Nonthermal plasma modification of polypropylene fibres for cementitious composites

**Abstract:** The plasma treatment of polypropylene fibres used as concrete admixtures for improving its mechanical properties is the focus of this research paper. A plasma treatment was conducted in a low-temperature plasma environment at atmospheric pressure in a DCSBD (Diffuse Coplanar Surface Barrier Discharge). The degree of hydrophilicity caused by the plasma treatment was determined by measuring the rate of penetration of water into the porous media, commonly referred to as the Washburn method. The influence of the addition of PP (polypropylene) fibres to the concrete matrix was investigated using a three point bending test which determined the flexural strength of concrete samples. Our experiments demonstrate that plasma improves both the wettability of PP fibres and its adhesion to the concrete matrix. The tests of flexural strength show that even a short plasma treatment (5 s) can have a significant impact on the mechanical properties of fibre-reinforced concrete composite.

**Keywords:** plasma treatment, DCSBD, polypropylene fibres, concrete, confocal microscope, Washburn method

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**1 Introduction**

Short staples of polypropylene (PP) fibres are becoming increasingly popular admixture to fibre-reinforced concrete. These PP fibres play an essential role during the early stages of concrete hardening, since their presence in the concrete matrix can significantly reduce the cracking of the concrete [1-3]. Polypropylene fibres can take over the tensile forces, that the concrete alone could not withstand. The dispersed fibres improve the integrity of the whole system, increase the ductility of concrete and can absorb energy in the forms of impacts and vibrations [4]. In comparison to other concrete admixtures, PP fibres have a small diameter (18 µm) and lower density \(900 \text{ kg m}^{-3}\) [5] and therefore it is possible to use large amounts of fibres in low amounts of concrete, *i.e.*, 1 kg can contain hundreds of millions of PP fibres. Due to its molecular structure, PP is a chemically inert material and this ensures its stability in the hostile alkalic environment of concrete [1]. However this property also makes it hydrophobic and causes a relatively low adhesion of the PP fibres to concrete matrix and therefore the fibre-reinforced composite cannot achieve its full potential.

At the moment this problem is addressed by a chemical treatment (sizing) on the surface of PP fibres to increase its surface free energy. The drawback of this approach is the necessity to select an appropriate sizing for each concrete composition, to thereby avoid possible sizing agents interference problems. In addition to that the use of chemical agents is in contradiction with current EU effort to replace the potentially harmful chemical technologies [6].

One of the alternative approaches to increasing the free surface energy of PP fibres is to use a plasma treatment. This concept is not entirely new. Plasma treatments of PP fibres for applications in concrete mixtures have already been investigated [7,8]. However these previous studies were carried out under low pressure conditions, which makes the studies unsuitable for industrial applications. Currently, there are multiple plasma sources at our disposal that can be used for plasma treatment of PP fibres at atmospheric pressure. In this work we have investigated the possibility of using plasma generated by Diffuse Coplanar Surface Barrier Discharge (DCSBD) [9] to...
replace a chemical treatment and to improve the structural integrity of final fibre-reinforced concrete.

2 Experimental procedure

2.1 Plasma treatment - DCSBD

A DCSBD (Diffuse Coplanar Surface Barrier Discharge) was developed by prof. Černák’s group in Bratislava and this technology is protected by several patents [10-12]. The system of conductive electrodes with a coplanar configuration is embedded in a ceramic plate made of 96% Al₂O₃ with dimensions 220×90×0.635 mm. The electrodes are energized by a harmonic high-voltage of 8 kV RMS, 15 kHz and 400 Watt input power at atmospheric pressure. As a result of this process, a thin layer (0.3 mm) of macroscopically uniform plasma, consisting of numerous H-shaped microfilaments, is deposited on the dielectric surface. The polypropylene fibres were brought into close contact with the layer of generated plasma, using the teflon pusher (Fig. 1) and forced to move at adjustable speed by a home-made winding apparatus (Fig. 2). Using this experimental setup the exposure times were varied from 1 s to 30 s.

2.2 Fibres

A multifilament yarn of PP fibres produced by KrampeHarex (Czech Republic) company was tested. The fibre diameter of a circular cross-section was (18 ± 2) µm; the density of fibres was 910 kg m⁻³ and tensile strength was (300 ± 45) N mm⁻² [5]. Fibres with no chemical sizing were used for the plasma treatment. For reference values, fibres with commercial proprietary sizing were tested as well. The fibres were supplied with proprietary chemical sizing, which cannot be avoided during the manufacturing process. The sizing had to be removed before activating by plasma and this was done by washing the fibres in a continuously flowing water for 3 hours followed by natural drying under standard conditions in laboratory for 2 days. After the plasma treatment, the fibres were cut to 12 mm staples.

2.3 Three-point bending test

A three-point bending test was used to determine the flexural strength of the concrete samples. These samples were reinforced with polypropylene fibres. The composition of the concrete mortar is given in Table 1. The water to cement ratio used for this study was 1:2. Mixing of mortar has been made in plastic bucket with electrically forced propeller with following procedure:

- mixing of cement and sand of 30 seconds
- addition of water and continued mixing for a further 1 minute
- addition of polypropylene fibres and continued mixing for a further 30 seconds
- manual mixing with shovel, attention was paid to bottom and corners and additional 1 minute mixing with electrically driven propeller to facilitate a randomized orientation of fibres.

Table 1: Composition of mortar.

|     | Mass [g] |
|-----|----------|
| Cement 32.5 R | 1110 |
| Aggregate 0-4 | 3053 |
| Water | 558 |
| PP fibres | 5 |

Figure 1: Schematic of the DCSBD setup for the treatment of PP fibres.

Figure 2: Experimental setup of DCSBD for the treatment of PP fibres (The pusher is not shown on the picture for the sake of clarity).
Testing samples with dimensions of $4 \times 4 \times 16$ cm were prepared by molding the mortar into the prepared forms, placing them on a vibrational table. The compaction time was 1 minute. After molding, a plastic foil was applied to protect the samples from loss of water due to evaporation, and the samples in mouldes were stored in the laboratory under standard conditions at 20°C (relative humidity was considered to have no effect because of plastic cover of samples). Demolding was realized just before the test, 12 hours after mixing.

During the tests the concrete sample was placed on two parallel rods. A third (central) rod was situated directly above the sample between the two lower rods. Afterwards the third rod was lowered in a defined fashion to break the concrete sample into two pieces. The loading of the third rod was measured. A Testometric M350-20 was used to record the working diagram. The test setup was a three-point bending with a span of 120 mm. Loading was obtained at a speed of 5 mm min$^{-1}$ with a total deflection of 5 mm. This method was used to monitor the behavior of fibres after the samples cracked. The residual strength after main peak (the failure of cement matrix) is related to fibres and the ability to transfer the force including strength of fibres and its bonding with the cement matrix. The tests resulted in the failure of the concrete sample in the manner shown on Fig. 3.

The measured dependence of the loading force on the deflection was also used to obtain the value of flexural strength:

$$\sigma_f = \frac{3FL}{2bd^3}$$  \hspace{1cm} (1)

work to fracture:

$$W_f = \frac{\int_0^D F\delta D}{db}$$  \hspace{1cm} (2)

and elastic modulus:

$$E_f = \frac{L^3m}{4bd^2}$$  \hspace{1cm} (3)

where the expression in the numerator of the work to fracture (ability to resist fracture) is called thoughness. The physical meaning of the rest of the variables is following: $F$ - load at a given point on the load deflection curve [mm]; $L$ - support span [mm]; $b$ - width of test sample [mm]; $d$ - depth of tested sample [mm]; $D$ - maximum deflection of the center of the sample [mm] and $m$ - the gradient (i.e., slope) of the initial straight-line portion of the load deflection curve [N mm$^{-1}$].

2.4 Washburn method

The test of mechanical performance of the fibre-reinforced concrete are also valid for evaluating the adhesion of fibres within the concrete matrix. However the concrete hardening takes quite a long time (days) and we needed a quicker method for evaluating the quality of plasma activated fibre surface. For this purpose we have decided to take a free surface energy of fibres as a qualitative measure of plasma treatment.

Traditional methods (goniometric or Wilhelmy plate method) used for evaluating the surface energy of materials are not suitable for porous samples such as a bundle of fibres primarily because the experimental liquid get drawn into the volume of the pores. The measured contact angle (goniometric method) and force (Wilhelmy method) are therefore not correct. A more appropriate Washburn method has been adopted instead.

The Washburn method is based on liquid uptake by the pores of investigated material. From the time dependence of uptaken mass of liquid we can determine

Figure 3: Concrete samples after three-point bending test of flexural strength.
parameters, which characterize the wetting properties of the sample. According to [13] the adsorption of liquid into porous medium can be described by

\[ m(t) = \frac{A}{B} \left[ 1 + W(-e^{-1-\frac{B^2}{A}}) \right] \]  

where \( W \) denotes Lambert W function, \( S_0 \) is specific surface of material, \( \sigma \) surface tension of liquid, \( \theta \) contact angle, \( R_s \) mean static radius, \( \rho \) density of liquid, \( \mu \) dynamic viscosity and \( \Omega \) cross-section of the tube filled with fibres of porosity \( \varepsilon \).

The fitting parameter, \( A = [kg^2 s^{-1}] \), contains the information on surface wettability (cos \( \theta \)), but also on the porosity of sample \( \varepsilon \), and is called the specific rate of wetting. A more suitable parameter for mutual comparison of the experimental data is \( A_n \) – normalized specific rate of wetting, which can be obtained by dividing Eq. 5 by porosity term as shown in Eq. 7. \( A_n \) is now directly proportional to the surface energy of the tested fibres.

\[ A_n = \frac{A}{e^\varepsilon (1-\varepsilon)^2} \]  

A yarn of PP fibres with a length of 2 m was folded 5 times in half and inserted into a glass tube with inner diameter of 11 mm. Both ends of the sample were cleanly cut to obtain a cylinder full of PP fibres with smooth bottoms. The lower bottom of fibres was jutting out approximately 2 mm from the glass tube. The glass tube with the sample was placed on the scales and connected to a PC and water was brought into contact with the fibres. The experimental setup used for this study is shown in Fig. 4a, the real model is shown in Fig. 4b. Using a simple program, we were able to load the dependence of mass measured by the scales versus time.

Unfortunately the mass measured by analytical balance is not equivalent to the mass of liquid inside the pores. Formed liquid “meniscus” at the water-sample interface causes an attractive force interaction between the sample and liquid. And due to this interaction, the scales show a greater mass. The water uptake by the pores comes from the liquid reservoir and clearly the liquid level in the beaker must fall. This way the meniscus is elongated. During our experiments we discovered, that the meniscus behaves like a spring or a rubberband. When extended it tries to reach its equilibrium position again and exerts additional force on the sample. During the real experiments the extension of the meniscus was in order of tenths of a mm. The effect was not visible by naked eye, but it was measurable.

In order to eliminate these parasitic effects following procedure was used at the end of each measurement:
when the liquid rise saturates and the measured mass is equal to $m_{\text{max}}$, the liquid reservoir is separated from the sample and brought into contact with the liquid reservoir again a few seconds later. After breaking the contact with liquid reservoir, only the pure mass of liquid inside the pores is recorded - $m_c$. When the sample is brought back into the contact with liquid and the meniscus is created again (this time not elongated), the recorded mass skips to the value $m_1$. The recorded values for $m_{\text{max}}$, $m_c$ and $m_1$ provide information concerning the contribution of the parasitic effects described above. We derived an equation that allowed us to calculate the mass of liquid inside the pores assuming the above mentioned constants are known:

$$M(t) = \frac{m(t) - m_1 - m_c}{1 + \frac{m_{\text{max}} - m_1 - m_c}{m_c}}$$  \hspace{1cm} (8)

where $m(t)$ is measured mass and $M(t)$ is the real mass of liquid inside the pores.

This procedure is illustrated in Fig. 5. Using two additional steps we are able to measure the additional values required to determine the real mass of liquid inside the pores. Afterwards the real mass was fitted to Eq. 4 and the parameter $A_n$ was calculated. Fig. 6 clearly shows that the influence of the meniscus on the measured mass is not negligible. This procedure for eliminating the parasitic effects of the liquid-sample interactions has not been considered by any groups working with the Washburn method to date.

The range of the fitted data had to be carefully chosen to not include the effects of step-like increase of mass due to the meniscus creation (lower boundary) and the influence of saturation due to the finite size of the sample (upper boundary). The range of the fit varied with each sample. Typically the lower boundary lied between 20-30% of $m_{\text{max}}$ and the upper boundary between 80-90% of $m_{\text{max}}$.

The experimental liquid in this study was water, since that is the liquid that wets the PP fibres in the concrete mixture. More information about mathematical model and data processing (including the elimination of the parasitic effect) can be found in [14,15].

### 2.5 Confocal microscope

The change of the surface of the PP fibres induced by plasma treatment was investigated using the confocal microscope. In comparison with conventional microscopes, confocal microscope has several advantages including: shallow depth of field, elimination of out-of-focus glare and mainly the ability to collect multiple optical sections from thick samples [16]. The last feature enables the user to obtain a 3D image of the observed object. In this work an Olympus LEXT OLS4000 confocal microscope was used. Its maximal vertical resolution is 10 nm. The pictures shown in this work were obtained using the objective lens with designation 100x. Fine scan was used in all cases. The contact between the lens and the fibres had to be avoided, otherwise the lens could be damaged and therefore the fibres were sticktaped onto a small plate in order to ensure the horizontal orientation of the fibres.
3 Results and discussion

Our first objective was to verify the reproducibility of the results obtained by Washburn method and to determine the influence of the time of exposure on the wettability of the plasma-treated fibres. The value of wettability $A_n$ could in principle be used in further calculations to obtain the surface energy of the fibres. However it would require the use of a method [17] based on the wetting of the porous materials by more liquids (at least 8-10). Also this method is still a subject of a discussion among the scientists which prompts us to be careful. For the sake of this article the comparison of the wettability is sufficient.

Fig. 7 shows the influence of plasma treatment on the wettability of PP fibres at various treatment times. The pure untreated PP fibres did not adsorb any water at all - $A_n = 0$. Within the investigated times of exposure, the longer plasma treatment results in higher wettability of fibres. It is also clear that the most significant improvement of wettability occurs during the first 10 s of plasma exposure. After this time interval it is no longer efficient to continue the plasma treatment, since the curve reaches saturation.

On the other hand the normalized specific rate of wetting the chemically treated fibres is $1.09 \pm 0.03$ g$^2$/s$^1$. This value is almost 10 times higher than the rate of wetting of the fibres treated by Diffuse Coplanar Surface Barrier Discharge (DCSBD). This study demonstrates that the plasma treatment by DCSBD can only achieve a fraction of the wettability provided by chemical treatment. However below we will show that this relatively big discrepancy does not have to be crucial in an actual concrete environment.

In further experiments the studying focused on the short periods of plasma exposure of polypropylene (PP) fibres by DCSBD, in order to obtain the results applicable for industrial application. The following experiments demonstrated the correlation between wettability of PP fibres induced by plasma treatment in DCSBD and the flexural strength of concrete samples reinforced by these fibres.

Fig. 8 illustrates the process of a three-point bending test to assess the flexural strength of the concrete samples. Lowering the central bar against the concrete sample (the value of deflection) results in a force being exerted on the sample and this force increases with increasing deflection until certain point, when the initial crack of the sample appears. The point when the initial crack occurs in the sample corresponds to the maximum point in the curve. After the maximum curve is obtained, the resistance of the sample against further deformation decreases and the residual strength is measured. Fig. 8 also shows that the samples without admixture of fibres exhibit almost no residual strength and these samples fall apart shortly after the initial crack. On the other hand the samples reinforced by PP fibres still poses certain residual strength even after further deformation of the sample and prevent its disintegration.

Fig. 9 compares the flexural strength of concrete samples with PP fibres with various surface modifications after 13 hours of hardening. The columns denoted as a maximum gives the force needed for initial cracking of the samples. Next columns list the force needed for further deformation of the sample. It can be seen that the biggest force needs to be exerted on the samples with PP fibres treated in DCSBD for 5 s. The other samples including those with chemically treated fibres lag significantly. After
the initial crack the highest residual flexural strengths were measured also for the PP fibres treated in DCSBD for 5 s. Fig. 9 also shows that concrete samples without admixture of fibres fall apart immediately after the initial cracking (additional columns are missing). Samples denoted as untreated correspond to native PP fibres which were prepared by the washing out the sizing of "as received" commercial (chemically treated) fibres. Although the initial flexural strength is similar to that of chemically treated fibres, it should be noted that these fibres are not used in real applications chiefly due to their electrostatic charging that complicates the manipulation with them. Surprisingly the plasma activation of the washed-out (untreated) samples was able to remove this undesirable charging effect.

Table 2 shows the calculated flexural strength, elastic modulus and work to fracture for concrete samples reinforced by polypropylene fibres with various surface treatment. Five second plasma treatment of PP fibres caused 28% improvement of the flexural strength of the resulting concrete sample relative to the untreated PP fibres. The "work to fracture" of the concrete sample was also improved by 20%. When comparing the "work to fracture" values, only the fibres with a chemical treatment ensured better results than 5 s plasma treatment. The concrete samples without any fibres exhibited extremely poor "work to fracture" values.

To our knowledge, only a few other authors have attempted to use a plasma treatment of PP fibres to improve the mechanical properties of fibre-reinforced cementitious composites. For example [7] modified the surface of PP fibres in low-frequency argon and oxygen plasma at 20 Pa. They achieved best results for 2 minutes exposition and power input 120 W. The improvement of flexural strength was 56% and the toughness (work to fracture multiplied by the width and depth of the tested sample) was improved by 54%. This research group [20] also reported an increase in the flexural strength and toughness of concrete samples when using PP fibres treated in cascade arc argon plasma at 36 Pa. Although both of these papers reported significant improvements of the mechanical properties, the use of vacuum systems and long treatment times (minutes) are required. This makes it unsuitable for industrial application, where only short exposure times are technically feasible and for this reason we focused our attention only on the treatment times up to 5s.

By comparing Figs. 7 and 9, a correlation between the wettability and flexural strength for fibres with plasma treatment is observed. However, there is a huge discrepancy for the fibres with a chemical treatment. The

| Plasma treatment | 1 s       | 3 s       | 5 s       | Untreated | No fibres | Chemical treatment |
|------------------|-----------|-----------|-----------|-----------|------------|-------------------|
| Flexural strength [MPa] | 0.80±0.05 | 0.78±0.06 | 1.13±0.07 | 0.82±0.03 | 0.82±0.05 | 0.82±0.04         |
| Elastic modulus [GPa] | 7.71±0.24 | 7.29±0.17 | 6.95±2.09 | 7.95±0.53 | 7.75±0.60 | 6.18±0.23         |
| Work to fracture [J mm^-2] | 0.19±0.02 | 0.18±0.04 | 0.25±0.08 | 0.20±0.04 | 0.19±0.05 | 0.25±0.04         |
perfectly wettable chemically treated fibres do not exhibit any special effect in initial cracking formation. In addition the post-cracking behavior of tested samples was inferior to that of plasma activated fibres. These results demonstrate that wettability alone cannot guarantee an improved structural integrity of a fibre-reinforced concrete. The effect of high wettability of chemically treated fibres can be most probably attributed to the release of sizing agents into the testing water and consequently a reduction of water free surface energy.

Both Fig. 7 and Fig. 9 show an improvement in the performance with increasing time of exposure to the plasma. Based on these results, we can conclude, that even a relatively small increase of wettability of fibres induced by plasma treatment can cause significant improvement in flexural strength of fibre-reinforced concrete.

The results of morphological changes obtained by confocal microscopic measurements are shown in Figs. 10a-10c. When comparing Figs. 10a and 10b, a difference in the appearance of PP fibre caused by plasma treatment in DCSBD can be seen. The non-treated fibre on Fig. 10a has a relatively smooth surface with several scratches which have probably arisen during the manufacturing process. On the other hand, the fibre treated in plasma has a densely spotted surface by small blisters with spacing often smaller than 1 µm. This fine structure was not observed on any of the non-treated fibres. We have suspected that the origin of these blisters comes from microcondensation of surrounding water vapours (or other liquid) on the plasma created functional sites. A similar phenomenon has been previously reported for hydrophobized glass beads [18].

In order to verify this suspicion we have exposed the same fibres for 24 hours to a closed box with saturated water vapours. The surface of the non-treated PP fibre remained the same. On the other hand, a comparison between Figures 10b and 10c reveals a significant change in the appearance of the fibre previously treated in plasma. Most of the small dots created by plasma treatment were not visible after 24 hours in water atmosphere. The remaining dots are more dissolved with less pronounced borders. The results demonstrate a presence of active surface towards water molecules on plasma treated fibres.

### 4 Conclusions

The influence of plasma treatment on polypropylene fibres was investigated by means of the Washburn method, three-point test of bending flexural strength and

![Image of fibres](image)

**Figure 10:** a) The surface of PP fibre without surface treatment b) The surface of PP fibre with plasma surface treatment in DCSBD c) The surface of PP fibre with plasma surface treatment in DCSBD after 24 hours in water vapours.
confocal microscope measurements in order to evaluate the wetting properties of fibres and mechanical properties of fibre-reinforced concrete samples. We showed that the plasma treatment process improves both the properties of the fibre-reinforced concrete and fibres themselves. Even the admixture of non-treated PP fibres improves the mechanical properties of concrete samples, since it prevents the complete desintegration of the sample after the initial cracking. However the admixture of plasma treated PP fibres can ensure even higher flexural strength of concrete. The best results were obtained using PP fibres with 5s plasma treatment in DCSBD. In general the time required for plasma treatment is of order of seconds and therefore the industrial application of such treatment is feasible.

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