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PULLOUT BEHAVIOR OF OXYGEN PLASMA TREATED POLYMER FIBERS FROM CEMENT MATRIX

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Abstract. The aim of this work is to describe bonding properties between surface treated polymer fibers and a cement matrix. In order to increase an interaction between the matrix and fiber surfaces, two fiber types having approx. 0.5 mm in diameter were modified by mean of oxygen plasma treatment.

Surface physical changes of treated fibers were examined using SEM morphology observation and interfacial adhesion mechanical tests. The principle of mechanical tests rested on a single fiber pulling out from the matrix (cement paste, CEM I 42.5 R, w/c 0.4). The embedded length was equal to 50 % of original fiber length (50 mm), where the fiber free-end displacement and force resisting to the displacement were monitored.

It was pointed out that interfacial shear stress needed to break the bond between the modified fibers and the matrix increased almost by 15–65 % if compared to reference fibers. When the fiber free-end displacement reached to 3.5 mm, the shear strength increased almost twice.

Keywords: Cement composites, fiber reinforcement, plasma treatment, morphology, pullout.

1. Introduction

A fiber-reinforced concrete (FRC) is a composite material containing fibers in an amount of 1 % of concrete volume standardly. The role of the fibers is to promote a crack distribution and to reduce crack widths. FRC mechanical properties are dependent on (i) properties of each components (by which we mean mainly cement matrix as a continual phase and fibers as reinforcement) and (ii) a mutual interaction between the two basic phases. The strong interaction characterized by the bond and the adhesion between the two phases plays an important role in the mechanical performance of the FRC [1–3].

The FRC may be reinforced with polymer fibers. The use of polymer instead of more widespread steel fibers brings a number of benefits: a corrosion resistance, a lower propensity to a balling fibers creation during a mixing process, a frugality to hosses and nozzles of shotcrete devices, etc [4].

Despite the above mentioned benefits, polymer fibers (including polypropylene, polyethylene, Nylon, PVA, etc.) have their significant limitations. This is primarily about poor adhesion and wettability to the cement matrix due to their chemical inertness, low surface energy and smooth surfaces [5, 6].

The smooth fiber surfaces can not guarantee required strong adhesion with the matrix. After the full debonding, when fibers are pulled out from the matrix, a weak abrasion effect results to FRC integrity infraction. To ensure reinforcing effect, high amount of fibers can be applied. Unfortunately, this access is inappropriate due to mixture workability reducing effect [3]. On the other hand, an interfacial bond strength enhancement seems to be the most effective way to improve FRC mechanical performance without undesirable side effects, especially in the field of polymer fiber reinforcement [7–9].

In order to modify polymer fiber surfaces, several types of treatment may be applied, e.g. chemical (e.g. use of high alkali solutions) and physical (e.g. mechanical roughening). Unfortunately, the first mentioned method we can not considered to be effective and environmentally friendly due to high time consumption (often crossing tens of hours), requirement of high temperature (almost 100 °C) and need to use aggressive chemical substances [9–11]. Next, it is difficult to control the mechanical methods and moreover, its effect has a very strong impact on fiber mechanical properties [12, 13].

To modify polymer fiber surfaces effectively, a plasma treatment seems to be good alternative to conventional methods mentioned earlier. An effect of the plasma treatment is twofold: chemical as well as physical. The chemical treatment rests in a polymer surface activation, when active polar groups are implemented onto fiber surfaces. As a consequence, the surface is modified from hydrophobic to hydrophilic and thus its reactiveness with polar liquid (water contained in cement paste) is increased [8, 14]. Next to that, the polymer surface is roughened via ion bombardment. In the case of the FRC containing polymer fibers, the second mentioned phenomenon is very important to achieve strong adhesion between

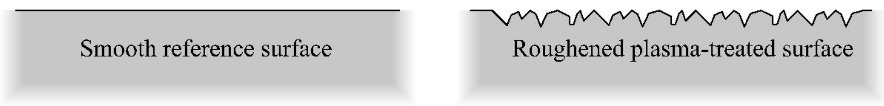

Figure 1. Principle of physical surfaces treatment (from own resources).

Name [-]	Material [-]	Diameter [µm]	Young modulus [GPa]	Length [mm]	Mass Density [kg/m^3]
Concrix	polyolefin	500	≥ 10	50	910
BeneSteel	PP, PE	480	5.17 ± 0.50	55	∼913

Table 1. Summary of basic fiber parameters.

the two materials when the fiber is pulled out from the matrix (called as bridging effect). In this study, we focus primarily just to the physical modifications and their effect. The theoretical principle of the plasma modification is imaged in the Figure 1.

As a proper indicator of the interaction rate between the modified fibers and the matrix, mechanical tests should be done. Indirect mechanical methods have been applied – for example bending tests of the composite material [8]. Nevertheless, pullout tests of the single fiber from the matrix provide clear information about the interaction between the two materials. Therefore, we focused to the second mentioned method. Moreover, the effect of ion bombardment may be examined using SEM morphology investigation and AFM surface scanning [8, 15].

2. Materials

2.1. Polymer fibers

Two types of polymer macro-fibers were used. Both of them are standardly used as randomly distributed and oriented reinforcement in the field of the FRCs to reduce creation and development of shrinkage cracks and to preserve construction integrity. Concrix fibers composing from two layers (shell and high-modulus core) were made from polyolefin (a specific type was not provided by the manufacturer) in Switzerland. BeneSteel fibers composing from PE (polyethylene) and PP (polypropylene) mixture were made in the Czech Republic. The basic fiber parameters provided by their manufacturers are summarized in Table 1.

2.2. Cement samples

Cement prismatic samples composed of Portland cement CEM I 42.5 R (water to cement ratio w/c 0.4) having dimensions equal to 25×20×25 mm were made and stored for 15 days (unmolded after 1 day of hardening) in standard laboratory conditions. A fiber embedded length was equal to 25 mm. The sample is captured in Figure 2.

Figure 2. Cement specimen with single fiber for pullout tests.

3. Methods

3.1. Plasma modification

In order to modify fiber surfaces physically, the oxygen cold plasma treatment was done using Tesla VT 214 device. The duration of plasma treatment was 30 and 480 seconds. The first mentioned duration (30 seconds) should guarantee required surface changes, but only to a minimal extend. On the other hand, the longer mentioned duration was established as the longest possible time (when the fiber were treated even longer, their melting temperature was reached). The power of RF source was 100 W, gas pressure 20 Pa.

3.2. SEM morphology analysis

To asses physical changes onto fiber surfaces properly, the scanning electron microscope observation was done by Zeiss Merlin (Carl Zeiss Microscopy GmbH). Using the plasma sputtering system (BOC Edward Scancoats Six), the fibers were coated by thin gold layer to eliminate surface charging during SEM analysis.

3.3. Pullout tests

Ass a proper indicator of the interaction of both reference and plasma treated fibers and the cement matrix, pullout tests of the single fiber were realized. The displacement controlled testing took place on the loading frame Web Tiv Ravestein FP100 at the constant rate of 0.8 mm/min until reaching 60 N and 0.6 mm/min further. As a result of the experiment, a dependence between the fiber free-end displacement and the force

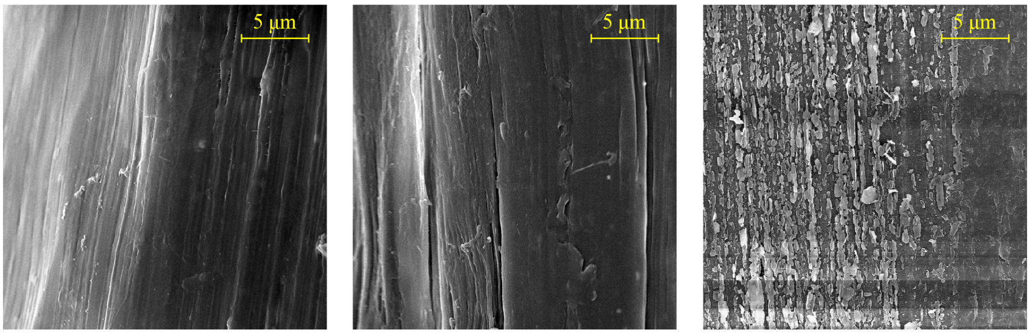

Figure 3. SEM images of reference (left), 30 s (middle) and 480 s (right) plasma treated Concrix fibers.

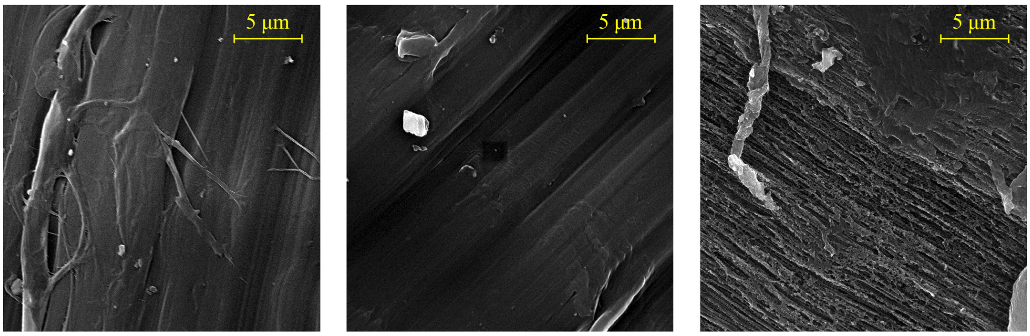

Figure 4. SEM images of reference (left), 30 s (middle) and 480 s (right) plasma treated BeneSteel fibers.

resisting to the displacement was recorded. To provide values normalized by the fiber surface area, the interfacial shear stress was calculated. We focused to two stages: (i) when the pullout force reached its maximum and (ii) when the fiber free-end was displaced by 3.5 mm. The mentioned shear stress was calculated as

$$\tau_{max} = \frac{F_{max}}{C_f l_e} \quad (1)$$

and

$$\tau_{3.5} = \frac{F_{3.5}}{C_f l_e} \quad (2)$$

where F_{max} and $F_{3.5}$ represent the maximal force and the force needed to reach the fiber free-end displacement of 3.5 mm, C_f is a fiber circumference and l_e is a fiber embedded length.

4. Results

4.1. SEM morphology analysis

The morphology changes onto Concrix and BeneSteel fiber surfaces are shown in the Figure 3 and Figure 4, respectively. The SEM images with magnificence of 5k showed that both types of untreated fibers had smooth surfaces having tiny grooves that originated probably from a production technology. The same can be said of fibers modified 30 seconds by plasma treatment. This treatment time turned out to be too short to achieve fiber surfaces physical changes via the ion bombardment but despite of this, tiny morphology changes were revealed. On the other side, the surfaces were significantly changed after 480 seconds of modifications. In the case of Concrix fibers, their surfaces were slightly damaged. A violation of the surfaces by scoops was observed. In the case of BeneSteel fibers, their surfaces after 480 seconds of plasma treatment can be described as significantly roughened by longitudinal grooves, if compared to reference fibers.

The roughening of fiber surfaces has twofold importance, as mentioned below.

- Increase of the surface area. Before full debonding, when is the FRC exposed to tensile load, chemical bonds between the two materials are realized on a larger area and thus a stronger mutual interaction is ensured.
- Increase of the shear stress. After full debonding, when are fibers pulled out from the matrix, the shear strength is increased due to the fiber surface roughness.

4.2. Pullout tests

Pullout tests of single fibers from cement matrix revealed the significant cohesion increase in the both stages – before and after the full debonding.

Before the full debonding, the maximal shear stress (τ_{max}) was increased by ca. 10 and 60 % regardless to the duration of the plasma modification in the case of Concrix and BeneSteel fibers, respectively. This phenomenon can be attributed to the increase of the contact area and to the activation of the surfaces by

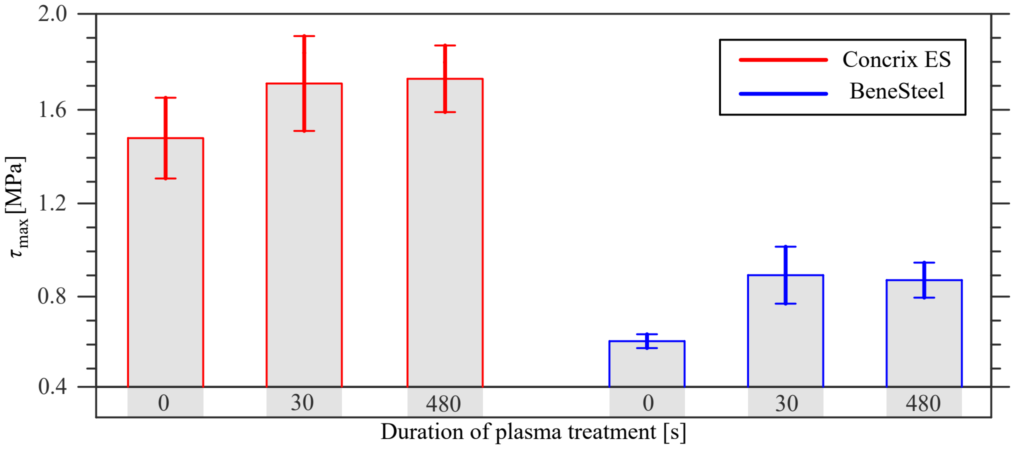

FIGURE 5. Maximal interfacial shear stresses for various treatment duration.

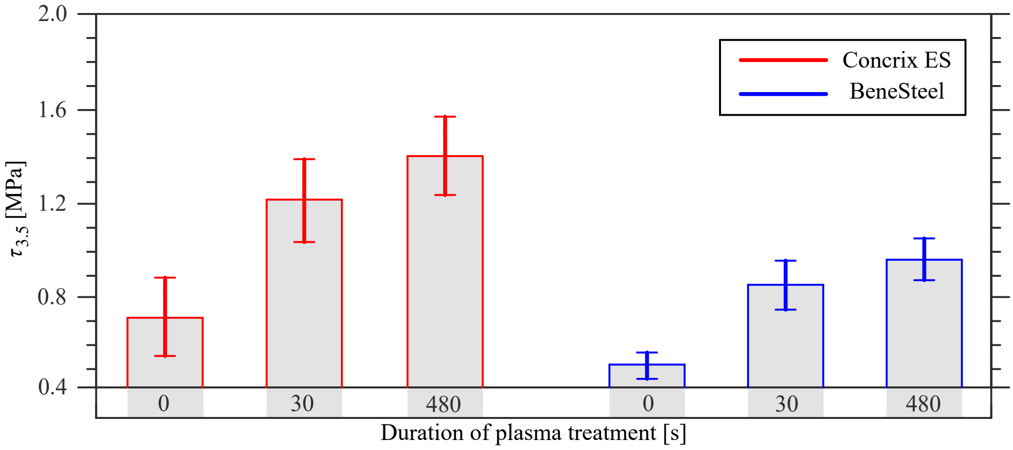

FIGURE 6. Interfacial shear stresses at 3.5 mm pullout for various treatment duration.

functional polar groups. The results are graphically shown in the Figure 5.

In this study, we focused especially on physical fiber surface changes, so we put more emphasis to the shear stress ($\tau_{3.5}$) monitored when fibers pulled out from the matrix by 3.5 mm (after the full debonding). The results revealed that the shear stress increased after 30 seconds of the plasma treatment by ca. 70 and 80 % in the case of Concrix and BeneSteel fibers, respectively. After 480 seconds of the treatment, an other shear stress increase was recorded. Concretely by 15 % identical for both fiber types as is shown in Figure 6. These phenomenons were caused by the increase of fiber surface roughness.

5. Conclusions

Two types of polyolefin macro-fibers having ca. 0.5 mm in diameter were surface treated by mean of the cold low-pressure oxygen plasma treatment in order to achieve their surface physical changes via ion bombardment and thus to enhance an interaction between their surfaces and the cement matrix.

The fibers were exposed to plasma by 30 and 480 seconds. To asses the plasma modification impact onto fiber surfaces, the scanning electron microscopy enabling an observation of morphology and single fiber pullout tests from the cement matrix (prismatic cement specimens composed of Portland cement CEM I 42.5 R, w/c ratio 0.4, dimensions 25×20×25 mm, embedded length 50 % of the fiber original length) pointing out on an interaction between the two materials directly were done. Interfacial shear stresses were calculated to mutual compare and normalize provided values. The stresses were assessed into two stages – when the value reached to its maximum (before the full debonding) and when the fiber free-end was pulled out from the matrix by 3.5 mm. Because we concerned primarily to the physical fiber surface modification, we focused on the shear stresses when was the fiber completely debonded from the matrix in detail. Based on the two experiments, we found out that:

- Fiber surfaces were roughened via ion bombardment especially in the case of modification lasting 480 seconds. Compared to reference fibers characterized by the smooth surface, modified samples were etched. Grooves and other surface damages were revealed (scales, depressions) using SEM.
- The cohesion between the two materials was significantly increased. The maximal interfacial shear stress increased by ca. 10 and 60 % for both treatment times (30 and 60 seconds) of plasma modification in the case of Concrix and BeneSteel fibers, respectively. After the full debonding, the cohesion between both fiber types was increased by 70–80 %, if compared to reference fibers.

All in all, it was demonstrated that plasma treatment is an effective method to modify polymer fibers surfaces in order to enhance their interaction with the cement matrix, as it was found also in [5, 8, 14]. This modifications may bring many benefits in the field of FRC production. To extend the plasma modification into the industrial use, it will be necessary to accelerate the treatment process.

Acknowledgements

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