INTERFACE ENHANCEMENT BETWEEN POLYMERIC MACRO FIBERS AND CEMENT MATRIX BY PLASMA TREATMENT

TREJBAL Jan[1], ŠMILAUER Vít[1], KOPECKÝ Lubomír[1], ARTEMENKO Anna[2], POTOCKÝ Štěpán[2]

[1]Czech Technical University in Prague, Faculty of Civil Engineering, Prague, Czech Republic, EU,
jan.trejbal@fsv.cvut.cz
[2]Czech Academy of Science, Institute of Physic, Prague, Czech Republic, EU

Abstract

Commercial polymeric macro fibers Concrix ES having 500 µm diameter were treated to attain stronger adhesion with cement matrix. In order to improve their wettability with water, low pressure inductively coupled oxygen plasma treatment was used. Thus treated fibers were investigated from chemical and physical perspective. A direct horizontal optical static method enabling contact angle measurement directly on the fiber surfaces revealed that fibers treated only 5 s exhibited significantly better water wettability (approximately two times) while their mechanical properties were not influenced, as found by fiber tensile strength tests. Fiber morphology changes were observed by scanning electron microscopy - in contrast with reference fibers, the surfaces of treated samples were significantly roughened. The XPS analysis confirmed an exchange of surface atoms by oxygen ones within the 5 s of plasma treatment. A practical indicator of executed modification, pull out tests of selected fibers from cement paste samples (water to cement ratio 0.4), were done. It was shown that plasma treated fibers exhibited stronger chemical interaction with cement matrix by approximately 30%.

Keywords: Plasma, oxygen, wettability, contact angle, pull-out tests, macro fibers

1. INTRODUCTION

Usage of synthetic fibers for reinforcement in composites becomes increasingly diversified. In the civil engineering, the fiber reinforcement is the most often used for the production of concrete materials, e.g. floors, foundation slabs, thin walled or impact-resistant precast and shotcrete [1-3]. In comparison with steel, synthetic (polymeric) fibers are characterized by low density, high chemical resistance and relatively low cost, whereas their mechanical properties (tensile strength and Young modulus) are sufficient [4]. On the other hand, smooth fiber surfaces and low wettability does not guarantee a strong (chemical and physical) interaction between fiber surfaces and composite matrix [5-7].

In order to improve interaction between reinforcement and matrix, fibers can be modified by mechanical or chemical treatment [7, 8]. Both mentioned methods have an impact rather on physical interaction (shear strength). To guarantee the Young modulus and tensile strength (or bending strength) enhancement of composites, it is necessary to increase especially the chemical interaction between reinforcement and matrix [9].

To increase chemical and physical interaction in interface zone, plasma treatment seems to be a progressive method. The low pressure plasma treatment represents a universal, efficient and eco-friendly alternative for surface modifications of almost any synthetics materials. The principle of modifications relays on surface activation (polar and functional groups formation - responsible for chemical bonds) and surface roughing (physical interaction) [10, 11].

In the present work, we report the results of oxygen plasma treatment of commercial polyolefin macro fibers Concrix ES. The influence of treatment time on fiber wettability, surface morphology and chemical composition, mechanical properties and pull-out behavior from cement matrix is studied.

2. MATERIALS AND METHODS

Concrix - Switzerland bi-components fibers having a diameter equal to 0.5 mm and 50 mm length were made from high E-modulus polyolefin. Their bulk was composed of two main parts - high E-modulus high strength core giving high-grade mechanical properties to fibers and structured shell giving resistance to surface damage and good processing to concrete mixture and fiber surface/concrete interface binding. Other fiber parameters were as follows: modulus of elasticity >10 GPa, density 0.91 g/cm^3, melting temperature ca. 150°C, tensile strength 600 MPa, inert alkali / acid resistance [3, 4].

All cement samples used in this study were made from cement paste based on Portland cement (Radotín in the Czech Republic, CEM I 42.5 R). Water to cement ratio was 0.4.

To improve the water wettability of fibers, oxygen treatment in inductively coupled plasma system (VT 214, Tesla) was done. Plasma treatment parameters were: total power 100 W, total gas pressure 60 Pa, 50 sccm O_2 flow, and the exposition time 5 to 480 s.

A direct horizontal optical method was used for fiber wettability evaluation [12]. The final contact angle value was averaged from 6 independent measurements.

Scanning electron microscope (Maia 3, Tescan) was used for fiber morphology analysis. To eliminate surface charging, the investigated fibers were overcoated by thin gold layer (BOC Edward Scancoats Six). The sputtering process parameters were: deposition time 40 s, sputter voltage 1.3 kV, electric current 35 mA, total gas pressure 26.6 Pa. The thickness of the gold layer was approximately 10 nm as measured by Veeco Dektak 150.

The chemical composition of the polyolefin fiber surfaces was analyzed by X-ray photoelectron spectroscopy (XPS) using XPS spectrometer (Kratos, AXIS Supra) equipped with a hemispherical analyzer and a monochromatic AlKα X-ray source (1486.6 eV). The experiment was executed on reference, 5 s, 30 s and 480 s plasma treated fibers. The XPS spectra were acquired from the area of 110 × 110 μm^2 with the take-off angle 90°. The survey XPS spectra were recorded with the pass energy of 80 eV, whereas the high resolution spectrum scans with a pass energy of 20 eV. The CasaXPS software with implemented linear baseline and Gaussian line shapes of variable widths for peak fitting was used for spectra processing. XPS peak positions were determined with an accuracy of 0.2 eV. The samples were calibrated on 285 eV (C-C bond) [13]. The deconvolution of C 1s peak was made into 4 peaks: C-C 285 eV, C-O 286.6 eV, C=O 287.8 and O-C=O 289 eV [13, 14].

Tensile strength test was carried out using loading frame Web Tiv Ravestein FP100. The experiment was displacement-controlled at a constant rate of 0.8 mm/min in the case of load up to 60 N and 0.6 mm/min in above 60 N, respectively. The value of fiber tensile strength and load carrying capacity (N/fiber) was averaged from six measurements.

Single fiber pull-out tests were realized in order to reveal interface bond between fiber surfaces and cement matrix. Prismatic samples having dimensions equal to 25 × 20 × 40 mm were made form cement paste. Each sample contained single fiber which was placed in an identical position with specimen center (longitude axis). The embedded length of the fiber was equal to the cement specimen length (i.e. 40 mm). Thus prepared samples were stored in laboratory conditions (room temperature, relative humidity of about 50%) for 28 days. Based on the previous experiments, reference and fibers treated by plasma for 30 s were chosen for this testing, each represented by 6 pieces. After mixture curing and hardening, single fiber pull-out tests were done using the same loading frame as in tensile strength tests. Cement sample part was fixed in the self-locking static chuck, while fiber free end was fixed in the movable chuck. The experiment was displacement-controlled at a constant rate of 2 mm/min.

3. RESULT AND DISCUSSION

The dependence between duration of plasma treatment and contact angle is shown in the **Figure 1**. An average contact angle measured on reference fibers was equal to 54.0±6.9°, while in all cases of plasma treated fibers this value oscillated between minimal 23.4±2.8° (treated 60 s) and maximal 27.7±4.8° (120 s). It is shown that too long plasma treatment duration is not effective. After first 5 seconds of plasma treatment, the wettability drops down to approx. 25°. The similar findings were described by B. Felekoglu et al. [6], who tried to modify polypropylene (PP) planar plates via oxygen and argon plasma. They found that the highest wettability enhancement was evident after first 2 seconds of treatment [6].

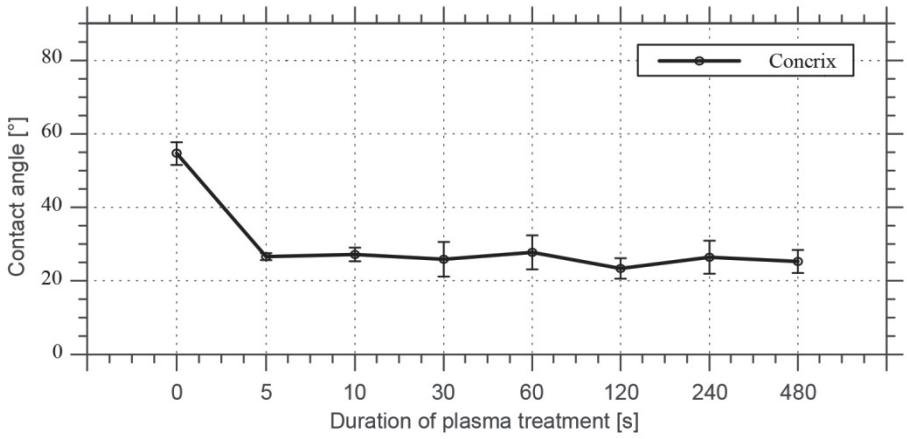

Figure 1 Contact angle values as a function of plasma treatment duration

The surface morphology changes of plasma treated fibers are shown in the **Figure 2**. While the surface of reference (marked as Concrix_R) and plasma treated fibers by 30 s (Concrix_P30) can be described as smooth and planar, significant morphology changes were present in the case of samples treated for 480 s (Concrix_P480). The surface of 480 s treated fibers was roughened and scaly in the monomolecular layer. Our finding corresponded with AFM analysis of dielectric barrier discharge treated PP films executed by Ch. Wang and X. He. They found out that treated samples were characterized by ca. 15 times greater roughness in comparison with untreated ones [15].

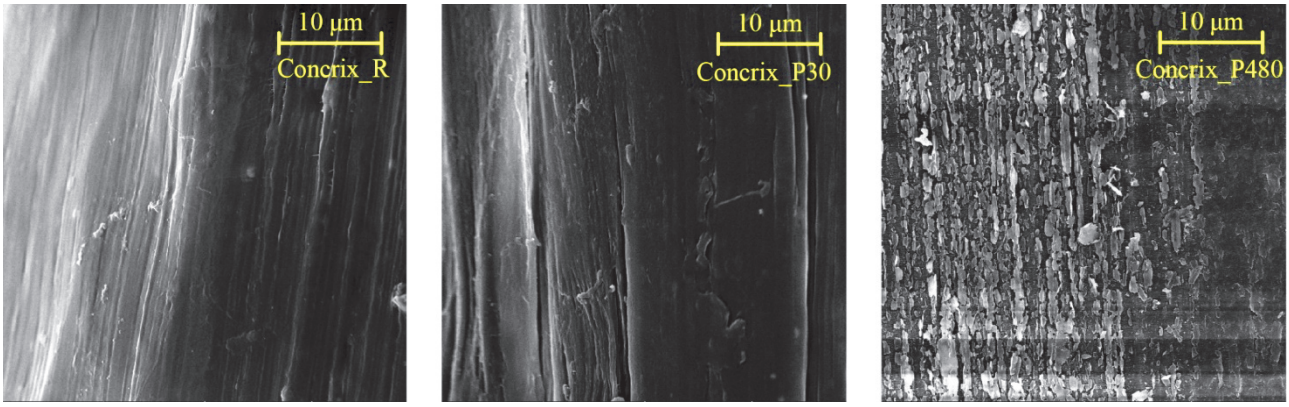

Figure 2 SEM image of reference (left) and plasma treated (30 s - center, 480 s - right) fibers

The **Figure 3** shows the C 1s XPS spectra of reference fiber (i.e. 0 min plasma treatment) and after O_2 plasma treatment (for 30 and 480 s). XPS spectra confirmed transformation of C-C/C-H bonds on untreated sample into C-O, C=O and O-C=O bonds. It is clear that already 5 s of O_2 plasma treatment resulted in a distinct

exchange of surface atoms with oxygen ones. Prolonged oxygen treatment does not increased significantly portion of oxygen bonds which is in agreement with results of water contact angle (see **Figure 1**).

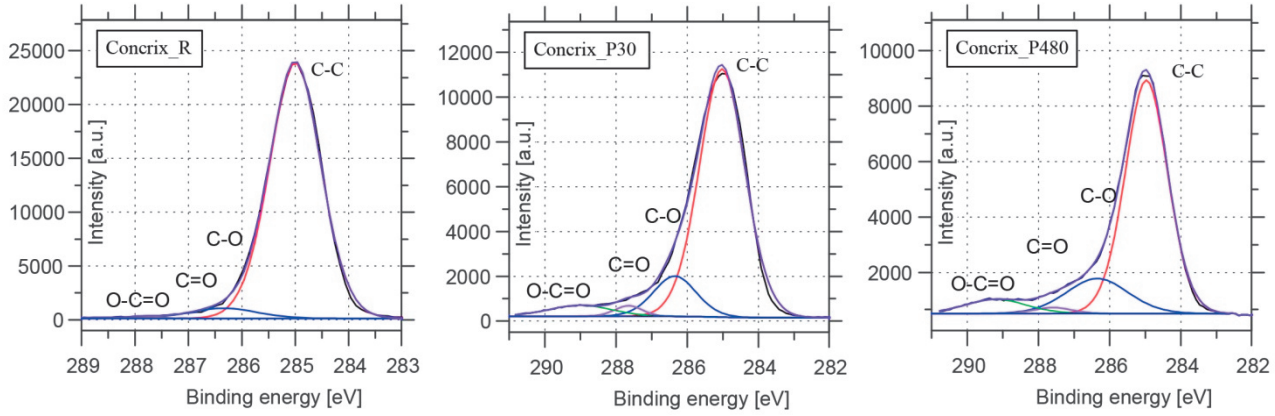

Figure 3 XPS spectra of reference 30 and 480 s treated fibers

Due to ion bombardment during plasma treatment, modified samples can be physically damaged. Fiber tensile strength tests were done as a proper indicator to reveal of plasma treatment impact on fibers mechanical properties. These tests showed that fiber load carrying capacity was equal to 97.1±3.7 N in the case of reference fibers, and the value oscillated about 90-100 N in the case of treated fibers, respectively. Thus we can conclude that plasma treatment did not influence mechanical properties of the fibers, despite the surface changes were found out by SEM analysis. An insignificant increase of load carrying capacity of treated fibers (mainly by 30-240 s) was presumably caused by experimental error. Low dependence of load carrying capacity is most probably caused by the stratified composition of tested fibers - the treatment influenced only shell, while load bearing core was not affected. Dependence between fiber load carrying capacity and plasma treatment duration is shown in the **Figure 4**.

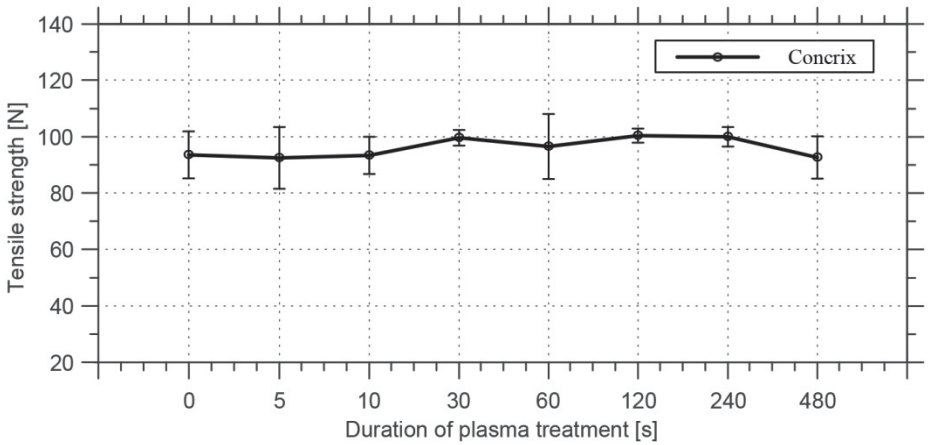

Figure 4 Tensile strength as a function of plasma treatment duration

Pull-out behavior of tested fibers is shown in the **Figure 5**. Expected results were obtained during fiber pull-out tests. While average force needed for reference fiber (Concrix_R) pull-out from cement matrix was equal to 74.4±7.2 N, 30 s plasma treated fibers (Concrix_P30) were pulled-out by higher force of 96.3±10.1 N. It is a nearly 30% increase of chemical interface bond between treated fibers and cement matrix. On the other hand, due to too long fiber embedded length, the increase of physical interface was not demonstrated. Four of six treated fibers were broken during pull-out test - their adhesion with matrix was stronger than their load carrying capacity. Because of this, average curve following slip-softening behavior cannot be calculated and

then compared with reference curve. It expected that for the shorter embedded length similar results to H. Wu and W. C. Li would be obtained. They increased both, chemical and physical bond between plasma treated polyethylene fibers and cement matrix [16].

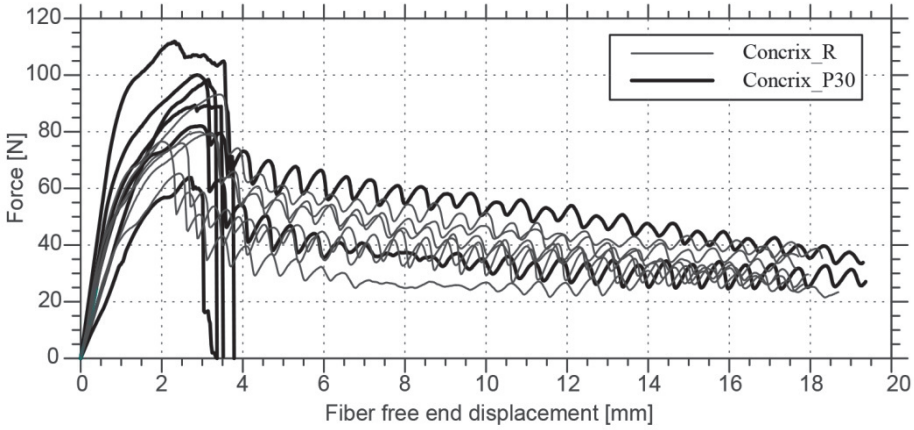

Figure 5 Pull-out behavior of reference and plasma treated (30 s) fibers

4. CONCLUSION

The low temperature oxygen coupled plasma treatments were used to attain the better interaction between polyolefin macro-fibers (called Concrix ES) and cement matrix. Water wettability of thus treated fibers increased more than two times after only 5 s treatment time. Physical and chemical surface changes were detected on fiber surfaces by SEM observation and XPS analysis. Due to ion bombardment, fiber surfaces were roughened as showed SEM pictures. The significant changes of chemical fiber surface composition and implementation of polar groups were detected by XPS. Despite these mentioned surface changes, the fiber load carrying capacity were not influenced as shown by tensile strength tests most probably due to the stratified composition of tested fibers. Finally, the effect of plasma treatment modification was proven practically - by pull out tests of a single fiber from cement matrix. This experiment demonstrated that plasma treated fibers by 30 s exhibited ca. 30% higher chemical adhesion between fiber surfaces and cement matrix.

ACKNOWLEDGEMENTS

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