Study on time-dependent surface properties of plasma treated polymer fibers

Jan Trejbal[1]*, Tereza Valentová[2], Zdeněk Prošek[1,3]

[1]Department of Mechanics, Faculty of Civil Engineering, CTU in Prague, Thákurova 7/2077, Prague, 166 29, Czech Republic
[2]Department of Road Structures, Faculty of Civil Engineering, CTU in Prague, Thákurova 7/2077, Prague, 166 29, Czech Republic
[3]University Centre for Energy Efficient Buildings, CTU in Prague, Třinecká 1024, Buštěhrad, 273 43, Czech Republic

*Corresponding author

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Abstract

This work focuses on a surface modification of polypropylene micro-fibers having 18 μm in diameter and 12 mm in length by means of the cold low-pressure oxygen plasma treatment. The main goal is to change fiber surface properties from hydrophobic to hydrophilic and from smooth to slightly roughened and thus to ensure a strong adhesion of their surfaces with a cement matrix. As a proper indicator of realised modifications, scanning electron microscopy (an assessment of surface roughening) and a wettability measurement with demineralized water were done. Moreover, in order to establish a time-dependent stability of the chemical changes onto fiber surfaces, the wettability measurement was repeated immediately after the treatment and with a time lag equal to 1, 7 and 30 days, when fibers were exposed to standard atmospheric conditions. To asses a rate of an adhesion between fibers and the cement matrix, mechanical four-point bending tests of prismatic cement samples (CEM I 42.5 R, w/c 0,4, dimensions 40×40×160 mm) reinforced with both reference and treated fibers were performed. SEM revealed slightly roughened fiber surfaces after plasma modifications. The treated fiber wettability with water increased almost twice, compared to reference fibers. Nevertheless, the wettability fast decreased to reference values.

Keywords: Polymer micro-fibers, oxygen plasma, surface properties, wettability.

Introduction

The fiber reinforced concrete (FRC) is a composite material conventionally containing randomly oriented fibers as a reinforcing discontinuous phase. Standardly, as a basic continuous phase, a concrete based on Portland cements is used. The second phase – the reinforcement is ordinary used in an amount equal to approx. up to 1 % of a concrete volume. For an idea, an equivalent of this amount is 78.5 and 9.1 kg of fibers per 1 m^3 of the concrete in the case of steel and standard polymer fibers (e.g. polypropylene or polyethylene), respectively [**1, 2**].

This material has become popular throughout the world in the field of a shotcretes production, flor structures, thin-walled precast products and the like due to its preferable material properties. FRCs often exhibit perfect mechanical properties in tension and bending, especially when compared to plain concretes [**2, 3**]. Constructions made from the FRC can be described as tough and durable [**4**].

The role of the reinforcement is to promote a crack creation and a distribution in the stages during the mixture hardening and to reduce crack widths and thus to prevent a material disintegration via so-called bridging effect in post-cracking stages when the material is overloaded [**2, 3**].

The fiber reinforcement is characterized by a material origin (steel, glass, carbon, polymer, plant- or animal-based, etc.), a relatively high tensile strength, a modulus of elasticity, a high aspect ratio (ratio of fiber length to diameter) and by an ability to create bonds with the cement matrix [**1**].

As the fiber reinforcement in FRCs, steel wires or fibers are the most used in the field of civil engineering. Unfortunately, the use of steel fibers has its limitations, e.g. as follows: a low-corrosion resistance (or high price for a use of stainless steel), a high propensity to a balling fibers creation during a mixing process, a low frugality to hoses and nozzles of shotcrete devices, etc. To eliminate these drawbacks, polymer fibers can be applied as an almost equivalent alternative to steel fibers [**5**].

However, it must be taken into an account, that surface of most polymer fibers (including the most used polypropylene and polyethylene) can be described as smooth and chemically insert, when related to the cement matrix. As the result of the phenomenon, the interaction between fiber surfaces and the matrix, playing an important role in FRC mechanical properties, is so poor. Consequently, when FRC based constructions are loaded by the tensile stress, the bridging effect mentioned earlier is insufficient. To maximize a reinforcing effect unfolding from the bridging effect, the amount of fibers or the fibers aspect ratio can be increased. Unfortunately, both of these approaches may cause a reduction of the mixture workability. On the other hand, surface modifications of polymer fibers can be done in order to change their surface properties from hydrophobic to hydrophilic (chemical change) and from smooth to roughened (physical change) and thus to ensure a strong bond (adhesion) with the cement matrix [**6, 7, 8**].

In order to modify polymer fiber surfaces, it is advisable to carry out several types of treatments. These treatments can be divided, in general, into two groups – physical and chemical methods. The first mentioned method rests in a mechanical roughening of fibers. However, the mechanical roughening has a strong impact also on fiber mechanical properties. Thus modified fibers can be significantly damaged and their ability to function as the reinforcement can be lost [**9, 10**]. Chemical methods are based on an etching of fiber surfaces by aggressive substances, e.g. by high alkali solutions (an alkaline hydrolysis using aqueous solutions of NaOH, $CaOH_2$, etc.). Neither these methods cannot be considered as effective. To achieve required changes onto fiber surfaces, fibers have to be exposed to solutions often up tens of hours. In addition, a high temperature of solutions is necessary for the etching process [**8, 11, 12**].

Compared to methods mentioned above, plasma treatment seems to be an efficient and an eco-friendly alternative for fiber surface modifications. Plasma can be defined as a ionized gas (composed of electrons, ions, and neutral species). The effect of the plasma treatment is twofold: chemical and physical. The chemical mechanism for the plasma surface modification relays on a surface atoms replacement by oxygen atoms and a formation of polar groups. The presence of polar or functional chemical groups enhances the reactivity with the cement matrix (contain water). Next to that, a physical mechanism rests in the surface roughening via a ion bombardment. The surface roughening increases an interfacial area and ensures an attainment of a friction between the two materials (the interfacial shear strength is thus increased) [**13, 14, 15**].

As is clear from the preceding paragraph, the plasma treatment becomes popular and often used in the field of polymer and other materials surface properties modifications. However, throughout the researches, there is a missing information about a time-dependence of modified surfaces, when they are exposed to standard atmospheric conditions. It is obvious that the mechanical modification (roughened surfaces) is irreversible. The same thing, however, cannot be said about chemical changes (presence of active polar groups). These groups may interact with an airborne dust and an air humidity contained in the atmosphere and thus the modified wettability may decreased to reference values. The main task is about the stability of activated bonding, when exposed to atmospheric conditions arises. The purpose of this work is to fill that void and to assess the rate at which the effect of plasma treatment decreases.

Experimental

Materials

Tested fibers: Polypropylene micro-fibers having 18 μm in diameter and 12 in length were used for purposes of this study. These fibers are standardly used as randomly dispersed and oriented reinforcement in the concrete mixture to avoid the creation of shrinkage cracks during the concrete hardening and to increase the construction fire-resistance. As provided by their manufacturer (Trevos, s. r. o., Czech Republic), fiber parameters are as follows: UTS ca. 273 MPa (a ultimate tensile strength, calculated from dTex unit), a ductility higher than 50 %, an industrial surface modification: a fabric water flushable softener. Fiber are shown in the **Fig. 1.**

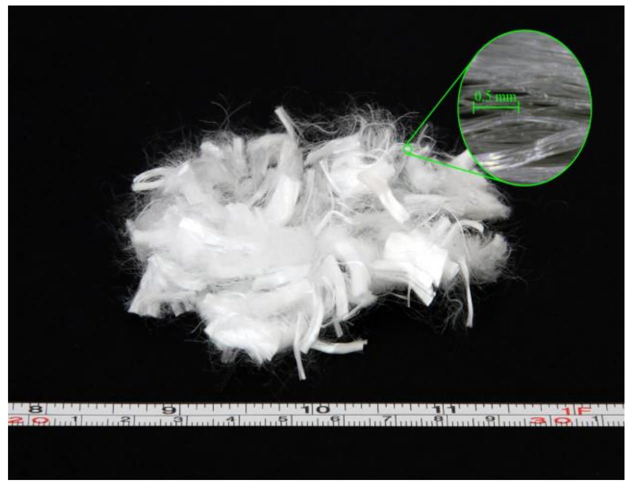

Fig. 1. Digital camera photo of tested fibers.

Cement samples: Prismatic cement paste specimens having dimensions equal to 40×40×160 mm were made using metal forms for further mechanical tests. The paste was composed from the Portland cement CEM I 42.5 R and water (water to cement ratio of 0.4). The paste was reinforced with both reference and modified fibers in an amount of 2 % of the paste volume. After 1 day, the prepared samples were cast out from forms and stored submerged into water 27 days (total age of samples equal to standard 28 days), when the samples were tested.

Methods

The plasma treatment: to improve fiber surface properties, the oxygen treatment in an inductively coupled plasma system (Tesla VT 214) was done. Constant plasma treatment process parameters were as follows: a total power 100 W, a total gas pressure 50 Pa and 50 sccm O_2 flow. The treatment was differed only by the exposition time (10, 60 and 240 seconds).

The wettability measurement: to assess the fibers surface wettability by demineralized water, the direct horizontal optical method allowing the contact angles measurement on the single fiber submerged into water was used. Both as received and modified fibers were placed vertically into the water level. The contact angle value was evaluated from a menisci of a liquid adhering on the fiber. This three phases interfacial contact was captured using an optical set. Thus obtained values were evaluated by means of CAMTIA – MatLab based on the in-house tool. The measurement was six times repeated in order to obtain statistically relevant data. The optical set is imaged in the **Fig. 2.** A demonstration of thus captured images is shown in the **Fig. 3.**

The scanning electron microscopy: SEM microscope (Zeiss Merlin, Carl Zeiss Microscopy GmbH) was used for the surface analysis allowing to determine morphology changes. To eliminate surface charging, the investigated fibers were overcoated by a thin gold layer using a plasma sputtering (BOC Edward Scancoats Six). The thickness of the gold layer was ca. 10 nm as measured by Veeco DekTak 150.

Bending tests: as an indicator of the interaction rate, a four-point bending displacement controlled test of cement samples reinforced with fibers was done. The result of the test was a dependence between the load and the displacement. The samples behavior recorded during the test allowed to evaluate the interaction (bond and adhesion) between the two materials indirectly. We focused especially on the maximum samples load-bearing capacity in the elastic stage and on the post-cracking behavior. The first mentioned parameter points out on the chemical interaction between fibers and the matrix, while the second parameter on adhesion, when the first crack occurred and fibers were pulled out from the matrix. The test was realized using the Web Tiv Ravestein FP 100 loading frame at the loading constant rate of 1 mm/min. Each type of the mixture was represented by 6 specimens in order to obtain a statistically relevant set of results.

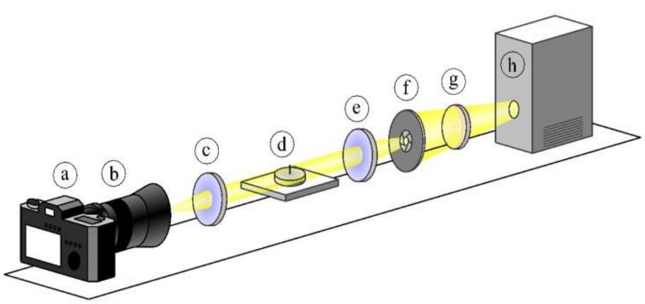

Fig. 2. Scheme of optical set using for contact angle measurement, from left: a) digital camera, b) zoom lens (f = 300 mm), c) convex lens (f = 50 mm), d) fiber submerged into the water, e) convex lens (f = 50 mm), f) circular aperture, g) light diffuser, h) light source.

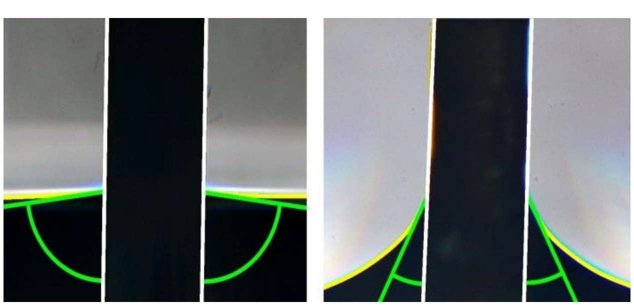

Fig. 3. Reference (left) and treated (right) fiber submerged into the water with outlined contours.

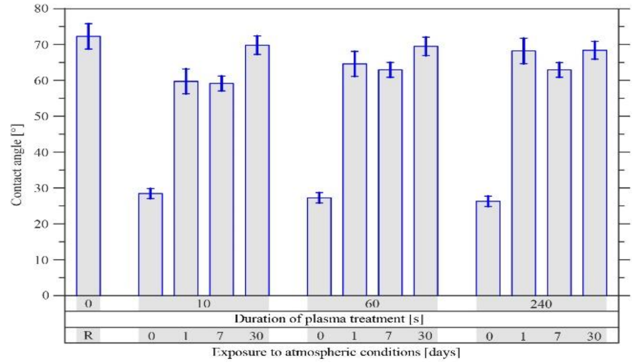

Fig. 4. Contact angles depending on the plasma treatment time and the exposition to atmospheric conditions measured on fibers.

Results and discussion

As-received fibers exhibited a relatively low wettability with demineralized water. In this case, the contact angle reached on 73.1 ± 2.1 °. In contrast with that, contact angles measured on treated fibers regardless to the treatment time did not overcome 30°, when measured immediately after the modification. It is clear that the wettability was improved more than twice. It can be assumed that this result ensures the stronger adhesion between fibers and the cement matrix (containing water). Nevertheless, when treated fibers were exposed to atmospheric conditions, their wettability was significantly deteriorated. Just 1 day after the treatment, contact angles were increased to approx. 60-65°. Values measured after 7 days were practically identical to contact angles after 1 day. In the case of fibers exposed to atmospheric conditions, contact angles increased about other 5°. It was found out that chemical changes onto modified fiber surfaces are reversible almost to reference values. These results are summarized and graphically shown in the **Fig. 4.**

Surface morphology changes of plasma treated fibers are shown in **Fig. 5**, as obtained using SEM. While the surface of reference fibers can be described as smooth or even shiny, some changes were present in the case of samples treated for 240 seconds. This surface was dim and roughened by small scratches. This phenomenon may contribute to increase of the adhesion between fiber surfaces and the cement matrix and thus to support the bridging effect when the matrix is tensile loaded. We found out the similar result in our other research [**7**].

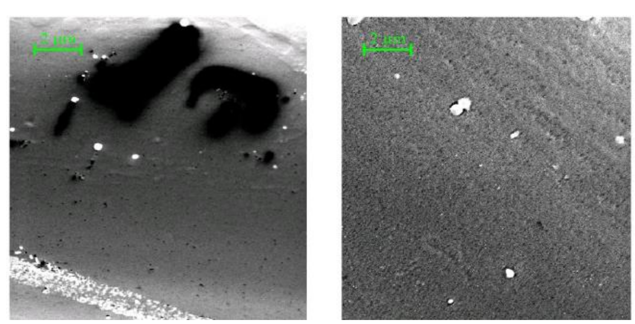

Fig. 5. SEM images of reference (left) and 240 seconds plasma treated (right) fibers.

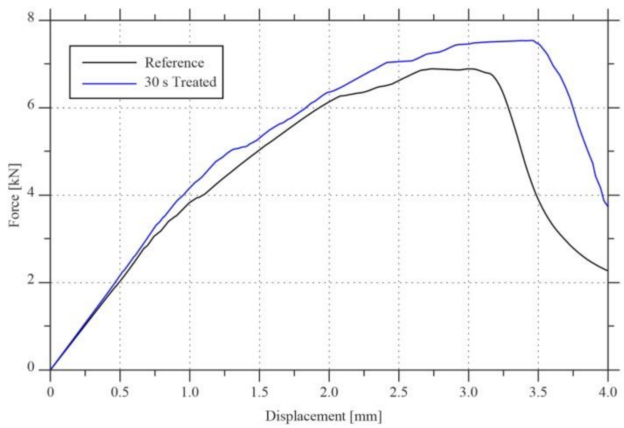

Fig. 6. Force-displacement diagram of cement samples reinforced with reference and 30 seconds plasma treated fibers.

Mechanical tests of prismatic cement-paste samples confirmed that surface changes onto fiber surfaces mentioned above have a positive impact on the mechanical behavior of the bending loaded specimens. As captured in the **Fig. 6**, the toughness of samples reinforced with modified fibers was higher at any displacement, if compared to samples made from the reference mixture. The increase of the initial toughness was caused probably by the reduction of the amount and width of shrinkage cracks created during mixture hardening. Next, the significant toughness increase was recorded in stages of post-cracking where the first cracking was occurred. The fiber surface roughness was responsible for the difference between the post-cracking behavior of two types of mixtures.

Conclusion

Polypropylene micro-fibers having 18 μm in diameter and 12 in length used as the reinforcement in fiber reinforced concretes were treated by means of the oxygen cold plasma treatment in order to achieve their surface changes and thus to ensure their interaction with the cement matrix. Both chemical and physical changes of treated fibers were examined using the contact angle measurement (wettability by water determination) and the scanning electron microscope (morphology assessment). In addition, to reveal the surface chemical changes stability of the treated fibers, wettability measurement was repeated immediately, 1, 7 and 30 days after the treatment, when fibers were exposed to standard atmospheric conditions. To detect the interaction between fibers and the cement matrix (CEM I 42.5 R, w/c ratio 0.4), four point bending tests of prismatic samples (dimension 40×40×160 mm) reinforced with reference and plasma treated fibers in the amount of 2 % of the cement paste volume were done.

It was found out, that the plasma treatment increased the fiber surface wettability with demineralized water more than twice. However, the wettability was deteriorated almost to reference values already after one day (after the treatment). SEM images revealed the increased roughness onto modified fibers. Mechanical tests showed indirectly on the interaction increase between modified fibers and the cement matrix.

Acknowledgements

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