CARBON MICROFIBERS SURFACE CHANGES INDUCED BY OXYGEN PLASMA TREATMENT

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Abstract

The reinforcement carbon fibers were modified using low pressure oxygen plasma treatment to attain the better adhesion between their surfaces and matrix of various composite materials. We investigated the influence of plasma treatment duration on the surface morphology, wettability and mechanical properties of carbon fibers. Three different times of plasma treatment were studied (1, 2 and 4 minutes) together with untreated samples. The fiber surface morphology changes were studied using scanning electron microscopy. The other studied parameters were the fiber modulus of elasticity and tensile strength. The results showed that 4 minutes of plasma treatment had a positive effect on the fibers surface morphology and wettability while no or limited effects on mechanical properties were found.

Keywords: Carbon fibers, plasma, SEM, tensile strength, modulus of elasticity

1. INTRODUCTION

Nowadays, carbon fibers are used in civil engineering mainly as an additional surface reinforcement. Carbon fiber reinforced polymer (CFRP) is used as plates of different shapes and dimensions. CFRP is an advanced material which is glued to already existing structures, mainly for undergoing reconstruction [1]. The result of CFRP application is increased flexural and shear strength of the construction. CFRP used as an additional reinforcement can improve only the deformation arising from further additional load [2], [3]. Another utilization of carbon fibers is as micro reinforcement in composite materials [4]. Applications of carbon fiber reinforcement with cement matrixes are limited due to their poor interaction with matrix of the composite material.

The carbon fibers have a circular shape, smooth surface, and a low cohesion with the cement matrix. Additionally, during fibers production process carbon fibers are fitted with sizing (surface finish) in order to improve consistency with epoxy resins. Unfortunately, this treatment is hardly compatible with cement matrix.

Beside the sizing treatment mentioned above, several types of fiber surface modifications can be used. These methods are based on mechanical treatments [5], chemical treatments [6], and plasma treatments [7]. An advantage of plasma treatments is low impact on mechanical properties and controlled chemistry given by selected gas species. The purpose of fiber surface modification is to improve the cohesion with cement matrix and thereby reduce anchorage length of fibers i.e. reduction of mass and length of fibers used in the composites.

In this work we focused on oxygen plasma treatment of carbon fibers. The plasma, an ionized gas composed of electrons, ions and neutral species, interacts with carbon fiber surface. This progressive modification is responsible for both, the chemical (interaction with radicals of working gas, O_2) and the physical (interaction with energetic particles) surface changes of thus treated fibers. The cohesion given by chemical bonds between treated fiber surfaces and reinforced matrix is enhanced by fiber surface activation (application of polar or chemical active groups responsible for wettability increase), while the physical cohesions is improved by surface roughening (morphology changes). The plasma treatment was successfully used for surface

modification of various (glass, polymer etc.) fiber materials [8]. We studied morphology changes by SEM, surface activation by indirect measurement of wettability and mechanical changes by uniaxial loading tests.

2. EXPERIMENTAL

We used the Tenax carbon fibers UTS50 F24 24K 1600tex DCP (Toho Tenax, Germany) having 7 µm diameter. The fibers were packed to filament yarn. Material parameters were as follows: 7 µm diameter, 265 GPa modulus of elasticity, 5100 MPa tensile strength, 1780 kgm^{-3} density, sizing based on polyurethane (2 wt. %).

A low-temperature oxygen plasma treatment was used for the surface modification of carbon fibers. The plasma treatment was performed in inductively coupled plasma system (VT 214, Tesla) with a total RF power of 100 W. The base pressure in the chamber was 20 Pa. Then the chamber was flashed with oxygen gas. Plasma treatment was done with 50 sccm O_2 flow and 59 Pa working pressure. The sample set description, plasma treatment duration and macroscopic characterization of carbon fibers are summarized in **Table 1**.

Table 1 Summary of plasma treatment duration and macroscopic characterization of carbon fibers

Set	Treatment duration [min.]	Length of fiber [m]	Weight of samples [g]	Amount of fibers [pcs]
CARBON 0´	0	1.058	0.0092	128
CARBON 1´	1	1.058	0.0100	139
CARBON 2´	2	1.058	0.0193	268
CARBON 4´	4	1.058	0.0192	266

The surface morphology of the carbon fibers was evaluated by scanning electron microscope (Maia 3, Tescan).

Classical methods of direct or indirect wetting and contact angle measurements of carbon fiber cannot be used due to the small size of the fibers. For this reason, indirect method of wettability intensity was chosen for measuring of carbon fiber. Measurement method was based on weight ratio of water adhering on the fibers and carbon fibers in dry conditions, according to the following formula:

$$m_w = \frac{m_m - m_d}{m_d} \cdot 100 \qquad (1)$$

where m_w is the intensity of wettability, m_m is the weight of wet fibers and m_d is the weight of dry fibers.

The mechanical tests represented by tensile strength and modulus of elasticity measurements were carried out using loading frame MTS system device, model MTS Alliance RT/30. The testing was displacement controlled at a constant rate of 0.2 mm/s. Two sets of (reference samples and 4 min. treatment) were tested to determine the effect of plasma treatment on the mechanical properties of carbon fibers and from each set six samples were evaluated.

3. RESULTS AND DISCUSSION

The **Figure 1** shows SEM images of plasma treated fibers (CARBON 0' to 4') in the electron microscope with same magnification. The SEM images (**Figures 1a-1d**) show that prolonged treatment time resulted in deepening of longitudinal grooves originally presented (see **Figure 1a**) on untreated carbon fibers. No visible

changes were seen between the sample CARBON 0' and CARBON 1' (**Figures 1a** and **1b**). **Figure 1c** shows protrusions on the surface of carbon fiber that protrude from the fiber surface. These protrusions may correspond to contamination from production of fibers, which adhered to the fiber surface. The sample CARBON 4' (**Figure 1d**) had approximately two times deeper grooves than the reference sample.

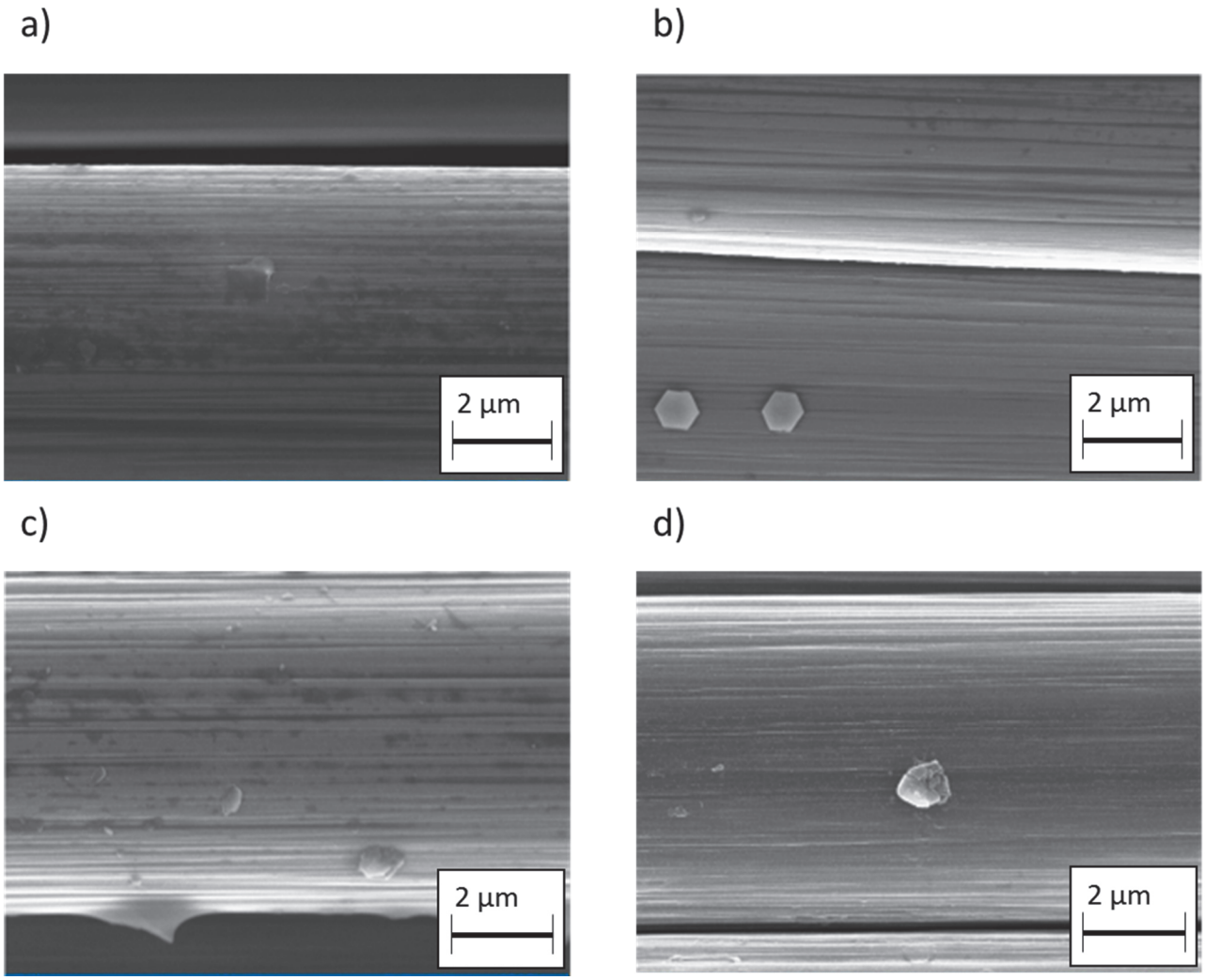

Figure 1 SEM images of the modified carbon fibers as a function of treatment time: a - reference sample (CARBON 0´), b - 1 min. treatment (CARBON 1´), c - 2 min. treatment (CARBON 2´), d - 4 min. treatment (CARBON 4´), scale bar is 2 µm

Figure 2 shows wettability changes of plasma treated fibers. Untreated fibers have wettability 41.5 %. Increasing treatment time resulted in increase of wettability. After 4 min of plasma treatment the average value of wettability increased 2.5 times compared to the reference sample. Improved wettability is caused by exchange of dangling bond and oxygen atoms during plasma treatment [9].

Improved surface cohesion with water has to be checked with mechanical properties of the fibers, which are important for future applications in the cement composites.

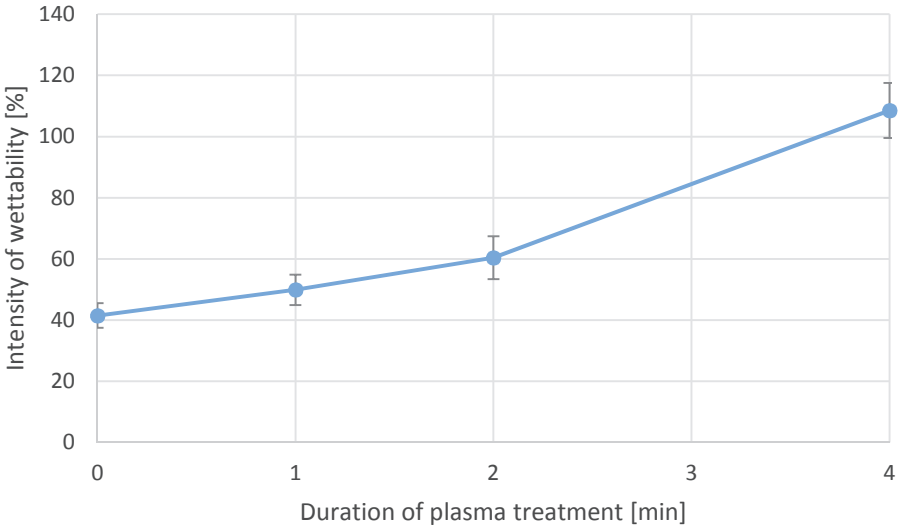

Figure 2 Intensity of wettability of the modified carbon fibers

The **Table 2** shows values of maximum tensile force, tensile strength and elasticity modulus of reference and CARBON 4' sample. The value of maximum tensile force of filament yarn was recalculated to the value of tensile strength because of different amounts of fibers in the filament yarn. After 4 min. plasma treatment the average value of tensile strength remained constant (5092 MPa) while an elasticity modulus decreased. The average values of elasticity modulus decreased by 31.2 % to the untreated sample. This difference of average values of elasticity modulus could be caused by different amounts of fibers in filament yarn, because fibers in filament yarn were not aligned and not all fibers are stressed.

Table 2 Mechanical properties of testing samples with standard deviations

Set	Time of treatment [min.]	Amount of fibers [pcs]	Maximal tensile force of filament yarn [N]	Tensile strength [MPa]	Modulus of elasticity [GPa]
CARBON 0´	0	128	25.06 ± 2.32	5092 ± 470	55.55 ± 6.56
CARBON 4´	4	266	52.21 ± 5.84	5092 ± 570	38.21 ± 5.21

4. CONCLUSION

The impact of the plasma treatment on the surface morphology and mechanical properties of the carbon fibers was studied. The results showed that the plasma treatment positively affected the carbon fiber surface morphology. Samples with 4 min. plasma treatment had approximately two times deeper grooves than the reference sample and thus it is expected their better physical cohesions. Moreover, the average value of wettability increased 2.5 times compared to the reference sample. The results of mechanical properties confirmed no changes in fiber tensile strength after 4 min. plasma treatment. On the other hand, the value of elasticity modulus decreased by 17 GPa.

These results are promising for usage of the plasma modified carbon fibers as a reinforcement of cement composites in civil engineering while optimization of plasma treatment is necessary to eliminate decrease of elasticity modulus. In the future we will focus on plasma treatment during longer times and pull out tests to confirm improved cohesion between fiber surfaces and cement matrix.

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