

# PLASMA SURFACE TREATMENT OF POLYPROPYLENE REINFORCING FIBRES BY DIELECTRIC BARRIER DISCHARGE

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**Abstract.** This article deals with plasma treatment of polypropylene fibres used as concrete admixtures for improving its mechanical properties. Plasma treatment was conducted in low-temperature plasma at atmospheric pressure. Dielectric barrier discharges in both coplanar and volume configuration of electrodes were used for this purpose. The degree of hydrophilicity caused by plasma treatment was determined by measuring the rate of penetration of liquids into the porous media, so called Washburn method. The optimized plasma treatment of industrially used polypropylene fibres ensured further 20% surface wettability improvement comparing to the standard chemical treatment.

## Introduction

### Polypropylene fibres as concrete admixtures

By adding the polypropylene (PP) fibres to concrete it is possible to improve the tensile strength of the concrete. Due to its chemical structure polypropylene is stable even in highly alkaline environment of concrete *Zheng et al.* [1995]. If the reinforcing PP fibres are equally distributed in the volume of concrete mixture, they can: improve the integrity of the whole system, increase the ductility of the concrete and absorb energy in the form of impacts and vibrations *Fischer et al.* [2007]. However the PP fibres must have sufficiently high surface energy.

Polypropylene chain is chemically inert and hydrophobic. Both of these properties are caused by the presence of the non-polar methyl group  $\text{CH}_3$ , which is bonded to the chain of carbon atoms. After mixing the PP fibres into the concrete mixture, the fibres will form clusters and the equal distribution will not be achieved. This is caused by its inherent hydrophobic nature. Clusters of fibres often trap considerable amount of air, which has a negative effect on the mechanical properties of the fibre-reinforced concrete *Kopkání et al.* [2010]. Therefore the industrially used fibres are chemically treated in order to increase its surface energy. However there is also another more eco-friendly way to increase the surface energy of polypropylene - plasma treatment. In this work we were treating the PP fibres by dielectric barrier discharge to increase its wettability.

### Plasma treatment of polypropylene fibre

Oxygen radicals created in plasma oxidize the carbon of the methyl group. Hence the methyl group is replaced by ether  $[-(\text{C}-\text{O})-]$ , ester  $[-(\text{C}=\text{O})-]$ , carboxyl  $[-(\text{C}=\text{O})-\text{O}-]$  or hydroxyl OH group *Cui et al.* [2002]. In comparison with the hydrophobic  $\text{CH}_3$  group, these new oxygen-containing groups are characteristic by their polar structure.

## Experimental

### Plasma sources

Following plasma sources were used to treat the surface of PP fibres:

- **Planar and curved DCSBD** *Simor et al.* [2002] - use a coplanar configuration of electrodes embedded in ceramics with 96% content of  $\text{Al}_2\text{O}_3$  was chosen as the dielectric material. Permittivity of this corund ceramics was  $\epsilon_r = 9,8$  and its thickness 0,635 mm. There were used silver electrodes with the width 1 mm and inter-electrode distance 1,5 mm. The lower part of the ceramics was

cooled by flowing oil. The dimensions of the surface of electrodes (the area of discharge) were 20 x 8 cm. For better contact with plasma, the fibres were pressed to the ceramics by a teflon pusher. Schemes of the planar and curved DCSBD reactors are shown on Figures 1 (a) and 2 (a).

- **VDBD** - uses volume configuration of electrodes separated by glass with permittivity  $\epsilon_r = 3 - 4$  and thickness 2 mm. Discharge gap was set to 1 mm. When we used the corund ceramics in this configuration of electrodes, a fast thermal degeneration of fibres occurred. The reason for this effect was a relatively big transferred charge caused by higher permittivity of corund and a relatively big inter-electrode distance. The scheme of VDBD reactor is shown on Figure 1 (b).
- **Device AHLBRANDT** - uses a volume configuration of electrodes isolated by a ceramics layer. This commercial device is used primarily for mass treatment of foil. Plasma burns between the rotating cylinder and a detachable electrode with gaps, which serve as air outlet. The fibres were coiled around the whole width of cylinder in order to achieve activation of multiple fibres at the same time and thus minimazing the treatment time. The scheme of its electrodes is shown on Figure 2 (b).

In all of the above mentioned plasma reactors, we used the highest power input, that did not cause the thermal damage to the fibres.

**Washburn method**

The influence of plasma treatment on the surface energy of polypropylene fibres was determined by measuring the rate of penetration of liquids into the porous media of fibres. This procedure is called the

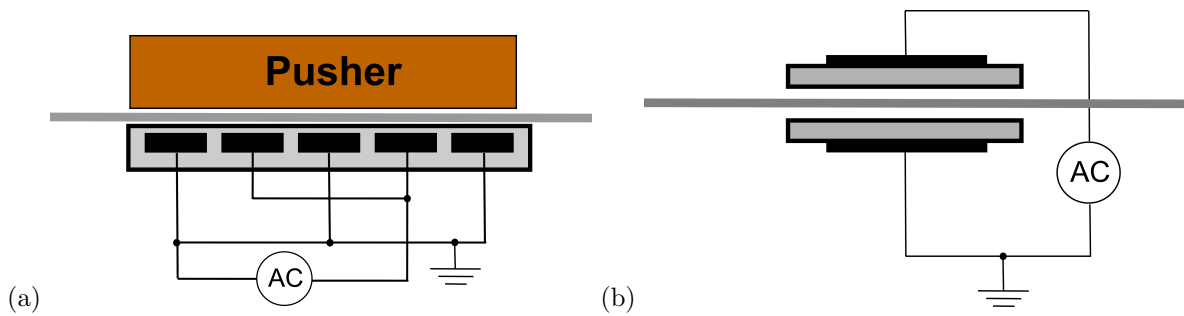


Figure 1. (a) planar DCSBD, (b) VDBD

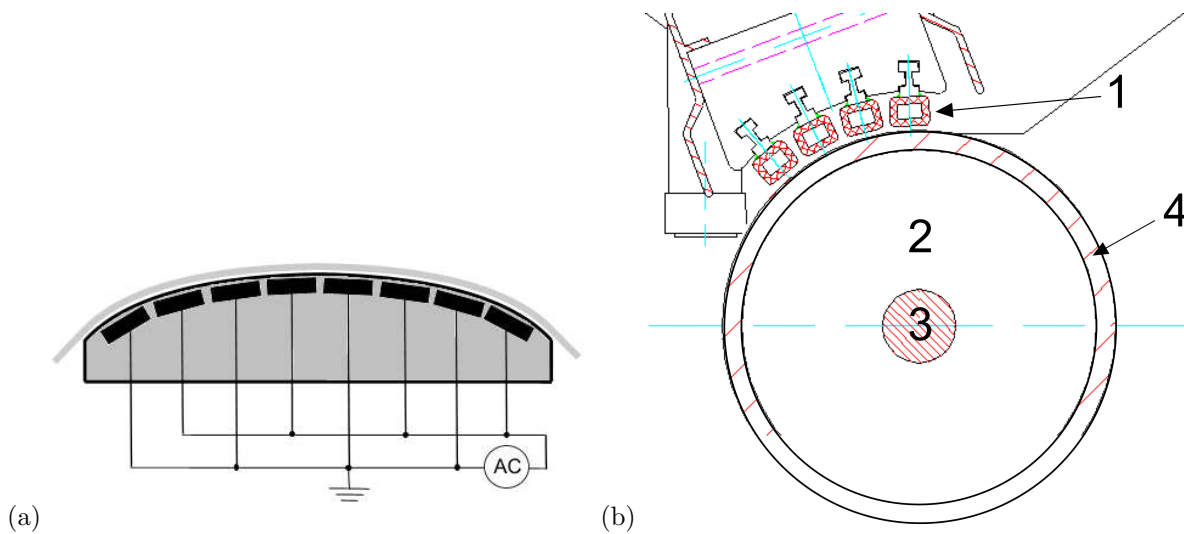


Figure 2. (a) curved DCSBD, (b) AHLBRANDT

Washburn method. It can be shown that the mass increment of liquid in pores is governed by equation [Fries *et al.*, 2010]:

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

with parameters:

$$A = \frac{\epsilon^4}{S_0^2(1-\epsilon)^2} \frac{\rho^2 \sigma_l \Omega^2 \cos \theta}{4\mu R_s} \quad (2)$$

and

$$B = \frac{\epsilon^3}{S_0^2(1-\epsilon)^2} \frac{\Omega \rho^2 g}{8\mu}, \quad (3)$$

where W denotes Lambert W function,  $S_0$  is specific surface of material,  $\sigma_l$  surface tension of liquid,  $\theta$  contact angle,  $R_s$  means static radius,  $R_h$  means hydraulic radius,  $\rho$  density of liquid, a  $\mu$  dynamic viscosity and  $\Omega$  cross-section of the tube filled with fibres of porosity  $\epsilon$ .

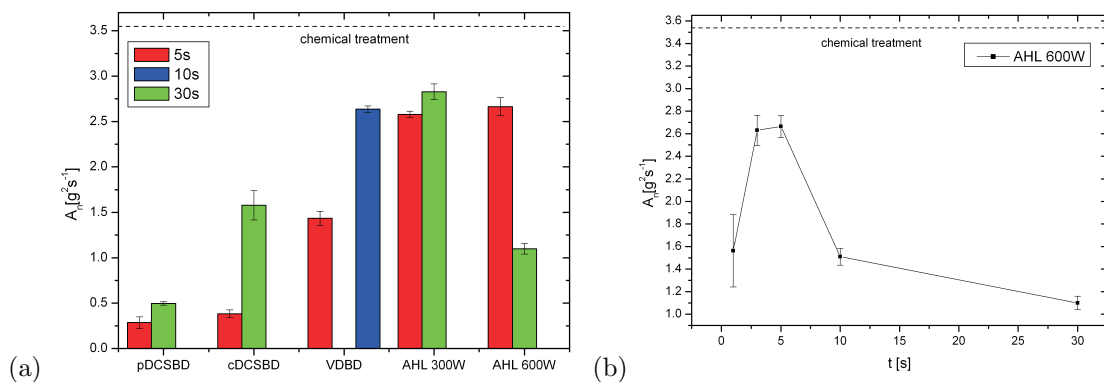
Parameter A [ $\text{kg}^2\text{s}^{-1}$ ] is called the specific rate of wetting and depends on the porosity of the sample, which is undesirable. The parameter of interest is  $A_n$ , which we named the normalized specific rate of wetting.  $A_n$  is not dependent on the porosity of the given sample, hence it is influenced only by the surface properties of the substrate. In our work we use  $A_n$  as the characteristic of the surface energy of polypropylene fibres.

$$A_n = \frac{A}{\frac{\epsilon^4}{(1-\epsilon)^2}}. \quad (4)$$

## Results

In our first experiments we tried to determine which DBD plasma reactor is most suitable for plasma treatment of PP fibres. Figure 3 (a) clearly shows, that plasma reactors with volume configuration are better suited for plasma treatment of polypropylene fibres than those with coplanar configuration. This observation can be explained by the way the filaments penetrate the volume of fibres. Filaments in the discharge with volume configuration are stationed perpendicular to the stack of fibres, hence they penetrate the whole volume of the stack. On the other hand the filaments in the discharge with coplanar configuration are stationed horizontally to the fibres and are not in contact with the whole cross-section of the stack. In further experiments we focused our attention on the commercial device AHLBRANDT. With input power of 600 W it proved to be the best possibility for short-period treatments of 5 s.

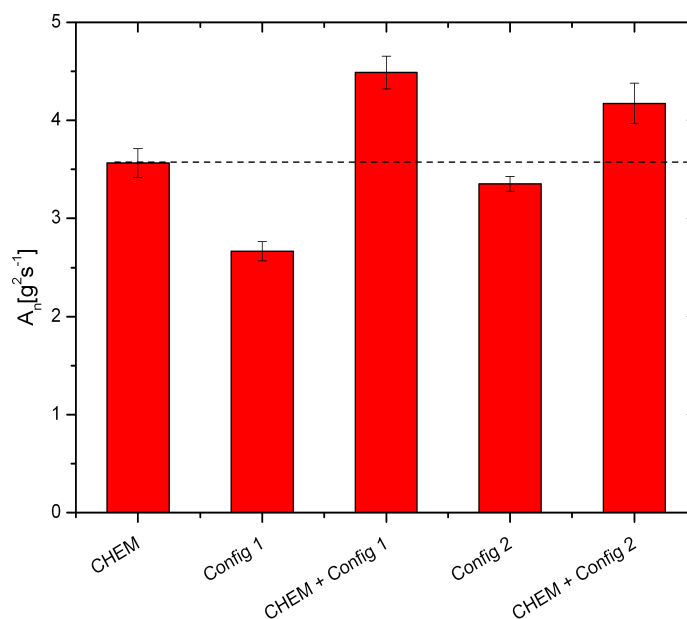
Figure 3 (b) shows the dependence of the normalized specific rate of wetting  $A_n$  on the treatment time of PF in device AHLBRANDT with input power of 600 W. It is apparent that the most effective treatment of PP fibres is achieved by the time of exposure in interval 3 - 5 s. The longer treatment times



**Figure 3.** (a) Comparison of  $A_n$  (normalized specific rate of wetting) for PP fibres treated in planar DCSBD, curved DCSBD, VDBD and commercial device AHLBRANDT, (b) Dependence of  $A_n$  on the exposure time for the PP fibres treated by plasma in the device AHLBRANDT with power input 600 W.

lead to the overexposure and undesired thermal degeneration. On the other hand the treatment times shorter than 1 s are not sufficient to effectively activate the surface of PP fibres.

From the industrial point of view, plasma treatment of pure polypropylene fibres is not so interesting. During the process of fibres production, small amount of chemical substance is spread over the surface of fibres. This is an inextricable part of the manufacturing process, since it allows for a carefree rewinding of fibres. This chemical treatment also improves the wetting of fibres. Therefore in further experiments we tried to treat these already chemically treated fibres with plasma. For this purpose we used the device AHLBRANDT with power input 300 W (Configuration 2) and 600 W (Configuration 1) with optimized treatment times. The results of this experiment are shown in Figure 4.



**Figure 4.**  $A_n$  (normalized specific rate of wetting) of PP fibres with different surface treatments.

Figure 4 shows that the plasma treatment with both configurations considerably improves the wetting of the chemically treated fibres. Configuration 1 caused 20% increase of rate of penetration and configuration 2 caused 15% increase. This result clearly indicates that the plasma treats mainly the surface of polypropylene and does not damage chemical treatment.

In our work we also used the XPS analysis to examine the chemical changes on the surface of fibres caused by plasma treatment. The scans of C 1s peak for pure PP fibres and plasma treated PP fibres show, that the plasma treatment caused additional binding of polar groups C=O and O-C-O/N-C=O, which is the reason for its improved wetting properties.

## Conclusion

Using the Washburn method it was determined that the plasma reactors with volume configuration of electrodes are well suited for the treatment of PP fibres. From among the used reactors the commercial device AHLBRANDT was shown to be the most efficient in improving the wettability of PP fibres and was used in further experiments. These experiments included the process of optimizing the exposure time for given power input and plasma treatment of chemically treated PP fibres under the optimized conditions. The latter showed, that the optimized plasma treatment of industrially used polypropylene fibres can ensure further 20% surface wettability improvement comparing to the standard chemical treatment. XPS analysis of the plasma treated fibres revealed that the improved wettability is caused by the binding of the polar groups C=O and O-C-O/N-C=O.

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