A Study on the Adhesion in the Interfacial Transition Zone Between Glass Fibre Reinforced Rebar and the Cement Matrix

Grigory Yakovlev1, Zarina Saidova1, Rostislav Drochytka2, Anastasiya Gordina1, Igor Pudov1, Natalia Kuzmina1, Ekaterina Begunova1, Ali Elsaed Mohamed Mohamed Elrefai3

1Kalashnikov Izhevsk State technical university, 426069, Izhevsk, Studencheskaya Str. 7, Russia
2Brno University of Technology, Institute of Technology of Building Materials and Components, Brno, Veveří 331/95, Czech Republic
3Egyptian Russian University, Cairo, 87 El-Tahrir St., Egypt

Abstract. This study is aimed at increasing the adhesion of the fibre-reinforced polymer rods to the binder in the cement-based composites in order to eliminate the problem of rod slippage under loading and broaden the application of composite reinforcement in the construction industry. It is assumed that the better adhesion of reinforcement rod to the cement matrix can be provided by increasing the cement stone structural density, and, in particular, by compacting the structure of the hydration products formed on the surface the fibre-reinforced polymer reinforcement rod. Such increase in strength and density can be achieved by adding nanodispersed additives such as metakaolin, the dispersion of carbon black and Peneco Nano Stachema primer into the composition of the cement matrix. Additional adhesion of the cement matrix to the reinforcement is ensured by coating it with the primer, which seals the structure of the cement matrix located in the interfacial transition zone between the reinforcing bar and the cement stone. Experimental study proved that the proposed approach allows the formation of a strong and dense structure in the interfacial transition zone between the cement matrix and the fibre-reinforced polymer reinforcement rod surface. The introduction of metakaolin and a dispersion of technical soot led to an increase in the adhesion strength of fibre-reinforced polymer rod with a cement matrix by 27% and 29%, respectively. The IR spectral analysis and DTA analysis results showed that the mineralogy and morphology of the hydration products was changed due to the addition of the modifying additives, thus improving the adhesion characteristics and corrosion resistance of fibre-reinforced polymer in the cement-based composites.

1. Introduction
Fibre reinforced polymer (FRP) composites have been increasingly used in civil engineering applications in the last few decades. These materials, consisting of mineral (glass, basalt, carbon) fibres with a diameter of up to 10-15 microns in combination with polymer binding compounds, primarily epoxy resins, provide a cost-effective alternative to conventional materials. Significantly lower weight of polymer-composite products, compared to the traditional metal analogues, sufficiently high corrosion and chemical resistance, as well as high tensile strength determine the growing demand of construction and operating companies for FRP materials. One of the drawbacks of the composite FRP products, however, and, particularly, fibreglass reinforcement, is a rather low modulus of elasticity, approximately 4 times lower than that of steel, which limits its use as the main reinforcement in the structures exposed to bending.
Besides, the combined action of composite rods and a cement matrix is a rather controversial issue. The adhesion between the cement binder and reinforcement is one of the most important factors affecting the mechanical characteristics of the cement concrete and its durability - strong adhesion provides the bearing capacity and reliability of the reinforced concrete structure.

It was observed that the bond between FRP reinforcement and concrete depends on several factors. These include friction due to surface roughness of FRP rebars, the mechanical interlock of the FRP rebars against the concrete, the chemical adhesion, the hydrostatic pressure against the FRP rebars due to the shrinkage of hardened concrete and the swelling of FRP rebars due to temperature change and moisture absorption [1-3].

Davalos et al. [4] used the pull-out test in order to study the effect of surface treatment of polymer-composite reinforcement (FRP) on the nature of the destruction under loading of the interphase layer between the reinforcing bar and the cement matrix in the high-strength concrete. Various types of composite rods surface treatment were used: periodic profile, sand-covered, and also roughened by sand-blasting to produce small deformations. Russian scientists Khozin et al. conducted a similar research [5], in which, based on the extensive experimental research, it was shown that the use of periodic profile is not recommended as a surface treatment type for the FRP rods. This is due to the fact that the winding of FRP rods, obtained by sticking a bundle of fibres impregnated with a binder on the rod surface, can be cut off the surface when the pull-out force is applied. It is also known, that the exposure of the rods to the solution of caustic alkalis before placing them in concrete [6], leads to a significant decrease in the adhesion strength of the composite reinforcement with the surrounding cement matrix, which is apparently caused by the destruction of the epoxy binder. Thus, in contrast to profiled steel reinforcement, the adhesion of FRP rods to concrete is ensured mainly due to the adhesion of cement stone with an epoxy coating, and not by mechanical engagement of the winding in a concrete matrix.

However, the lack of chemical affinity between the main components of the cement matrix (crystalline hydrate formations) and the polymer component of the composite reinforcement (Figure 1a), reduces the interfacial bond between FRP and cement matrix. Besides, in the course of the cement hydration process, a shell, consisting of calcium oxide hydrate, is formed on the surface of the composite bar, which has low shear strength due to the lamellar structure of the crystalline formations. Besides, the high porosity of the structure formed around the composite rod can affect the adhesion characteristics (Figure 1b).

Figure 1. Microstructure of the interphase layer between the FRP rod and the cement-based composite: a) calcium hydrates in the contact zone, b) porous structure of the new formations

The analysis of the test results [7] showed that the highest pull-out strength is provided when FRP rod is “squeezed” by a thin bundle of fibres with a step equal to 1 or 2 rod diameters. This increases the specific area of FRP contact with concrete and improves the conditions for the joint operation of the rod with concrete under loading, which makes it possible to use the strength properties of the to the full. Besides, sanding of the composite reinforcement surface is an effective method of increasing adhesion.
The use of fine sand leads to a good chemical adhesion to the concrete due to higher surface area. However, the use of coarse sand produces higher bond strength between the rebar and the concrete due to friction and interlocking forces prevailing over the chemical adhesion mechanism [8].

It is also possible to use special gripping and anchoring devices [9] both for fixing the composite polymer reinforcement in the concrete body and to ensure its pre-tensioning [10]. The solutions based on placing the end of the reinforcing bar in a sleeve [11], steel tube or tip [12] with the further polymerization of an adhesive or glass-filled epoxy resin in them are found to be the one of the most effective ways to provide adhesion in terms of the absence of initial deformations in the area of reinforcing bar attachment, and due to the maximum contact area and adhesion coefficient.

Moreover, in order to provide the maximum strength properties of the contact area between FRP rods and the cement matrix, it is recommended [13] to use increased-strength concretes of class M40 and higher. This means that the use of composite reinforcement in concretes of normal strength is complicated by the weak adhesion of the cement matrix to the surface of the rod. In this case, better adhesion of reinforcement to the cement matrix can be provided by increasing the cement stone structural density [14], and, in particular, by compacting the structure of new formations located around the composite reinforcement. Such increase in strength and density can be achieved by adding nanodispersed additives such as metakaolin, carbon black and multicomponent primer Peneco Nano Stachema (Czech Republic) into the composition of the cement matrix. Additional adhesion of the cement matrix to the reinforcement is ensured by coating it with this primer and sealing the structure of the cement matrix located in the interphase layer between the reinforcing bar and the cement stone.

Thus, the two solutions that are proposed in this article aimed at increasing the adhesion of cement stone to composite reinforcement should eliminate the problem of rod slippage under loading and broaden the application of composite reinforcement in the construction industry.

2. Materials and methods

Physical and mechanical tests of the reference and modified samples (Figure 2) were carried out at the Research and Education Center "Technologies" (KGASU, Kazan, Russia) in accordance with GOST 32492-2015 "Polymer composite reinforcement for reinforcing concrete structures. Methods for determining the physical and mechanical characteristics" [15].

The adhesion strength of composite reinforcement to concrete was determined using glass fibre reinforced polymer GFRP reinforcement rods produced by KomAR LLC (Izhevsk, Russia), that was vertically installed in the center of standard concrete cubes with dimensions of 100x100x100 mm. In order to provide the uniform distribution of load, a test sleeve was previously fixed at one end of the rod [16].
The following additives were used as modifiers of the structure of the cement matrix in the interfacial layer between GFRP rods and the composite reinforcement:
- primer dispersion Peneco Nano Stachema (Czech Republic);
- metakaolin with an average particle size of 19 nm dispersed in a hydrodynamic cavitator (Figure 3);
- dispersion of carbon black (Figure 4) produced by Palizh™ (Novy Dom LLC) with an average particle size of 30 nm and a specific surface area of 65-100 m²/g. The pigment content in the paste is 34%.

Additionally, the adhesion of the GFRP rod to the cement matrix was provided by coating the surface of the rod with Peneco Nano Stachema primer.

The analysis of the microstructure of the interfacial layer and the X-ray microanalysis of the contact zone to determine of the elemental composition was carried out on a scanning electron microscope MIRA3 TESCAM at the AdMAS research center at the Technical University of Brno (Brno, Czech Republic).

Differential thermal analysis was carried out on a TGA/DSC1 Star system derivatograph manufactured by Mettler Toledo in the temperature range from 60 °C to 1100 °C at the heating rate of 30 °C/min, and IR spectral analysis was performed in the frequency range 400 - 4000 cm⁻¹ using Fourier transform infrared spectrophotometer IRAffinity-1 manufactured by Shimadzu.
3. Results and discussion

To increase the adhesion of the cement matrix and the surface of the GFRP reinforcement bar, it is proposed to use additives that can change the phase composition, mineralogy and morphology of the hydration products in the interfacial transition zone, with the conversion of calcium hydroxide into a more durable and stable phase, morphology of which excludes slipping and the alkaline corrosion of the reinforcing bar in cement-based composites.

The results of mechanical tests of the samples are presented in the Table 1. The concentration of modifying additives in the composition of the cement-based composite was established from the hypothesis that improving the adhesion of GFRP with a cement matrix can be achieved by increasing the strength of the original concrete [13]. Therefore, the choice of the additives’ concentration was determined by the previous studies [17, 18]. According to the manufacturer’s recommendations, 1 litre of Peneco Nano Stachema dispersion was added per 30 kg of cement.

| Sample Description                        | Pull-out strength, MPa |
|-------------------------------------------|------------------------|
| Reference                                 | 14.39                  |
| Modified by Peneco Nano Stachema          | 15.78                  |
| Modified by 3% of metakaolin              | 18.23                  |
| Modified by the dispersion of carbon black | 18.59                  |

As seen from table 1, the introduction of modifying components into the composition of cement-based composites results in the increase of the adhesion of fiberglass reinforcement to the binder. The introduction of metakaolin and a dispersion of technical soot resulted in the increase of the adhesion strength of GFRP with a cement matrix by 27% and 29%, respectively.

In order to analyze the structure formed at the interfacial transition zone between fiberglass reinforcement and cement matrix, microstructure analysis of the interfacial layer was conducted using a MIRA3 TESCAM scanning electron microscope.

Metakaolin (also known as nano-clay) was one of the nanostructuring additives introduced into the composition of cement-based composite in order to ensure increased adhesion between the GFRP reinforcement and the cement matrix (Figure 5a). Due to the interaction between metakaolin and calcium hydrates during hardening, new hydration products are formed on the surface of the composite reinforcing bar, namely, calcium sulfoaluminate hydrates (hydrogarnets), tightly adhering to the surface of the composite bar (Figure 5a). This correlates with the data provided by Gorshkov [19]. These new formations provide better adhesion of the bar surface to the cement matrix, preventing the slippage of the reinforcing bar under loading. Besides, hydrogarnets increase the chemical resistance of GFRP, which was confirmed by Saraykina et al. [14]. The study of Purnell et all [20] also confirms the effectiveness of metakaolin in increasing glass fibre reinforced cement durability and demonstrates that pH of the pore water is reduced when 20% of the cement is substituted by metakaolin. Additionally, they concluded that with 20% of metakaolin, the glass fibres are covered by a mineral phase other than calcium hydrate. So metakaolin seems to be more effective in protecting alkali sensitive fibres from degradation [21].

A nanomodifying additive Peneco Nano Stachema was also introduced into the composition of the cement-based material (Figure 5b), which led to the formation of a complex polymorphic structure with a predominance of tobermorite-like calcium silicates hydrates CSH (I), visually resembling a twisted foil. Considering the absence of lamellar loosely bound calcium hydrate crystals, and the presence of calcium silicate hydrates with an increased surface area, it is expected that the adhesion of the cement matrix to the surface of the GFRP rod will improve.
The modification of the composition with a dispersion of technical soot (Figure 6) led to the compaction of the material structure (Figure 6a). The adhesion of the cement matrix to the surface of the composite rod was increased, which, under loading, resulted in the destruction of glass fibres in the GFRP rather than in the interfacial transition zone between the cement matrix and the rod surface (Figure 6b).

Figure 5. Microstructure of the interfacial transition zone in the test samples: (a) with the dispersion of metakaolin, (b) with the dispersions of Peneco Nano Stachema

Figure 6. The microstructure of the interfacial transition zone in the test samples when the dispersion of carbon black is added to the cement matrix: (a) at 1000-fold magnification, (b) - a fragment of the microstructure at 5000-fold magnification

Figure 7a shows that the use of carbon soot as a modifier of the cement-based composites leads to a change in the crystalline structure of hydration products along the surface of the GFRP rod, creating a dense and low-permeable shell around the rod. X-ray microanalysis of the interfacial transition zone between the cement matrix and the glass fibre (Figure 7) showed that, in addition to calcium (Ca), silicon (Si), oxygen (O) atoms included in calcium silicate hydrates, the presence of carbon atoms (C), characteristic of soot, and aluminium atoms (Al), forming aluminoborosilicate glass, was also noted.
Figure 7. Microstructural analysis of the interfacial transition zone between the cement matrix modified with a dispersion of carbon black and the glass fiber surface: a) the studied area of the cement matrix on the glass fiber surface, b) X-ray microanalysis spectrum

Additionally, the adhesion of the cement matrix to the reinforcement rod was ensured by coating it with Peneco Nano primer manufactured by Stachema. It can be seen from Figure 8 that in this case the adhesion of the cement concrete to the epoxy coating exceeded the cohesive strength of concrete and is thus sufficient for anchoring the reinforcing bar in it.

Figure 8. Microstructure of the interfacial transition zone in the sample with nanostructuring additives: a) cohesive rupture of the polymer in the GFRP reinforcement rod, b) adhesion between calcium silicate hydrates C-S-H and the surface of the polymer reinforcement rod

The IR spectrum of the interfacial transition zone between the modified cement matrix and glass fiber (Figure 9b) shows the intensification of the absorption lines around 1080 cm⁻¹ and a significant decrease in the intensity of absorption lines at 968 cm⁻¹, both when the structure was modified with metakaolin (Figure 9b) and technical soot with additional surface treatment of the reinforcement rod with Peneco Nano Stachema primer. This indicates a significant change not only in the morphology of the new formations (Figures 5, 6, 7a), but also in their mineralogy, which, in turn, leads to a change in the composition of the hydration products.

The results of IR spectral analysis are confirmed by the Differential thermal analysis (Figure 9). The endothermic effect in the temperature range 512 °C for the control sample shifts to 499 °C when modified with metakaolin and 506 °C when modified with technical soot. A decrease in the weight loss in the temperature range of 500-506°C was noted for the samples modified with metakaolin and technical soot dispersion, which confirms the decrease in calcium hydroxide content in the cement matrix due to the
pozzolanic activity of the additives and the binding of calcium hydroxide into calcium silicate and aluminosilicate hydrates. The formation of calcium aluminosilicate hydrates in the samples modified with metakaolin was confirmed by X-ray microanalysis, the spectrum of which shows the presence of aluminum atoms (Figure 7b). When the cement matrix is modified with technical soot dispersion, an increase in the endothermic effect at a temperature of 801.6 °C is noted, which can be caused by a more intense conversion of calcium hydroxide into calcium silicates hydrates (Figure 9f). In this case, the TG line shows that the weight loss of the sample upon reaching this temperature increased by 25% in comparison with the sample modified by metakaolin. This can be due to the fact that calcium aluminosilicate hydrates contain a smaller amount of bound water in the crystal structure.

The changes in the DTA spectra, the strengthening of absorption lines in the region of 1080 cm\(^{-1}\), the appearance of new absorption lines in the regions of 779 cm\(^{-1}\) and 694 cm\(^{-1}\) confirm the possibility of changing the mineralogical composition of the cement matrix by modifying it with metakaolin and the dispersion of technical soot.

![Figure 9. IR and DSC (TGA) spectra: a, b) a reference sample, c, d) a sample modified with metakaolin, e, f) a sample modified with a dispersion of carbon black](image-url)
4. Conclusions
Thus, certain steps were taken towards strengthening the bond between the surface of the GFRP reinforcement rod and the cement matrix in the interfacial transition zone. It was found that the integrity of FRP reinforced concrete depends mainly on the ability of the composite reinforcement to work together with the adhesively bonded concrete layers. This bond can have both mechanical and chemical nature. When modifying additives are applied to the surface of the reinforcement rod, hydration products with higher density and strength are formed, mainly calcium silicate hydrates C-S-H of lower basicity. When metakaolin is used as a modifier, calcium aluminosilicate hydrates are formed on the surface of the rod, protecting it from alkaline environment in the concrete and providing better bond with the cement matrix. The introduction of metakaolin and a dispersion of technical soot led to an increase in the adhesion strength of GFRP rod with a cement matrix by 27% and 29%, respectively.

The proposed approach allows the formation of a strong and dense structure in the interfacial transition zone between the cement matrix and the GFRP reinforcement rod surface. The mineralogy and morphology of the hydration products is also changed due to the addition of the modifying additives, which improves the adhesion characteristics and corrosion resistance of GFRP in the cement-based composites.

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