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TREATMENT OF POLYPROPYLENE MICROFIBERS BY ATMOSPHERIC AND LOW-PRESSURE PLASMA – APPLICATION TO A REINFORCED CEMENT COMPOSITE CONTAINING RECYCLED CONCRETE

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Abstract. The effect of atmospheric and low-pressure plasma modification on polypropylene (PP) microfibers was examined. Mechanical changes on the microfiber surfaces were observed using scanning electron microscopy (SEM). Next, wettability was measured using the packed-cell method. The fibers were applied into a cement matrix containing micro-milled recycled concrete. Test specimens were made and then the dynamic modulus of elasticity was continuously measured. After 28 days were made in the test specimens central notches to a depth of 14 mm. Finally, bending tests were performed. From the results, the fracture energy of the composite material was calculated. It was proven that low-pressure plasma modification as well as atmospheric plasma modification increases the wettability of PP fibers with water. Furthermore, it was found that samples containing plasma-modified microfibers have a higher fracture energy compared to the same samples with fibers without plasma modification. Conversely, plasma modification had no effect on the dynamic modulus of elasticity.

Keywords: Atmospheric plasma, plasma modification, plasma treatment, polypropylene microfiber, oxygen plasma, wettability, fracture energy, SEM.

1. Introduction

Nowadays, proper waste management is very important. Old waste concrete can be recycled and subsequently reused. It is most often used as a bottom layer for roads. In this work, recycled concrete was ground using a high-speed mill and then used as a filler for the cement composite material. The advantage of this use is possibility to use all fractions of recycled concrete and possibility to activate some non-hydrated cement in recycled concrete [1, 2]. The cementitious composite material was reinforced using polypropylene (PP) microfiber reinforcement. The properties of the resulting composite material depend, among other things, on the interfacial transition zone (ITZ). In this zone occurs interaction between the cement matrix and the fibers [3]. To improve the adhesion between the fiber and the matrix, it is possible to modify the surface of the fibers, which will lead to an improvement of the mechanical properties final composite material. Using plasma, we can modify the fiber surface both mechanically and chemically [4]. The mechanical effect of plasma modification is caused by ion bombardment. The chemical effect of plasma modification is mainly caused by the many chemical groups that are generated during modification [5, 6]. The effect of plasma modification on microfibers surface depends on many parameters, including time, gas, power, and device. Plasma treatments are performed in a low-pressure chamber or at atmospheric pressure [7, 8].

2. Materials and specimens

Portland cement, micro-milled recycled concrete, plasma treated polypropylene (PP) microfibers and water were used to produce the test samples. The ratio of cement to recycled was 1:1. The water ratio W/C+R was 0.32 for each sample. Portland cement CEM I 42.5 R Radotín (Českomoravský cement, Czechia) was used. Micro-milled recycled concrete (Lavaris, Czechia) was made from concrete drainage gutters using a high-speed mill. The specific surface of micro-milled recycled concrete is around 36 m^2/kg. Microfibers Fibrofor Multi (Contec Fiber, Switzerland) were made of polypropylene. The fibers are made in bundles (type 127), the diameter of individual filament is about 32 µm and the microfiber length is 12 mm ±5 %. The surface of the microfibers was modified using atmospheric or low-pressure plasma. Low-pressure plasma treatment was performed by Tesla VT214 device using an RF source – gas pressure in the chamber of device was 20 Pa. Atmospheric pressure modification was performed by Roplass RPS 400 device using a dielectric barrier discharge. The process parameters of oxygen low-pressure plasma modification were chosen based on previous experiments [9].

Set	Device	Input power [W]	Time [s]	Gas	Pressure [Pa]
REF	-	-	-	-	
A	Roplass RPS 400	300	480 (4×120)	Air	Atmospheric
T	Tesla VT213	100	480 (2x×240)	Oxygen	20

TABLE 1. Process parametrs of plasma modification.

Set	Cement [g]	Recyclate [g]	Water [g]	W/C+R	Microfibers [g]	Microfibers [%]
REF	1500	1500	960	0.32	28.0	2
A	1500	1500	960	0.32	28.0	2
T	1500	1500	960	0.32	28.0	2

TABLE 2. Composition of the samples.

The oxygen low-pressure plasma modification of the microfibers was performed for a total of 480 s, while the process was paused after 240 s, the fibers were mixed and then the process was started again. For the same duration, the fibers were modified in atmospheric pressure plasma, where the working was atmospheric air. To achieve a uniform modification of the surface of the fibers, the fibers were mixed during the process after every 120 s. The process parameters of plasma modification are in Table 1.

A total of three sets specimens were made, each set containing six test specimens. The dimensions of the test specimens were $40 \times 40 \times 160$ mm. Samples were unmolded 24 hours after production and were stored 28 days in standard laboratory environment. Composition of the samples is shown in the Table 2.

3. Experimental methods

Fiber surface was examined by scanning electron microscopy (SEM). First, a thin layer of platinum was sputted on the surface of the fibers using a Mini Sputter Coater Quorum SC7620 at a pressure of 8 Pa. Subsequently, the surface of the fibers was examined using a Merlin Zeiss SEM. The surface of the fibers was examined at a magnification of 20,000× (Figure 1).

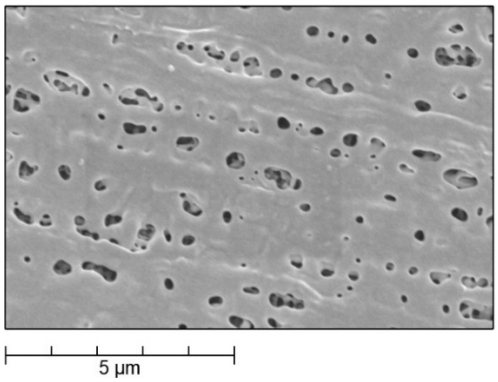
The wettability of the fibers was measured by the packed-cell method. The fibers were insert into a container with a perforated bottom, after that this container was immersed into water for 60 seconds. Container with the fibers was weighed on the laboratory scale before immersion and 120 seconds after immersion. Finally, the percentage weight of water to weight of fibers was calculated (1) [10]:

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

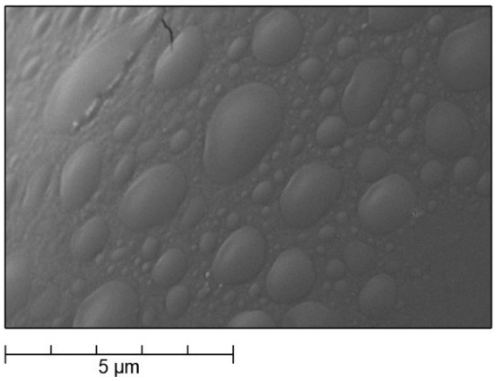
where

m_v the weight of water to the weight of fibers ratio [%],

m_m the weight of wet fibers and packed-cell measuring set [g],



(A). Plasma modification in low-pressure by oxygen.



(B). Plasma modification in atmospheric pressure by air.

FIGURE 1. SEM image – microfiber surface after modicifation.

m_s the weight of dry fibers and packed-cellmeasuring set [g],

m_n the weight of packed-cell measuring set [g].

The dynamic modulus of elasticity of the samples was continuously measured by the resonance method (Brüel&Kjær, Denmark). The modulus of elasticity was measured 7, 14, 21 and 28 days after samples production. The measuring system includes an impulse hammer Brüel&Kjær type 8206, response sensor Brüel&Kjær type 4519-003 and measure device Brüel&Kjær Front-end 3560B-120. The dynamic mod-

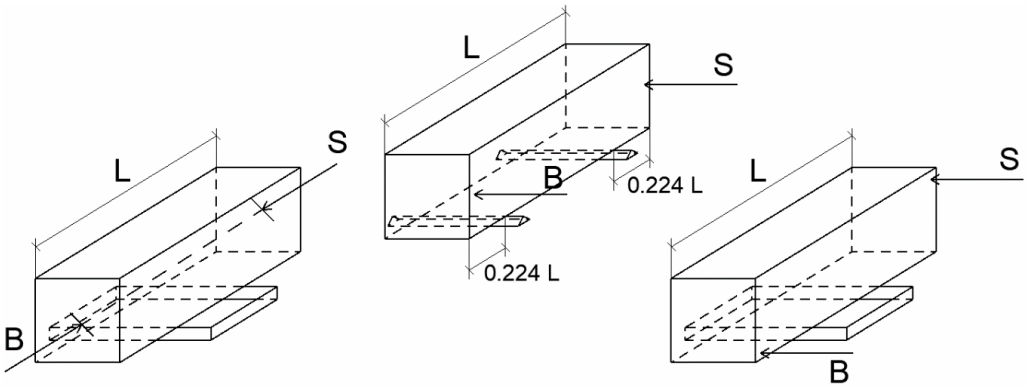


Figure 2. Position of the sensor and the impulse hammer on the sample to measure the fundamental frequencies from longitudinal (left), transverse (center), and torsional (right) oscillations; S – sensor, B – impact hammer [11].

ulus of elasticity was determined from longitudinal, transverse and torsional oscillations (Figure 2). Finally, the dynamic modulus of elasticity was calculated using PULSE LabShop software version 14.0.1.

For measurement of fracture energy was performed a notch in the middle of the length test specimens. Notch was performed using an automatic saw with a water-cooled diamond blade (Achilli, Italy). The depth of the notch was 14 mm, which is approximately one third of the height of the specimen. The notch width was 3 mm. Subsequently, a three-point bending test was performed. Samples were loaded by electromechanical press (MTS, USA). Samples were loaded with constant displacement at a speed of 1.5 mm/min. The fracture energy was calculated using the formula (2):

$$G_f = \frac{A_f}{BW}, \tag{2}$$

where

G_f fracture energy [J/m^2],

A_f the work of loading force [J],

BW the area of the crack ligament [m^2].

The work of the loading force was calculated as the integral of the function from the force-displacement graph:

$$A_f = \int_0^{s_{\max}} F d_s, \tag{3}$$

where

s displacement during loading test,

F force during loading test.

4. Results and Discussion

In the SEM images were observed on the fiber surfaces significant mechanical changes compared to the reference fibers for both types of modification. However, the changes on the fiber surfaces are different for each type of modification. Fibers modified by low-pressure oxygen plasma have holes on their surfaces. Fibers modified by atmospheric pressure plasma have pimples (drops) on their surfaces. The wettability of the

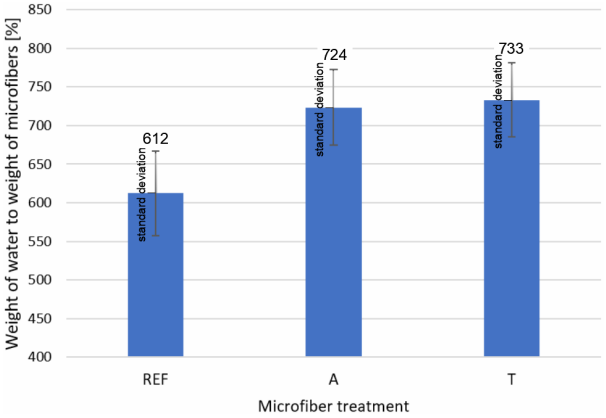


Figure 3. Weight of water to weight of microfibers.

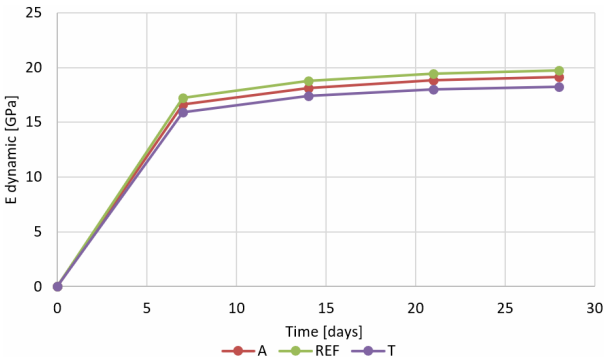


Figure 4. Dynamic modulus of elasticity from 0 to 28 days.

fibers increased after both modifications, the amount of water between the fibers increased in both cases by approximately 20 % compared to the reference values. The chemical effect of plasma modification is approximately the same in both cases (Figure 3). The dynamic modulus of elasticity was slightly lower for the samples containing plasma-modified fibers than the reference samples. For fibers modified by atmospheric plasma, modulus of elasticity decreased by approximately 1 %, for fibers modified by low-pressure oxygen plasma decreased by 3.5 % (Figure 4). Decrease in modulus of elasticity is negligible, most likely it was

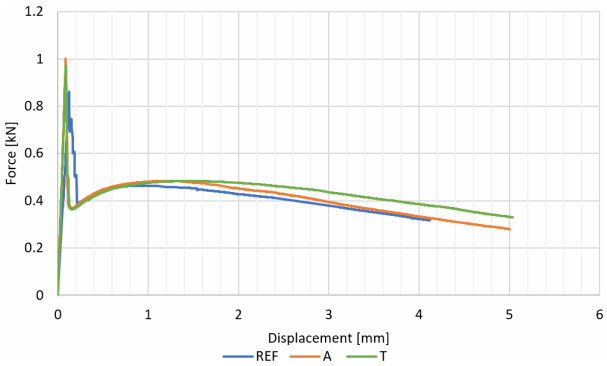


FIGURE 5. Flexural test – force-displacement graph.

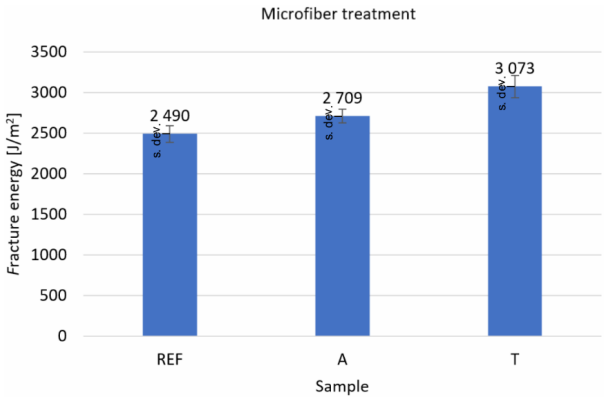


FIGURE 6. Fracture energy of samples.

caused by slightly worse workability of the cement mixture. That corresponds to a slightly lower density of samples with plasma-modified fibers compared to the reference samples. The fracture energy was higher for the samples with plasma-modified fibers compared to the reference samples. For samples containing fibers modified by atmospheric pressure plasma, it was an increase of approximately 8 %, for samples containing fibers modified by low-pressure oxygen plasma, it was an increase of approximately 25 % (Figures 5, 6).

5. CONCLUSION

The surface of the fibers was modified both mechanically and chemically. Based on the experiment, we can conclude that:

- Modification by oxygen low pressure plasma caused mechanical changes on the fibers surfaces. There were observed by SEM (magnification 20,000×) holes caused by this modification.
- Modification by atmospheric pressure plasma caused mechanical changes on the fibers surfaces. On the fiber surface were observed by SEM (magnification 20,000×) formations that look like drops or pimples caused by this modification.
- The wettability increased approximately the same after both modifications. The amount of water between the fibers increased by approximately 20 % in both cases.
- Modifications had almost no effect on the modulus of elasticity. The modulus of elasticity slightly decreased, for samples containing microfibers modified by atmospheric plasma decreased by 1 %, for samples containing microfibers modified by low-pressure oxygen plasma decreased by 3.5 %. This decrease was probably caused by the slightly worse workability of the fresh cement composite mixture for the samples containing plasma-modified fibers compared to the reference samples.
- The fracture energy of samples with plasma-modified fibers increased in both cases of modification. For samples modified by atmospheric pressure plasma, it increased by 8 %, for samples modified by low-pressure oxygen plasma, it increased by 25 %. The increase in fracture energy was mainly caused by the mechanical effect of plasma modification.

The tested plasma modifications succeeded in increasing the fracture energy of the cement composite material containing micro-milled recycled concrete. Both tested modifications were suitable. Samples containing fibers modified by low-pressure oxygen plasma had a higher fracture energy than samples containing fibers modified by atmospheric pressure plasma. On the other hand, plasma modification performed in atmospheric pressure is significantly easier to apply in mass production compared to modification performed in low-pressure. The workflow and devices for low-pressure plasma are more complicated compared to atmospheric plasma devices.

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