

Structures and buildings rehabilitated with FRP: durability issues and challenges for materials advancements

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ABSTRACT: The use of fiber reinforced polymer (FRP) composites for the rehabilitation of buildings or infrastructures is increasingly becoming an effective and popular solution, being able to overcome some of the drawbacks experienced with traditional interventions and/or traditional materials. The knowledge of long-term performance and of durability behavior of FRP, in terms of their degradation/aging causes and mechanisms taking place in common as well as in harsh environmental conditions, still represents a critical issue for a safe and advantageous implementation of such advanced materials.

1 INTRODUCTION

Fiber reinforced polymers (FRP) are already used in the rehabilitation/strengthening of built infrastructures realized in concrete and in masonry, although the lack of fundamental information on their long-term behavior if exposed to different, possibly severe, environments somehow limits a wider exploit of such systems [Motavalli, and Czaderski (2007)].

Their good success is due to a variety of different properties displayed by FRP, such as high specific strength and specific stiffness, high durability against corrosion, lower weight, ease of installation and reduced manufacture time. All these latter properties make FRP preferred to traditional construction materials, such as steel and concrete. Furthermore, a wide choice of materials (polymeric resins and fibers) is commercially available: different structures/components can be created from their combination, with tailored anisotropy and geometry able to satisfy the project requirements. Nevertheless, there are several aspects of this relatively new technology that still need further research and development, in particular concerning their durability.

Existing data on the durability of FRP's employed in this specific field are still not organically collected and rationalized. Discrepancies between results obtained by different durability studies have been even observed and possibly attributed to different materials, processing or conditioning conditions employed (for instance: different times elapsed before the execution of durability tests), being all fundamental information's for a complete understanding of the effects of the external environment on properties of materials and for an accurate prediction of their behavior over their lifetime. This uncertainty, on the other hand, hampers the enormous potential of composites in the rehabilitation of constructions, since the acceptable lifetime of products employed in this field should be in the order of one hundred years [Bakis et al (2002)].

Then, from one side, there is a need to find reasonable tools not only for the prediction of change in properties of these materials with time when hardened (i.e. cured) in different but realistic thermo-hygrometric conditions but also for the determination of the remaining service-life of a structure working in widely variable service conditions. From another side, the implementation of materials, i.e. the development of long-lasting matrices/adhesives for FRP, is compulsory. For both issues, although the efforts of research are rather active worldwide, no conclusive solutions have been identified yet.

2 COMPONENTS FOR FRP

The performance and durability of FRP's employed in rehabilitation of civil infrastructures mainly depend on the choice of constituent materials to manufacture the FRP, on the process used to manufacture and to apply the composite, on the load regime and on the kind/level of the environmental exposure. FRP composites for such applications are typically composed by continuous fibers (carbon, glass, aramid) embedded in a thermosetting resin matrix (epoxy, vinyl ester or polyester resins) that holds together the fibers and transfers the load between them. A thermosetting resin (the same composing the matrix of FRP or a different one) is also employed to act as adhesive between the FRP and the (concrete/masonry) substrate. The chemical nature of the matrix/adhesive for the composite as well as the conditions used to set and harden it will have a decisive influence on the performance and behavior of the FRP and on the effectiveness of the whole intervention.

The behavior and integrity of an element reinforced by FRP depend not only on the properties of the individual materials but also on the performance of the FRP-adhesive and adhesive-substrate interface bonds. Therefore, the reliability of the rehabilitation intervention using externally bonded FRP materials depends to a large extent on the bond between the reinforcement and the substrate and, therefore, on the ability to transfer the stresses at the interface.

FRP can be applied following two different procedures: a) the precured FRP prepregs are adhesively bonded as prefabricated elements to the concrete (or masonry) substrate; b) the composite is applied through a "wet lay-up" of fabrics directly onto the substrate.

In the first case, the application of prefabricated (often pultruded) laminates ensures the use of precured materials, produced in factories through industrially controlled processes, thus achieving a high level of uniformity in the final product that will display high properties. On the negative side, prefabricated FRP elements are less flexible and not adaptable for unpredicted configurations that can be found in the field applications (i.e. the confinement of cylindrical concrete columns, the strengthening of arches and vaults in masonry constructions). Moreover, the application of a precured FRP element to a concrete/masonry substrate is carried out by means of a thermosetting adhesive applied and hardened on site. This, therefore, implies the introduction of an adhesive interphase between the already cured FRP and the substrate [Karbhari (2002)].

The use of the wet lay-up technique (i.e. the FRP is applied and formed *in situ*) provides enormous flexibility, since the pre-impregnated fabrics can closely follow the geometrical configuration of the structure to be rehabilitated. Moreover, the bond between the FRP and the substrate is guaranteed by an adhesive resin that is very similar to the matrix of the composite, i.e. it is able to form a continuum between the FRP and the substrate. The lack of a careful

control of the curing process, however, leads to a significant higher level of variation in the final performance of the intervention.

In both the described techniques, the weakest link is represented by a cold-cured thermosetting resins, often epoxy, used as adhesive in the first case and as matrix/adhesive in the second one. While the resin is responsible for the overall integrity of the rehabilitated structure, since it must assure an effective stress transfer among the structure and the FRP reinforcement, it can undergo both chemical and physical degradation by environmental actions and mechanical stresses.

2.1 Cold-cured thermosetting (epoxy) resins

Among the polymers employed in this field, epoxy resins are without a doubt the most used for their excellent properties. They can be formulated into low viscosity systems which “cure” (i.e. form cross-links throughout the structure and, as a consequence, harden) at room temperature with a minimal shrinkage; when correctly formulated and cured, they exhibit a good combination of mechanical properties and chemical resistance towards environmental agents; compared to other resins, cured epoxy systems are known to have excellent adhesion to a broad range of substrates and reinforcing materials. For the strengthening/repairing applications through FRP’s, epoxies are frequently preferred to both vinyl ester and unsaturated polyester resins, both characterized by an excessive shrinkage during curing, with the possible formation of micro-cracks or micro-gels, resulting in micro inhomogeneities and incomplete polymerization [Mays, and Hutchinson (1992)]. Unsaturated polyester resins, in addition, display high susceptibility to moisture and low bonding efficiency in damp or wet conditions and when exposed to alkaline environments.

The polymerization (curing) reactions of an epoxy (part A of the system), giving rise to a rigid network-type structure, occurs in presence of a suitable curing agent (hardener, part B of the system) and is favored by heat/radiations, depending on the ingredients (Part A and B) and on the curing mechanism. In particular, the kind and amount of the harder are selected on the basis of the resin and on the available curing conditions and have both an appreciable influence on the final performance of the cured epoxy.

For economic and practical reasons, the resins used as matrix and/or adhesive for FRP components employed for the rehabilitation of constructions are “cold-cured” types, typically based on bis-phenolic epoxies, cured at ambient temperatures on site with the addition of aliphatic amines [Hollaway (2010)]. Unlike the epoxy resins employed as matrices for FRP and adhesives in the much more demanding aeronautical/aerospace or automotive industries (that are typically cured employing curing cycles characterized by very high temperatures with the addition of curing agents, i.e. aromatic amines or anhydrides, active only at these temperatures), epoxy resins used in the construction industry, where large surfaces must be strengthened by an FRP often formed on field (i.e. *in situ*), are cross-linked without the possibility to effectively control and keep constant the manufacturing procedures as well as the (outdoor) conditions for the processing (hardening) of the adhesive/matrix resin. Providing any kind of heat sources over the large areas required for the described applications, in fact, is very difficult and prohibitively expensive.

The main consequences of a cure at ambient (often not-constant and uncontrolled) temperatures of epoxy adhesives are: i) long curing times (in the order of weeks) are necessary to achieve sufficient mechanical properties, the lower the curing temperature, the longer the curing time; ii) the curing (cross-linking) reactions taking place at ambient temperatures are often not

completed due to kinetic restrains; iii) a moderate glass transition temperature (T_g), in practice never greater than 65–70°C, is attainable by these systems, particularly if the curing of the resin occurs at low winter temperatures [Frigione et al. (2006a); Frigione et al (2006b); Frigione, and Lettieri (2008); Sciolti et al (2010); Michels et al (2015); Savvilotidou et al (2017a)]. In addition, the absorption of external water (for example, as atmospheric moisture or rain) produces a decrease in the initial T_g of the resin, with consequent negative effects on mechanical and adhesive properties.

When the T_g is approached and surpassed by an even mild external temperature, the adhesion between the FRP element and the substrate (concrete/masonry) is likely to be reduced. Furthermore, the exposure to moderate temperatures (above the T_g) of not fully cross-linked thermoset polymers can promote their post-cure. The post-cure is usually reflected in increment of T_g and of stiffness of the resin [Silva et al (2016)]. However, T_g 's never exceeding 75°C are generally found for an epoxy/aliphatic amine couple, even if the cross-linking of the resin has been completed through a post-cure procedure [Savvilotidou et al (2017a)]. These systems, therefore, operate in a non-equilibrium state, with the properties evolving in time and as a consequence of the variable external conditions.

2.2 *Fibers and Configuration of FRP*

Referring to the fibers, carbon is the most commonly fiber used in FRP systems for rehabilitation applications where exposure to aggressive environments is expected. Carbon fibers are, in fact, considered to be inert to the most of the environments that can be found in civil infrastructure applications. The less expansive glass fibers, on the other hand, are more susceptible to harsh environments, especially moisture/alkaline ones, the latter producing loss in toughness, strength and embrittlement. Nevertheless, the durability of glass fibers upon exposure to typical outdoor applications is still satisfactory, especially if they are suitably protected against harsh agents by tailored sizing coatings, also acting as a bond-enhancement. Durability of glass fiber reinforced polymers (GFRP) can be even improved by using hybrid glass-carbon fabrics.

Other parameters have a crucial influence on the behavior of the FRP-rehabilitated structures, i.e. the number of composite plies, the direction and disposition of fibers in each ply and their weave pattern. The configuration of FRP components, in fact, must be properly designed taking into account the complex system of forces to which the structure rehabilitated with the FRP's will be subjected over its lifetime.

3 DURABILITY OF FRP'S IN COMMON OR HARSH ENVIRONMENTS

The environmental conditions to which FRP's for rehabilitation of structures are more frequently exposed during their service life are neither constant nor predictable and depend on several parameters, such as: the latitude and the altitude of the site, the season, the distance from sea, the local weather. Environmental factors can severely affect the performance in service of each element composing the FRP and of the whole FRP, even after a short time from its installation, due to specific processes, either reversible or permanent, taking place between the external agents and the materials composing the FRP. In particular, the role of the matrix/adhesive on the behavior of the FRP system is crucial. Due to the peculiarities of cold-cured epoxy resins, in fact, the environmental conditions most frequently encountered in civil infrastructures may severely affect the performance of wet lay-up type FRP and more generally the integrity of FRP-to-FRP and FRP-to-substrate bonds.

The service conditions characteristic of the common outdoor applications include: atmospheric humidity, rain, solar (UV) radiations, large variations in temperature, freeze-thaw regimes, acid rain, sea-water, deicing chemicals, alkaline environment when in the proximity of Portland cement concrete, sustained loads. Polymer composites can be also accidentally exposed to extreme environments, such as: fire, earthquake, explosive blasts.

The presence of humidity in the air, either in the form of moisture or actual water through rain, is probably the most harmful environment that can be encountered by matrices and adhesives employed in FRP's for civil engineering applications. Epoxy resins are able to absorb substantial amounts of water due to the presence of polar groups able to attract water molecules. The ingress of moisture over time is particularly significant if the polymer is permanently immersed in water, or salt or alkaline solutions, or if it is exposed to deicing salt solutions. An excessive penetration of water is generally considered harmful since it leads to a reduction in stiffness (even halved) and strength of the resin, with a consequent remarkable reduction of the Tg of the resin and a marked decrease of load-bearing capacity, due to plasticization effects [Frigione et al (2006a), Frigione et al (2006b), Savvilotidou et al (2017b)].

When the service temperature approaches the Tg of the resin, a dramatic decrease (up to 70%) of the (mechanical, adhesive) properties of the cold-cured resin occurs: approaching the Tg, the behavior of the resin drastically changes from that of a solid adhesive, able to effectively bond two different materials, to that of a soft material, unable to guarantee the stress transfer between the same materials. An even moderate service temperature, therefore, is able to reduce appreciably the adhesion strength to concrete, i.e. by over 80% at 50°C, as well as the fatigue resistance [Aiello et al (2002)]. As the temperature increases, the mechanism of failure occurring in the samples changed, from predominantly concrete failure to mixed failure of epoxy and at the interface. The service temperatures encountered in practice by these systems may be close or even higher than their Tg: even if the air temperature measured in Mediterranean areas usually does not exceed 40-45°C even in summer, the temperature of a surface irradiated by sun can be appreciably higher, i.e. even greater than the Tg of the matrix/adhesive resin.

The detrimental effects of water or moisture and of moderate temperatures on the performance of a cold-cured epoxy resin are reproduced also on its behavior as adhesive. It was found, in fact, that both agents are able to reduce appreciably the bond properties between an epoxy adhesive and concrete elements. As a general conclusion, when using the cold-cured resins, due to their moderate Tg, attention must be given to the site temperature: the (maximum) environmental temperature under working conditions should be at least 20°C below the expected glass transition temperature of the resin [Hollaway (2010)].

Referring to the influence of water/moisture on performance of FRP, apart from the kind of matrix resin and fibers used (carbon vs. glass), it mainly depends on the configuration of fabrics and on the direction of application of the load. In the case of in-plane tensile tests performed on unidirectional single ply wet lay-up FRP, for instance, only a negligible influence of presence of water was found [Sciolti et al (2010)]. On the other hand, in laminates composed by several plies, the presence of water at the interface between the adjacent layers is likely to be severely harmful. Since the matrix resin is also responsible for the adhesion between plies, greater reductions in tensile strength are found for thicker specimens, i.e. composed by a large number of plies. Similarly, the presence of water/moisture at the adhesive/fibers/substrate interfaces is detrimental when the FRP is applied to a concrete/masonry substrate [Dai et al (2010)].

Severe degradation in FRP properties occurs upon exposure to freeze-thaw regimes due to the stiffening and embrittlement of the matrix, with possible formation of micro-cracks. Fiber-matrix debonding and a local loss of adhesion strength towards substrate may take place due to the difference in coefficients of thermal expansion. Reductions in tensile strength and interlaminar fracture toughness are generally observed after freeze-thaw repeated cycles. The loss in strength is even more severe when the thaw regime is performed in saline environments. Seawater, deicing salts, alkaline and acid solutions are particularly harmful for AFRP (aramid fiber reinforced polymers) and GFRP, producing in both damage at the fiber/resin interface and the degradation of the glass fibers in GFRP. The tensile properties of CFRP (carbon fiber reinforced polymers) are scarcely affected by immersion in alkaline and acid solutions, while their flexural and interlaminar characteristics are affected by both chemicals.

A part from the degradation of bond performance, as in the case of exposure to elevated temperatures already discussed, polymer composites display a huge vulnerability against fire, since resins are organic materials mainly composed of carbon and hydrogen, both highly flammable. The performance and behavior of a repaired concrete beam under fire depend also on the type of cracks, repaired using epoxy, and on the extent of repair [Plecnik et al (1986)]. In addition, severe health hazard derived from polymers and composites in a fire accident is generated from the toxic combustion products created during burning of materials.

In order to reduce the fire hazards in FRP, therefore, it is recommended to: i) provide thermal protection for structures on site; ii) to introduce flame retardant agents (i.e. halogen based) into the resin formulations; iii) or to apply a protective intumescent coating on the surface of the manufactured composite [Hollaway (2010)].

Although fillers like aluminum or magnesium hydroxides are among the cheapest and effective fire retardant agents, they significantly deteriorate the mechanical and electrical properties and the rheology of the pristine resin. Halogen additives, on the other hand, are among the most effective agents for reducing the rate of heat release of phenolic, epoxy or bismaleimide resins; however, a high loading of such additives is often required, with associated cost, processability and property penalties.

When phosphorous-based flame retardants are purely blended with epoxy resins, they, not being chemically bonded to the network, can migrate toward the surface of components before cross-linking, reducing the glass transition temperature of the cured resin by acting as plasticizer [Frigione et al (2003)]. On the other hand, reactive organo-phosphorus compounds show more excellent flame retardant efficiency: the reactive flame retardants can be directly incorporated into the backbone of the epoxy network, either as a part of the curing agent or the epoxy itself, exploiting their capability to the best.

4 DEVELOPMENT OF IMPROVED MATERIALS

The use of nano-structured polymers as matrix/adhesive for FRP is expected to become a realistic alternative to traditional polymeric products also in civil engineering field, due to their superior properties and greater durability against moisture, temperatures, harsh environments, fire. Nano-structured polymers are typically produced as nano-composites, based on preformed nano-sized inorganic (silica, clay, carbon nano-tube) particles dispersed of into the resin, or organic-inorganic hybrid materials, where the two different nano-phases are strictly interconnected at a nano-scale level. The efforts of academic and industrial research in this field must be mainly devoted to the development of more durable thermosetting matrix/adhesive resins at affordable costs, also able to achieve a stable thermodynamic state after short curing

times in different thermo-hygrometric conditions, with a consequent improvement in the long-term performance of FRP's. The formulation strategy of these systems, then, must be aimed at increasing the T_g and the elastic modulus in the rubbery region of the resin as well as at improving their performance under different environmental regimes, irrespective to the curing conditions [Lionetto, and Frigione (2015)].

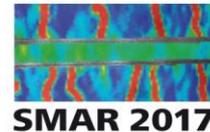
At the present time, however, the production processes of such nano-structured polymers are still complicated and expensive to be conveniently applied in the construction industry.

5 CONCLUSIONS

Due to the heavy concerns about durability of FRP materials intended for rehabilitation of constructions, in common as well as in harsh environments, research should be forced to the development of new epoxy resins, still able to set and cure at ordinary temperatures and humidity levels but displaying much greater T_g values, lower curing times and less durability concerns than those commercially available at the present time. Despite to the described drawbacks, these resins still represent a viable solution to assemble and/or to apply FRP repairing elements. These latter, in turn, display several advantages over traditional materials in terms of high strength-to-weight and stiffness-to-weight ratio's, great versatility, shorter times for the interventions and, consequently, of activities interruption, with a consequent reduction of the overall costs. Maintenance operations are also cut when polymer composites are applied in substitution of traditional construction materials. The collaboration between experts possessing different scientific background and expertise is, therefore, greatly encouraged for a stronger deeper comprehension of durability phenomena and a faster successful identification of practicable solutions.

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