 2009.
63. Hashemi S, Al-Mahaidi R. (2010). "Investigation of bond strength and flexural behavior of FRP strengthened RC beams using cement-based adhesives". *Structures Congress* , May 12-15, Orlando, Florida, United States, PP. 689-700.
64. Al-Abdwais, A., and Al-Mahaidi, R. (2016). "Modified cement-based adhesive for near-surface mounted CFRP strengthening system". *Construction and building materials*, Vol.124, pp. 794-800.
65. Sveinsdóttir, S. L. (2012). "Experimental research on strengthening of concrete beams by the use of epoxy adhesive and cement-based bonding material". Master Thesis, Civil Engineering with Specialization in Structural Design and Concrete Technology, School of Science and Engineering, Reykjavík University, Iceland.
66. Al-Safy, R., Al-Mosawe, A., Al-Mahaidi, R. (2019). "Utilization of magnetic water in cementitious adhesive for near-surface mounted CFRP strengthening system". *Construction and Building Materials*, Vol.197, pp. 474-488.

67. Mohammed, A., Al-Saadi, N.T.K and Al-Mahaidi, R. (2017). "*Utilization of Graphene Oxide to Synthesize High-Strength Cement-Based Adhesive*". Journal of Materials in Civil Engineering, Vol.29, No.4, 7 pages.
68. Vasconcelos, E., Fernandes, S., Aguiar, B., Pacheco-Torgal, F. (2011). "*Concrete retrofitting using metakaolin geopolymer mortars and CFRP*". Construction and Building Materials , Vol 25, No. 8, pp.3213-3221.