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Review

Surface Modification of Glass Textile for the Reinforcement of a Cement-Based Composite: A Review

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Featured Application: Authors are encouraged to provide a concise description of the specific application or a potential application of the work. This section is not mandatory.

Abstract: The mechanical properties of cement-based composites reinforced with glass textile are strongly affected by the low ability of the inorganic matrix to penetrate within the single filaments, and by the low durability of the fibers in an alkaline environment. Over the last decades, different studies have investigated the possibility to improve the mechanical properties and the durability of this class of composites by modifying the surface of the reinforcement, mainly using different types of organic or inorganic coatings. Although different solutions have been proposed, the feasibility of applying these techniques strictly depend on the final application of the composite. This review aims to give an overview of the different methods that have been proposed in the literature and to highlight advantages and drawbacks.

Keywords: glass fibers; surface modification; GRC; FRCM; TRC; cement-based composite; interface; coatings

Citation: Bompadre, F.; Donnini, J. Surface Modification of Glass Textile for the Reinforcement of a Cement-Based Composite: A Review. *Appl. Sci.* **2021**, *11*, 2028. https://doi.org/10.3390/app11052028

Academic Editor: Christina Scheffler

Received: 25 December 2020
Accepted: 12 February 2021
Published: 25 February 2021

1. Introduction

Thanks to their highly attractive performance to price ratio, glass fibers are nowadays one of the most widely employed reinforcement for the production of composite materials. Glass reinforced polymers (GRP) account for more than 95% in terms of volume of the total production of reinforced polymers, and their wide applications range from the construction of wind turbine to the production of consumable goods [1]. Glass can be used in the form of continuous filament woven in textiles or meshes, or as short fibers dispersed in the matrix. The great success of glass fiber as reinforcement for GRP has prompted the research and the development of manufacturing processes and technological instruments for their production, so that nowadays a wide scientific literature and technological know-how is available on this topic. Particularly, both academia and industry have put great effort into investigating the fiber/matrix interface as the key factor for controlling the stress transfer between matrix and reinforcement and determinate the composite mechanical behavior. Modification of fiber surface for tailoring the fiber-matrix interface and, as a consequence, the resulting properties of the composite, is a common practice that has been widely employed for the development of high technological materials [2–4]. For this purpose, a great variety of instruments have been developed, including: application of sizing and coating [1,3,5], polymer grafting [4] and plasma treatments [2,6]. Although more than 80% of glass filament or spun glass fiber yarns are used to reinforce plastics [7] since the beginning of the 1960s glass fibers have been employed also for the reinforcement of cement-based matrices [8]. The first applications mainly made use of discontinuous (or short) fibers randomly dispersed in the matrix. More recently, cement-based composites have been developed, in which the reinforcement is applied in the form of continuous multi-filament textile or fabric. These composites take the name of Textile Reinforced Concrete (TRC) and

Fabric Reinforced Cementitious Matrix (FRCM) systems. Both systems make use of the same kind of reinforcements, which are made up of continuous multi-filament strands, assembled in different geometry by various means such as weaving, knitting, tufting, felting, braiding, or bonding. Application can range from the production of composite for the rehabilitation and reinforcement of concrete and masonry structures [9–13] or the production of high performance cementitious composites with unique tensile strength and ductility [8,14,15]. Several studies have been conducted on the use of inorganic based composites as external reinforcement of masonry walls subjected to in-plane [16] and out-of-plane [17] loads, confining of masonry and concrete columns [18,19], arches [20] and strengthening of concrete structures [21,22]. Of course, the stress transfer at the fiber–matrix interface is fundamental also for this class of composites. However, along with the stress transfer between the matrix and the reinforcement, the mechanical properties of TRC and FRCM also depend on the stress transfer between the single filaments that make up the reinforcement. Indeed, tensile tests conducted on TRC and FRCM highlight that the composite strength is much lower than that of the reinforcement, because only the external filaments of the yarns are directly involved in the stress distribution. This phenomenon is due to the big dimensions of the cement grains, compared to the small size of the spaces between the filaments, that account for an incomplete embedding of the yarn in the matrix. As a consequence, only the outer filaments are directly anchored to the surrounding matrix, and since the low friction between the filaments is not sufficient to redistribute the stress between them, the composite fails when the outer filaments reach their ultimate tensile strength, while the inner filaments slip within the yarn [11,12,14,23,24]. It should be stressed out that, unlike carbon fibers, glass fibers have good adhesion to cement-based matrices [25]. Therefore, the first goal of any surface modifications introduced is not to improve the adhesion to the matrix, but rather to improve the stress transfer between the fibers. This dual necessity of improving the stress transfer between the single filaments in the yarn, while maintaining a good interfacial adhesion with the cementitious matrix, it is often a challenge in the development of TRC and FRCM composite materials. Furthermore, great care must be taken when using glass fibers in cement-based matrices due to the high alkalinity of the matrix. To address this issue, fibers produced for cement-based composites, known as alkali-resistant glass fiber (ARG), are manufactured by adding a high percentage of zirconia (typically 15–23% by weight) [1]. However, it has been proved that, although ARG fibers are less affected by alkaline attack and the loss in mechanical properties over time is reduced compared to glass-reinforced concrete (GRC) with E-glass, they are not immune to chemical corrosion in OH^- rich environments [26–28]. The direct chemical attack on the fibers is not the only factor influencing the durability of GRC over time. Some of the chemical reactions responsible for the curing of the matrix are reported to modify the fiber–matrix interface, also affecting the mechanical behavior of the composite [29,30]. Because of the peculiar chemical-physical conditions that glass fabric embedded in the cementitious matrix has to withstand, surface modifications of glass fibers for cementitious composites must fulfill specific requirements. The increase of the stress transfer between the filaments, and the improvement of the glass fibers durability are the two most important aspects that need to be addressed to improve the properties of these composite systems. However, for practical applications other requirements should also be taken into consideration. For example, fabrics employed for the reinforcement of existing structures with complex geometry have to be enough flexible to be easily adapted to the substrate. Moreover, protect the textile from external abrasion can prevent the reinforcement to be damaged when handled, making easier its application. In order to address these requirements, different coatings have been successfully employed. Polymeric coatings are the first and most widely employed ones, but more recently inorganic coatings have also been proposed. Alternatively, some studies investigated the possibility to modify organic coatings with nanoclay particles to improve the chemical interaction of the polymer with the matrix and to enhance the durability in alkaline environments. The aim of this review is to present the different methods that have been proposed for the modification of glass textiles employed in cement-based composites, and to give an overview of their main advantages and drawbacks.

2. FRCM and TRC

Before presenting the techniques reported in the literature for the modification of textile employed in cement-based composites, this chapter wants to give a short overview on FRCM and TRC composites, to explain their main differences and clarify some terms that will be further used in the paper. Naaman define TRC as "a type of reinforced concrete commonly constructed of hydraulic–cement matrix reinforced with several layers of closely spaced continuous 2D textiles, or one or several layers of 3D textiles" [31], while FRCM has been defined in the ACI 549 as "a composite material consisting of one or more layers of cement-based matrix with a maximum organic content of 5%, reinforced with dry fibers in the form of open mesh or fabric. The cement-based matrices are typically made of combinations of Portland cement, silica fume, and fly ash as the binder" [32]. Since these composites are conceptually similar, literature studies conducted on both TRC and FRCM composites are reported, considering them within the class of composite materials with cementitious matrices. However, the reader should keep in mind that usually TRCs are associated with new industrial products, while FRCMs have been specifically designed for the repair and rehabilitation of concrete and masonry structures. This is important, on one hand, because of the different specific needs that the composite should address and, on the other hand, because of the difference in the inorganic matrix employed. Indeed, TRCs usually make use of the so-called fine concrete matrix, where the binder used is always a hydraulic-cement and the cured matrix owns high compression and flexural strength [33]. FRCM systems are designed for the rehabilitation of existing structures, which also includes masonry constructions, where high performance concrete matrix is not required, and mortars with much lower mechanical properties are employed. Particularly for the rehabilitation of historical structures, the use of lime-based mortar is recommended, which besides having different mechanical properties also has a different curing mechanism than the cement-based matrix [34,35]. However, both systems can be reinforced with continuous multi-filament glass fibers assembled in textiles or fabrics. The continuous strands of fibers, that make up the textile reinforcement, are called yarns. In the spun yarn production, the sliver that has been drafted, twisted, doubled and redoubled is called roving, which can be considered as an intermediate element between sliver and yarn. A more extended explanation of textile terminology can be found in [36]. Unfortunately, the terminology employed in different studies from the literature is not always univocal. As far as possible, in the following chapters the same names reported by the authors will be used. However, both yarn and roving should be considered as a bundle of multi-filament fibers.

3. Durability of Glass Fibers in Cement-Based Composites

When glass fibers were first used for the production of GRC, the main problem was the low alkali resistance of E-glass fibers, which were commonly employed in polymer-based composites. The rapid deterioration process of glass fibers in cementitious matrices can be attributed to the breakdown of the Si–O–Si bonds, that make up the fiber backbone, by the OH^- ions that are highly concentrated in the alkaline pore solution.

At the end of the 1960s, Majumdar developed glass fibers with a particular composition, which mainly differs from E-glass fiber for the addition of ZrO_2, observing high chemical stability in alkaline solutions. The higher stability of glass at high pH value is attributed to very stable hydrated ZrO_2 that forms on the glass surface, offering a barrier for the diffusion of OH^- ions [37]. The incorporation of $\sim$16% ZrO_2 in the glass composition is currently the most efficient way to enhance the resistance of glass fibers in alkaline environments. However, the ZrO_2 layer formed on the glass surface can only slow down the diffusion of the OH^- ions into the glass network, but can not prevent them to react with the SiO_2, so that in their service life AR-glass fibers do not have complete resistance to alkali attack. Moreover, studies conducted on the durability of GRC and TRC show that the corrosion of the fibers due to chemical attack is not the only degradation mechanism in glass fiber reinforced cementitious matrices. Different studies report that the degradation of glass fibers, with consequent strength loss, plays a minor role in the embrittlement of GRC composite over time [27,38,39]. According to Bentur et al., the microstructural changes, that occur over time in the matrix around the fibers, lead to the enhancement of the bond between fiber and matrix and to the stiffening of the interfacial transition zone (ITZ), resulting in a reduction of the mechanical properties of the composite [40]. These results were confirmed by Butler et al., who investigated the durability of fibre–matrix interfaces in textile-reinforced concrete using different matrix compositions, concluding that losses in the mechanical performance of the composite are the result of both the formation of new solid products on and among the filaments, mainly brittle Portlandite, and the reduction of the filaments tensile strength, caused by defects growth [41]. Since both chemical attack and densification of the matrix adjacent to the filaments are phenomena that take place at the fiber-matrix interface, the modification of the fibers surface, in order to improve their resistance to alkaline corrosion and reduce the formation of a brittle matrix between the filaments, is commonly adopted to preserve the performance of the composite.

4. Modification Techniques of Glass Fibers

Before presenting a more detailed description of some glass fiber modification techniques, in the authors' opinion a brief discussion on the use of the term coating in the scientific literature is needed. A coating can be generally defined as a continuous or discontinuous layer of some compound, whose chemical nature can vary from thermoplastic or thermoset polymer to thin inorganic particles, which is applied on a substrate for functional and/or decorative purposes. The ambiguous meaning of the term coating can be sometimes misleading and makes it difficult to analyze and compare different results presented in the scientific literature. For example, in some studies the fibers are described as uncoated, although all fibers available in the market are covered with a thin layer of polymeric coating, usually indicated as size or sizing. Figure 1 shows the different surfaces of glass fiber with and without sizing.

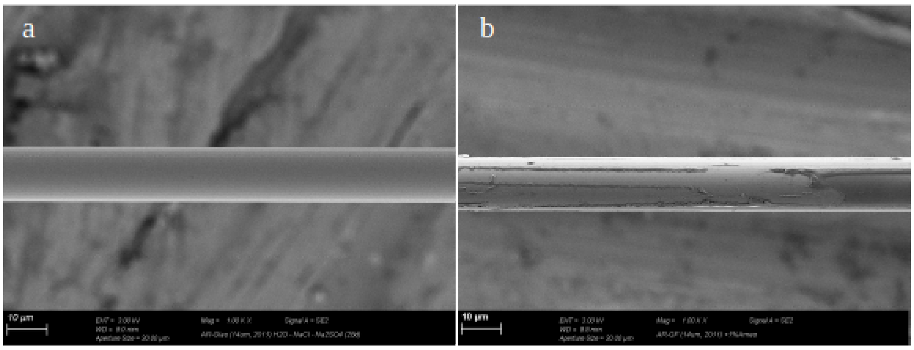

Figure 1. Glass fibres (**a**) without and (**b**) with sizing produced at the Leibniz-Institut für Polymerforschung Dresden e. V. (IPF), Germany. SEM images performed with Ultra plus (Carl Zeiss NTS) in high vacuum and an accelerating voltage of 3 kV, provided by Steffi Preßler (IPF, Dresden). Magnification ×100.

The content of sizing usually ranges between 0.5–2% by weight of the finished products [7], and it forms a thin polymeric film on the fiber surface, which is in the range of some tens of nanometers. When an additional polymer is applied to the yarns that make up the fabric or textile, this is usually called coating. However, the amount of coating applied to the fabric can be very variable. Often the same term is employed to indicate both materials where the coating makes up 5–10% in weight of the reinforcement, forming a thin layer on the fiber's surface (Figure 2), as well as fabric with a polymeric content over 30%, where the reinforcement itself can be considered an FRP composite (Figure 3).

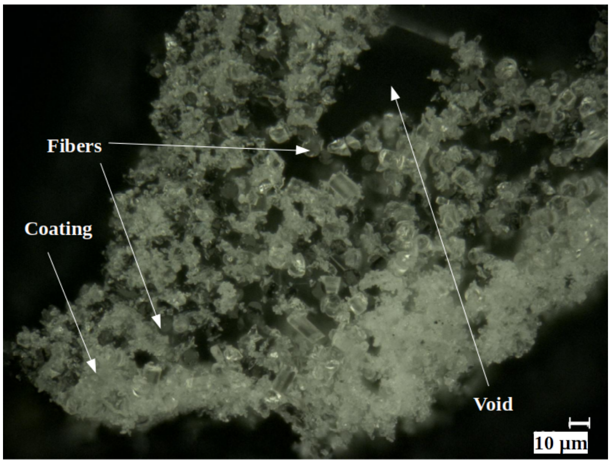

Figure 2. ARG roving with 6% SB coating produced at the Leibniz-Institut für Polymerforschung Dresden e. V., Germany. Image acquired with a Digital-Microscop Keyence VHX2000.

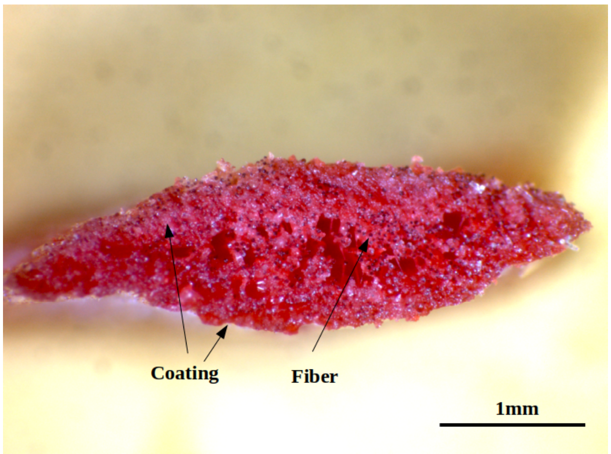

Figure 3. Cross section of a yarn cuted from a commercial avaiable ARG fabric impregnated with a SB coating. Coating content according to the producer 35%. Immage acquired with a optical macroscope Leica DFC320.

Unfortunately, information about the content of coatings is not always available in literature studies. Moreover, if reported, they are usually indicated in terms of weight percentage, which do not indicate the exact thickness of the coating layer that covers the fibers, although the thickness of the material plays an important role on both the mechanical performances and on the durability of the reinforcement. Since, based on the information available, it is not possible to classify different systems according to the thickness of the applied coating, this parameter will be marginally considered in this paper.

In the following sections, results of literature studies will be presented, making the first major distinction between organic and inorganic coatings and analyzing the effects of different surface modifications on both fibers and yarns.

4.1. Sizing

All commercialized fibers are covered with a thin polymeric film, named size or sizing. Typically the size is applied to freshly pulled glass fibers by means of a sizing applicator, which normally consists of a roller, positioned with its lower portion in a size reservoir 1–2 m below the bushing plate, that rotates at a fixed rate, picking up a layer of the size on its surface. Sizing formulations almost always contain an organofunctional silane, a polymeric film former, that usually make up 70–90% of the sizing and a lubricant. Organosilanes, typically organofunctional alkoxy silane, are a class of molecules that presents two moieties attached to the silicon atom: an hydrolyzable group, like a methoxy or ethoxy group, that can react with the siliceous backbone of the glass fibers, and an organic moiety that can react with other functional groups such amino, epoxy, vinyl or other typical groups of organic polymers. Despite the great variety of organosilanes available on the market, according to Thomason, γ-aminopropyltriethoxysilane (APTES), γ-glycidoxypropyltrimethoxysilane (GPTMS), γ-methacryloxypropyltrimethoxysilane (MPTMS) and vinyltriethoxysilane (VTES) made up the majority of all the sizing employed on commercial and laboratory scale [5]. This depends on the fact that sizing formulations have been mainly designed in order to promote the interaction between the fibers and polymeric matrices, so that silane and film formers are usually chosen in order to be compatible with the intended polymer matrix as much as possible. Therefore, the range of their chemical composition reflects the range of the most common matrix employed for FRP materials. In the case of GRC, where the reinforcement already has high chemical compatibility with the matrix, the organosilane does not have a primary role as an adhesion promoter. However, also for glass fibers employed for the reinforcement of inorganic matrix, the sizing application remains a crucial manufacturing step, because organosilanes perform many other roles besides improving the bond at the fiber-to-matrix interface. Sizing is known to play a key role also on the processability and performance of glass fibers, by preventing mechanical abrasion during the spinning process, protecting the fibers against physical, chemical and environmental degradation, and maintaining the highest potential level of fiber strength [5]. Particularly the tensile strength of the fibers is reported to be increased thanks to the ability of the sizing to mitigate surface defects, inducing healing of surface flaws and preventing the possibility of creating new defects [42–44]. For what it specifically concerns the employment of glass fibers for the reinforcement of cementitious matrices, some studies suggest that optimization of the sizing formulation can lead to enhanced durability of glass fibers in an alkaline environment. Butler et al. observed significant differences in the alternation of the mechanical performance of textile-reinforced concrete using commercial yarn with different sizing formulations [30]. Mäder et al., investigated the durability in alkaline environment of two different commercial glass fibers by immersing them in NaOH solution and observed that the residual content of sizing on the fiber, after accelerated aging, depends on both chemical formulation of the sizing and sizing content of the virgin fibers [45]. Unfortunately, studies focused on the relationship between the chemical composition of the sizing and the improvement of the fiber durability are often limited because of the unknown sizing composition of commercial fibers. Igarashi et al., investigated the effect of vinyl chloride-ethylene copolymer, polyvinyl–acetate and polyvinyl alcohol-based sizing on the microstructure of the ITZ around bundle fibers over a period of 180 days by means of microhardeness measurements and on the flexural behavior of continuously arranged fiber-reinforced composites prisms [46]. They report that the sizing formulation influences the formation of the ITZ, promoting the formation of a soft zone, which is wider for polyvinyl alcohol-based sizing, followed by polyvinyl-acetate and vinyl chloride-ethylene copolymer. The authors attribute the softer region, found at the interface with sized fibers, with the inhibition of hydration processes, which is reported to occur in presence of polyvinyl alcohol, and argue that a similar mechanism occurred in presence of polyvinyl-acetate because of their conversion in polyvinyl alcohol in an alkaline environment. A correlation between the width of the soft region in the ITZ and the behavior of the composite was observed in the load-deflection curves obtained by flexural tests, where composites reinforced with polyvinyl acetate-sized fibers reached a higher maximum load after the first cracking, compared to polyvinyl alcohol-treated fibers. Scheffler et al., investigated the degradation process of unsized fibers and fibers modified with four different sizings, after immersion in a 5% NaOH solution for 7 and 15 days [26]. According to the authors, the corrosion mechanism induced by NaOH solution hardly consents to drawing conclusions about the sizing effects on the failure stress distribution by means of tensile test. That is because, unlike exposure to cement solution, NaOH-attack is characterized by the peeling of the external shell of the fibers. Nevertheless, they could observe a correlation between the chemical composition of the sizing and the resistance of the fiber to alkaline attack. In particular, they report the beneficial effect of adding SiO_2 particles to the sizing formulation, which builds a sort of sacrificial layer, that gradually dissolves instead of the Si–O–Si-network of the glass. The proper formulation of the sizing also plays an important role in the perspective of further fiber modification, as for instance the application of an organic coating. According to Scheffler et al., the tailoring of the sizing formulation provides a basis to achieve enhanced mechanical performance when organic coatings are applied on multifilament rovings [47]. Further details on the role of coatings on the mechanical performance and durability of glass fiber reinforcement will be presented in the next section.

4.2. Organic Coatings

The application of organic coatings is a widespread and well-established manufacturing technique, employed for the modification of fibers surface and finishing of textiles [48,49]. Both short fibers and AR glass fabric modified with organic coating are already available on the market [50]. Because of the great variety of organic polymers available, this modification technique theoretically offers an extended array of products, whose characteristics can be adjusted to meet specific needs by varying the chemical formulation of the coatings. The use of organic coatings for the modification of AR-glass fibers was first introduced in order to improve their alkali-resistance, but more recently the impregnation of multi-filaments fabric and textile has been proposed on both laboratory and commercial scale, also for the improvement of the stress transfer between the filaments. Despite the great variety of polymers available on the market, the majority of studies conducted on the improvement of glass fibers fabric reinforced concrete are basically based on epoxy resin and styrene-butadiene copolymer. Epoxy resins have been successfully employed in different studies to improve the load bearing capacity of FRCM systems [51–60]. Hegger et al., report that by impregnating the AR-glass fabric with epoxy resin, the maximum tensile strength of the composite could be triplicated [57]. Büttner et al., obtained an improvement of the 70% in the load-bearing capacity of epoxy impregnated AR-glass fabric compared to the uncoated system [59]. Messori et al., report an increase in the tensile strength of FRCM composites, reinforced with epoxy coated fabrics [51]. The increased mechanical performance observed for coated systems, compared to the dry one, is attributed to the ability of the resin to penetrate into the yarn, increasing the stress transfer between the single filaments (Figure 4).

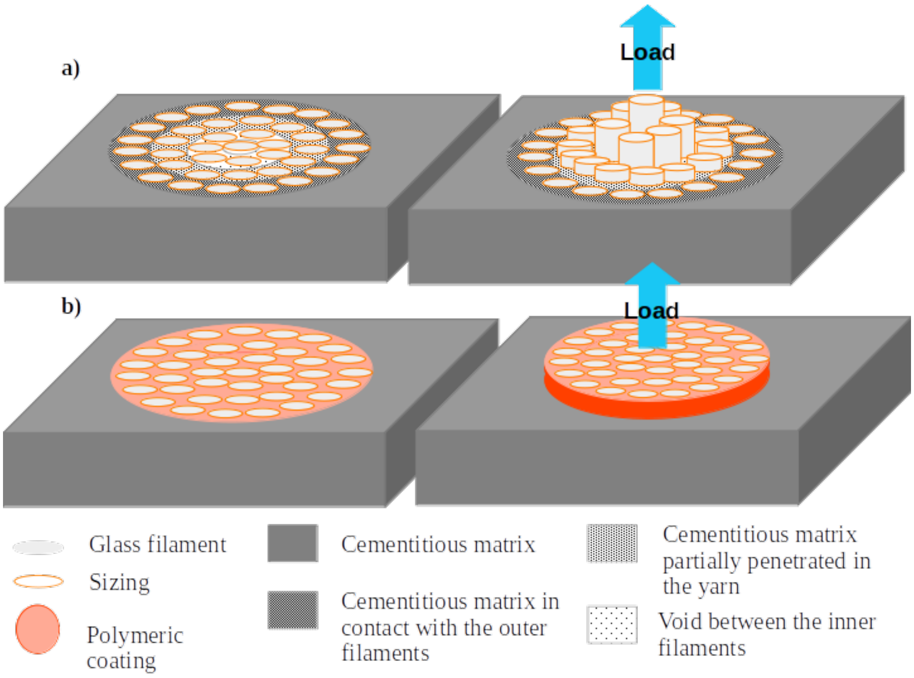

Figure 4. Schematic representation of (**a**) uncoated and (**b**) coated yarn embedded in a cementitious matrix.

As a consequence, a larger load-bearing cross-section can be activated in the yarn, leading to an improvement in the efficiency of the mechanical properties of the reinforcement. Raupach et al., compared the utilization of the reinforcement for dry and epoxy impregnated systems, defined as the ratio between the maximal tensile strength, obtained by a uniaxial tensile test conducted on dog-bone shaped specimens, and the theoretical maximum tensile strength, calculated out of the tensile strength of one single filament and the number of filaments used in one yarn [53]. The reinforcement utilization for the dry fabric was only 43%, while employing an epoxy-coated fabric it increased to 75%. Of course, in order to maximize the number of filaments engaged in the stress transfer, it is necessary that the epoxy coating fully penetrates in the fabric yarn. Epoxies have a good wetting behavior, however, the efficiency of the coating process also depends on the rheological properties of the coating employed. Signorini et al., demonstrated that by diluting the epoxy resin used for impregnation of AR-glass fabric with acetone, superior tensile strength of the composite can be obtained [55]. The authors correlated the viscosity of the coating with the tensile strength obtained for the composite and found out that the optimal coating formulation was achieved by a dilution degree of 75% (75 g acetone, 28 g epoxy resin). Although the dilution degree looks high, it should be noted that the solid content of polymeric water-based dispersion, employed for textile coatings, are often reported to be lower than 50% [45,56,61]. Indeed, although the great majority of the epoxy employed in experimental studies for the modification of reinforcement fabric are standard bi-component epoxy resins, some studies also reported the use of water-based epoxy coatings [28,56,61,62]. Dilthey et al., suggest that waterborne epoxy coatings are particularly promising for the fresh on fresh coating application method, in which the polymer impregnated textile is embedded in the cementitious matrix directly after application of the liquid resin [56]. Indeed, according to the authors, hardened epoxy resin has no interaction with the cementitious matrix, as could be proved from EDX analysis at the fiber-matrix interface-zone. As a consequence, the improvement in the load-bearing capacity of the composite is not attributed to a stronger chemical interaction between the epoxy resin and the inorganic matrix, but rather to the high friction that can be transmitted via shear bond, thanks to the close contact between the matrix and the reinforcement.

Because of the absence of good chemical interaction and therefore of good adhesion between the epoxy resin and concrete, the coated reinforcement can act as a separating layer, resulting in delamination failure, as reported in some studies [14,51]. On the contrary, fresh waterborne epoxy coating can improve the interaction of the reinforcement with the matrix by homogenization of the interface-zone. Büttner et al. performed tensile tests on dog-bone-shaped specimens reinforced with water-born epoxy impregnated AR-glass fabric, using both the fresh to hard (f/h) and fresh to fresh (f/f) methods, and observed that in the sample prepared with the f/f technique, the unhardened epoxy was able to admix and interact with the fresh concrete, forming a homogenized interfacial zone, while on f/h application method a clear-cut interface between concrete and reinforcement is formed [59]. Improvement of the mechanical properties of the composite by f/f method has been reported also by Cohen and Peled for styrene-acrylic polymer [63]. However, in the same work, the authors also report that, although the wet process lead to an improvement of the initial mechanical properties of the composite, specimens subjected to accelerated aging experience a lower decrease of the tensile strength when realized with the fresh-to-hard method, since precuring the polymeric coating allows a polymeric film to be formed around the fiber bundle, which protects the glass filaments from alkali degradation.

A promising alternative to epoxy resin are styrene–butadiene coatings,which have been reported to improve the interaction at the fiber-matrix interface [45,47,64]. Mäder et al., investigated the effect of different styrene-butadiene coating formulations on the mechanical properties and durability of two types of commercial AR-glass fibers [45]. In order to evaluate the impact of the coatings on the interface and the consequence of surface modification on the overall mechanical properties of the composite, the authors compared the results of the single fiber pull-out test, yarn pull-out test and tensile test performed on concrete specimens reinforced with continuous rovings. The authors calculated both the adhesion strength and interfacial friction for the coated and uncoated fibers, and report that the selected styrene-butadiene coating provide a superior adhesion with the cementitious matrix.

Interestingly they found out that by employing the selected coatings on two different commercial AR-glass yarns, although both coated yarns displayed improved tensile strength, the overall mechanical properties of the composite were not always increased. Similar results have been reported by Scheffler et al. [47], which were attributed to the superior compatibility between sizing and coatings. Interestingly the authors demonstrated that by tailoring the compatibility of coatings and sizing, rovings characterized by a lower initial tensile strength lead to composite with superior performances.

Styrene–butadiene coatings also have been employed to increase the durability of glass fibers to alkali attack. Gao et al., performed single fiber tensile tests on AR-glass fibers coated with two styrene-butadiene coatings before and after immersion in alkaline solution for 28 days at room temperate, and reported that, unlike the uncoated control fibers, no significant decrease of the mechanical performance was observed [64]. By performing Atomic Force Microscopy (AFM) and FTIR-ATR spectroscopy measurements the authors could verify that the coating was partially removed, but it had undergone no chemical modification after alkaline exposure, and conclude that the selected coating was chemically resistant to alkali attack. In a successive study Gao et al., developed a nanostructured styrene-butadiene coating, by intercalating nanoclay particles in the polymeric matrix, in order to improve the moisture barrier level of the coatings [65].

Water vapor sorption isotherm and AFM analysis of the fiber's surface before and after immersion in alkaline solution show that the coating with intercalated nanoclay has superior barrier properties against alkaline attack.

However, the tensile test conducted by Scheffler et al., after accelerated aging on roving coated with styren butadiene, with and with-out nanoclay, show that if the nanoclay are agglomerated in the coating, rather than well intercalated, an opposite effect of reduced durability can be obtained [66].

The addition of nanoclay particles in the polymeric coating was also reported to modify the interaction of styrene-butadiene coating with the cementitious matrix [47,67]. Scheffler et al., report that glass fiber reinforcements coated with styrene–butadiene coating containing 5% of nanoclay show a significantly steeper pull-out behavior at small crack width compared to roving modified with the same polymer but without clay [47]. This is due to a strong interaction between the nanoclay-contaning coating and the matrix, as confirmed by ESEM-images of the fracture interphases where a rising number of calcium-silicate-hydrate phases was observed at the surface with polymer with increased content of clay. This phenomenon has been attributed to the ability of clay-aluminates to serve as nucleation points for the development of hydration products. Although on a short-term period the intensification of the connection of the coated yarn with nanoclay particles increases the load-bearing capacities of the composites, Hempel et al., show that, after prolonged exposure to fog chamber, the very thick and stiff layer of hydration products formed at the fiber-matrix interface led to embrittlement and stiffening of the polymer, causing the failure of the reinforcement at a smaller load value compared to the same composite obtained without the addition of nanoclay [67].

4.3. Inorganic Coatings

When yarns are pre-impregnated with polymeric coatings, the penetration of the mortar within the filaments is prevented, so that the stress transfer between the filaments is no longer dependent on the ability of the mortar to penetrate into the yarn but rather from the bond at the interface between coating and matrix. In this case, the system is actually a glass–fiber polymer composite embedded in a cementitious matrix. Furthermore, since the coating prevents the penetration of the cementitious matrix into the yarn, the stress transfer between filaments strongly depends on the physical-mechanical properties of the coating itself. Moreover, some studies argue that the introduction of a polymeric layer between the reinforcement and the matrix can make the composite more sensitive to high temperatures and compromise its fire resistance [68,69]. Indeed, the reduction of the mechanical performance of FRCM composites exposed to temperature over 80 °C was reported for epoxy pre-impregnated carbon fabrics [68]. In order to overcome this issue, some studies propose the application of inorganic coatings instead of polymer based coatings [63,70–78]. Weichold at al. prepared a cement-in-polymer dispersion using a ultra-fine grained cement with a particle size of <7 μm and water-soluble polymers (poly vinyl alchol (PVA), poly(ethylene-co-vinyl acetate) (EVA), and poly(vinyl acetate) (PVAc)) [77,79]. They report that composites realized using the AR-Glass roving impregnated with the inorganic coating show maximum peak stress three times higher than the value obtained for the same sample reinforced with the untreated commercial fabric. The inorganic coating is also reported to change the pull-out behavior of the composite, which instead of experimenting with a sudden drop of the pull-out load after debonding displays a further increase. By conducing SEM-EDX analysis the authors could verify that the superior properties observed are due to the full penetration of the inorganic matrix into the yarn. Indeed, according to the author, the small amount of polymer contained in the applied coating (80% cement, 20% polymer) forms a thin film on the cement grains and the glass filament which dissolves when it comes in contact with the fresh cement-paste. In this way the non-hydrated cement contained in the inorganic coating can react with the Portland cement and improve the reinforcement embedding within the inorganic matrix. However, the high content of Portland cement contained in the coating provides a highly alkaline environment close to the glass fibers, which leads to a sever loss of the composite tensile strength over time. In another study the authors proposed the addition of active pozzolans in the coatings (metakaolin, and silicon dioxides), as a possible solution to decrease the pH in the vicinity of the glass filaments [80]. Although in general the increase of the pull-out load was lower compared to fibers coated with the cement/PVAc coating, the replacement of Portland cement with silica leads to a 1.6-fold increase in the residual tensile strength of the composite. Homoro et al. proposed a dry process for the pre-impregnation of glass yarn with inorganic powder, which makes use of a high-intensity alternating electrostatic field to facilitate the penetration of the powder into the yarn [70]. The process consists of passing the yarn covered with the powder between two electrodes where a strong alternative electrostatic field is created by applying high tension. When the yarn exits the dielectrics, the powder has homogeneously penetrated between the single filaments. Before casting the yarns are sprayed with water. The authors report an improved matrix penetration between the filaments which corresponds to superior tensile properties of the composite. Different studies propose the impregnation of the reinforcement with inorganic coating based on silica particles [63,72,75,76]. Silica coatings can be obtained by using silica particles of different dimensions. Signorini compared the effects of nano-silica and micro-silica coatings on the tensile strength properties of a lime-cement matrix reinforced with an open-square-mesh biaxial ARG fabric [72]. The nano-silica coating was prepared using the sol-gel method, where tetraethyl orthosilicate (TEOS) was employed as SiO_2 precursor and the fabrics were impregnated by bathing the fibers for 5 min in the colloidal solution obtained by acid-catalyzed condensation of TEOS in a isopropanol/water solution. The wet fabric was left to dry in oven at 105 °C for 15 min. For the coating with micro-silica particles, the reinforcement was immersed in an aqueous suspension obtained by stirring silica fumes with particle size of 0.15 μm for one hour in distilled water and successive sonicated for 10 min. In this case, after dipping the fabric in the suspension, it was left to dry at room temperature. For both coatings, SEM images show the presence of diffuse mortar patches attached to the fabric after the failure of the composite, which were not detected on the untreated reinforcement. The strong coupling effects of the silica coating with the reinforcement interphase are confirmed by the increase of the tensile strength of 60.3% and 96.7% for the fabric with nano-silica and micro-silica, respectively, with respect to dry systems. Cohen and Peled report an increase of the maximum tensile stress of the composite by coating the reinforcement with 200 nm silica fume particles [63]. However, in the same study, when using fillers with smaller particles dimension (50 nm) no increase in the composite mechanical properties was observed. According to the authors, this is partially due to the wash-out that small particles undergo when the reinforcement is immersed in the fresh cementitious paste. The authors also report that large silica fume particles have a beneficial effect on the durability of the composite because of the pozzolanic reaction between the amorphous silica and the portlandite. Instead of silica fume particles Quadflieg et al., report the use of a potassium silicate dispersion for the impregnation of AR-glass fabric [71]. The inorganic coating was applied on the AR-glass fabric using a coating machine with roll-to-roll technique. Specimens with the potassium silicate reinforcement showed an increase of the tensile strength of 18%, compared to samples with the uncoated fabric. Moreover, also the flexural strength of the composite subjected to four-point bending test increased by coating the fabric with potassium silicate. According to the authors, the inorganic coating reacts with the cementitious matrix, allowing better penetration of the matrix itself within the reinforcement and improving the adhesion at the fibers-to-matrix interface.

4.4. Comparison of Different Coatings

Because of the different materials, test methods and experimental protocols adopted in literature studies, the results obtained from experiments on the effects of coatings on both mechanical properties and durability of AR-glass reinforced cementitious composites are difficult to compare. In order to partially address this issue, this section tries to evaluate the advantages and drawbacks of the different techniques reported in literature studies based on the results obtained employing different coatings but maintaining unchanged the cementitious matrix and the test methods. Schleser et al. investigated the tensile strength of AR-glass roving impregnated with polymeric dispersions of chloroprene, polyurethane, acrylate, and an epoxy resin [54]. The epoxy impregnated yarns display the highest tensile strength and elastic modulus. For the rovings modified with the polymeric dispersion, no change in the elastic modulus was observed.

The acrylic polymer leads to an increase of the tensile strength slightly lower than that obtained with the epoxy resin. Polyurethane and chloroprene polymers also lead to an increase of the tensile strength compared to the dry rovings, but the performance obtained is far lower than the epoxy and acrylic impregnated yarn. The authors attribute the superior tensile properties of the epoxy impregnated roving to the high modulus of the epoxy resin (3.3 $\mathrm{kN/mm^2}$), which results in two orders of magnitude higher than the one of the acrylic polymer (10 $\mathrm{N/mm^2}$). Unfortunately, the study provides no information about the behavior of the composites. Rampini et al. compared the tensile behavior of cement-based composites obtained using four commercially available AR-glass fabrics, with two geometrical configurations, provided by the producer with epoxy and styrene-butadiene coatings [81]. They report that, although the tensile strength of the fabrics was marginally influenced by the coating, the maximum tensile strength of the composite reinforced using the epoxy impregnated fabrics was 50% to 60% higher compared to the styrene-butadiene impregnated coating. The authors attribute the superior performance obtained with the epoxy impregnated reinforcement mainly to the better ability of the resins to penetrate and impregnate the glass filaments and to stiffening the nodal connections between the yarns, which enable the weft strands to provide a greater anchorage when the specimen is loaded in the warp direction. An extended study on the effect of different sizing and coatings formulation on the durability of AR-glass fibers in alkali environment was conducted by Scheffler [28]. The author compared the alkali-resistance of AR-glass roving coated with a thermoplastic and a cross-linked styrene–butadiene polymers and an epoxy resin dispersion by immersing the roving in two alkaline solutions (5% NaOH and cement solution) and by accelerating aging of the cement-based composite obtained with the coated rovings. Rovings coated with the epoxy resin dispersion show an increase of tensile strength compared to the dry fibers, which is two times the increase obtained with styrene-butadiene coatings. After immersion in the alkali solutions for 28 days at 20 °C, the styrene-butadiene coatings proved to be more resistant than the epoxy coating. However, because of the better distribution of the epoxy coating on the filaments surface, it provides better protection of the glass fibers under more aggressive aging conditions. The influence of aging on the composite properties was verified by two sides pull-out test before and after exposure to different protocols. In general, if compared to styrene-butadiene, the epoxy coating leads to a higher increase of the loading force of the composite after the failure of the cementitious matrix. As a consequence, the epoxy impregnated reinforcement leads to a maximum pull-out load of the composite (about 200 N higher than that obtained for styrene–butadiene coated rovings), but smaller pull-out work. The pull-out results obtained after aging show that the best composite properties are obtained for the reinforcement coated with the epoxy resin dispersion. Quadflieg et al., investigated the effects of epoxy and styrene-butadiene impregnation among with the use of inorganic potassium silicate coating for the modification of AR-glass fabric [71]. Interestingly the authors use an automatic coating plant for the impregnation of the fabric, making some considerations on the process feasibility. All fabric samples were coated continually roll-to-roll, with the fabric being immersed in a Foulard containing the polymer and then squeezed by rollers before entering the curing oven. Since the penetration of the coating into the yarn is directly proportional to its viscosity, for aqueous potassium silicate dispersion a coating speed of 0.7 m/min was used, while for the much more viscose epoxy resin the process was slowed down to 0.2 m/min. Moreover, in order to facilitate the coating process, when the epoxy resin was applied, the Foulard and the squeezing rollers were heated to a temperature of 80 °C, to decrease the viscosity. The authors also report that the use of a two-component epoxy resin constrains the coating process due to the curing of the epoxy, which limited the coating usage time. Regarding the mechanical properties of the composite obtained with the coated fabrics, tensile tests showed similar results for epoxy and styrene-butadiene coatings, with the first one leading to slightly higher mechanical properties. The inorganic coating also led to an increase of the composite tensile strength but more moderate compared to the organic coatings. According to the authors, the superior load-bearing capacity of the composite observed for the polymer coated fabrics is due to the higher impregnation grade obtained. A cross-section of the coated roving reveals that for the epoxy resin the multi-filaments are completely impregnated, in the styrene–butadiene coated roving the core filaments remained uncoated and the potassium silicate coating, on and in the fabric, was randomly distributed with very little volume fractions. Different results were obtained by evaluating the effect of the coatings on the composite bending properties. First of all, the strength at the limit of proportionality (LOP), that for the dry and inorganic coated systems also corresponded to the maximum flexural strength (MFS), was much higher for the dry and potassium silicate-coated fabric than for the epoxy impregnated reinforcement. Indeed, while the inorganic coatings lead to a considerable increase of the first crack peak, for the epoxy fabric the LOP is almost the same as for the unreinforced matrix, which reflects the lower adhesion of the coated fabric with the matrix. For both styrene-butadiene and epoxy coated fabrics, after reaching the first peak, an increase in the bending strength is observed, leading to the formation of different peaks before reaching the MFS. The very high residual strength of these composites is attributed to the higher tensile strength of the polymer impregnated fabrics, although for the styrene-butadiene coating higher MFS are reached, probably due to the superior flexibility of the reinforcement.

Based on the information reported on the studies reviewed, some considerations can be made on the advantages and drawbacks of different techniques. Table 1 schematizes the different techniques analyzed in this review and summarizes their effect on: the load distribution between the single filaments (stress-transfer), the interaction with the cementitious matrix and the effect on fibers durability (alkali-resistance).

Table 1. Effects of different surface modification of glass fibers on the properties of cement-based composites.

Modification Techniques			**Stress Transfer**	**Interaction with the Matrix**	**Alkali-Resistance**	**Technology Readiness Level**	**Advantages**	**Drawbacks**	
Sizing			Limited	Good	Limited [26]	Standard procedure for the production of glass fibers	Easy to implement in production processes	Limited improvement of durability, stress transfer and textile handability	
Organic coating	Hardened coating (h/f)	Epoxy resin	Good to very good. Depending on the viscosity and solid content of the resin or polymeric dispersion [55]	Depends on chemical composition [14,45,47,51,64]	Improved [53]	Commercially available	High increase of the composite tensile strength [51–60]	Low flexibility: not adequate for reinforcement of structures with complex geometry	Low resistance to high temperatures [68,69]
		SB			Improved [64]		Increase of the composite tensile strength without loss of flexibility [71]	Lower increase of the fabric tensile strength compared with epoxy coating [81]	
	Fresh coating (f/f)	Epoxy or SB		Very good [59,63]	Lower compared to h/f method [63]	Commercially available	Improved interaction with the matrix compared with h/f method [59]	Difficult to apply in FRCM systems	

Table 1. *Cont.*

Modification Techniques	Stress Transfer	Interaction with the Matrix	Alkali-Resistance	Technology Readiness Level	Advantages	Drawbacks
SB-nanoclay coating		Very good [47,67]	Improved for nanostructured coating, otherwise reduced [65,67]	Laboratory scale	Improvement of the interaction between matrix and coating	Need implementation No infromation about resistance to high temperatures
Inorganic coating	Good to very good. Depending on the impregnation method	Very good	Improved by addition of silica [80]	Laboratory scale	Very good fiber-matrix interaction. Resistance to high temperature [78]	Need manufacturing implementation

5. Conclusions

Although the number of studies conducted on the surface modification of glass fibers for the reinforcement of cementitious matrices is still limited, compared to the wide scientific production available for organic matrices, different promising techniques have been described in the literature and can be used to improve the mechanical performance and durability of this class of composites. Because of the great variety of cementitious matrices that can be employed, as well as their different applications, that ranges from the production of high-performance building elements to the reinforcement of existing structures, there is no single solution. On the contrary, the possibility of using different techniques allows us to tailor the reinforcement and the fiber-matrix interface properties according to the specific application.

Based on the results presented, some conclusions can be drawn:

- In general the improvement of the load-bearing capacities of the composites by impregnation of the reinforcement with a polymeric coating is mainly due to the superior wettability of the polymer compared to the cementitious matrix, and its ability to fully penetrate in multi-filament yarns promoting a superior stress-transfer between the fibers.
- On the basis of the studies available it is not possible to state which polymeric coating provides the highest performance. In general, it has been observed that stiffer coatings like epoxy resins improve the composite tensile strength. However, epoxy impregnated reinforcements are also reported to have low flexibility, which can be a disadvantage when fabrics are meant to be used for the reinforcement of existing structures with complex geometry. Moreover, although a stiffer reinforcement can improve the tensile strength of the composite, flexible textiles performed better under flexural load. These parameters should be considered according to each specific use.
- For what it concerns the fiber-matrix interface, the interaction between polymeric coatings and inorganic matrices strongly depend on the chemical composition of the coating and can be improved by using the fresh to fresh methods or by incorporating inorganic particles, such as nanoclay, in the polymeric matrix. Since the first method is less feasible for strengthening interventions, it seems more suitable for the production of TRC elements rather than for FRCM applications. On the contrary, the second method can be used also for the production of pre-impregnated fabrics for the rehabilitation of existing structures.
- A stronger fiber-matrix interaction can be obtained by using inorganic coatings, which can chemically react with the cementitious matrix, providing a better adhesion at the fiber-to-matrix interface. However, a strong fiber-matrix interaction also results in a stiffer fiber-matrix interface, which could make the composite more brittle and lead to a reduction of the mechanical performance over time.

Author Contributions: Conceptualization, F.B. and J.D.; writing—original draft preparation, F.B.; writing—review and editing, F.B. and J.D.; visualization, F.B.; supervision, J.D.; All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Informed Consent Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

Abbreviations

The following abbreviations are used in this manuscript:

FRCM	Fabric Reinforced Cementitious Matrix
TRC	Textile Reinforced Concrete
ARG	Alkali Resistant Glass
ITZ	Interfacial Transition Zone
APTES	γ-aminopropyltriethoxysilane
GPTMS	γ-glycidoxypropyltrimethoxysilane
MPTMS	γ-methacryloxypropyltrimethoxysilane
VTES	vinyltriethoxysilane
f/h	fresh to hard
f/f	fresh to fresh
AFM	Atomic Force Microscopy
FTIR-ATR	Fourier-Transform Infrared-Attenuated Total Reflection
SEM	Scanning Electron Microscope
SEM-EDX	Scanning Electron Microscope-Energy-Dispersive X-ray
TEOS	tetraethyl orthosilicate
LOP	Limit Of Proportionality
MFS	Maximum Flexural Strength

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