

## PLASMA TREATMENT IMPACT ON PHYSICAL AND CHEMICAL PROPERTIES OF POLYMERIC FIBERS

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**ABSTRACT.** Presented work focuses on chemical and physical properties of plasma modified polymeric macro-fibers. Polyethylene terephthalate (PET) and polypropylene (PP) fibers having approx. 300  $\mu\text{m}$  in diameter were modified using cold oxygen plasma in order to achieve their surface changes needed for durable bond and adhesion with cement matrixes. A duration of plasma modification differed between 5 to 480 seconds, where an effect of the treatment was examined. Fiber surfaces chemical changes were researched via wettability measurement with demineralized water (the measurement was repeated immediately and after 1, 7 and 30 days to find out the changes stability). Physical changes were studied by means of weight balance (determination of weight loss) and tensile strength tests. It was found that wettability was enhanced significantly – up to two times, while mechanical properties of treated fibers decreased only slightly.

**KEYWORDS:** polymer macro-fibers, plasma treatment, wettability, tensile strength.

### 1. INTRODUCTION

Usage of man-made macro fibers as reinforcement of any composites become a commonality in majority of industry fields, civil engineering including. In the final consequence, a small bulk property improvement has strong impact in civil engineering due to mass production [1]. Fiber-reinforced materials exhibit good mechanical properties, e.g. high mechanical resistance (abrasion, impact resistance), ductility, water resistance etc. [2, 3].

The main task of the macro fiber addition is the distribution of shrinkage into several small cracks in the case of materials based on shrinking binders (mainly lime and cement), and to prevent the single crack openings after linear elastic response in the case of loaded samples [1]. In the civil engineering, the macro fiber reinforcement is the most often used for a) production of watertight concretes and concretes exposed to risk of steel reinforcement corrosion (absence of cracks disallows water penetration), and b) for production of large-scale construction exposed to temperature or moisture changes, dynamic loads, point loads (the fiber reinforcement provides a compactness – hence usability – of materials after the crossing the material loading capacity) [4, 5].

The fiber reinforcement can be classified by fibers material, diameter, tensile strength and their modulus of elasticity. As material, polymeric fibers can be used. Both polymeric (in particular PET and PP) fibers have high tensile strength equal to about hundred or

even thousands MPa. Their diameter is equal to tens or hundreds micrometers. Other characteristic property is low ratio of diameter to length (and related high specific surface enabling better stress transferring from matrix to fibers) and favorable cost [6, 7]. Polymeric fibers reveal low surface wettability (hydrophobicity). On the other hand, fiber reinforcement requires good adhesion between the fiber surface and matrix. To improve the mechanical strength of reinforced materials, adhesion between the fiber surfaces and matrix must be unambiguously ensured [5, 8].

The required adhesion can be modified by fiber surface treatment by chemical and physical methods [7, 9–13]. Currently, the newly introduced plasma treatment becomes popular as a progressive physico-chemical method. The low-pressure plasma treatment represents a universal, efficient and eco-friendly alternative for surface modifications. Plasma can be defined as ionized gas (composed of electrons, ions, and neutral species). The mechanism for plasma surface modification relays on surface atoms replacement by oxygen atoms and formation of polar groups. The presence of polar or functional chemical groups enhances the reactivity with the matrix based on cement or lime binder (both contain water) [5].

In the present work, we report on the modification of polyethylene terephthalate (PET) and polypropylene (PP) fibers by oxygen plasma treatment. The influence of the plasma treatment on the contact angle, the weight and the tensile strength of the fibers is studied.

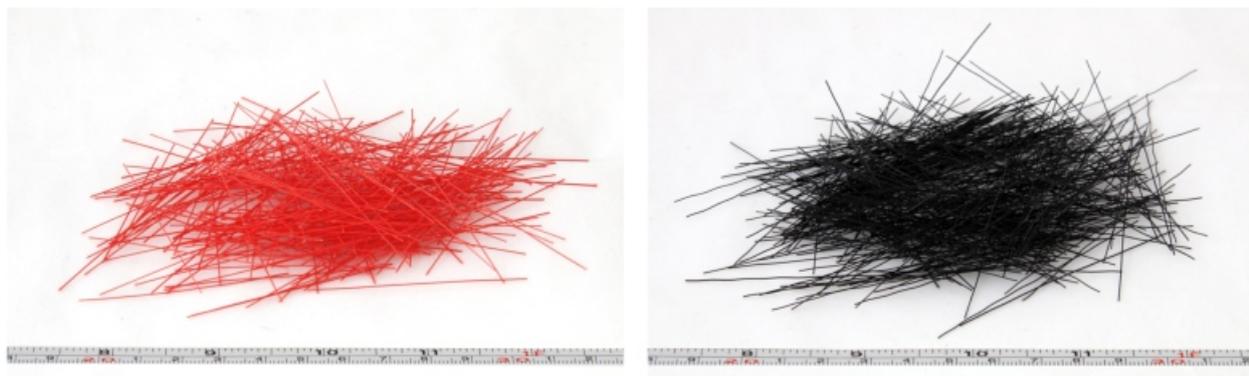


FIGURE 1. Digital camera photo of PET (left), PP fibers (right).

## 2. MATERIALS

### 2.1. POLYMER MACRO-FIBERS

Two different types of fibers were used: PET and PP. Both of them were made by Spokar manufacturer (Czech Republic). They were primarily made for the production of most types of brushes (tooth, paint etc.) and brooms [14]. The fibers had diameter equal to approx. 300  $\mu\text{m}$  (measured using mechanical micrometer), original length was 1200 mm (subsequently chopped according to need). An industrial water flushable sizing is standardly applied onto fiber surfaces as an integral part of their production. Fibers are shown in Figure 1.

## 3. EXPERIMENTAL METHODS

### 3.1. PLASMA TREATMENT

To improve the wettability and related adhesion between fiber surfaces and surrounded matrix, oxygen treatment in inductively coupled plasma was realized using device Tesla VT 214 (13.56 MHz). Parameters of the whole process differing only in exposition time from 5 to 480 seconds, the others were constant; total power of RF source 100 W, total gas pressure 20 Pa, oxygen flow 50 sccm.

### 3.2. CONTACT ANGLE MEASUREMENT

According to reference [15], using horizontal direct optical method, contact angles were measured between meniscus of distilled water (adhering on fiber surfaces) and fiber perpendicularly submerged into the water. Thus obtained results were averaged from 6 independent measurements.

### 3.3. WEIGHT RATIO ANALYSIS

Due to ion bombardments and polymer oxidation and surface structuring (etching) during the plasma treatment, the fibers can be damaged. Weight ratio observation carried out before and after treatment enables to assess the fiber weight loss, which is connected to tensile strength capacity loss. In order to quantify the fiber weight loss, fibers were weighed before and immediately after plasma treatment on weighing-machine Kern ALJ 120-4 ( $d = 0.1 \text{ mg}$ ).

### 3.4. TENSILE STRENGTH TESTS

Physical and chemical processes mentioned earlier can influence the fibers tensile strength. To determine the extent of fibers mechanical properties damage, tensile strength test was carried out using loading frame Web Tiv Ravestein FP100. The test was displacement controlled at a constant rate equal to 6 mm/min in the case of PET and 3 mm/min in the case of PP fibers, respectively. The results were averaged from 6 independent experiments for each plasma treatment time of both fiber types.

## 4. RESULTS AND DISCUSSIONS

### 4.1. CONTACT ANGLE MEASUREMENT

Contact angle measurement revealed  $84.7 \pm 2.2^\circ$  on untreated PET fibers and  $88.3 \pm 0.6^\circ$  on untreated PP fibers. The results provided on the treated fibers showed the unexceptionable positive plasma impact of the fibers wettability. All treated fibers independently on plasma exposition time showed significant decrease of contact angle. The angle measured immediately after plasma treatment on both types of fibers was moving between approx.  $25\text{--}30^\circ$ . After 1, 7 and 30 days from the treatment, contact angle increased up to  $65\text{--}70^\circ$  for PET fibers and for the PP fibers up to  $55\text{--}70^\circ$ . Besides, the results showed that it is not effective to do any treatment longer duration than several seconds. Another finding is the fact that storage of fibers, even for one day, is very inefficient, and the contact angle increase rapidly towards the reference values. Dependence between contact angle, duration of plasma treatment and time of storage in atmospheric conditions is shown in Figure 2 and Figure 3. Based on these finding, it was decided that plasma treatment duration realized within other experiments throughout the study were shortened to 120 seconds only. Demonstration of the fibers wettability captured during contact angle measurement is shown in Figure 4.

### 4.2. WEIGHT RATIO ANALYSIS

Weight ratio observation performed on fibers before and after plasma treatment showed that the weight

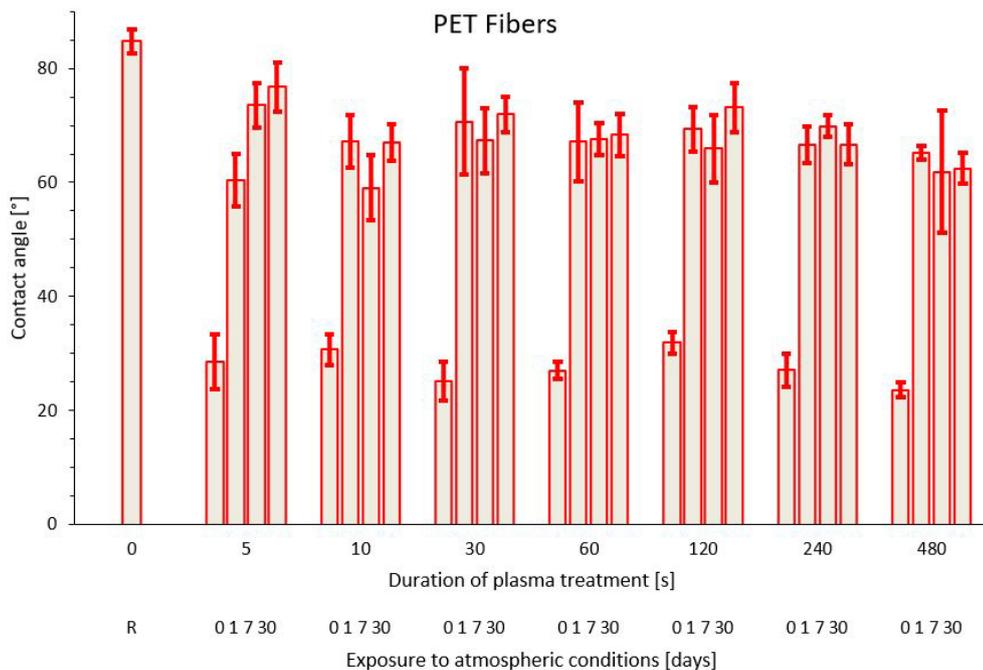


FIGURE 2. PET fibers – dependence between contact angle, duration of plasma treatment and time of exposure to atmospheric conditions.

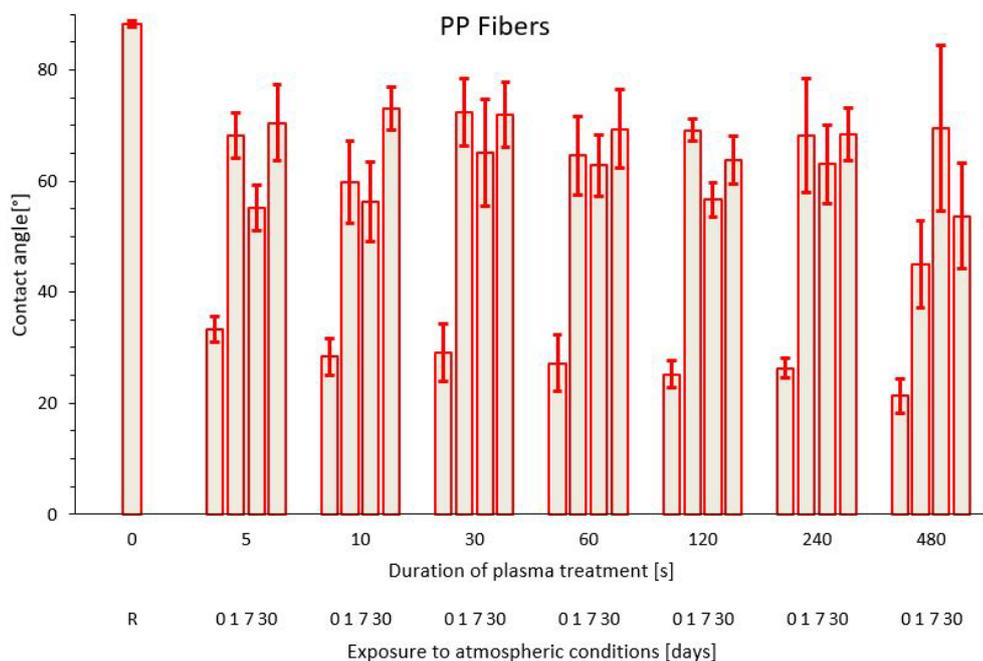


FIGURE 3. PP fibers – dependence between contact angle, duration of plasma treatment and time of exposure to atmospheric conditions

loss is negligible. Fibers treated by 120 seconds exhibited practically no weight loss, just less than 0.25%. Comparing both types of fibers, it can be said that the weight loss is the same until 30 seconds of plasma treatment. After 30 seconds of treatment, there are some small difference between PET and PP fibers. After the longest time of treatment (120 seconds), the

maximum averaged weight loss was 0.06 % and 0.21 % for PET and PP fibers, respectively. Based on these findings, it can be assumed that mechanical properties of treated fiber were not affected by plasma treatment, which is a positive result. Graphic relation between weight loss and duration of plasma treatment is shown in Figure 5.

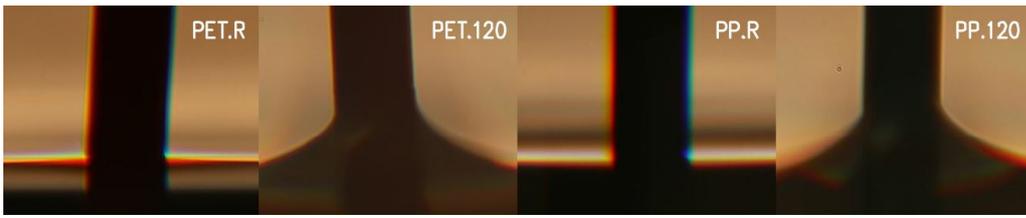


FIGURE 4. Contact angles captured during the wettability measurement

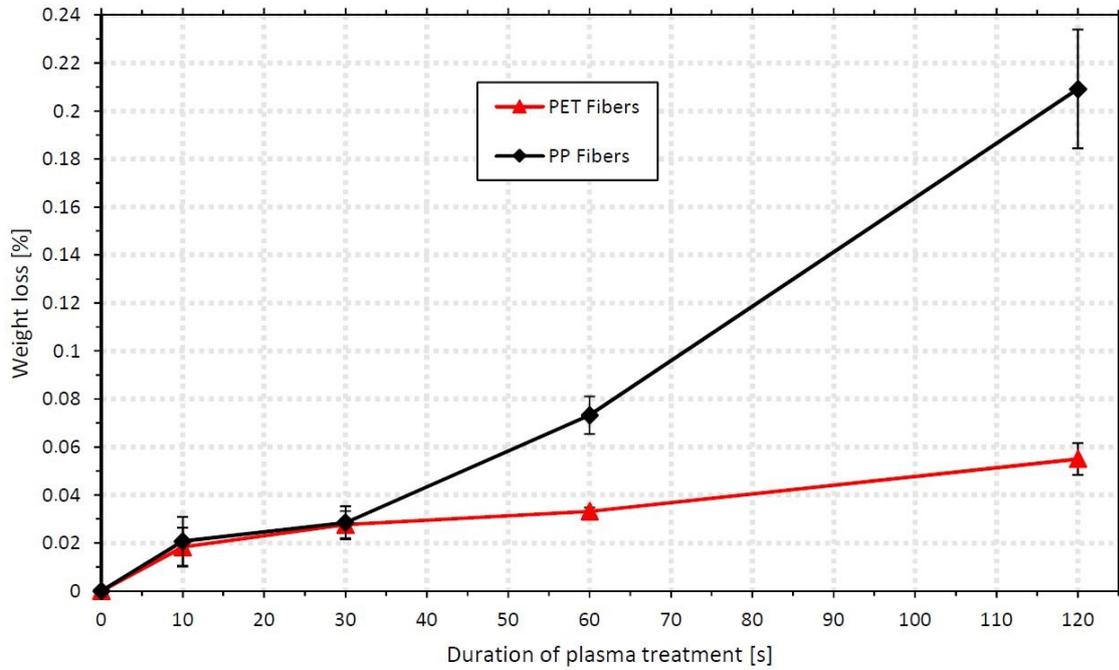


FIGURE 5. Relation between fibers weight loss and duration of plasma treatment obtained before and after plasma treatment.

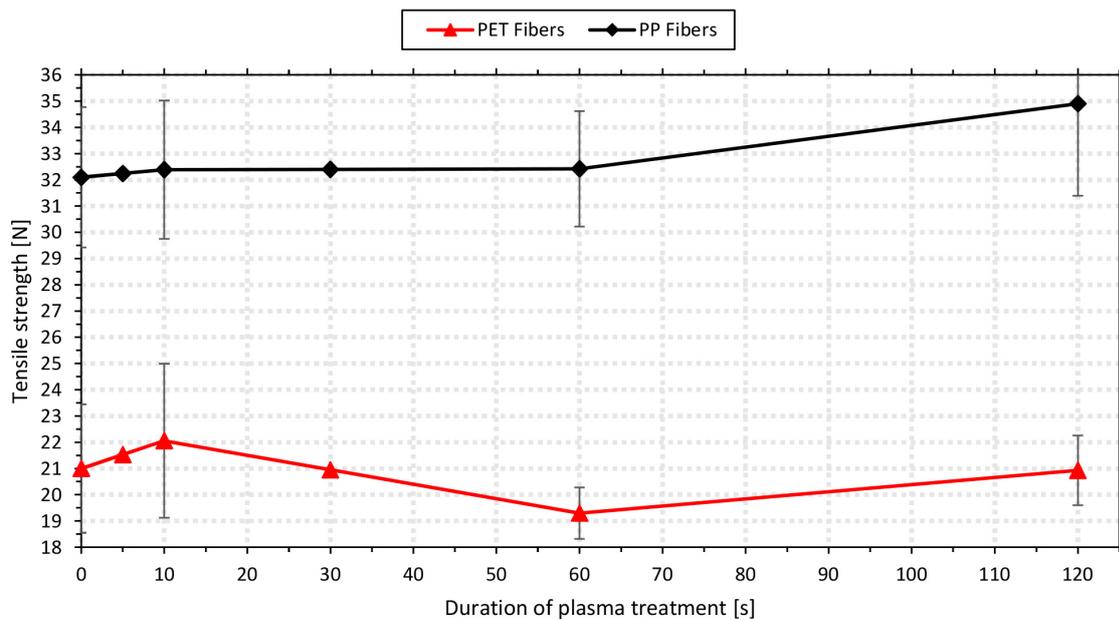


FIGURE 6. Dependence between fibers tensile strength and duration of plasma treatment.

### 4.3. TENSILE STRENGTH TESTS

Tensile strength (more precisely load carrying capacity) of reference and plasma treated fibers was approximately constant for all plasma treatment times (measured on reference, 10, 60 and 120 seconds treated fibers). PET fibers reached on approx. 20 N, while PP fibers on approx. 32 N. As it was already shown by weight loss ratio mentioned earlier, fiber tensile strength test confirmed that the plasma treatment had no significant effect on fiber mechanical performance. The relation between fibers tensile strength and duration of plasma treatment is shown in Figure 6.

## 5. CONCLUSIONS

Polypropylene (PP) and polyethylene terephthalate (PET) commercial macro fibers Spokar having approx. 300  $\mu\text{m}$  in diameter were surface treated by mean of low-pressure cool oxygen plasma treatment in order to achieve their chemical and physical surface changes. The aim of the executed treatment was to improve fiber surface wettability (from hydrophobic to hydrophilic) and morphology (from smooth to roughened), both standardly required for strong interphase interaction with cement matrix, when fibers used as reinforcement.

The plasma modification differed in duration (from 5 to 480 seconds). An effect on physico-chemical changes on fiber surfaces was examined by wettability measurement, weight loss ratio (fibers were weighed before and after plasma treatment) and finally by fiber tensile strength tests, when the main focus of the research was targeted to impact of plasma treatment on fiber mechanical performance. Besides, time-stability of chemical changes on modified fibers was researched – wettability between fiber surfaces and distilled water was examined using direct optical set for contact angle measurement immediately, 1, 7 and 30 days after plasma modifications. It was found out that:

- The wettability of plasma treated (regardless to duration of treatment time) both PP and PET fibers increased almost three times, if compared to reference samples.
- The modified wettability was very short-term. It was degraded almost to reference values already after one day, when fibers exposed to standard atmospheric conditions.
- Impact of realized treatment did not have no obvious effect on fiber mechanical performance, as demonstrated by no weight loss and no tensile strength changes for much as treated fibers.

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### REFERENCES

- [1] P. K. Mallick. Materials. In *Fiber-reinforced composites, materials, manufacturing and design*, chap. 2. CRC Press, 2007.
- [2] J. Trejbal, L. Kopecký, S. Potocký, J. Fládr. The effect of glass fiber reinforcement on flexural strength of lime-based mortars. In *53rd conference on experimental stress analysis*, pp. 450–453. Czech Technical University in Prague, 2015.
- [3] K. Šeps, J. Vodička. Fibre reinforced concrete with recycled concrete and insulation material stered. *Advanced Materials Research* **1054**:262–266, 2014. DOI:10.4028/www.scientific.net/AMR.1054.262.
- [4] Z. Lin, V. Li. Crack bridging in fiber reinforced cementitious composites with slip-hardening interfaces. *Journal of the Mechanics and Physics of Solids* **45**(5):763–787, 1991.
- [5] J. Trejbal, V. Šmilauer, A. Kromka, et al. Wettability enhancement of polymeric and glass micro fiber reinforcement by plasma treatment. In *Nanocon 2015 7th international conference on nanomaterials – research and application – conference proceedings*, pp. 315–320. Tangerang, 2015.
- [6] J. Bartoš. *Modification of PET fiber surfaces to increase their cohesion with cement matrix*. Diploma thesis. Czech Technical University in Prague, 2014.
- [7] J. Trejbal. *Modification of glass fibers surface and their application in mortars used for reconstructions of historical buildings*. Diploma thesis. Czech Technical University in Prague, 2014.
- [8] P. Chen. Influence of fiber wettability on the interfacial adhesion of continuous fiber-reinforced ppsk composite. *Journal of Applied Polymer Science* **102**:2544–2551, 2006. DOI:10.1002/app.24681.
- [9] S. Elsaka. Influence of chemical surface treatments on adhesion of fiber posts to composite resin core materials. *Dental materials* **29**:550–558, 2013. DOI:10.1016/j.dental.2013.03.004.
- [10] D. Cökeliler, S. Erkut, J. Zemek, et al. Modification of glass fibers to improve reinforcement: A plasma polymerization technique. *Dental materials* **23**(3):335–342, 2007. DOI:10.1016/j.dental.2006.01.023.
- [11] M. Kim, M. Kim, K. Rhee, S. Park. Study on an oxygen plasma treatment of a basalt fiber and its effect on the interlaminar fracture property of basalt/epoxy woven composites. *Composites Part B: Engineering* **42**(3):499–504, 2011. DOI:10.1016/j.compositesb.2010.12.001.
- [12] H. Wu, V. Li. Fiber/cement interface tailoring with plasma treatment. *Cement and Concrete Composites* **21**(3):205–212, 1999. DOI:10.1016/S0958-9465(98)00053-5.
- [13] J. Trejbal, J. Fládr, L. Kopecký. Utilization of plasma treated polymeric macro-fibers as reinforcement in concrete constructions. *Advanced Materials Research* **1144**:70–75, 2017. DOI:10.4028/www.scientific.net/AMR.1144.70.

- [14] Spokar a.s. Fiber production. <http://www.spokar.com/cz/technologie/vyroba-vlaken>.
- [15] J. Trejbal, L. Kopecký, S. Potocký, Z. Remeš. Direct optical method for contact angle measurement on micro fibers. In *Nanomaterials and nanotechnology in civil engineering 2015 – conference proceedings*, pp. 89–90. Czech Technical University in Prague, 2015.