

# INFLUENCE OF OXYGEN AND ARGON PLASMA TREATMENT ON WETTABILITY AND SURFACE MORPHOLOGY OF POLYPROPYLENE MICROFIBERS

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**ABSTRACT.** The surface treatment of polypropylene microfibers by plasma processing in oxygen and argon was studied with the motivation to increase their cohesion with the cement matrix. By plasma treatment, it is possible to modify the surface of the microfibers mechanically, chemically or with a combination of both. The microfibers were modified using the reactive ion etching plasma system. The surface of the microfibers was modified by oxygen and argon plasma. The wettability of the microfibers was measured using the Packed Cell method. Furthermore, the weight of the microfibers before and after plasma modification was measured. Finally, the surface of the modified microfibers was examined by scanning electron microscopy. Almost all modifications of the microfiber surfaces were able to increase their wettability with water. The wettability of the oxygen plasma treated microfibers increased on average by about 11%, the wettability of the argon plasma treated microfibers increased on average by about 6% compared to the fibers without modification. The mechanical effect of plasma treatment was proven only for microfibers modified by oxygen plasma.

**KEYWORDS:** Oxygen plasma, argon plasma, plasma treatment, plasma modification of microfibers, polypropylene, SEM, wettability.

## 1. INTRODUCTION

The interfacial transition zone significantly influences the properties of cement composite materials containing fibrous reinforcement at the interface between the fiber and the cement matrix [1, 2]. To achieve suitable mechanical properties of the fibers reinforced cement composite material, it is desirable to increase the wettability by water and mainly mechanically modify the fiber's surface [3]. By plasma modification, it is possible to modify the surface of the fibers both chemically and mechanically. Previous experiments proved that plasma modification by oxygen plasma could sufficiently increase the wettability of polypropylene (PP) fibers with water [4, 5]. However, the mechanical effect of plasma modification, realized by inductively coupled plasma, was insufficient on the surface of microfibers [4, 5]. The increased physical effect of plasma modification can be achieved by the impact of energetic ions i.e., with plasma system generally used for ion etching which utilizes ion bombardment process [6]. A typical representative of such systems is the reactive ion etching (RIE) system intensively etching the material's surface [7]. To increase the physical modification of PP microfibers, we present a study of oxygen and argon PP microfibers modifications by the RIE system to their wettability and surface morphology.

## 2. MATERIALS AND METHODS

Polypropylene microfibers Fibrifor Multi (Contec Fiber AG, Switzerland) were used. The microfibers are made in bundles (type 127) with the diameter of each individual microfiber around 32  $\mu\text{m}$  and the length of 12 mm  $\pm$  5 %. The properties of the microfibers are summarized in Table 1. The surface of the fibers was modified using the RIE system (Phantom III, Trion Technology Inc., USA). Microfibers weighing approximately 5 g were inserted into a Petri dish. Three Petri dishes with microfibers were inserted into the RIE system and pumped down to the pressure  $<1 \cdot 10^{-3}$  Pa. After that, the chamber was filled (50 sccm) by selected gas (oxygen or argon) and maintained at pressure 13.3 Pa. The plasma modification time was set from 30 to 480 seconds. The influence of RF power on microfibers was tested in the range of 100 W to 500 W for a fixed treatment time of 60 seconds. The influence of working gas atmosphere was studied at fixed RF power 100 W and various treatment times were studied. After the plasma modification process, the chamber was evacuated, vented with nitrogen and the microfibers were removed. The microfibers were stored in airtight bags. To determine the treatment stability, part of the samples was exposed to ambient conditions in a laboratory environment at a temperature of about 22 ° C and relative

humidity of about 50 % for 12 hours. The sample description with relevant process parameters of the RIE is in Table 2.

Fibers Material		Fibrofor multi Polypropylene
Diameter	[ $\mu\text{m}$ ]	32
Length	[mm]	12
Tensile strength	[MPa]	270
Melting point	[ $^{\circ}\text{C}$ ]	160
Bulk density	[ $\text{g}/\text{cm}^3$ ]	0.91

TABLE 1. Properties of selected fibers.

Designation	Input power [W]	Modifica- tion time [s]	Gas
A200W	200	60	argon
A300W	300	60	argon
A400W	400	60	argon
A500W	500	60	argon
A30	100	30	argon
A60	100	60	argon
A120	100	120	argon
A240	100	240	argon
A480	100	480	argon
O30	100	30	oxygen
O60	100	60	oxygen
O120	100	120	oxygen
O240	100	240	oxygen
O480	100	480	oxygen

TABLE 2. Designation and device settings during plasma treatment of microfibers.

All microfibers with the Petri dishes were weighed on a laboratory scale Denver Instrument S-64 (Denver Instrument Company, USA) before and after plasma modification. The wettability of microfibers was measured by the packed-cell method. The microfibers were in a perforated container and loaded by a lead weighing 53.55 g. The weight of the container was 9.45 g. Subsequently, the sample (microfibers, container, and lead) was weighed on a Kern ABS (KERN & SOHN GmbH, Germany) laboratory scale. Weight values were rounded to tens of mg. Next, the sample was dipped into the water for 10 seconds, removed from the water and placed in the holder for 120 s, during which time excess water could drain from the container. Finally, the sample was weighed again. From the measured weights, the percentage weight of water compared to the weight of microfibers was calculated according to Equation 1 [8].

$$m_v = \frac{(m_m - m_n) - (m_s - m_n)}{(m_s - m_n)} \cdot 100, \quad (1)$$

where:  $m_v$  – weight of water to weight of microfibers [%],  $m_m$  – weight of wet microfibers with container and lead [g],  $m_s$  – weight of dry microfibers with container and lead [g],  $m_n$  – weight of a wet container with wet lead [g].

The surface morphology of the microfibers was examined by electron scanning microscopy (SEM, Phenom XL, USA). To observe objects using SEM, the surface of these objects must be conductive. For this reason, a thin layer of platinum was applied to the surface of the microfibers using a Mini Sputter Coater Quorum SC7620 (Quorum Technologies, UK). Platinum was sputtered at a pressure of 8 Pa for 120 seconds resulting in approx. 10 nm thin Pt layer. The SEM was set to high resolution (10 kV) with low current intensity. A SED detector was used. The high vacuum option on the SEM was chosen, this option set pressure in the chamber of the device to 1 Pa. Images of fiber surfaces from SEM were magnified 10,000 $\times$ .

### 3. RESULTS AND DISCUSSION

The surface of the fibers was modified by oxygen plasma and by argon plasma. A more pronounced effect of mechanical modification was expected with argon plasma treatment because argon ions have a higher mass than oxygen ions [9]. In the preliminary runs we tested different RF power inputs from 100 W to 500 W at constant time of 60 s in argon atmosphere. As the power input increases, the temperature loading also increases. At a power input of 300 W and higher (samples A300W, A400W and A500W), the microfibers fused together by heat and started to melt. The temperature of the microfibers during the modification has to reach their melting point, which is around 160  $^{\circ}\text{C}$ . Due to this fact further testing was performed at a fixed RF power of 100 W.

At a fixed RF power of 100 W, we tested different times from 30 s to 480 s in argon or oxygen atmosphere. The weight loss of the microfibers during the plasma modification process was almost negligible, the maximum weight loss was about 0.12 % (sample O480). For microfibers modified by oxygen plasma for 240 s and 480 s, the weight loss was significantly higher compared to other types of plasma modification. Weight loss is mainly caused by etching of the microfiber surface during modification. Therefore, we can conclude that oxygen plasma changes the morphology of the microfiber surface more than argon plasma. The summary of microfibers weight losses after the plasma modification is shown in Figure 1.

The wettability of the microfibers was slightly higher after almost all performed plasma modifications. The weight of water between the microfibers in the samples after argon plasma treatment increased on average by about 6 % compared to the microfibers without modification. The weight of water between

the microfibers in the samples after oxygen plasma treatment increased on average by about 11 % compared to the microfibers without modification. The microfibers that were left in the laboratory environment for 12 hours (12H added to sample description) after the plasma modification had similar results of wettability as measured immediately after the plasma modification. The weight of water between the microfibers to weight of microfibers is given in Figure 2.

Morphological changes were observed on the surface of microfibers modified by oxygen plasma for 60 seconds or more by the SEM. With increasing time, the mechanical effect of plasma modification due to the ion bombardment was increased. In the SEM images we can observe that the mechanical modifications occurred preferentially in one direction. The most pronounced changes were observed on top of the samples (microfibers) placed in the chamber of the RIE system. The typical SEM images are shown in Fig. 3. No morphological changes were observed by SEM on the surfaces of the argon modified fibers, so not only the ion bombardment process but also the chemical effect of plasma modification is important to achieve morphological changes on the surface of microfibers. According to the results, to achieve more significant morphological changes, it may be appropriate to extend the modification time, increase the RF power of the RIE system or use a mixture of gases (oxygen and argon) during the modification.

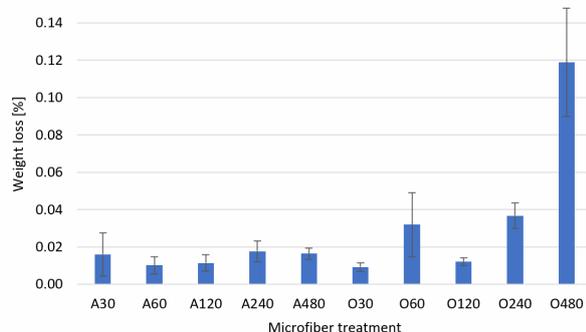


FIGURE 1. Percentage weight loss of microfibers after argon and oxygen plasma treatment (A, O) and respective time in seconds (30, 60, 120, 240 and 480).

#### 4. CONCLUSION

Plasma modifications of polypropylene microfibers was performed using the RIE system and compared the wettability and mass changes depending on plasma process parameters. We studied the influence of, plasma modification times (30–480 s), and working gases (argon or oxygen). Based on the performed measurements and results, we can conclude:

- Polypropylene microfibers begin to melt when the power input of the plasma modification device is set to 300W or more for Ar plasma and tested time of 60 s.

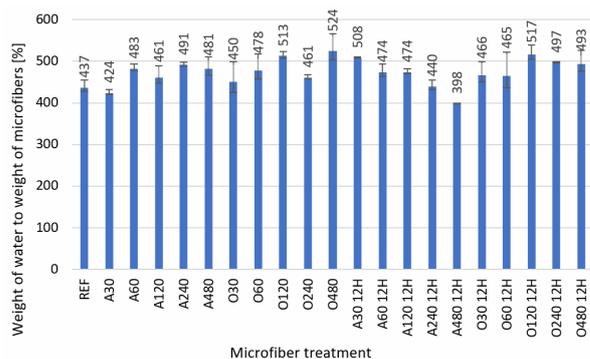


FIGURE 2. Wettability measured by the indirect Packed Cell method – reference microfibers (REF) microfibers after argon and oxygen plasma treatment (A, O), respective time in seconds (30, 60, 120, 240 and 480) and samples that were tested after 12 hours in a laboratory environment (12H).

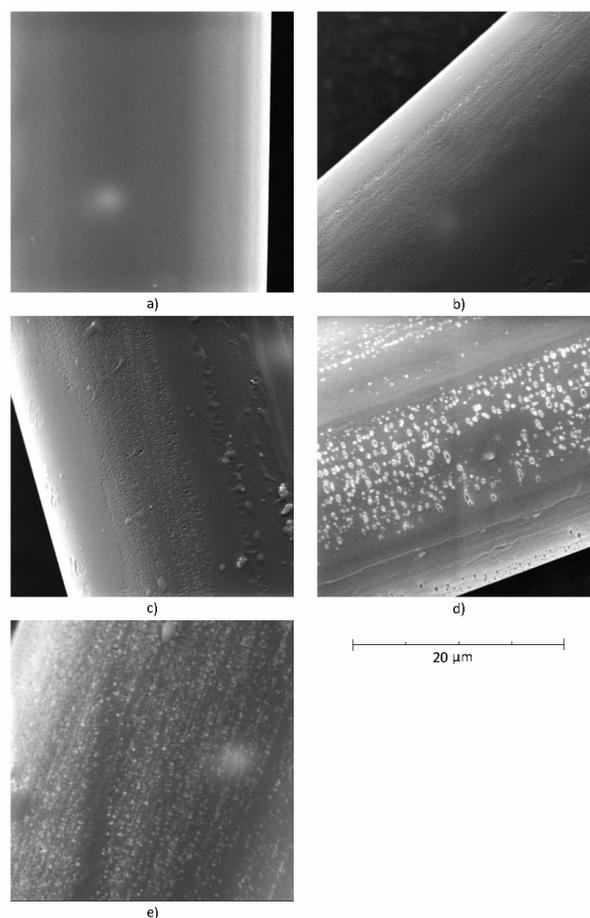


FIGURE 3. SEM images of treated microfibers: a) reference (REF), b) O60, c) O120, d) O240, e) O480.

- Plasma modifies only the microfiber surfaces. The highest weight loss did not exceed 0.12 % of the initial weight, so that the cross-sectional area of the microfiber almost did not decrease.
- At a RF power of 100 W, modification with oxygen plasma for 240 s and 480 s is most suitable – the greatest weight losses occurred during the

modification, while the reduction of the microfiber cross-sectional area is negligible.

- A slight increase in wettability occurred in almost all samples after plasma treatment. There was on average a more significant increase in wettability of the microfibers comparing oxygen to argon plasma modification. Leaving the microfibers in a laboratory environment for 12 hours after plasma modification had no significant effect on their wettability.
- Significant mechanical changes were observed on the surface of the oxygen plasma treated microfibers at 10,000× magnification. With increasing plasma modification time, the changes were more pronounced. The first mechanical changes have already been observed on fibers treated at 100 W after 60 s.
- No morphological changes were observed on the surface of the argon plasma treated microfibers at 10,000× magnification. Treatment of the microfiber surface only by argon plasma appears to be inappropriate.
- The morphological modification of the microfibers by oxygen plasma was very different on each section of the fiber surface, the fibers were mostly modified only from one direction. To achieve a uniform surface treatment, it would be necessary to carry out the plasma modification several times and to mix the fibers between each modification or to use a mixer during the plasma processing.

The results show that the mechanical effect of the plasma modification depends not only on the mass of ions, but also significantly depends on the chemical processes that occur during the plasma modification. Maybe it could be achieved better results by using a mixture of oxygen and argon gas during the plasma modification process. Better results could be also achieved by increasing the RF power or extending the modification time.

## 5. ACKNOWLEDGEMENTS

This work was financially supported by the Czech Technical University in Prague – the project SGS19/148/OHK1/3T/11 and TAČR SS03010302. The authors also thank the Center for Nanotechnology in Civil Engineering at the Faculty of Civil Engineering, Czech Technical University in Prague.

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