

# Hydrophylisation of non-woven polypropylene textiles using atmospheric pressure surface barrier discharge

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The aim of the present work was to investigate the surface modification of non-woven polypropylene textiles by means of plasma treatment at atmospheric pressure in order to improve their hydrophilic properties. The polypropylene non-woven spun-bond textiles with surface weight of 20 g/m<sup>2</sup> were used as the samples. The surface activation was provided by surface barrier discharge at atmospheric pressure where the operation frequency was 6 kHz. The surface energy of treated and untreated textile was investigated by means of contact angle measurement with four different liquids using the Surface Energy Evaluation System (SEE System). The surface energy was calculated according to LW/AB theory. The surface energy was correlated to the wetting properties of the materials studied by industrial permeability tests. In the present paper the hydrophilic properties and aging of plasma treated polypropylene samples with the plasma conditions and plasma exposition time are discussed.

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*Keywords:* Surface barrier discharge, Plasma treatment, Surface free energy

## 1. Introduction

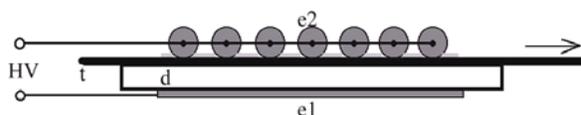
There is a wide range of methods for the surface modification of polymers in low-temperature plasma at reduced pressures in the order of 1 – 10 Pa. For such low pressure, the vacuum pumping system requires high costs and there are also difficulties to arrange the treatments of large-scale substrates such as long polymer textile rolls. Recently plasma treatment of polymers at atmospheric pressure appears as one of the most prospective and cheap solutions.

The aim of the present work is to investigate the surface modification of non-woven polypropylene textiles by means of plasma treatment at atmospheric pressure to improve their wetting properties. Polypropylene materials have many desirable properties such as high strength to weight ratio, good chemical resistance and thermal stability, relatively low cost and ability to recycle. However, the surface free energy is very low (approximately 20-25 mJ/m<sup>2</sup>), therefore their adhesion to other materials is very weak.

## 2. Experimental

The plasma activation of polypropylene textiles was carried out by surface discharges (SD) [1] operated at atmospheric pressure. The surface discharge was created on the surface of the insulating glass plate, which was from one side fully covered with metal electrode. On the other side of the glass plate the metal electrode consisted of 7 connected rotating rods with 9 mm gap. The rods were 6 cm long. The whole arrangement was placed in deposition chamber. The non-woven textile strips were

drawn with controlled speed through the chamber between the metal electrodes and the glass insulator plate. The discharge appeared along the insulator and the substrate surface in the decreasing initial electric field from the side of the rod metal electrodes [1]. The surface power density was kept at 0.4 W/cm<sup>2</sup> in all cases. Configuration of the reactor is shown in Fig. 1.



*Fig. 1 Configuration of the deposition reactor. The bottom metal electrode is marked as  $e_1$ , the upper rotating electrodes are marked as  $e_2$ ,  $d$  is the insulating glass plate,  $t$  is the paper strip and the arrow indicates its movement.*

In these experiments dry air was used as the buffer gas. The studied textiles were produced by Pegas a.s. Bučovice and surface density of polypropylene (PP) textiles was 20 g/m<sup>2</sup>.

The contact angle was measured directly from the observation of the solid-liquid meniscus. This method is often used for smooth surfaces, however its application for wettable materials is more complicated. In this case the determination of the contact angle immediately after the liquid was dropped on the PP surface is of crucial importance. After dropping a series of sessile drop images were taken by CCD camera in order to determine not only

the initial contact angle, but also the change of the drop profile in time due to wetting of the PP material.

For the determination of total surface energy from contact angles for example Owens-Wendt-Kaeble equation [2] can be used. The Owens-Wendt-Kaeble method enables to determine also the polar and apolar (dispersion) part of the total surface energy. However, this method does not give information about the acid-base character of the modified surface. For example it is well established that oxygen plasma surface treatment of polypropylene causes more acidic behaviour, whereas nitrogen based plasma introduces basic nitrogen-containing groups. It was shown in [3] that either acidity or basicity could be important for the increase of the surface energy of polypropylene. That is, why we used for detail analysis of some chosen samples the so-called “acid –base” theory enabling to determine also the electron-acceptor and electron-donor parameter of the surface tension.

The total surface tension is a sum of its apolar and polar components:

$$\gamma_i = \gamma_i^{LW} + \gamma_i^{AB} \quad (1)$$

where LW indicates the total apolar (dispersive), Lifshitz-van der Waals interaction, and AB refers to the acid-base or electron-acceptor/ electron-donor interaction according to Lewis.

The surface energy can be calculated according to Young-Dupré equation expressed by terms as electron-donor  $\gamma^+$  and electron acceptor  $\gamma^-$  parameters:

$$(1 + \cos \theta) \gamma_i = 2(\sqrt{\gamma_i^{LW} \gamma_j^{LW}} + \sqrt{\gamma_i^+ \gamma_j^-} + \sqrt{\gamma_i^- \gamma_j^+}) \quad (2)$$

where i refers to liquid and j refers to solid material. The values can be determined from contact angle measurement with three liquids of which two of them must have polar component. The liquids and their characteristic parameters used for contact angle measurement are listed in Table 1.

Water permeability of samples before and after plasma treatment was determined as the time necessary for the penetration of 5 ml of the testing liquid across the sample. Permeability tests were consistent with the norm ISO 9073-8:1995

Table 1. List of testing liquids used. The total surface tensions of liquids and their components are given in mJ/m<sup>2</sup>.

Testing liquid	$\gamma_{\text{tot}}$	$\gamma^{LW}$	$\gamma^{AB}$	$\gamma^+$	$\gamma^-$
Distilled water	72.8	21.8	52.0	25.5	25.5
glycerol	64.0	34.0	30.0	3.9	57.4
Ethylene glycol	48.0	29.0	19.0	3.0	30.1
Diiodinmethane	50.8	50.8	0	0	0

Young's equation, which is used for surface free energy evaluation, applies to ideal surfaces that are perfectly smooth. It is well known, that the roughness significantly influences the wetting properties of the solid surface. It enhances the hydrophobicity of hydrophobic surfaces as well as the hydrophilicity of hydrophilic surfaces. Two distinct hypotheses are classically proposed to describe the effect of the roughness on the wetting properties. According to Wenzel's hypothesis [4] the testing liquid completely fills the depressions in rough solid, so the roughness increases the surface area of the solid. The apparent contact angle  $\theta^*$  may be expressed as

$$\cos \theta^* = \rho \cos \theta, \quad (3)$$

where  $\rho$  is the surface roughness parameter. The surface roughness parameter gives the ratio between the ideal surface area and the increased surface area due to roughness and may be expressed as

$$\rho = \left( \frac{L}{l} \right)^{D-2}, \quad (4)$$

where D is the fractal dimension of the surface between the upper L and lower l scale limits. The apparent contact angle  $\theta^*$  is lower than  $\theta$  in case of  $\theta < \pi/2$  and  $\theta^* > \theta$  in case of  $\theta > \pi/2$ . That means that the roughness amplifies the hydrophobic as well as the hydrophilic surface properties.

According to Cassi's hypothesis [5] air can remain trapped in holes below the liquid drop and the drop sits on composite surface: partially on air, partially on the solid material.

The apparent contact angle may be expressed as

$$\cos \theta^* = -1 + \Phi_s (\cos \theta + 1), \quad (5)$$

where  $\Phi_s$  is the solid fraction of the surface. The Cassi's approach is used only for hydrophobic surfaces. In Fig. 2b this approach combined with Cassi-Baxter's approach

$$\cos \theta^* = -1 + \Phi_s (\cos \theta + 1)^2 \quad (6)$$

is compared with the theoretical results obtained on the smooth surface.  $\Phi_s$  is the solid fraction of the surface. The Cassi's approach is valid only for  $\theta > \pi/2$ , i.e. only for hydrophobic surfaces. The combined Cassi-Baxter approach gives better results. According to Fig. 2 the hydrophilic surface may be changed to hydrophobic also with variation in the surface roughness. This is not really true. It is possible to obtain contact angles higher than  $\pi/2$  on hydrophilic surfaces, however these contact angles are metastable.

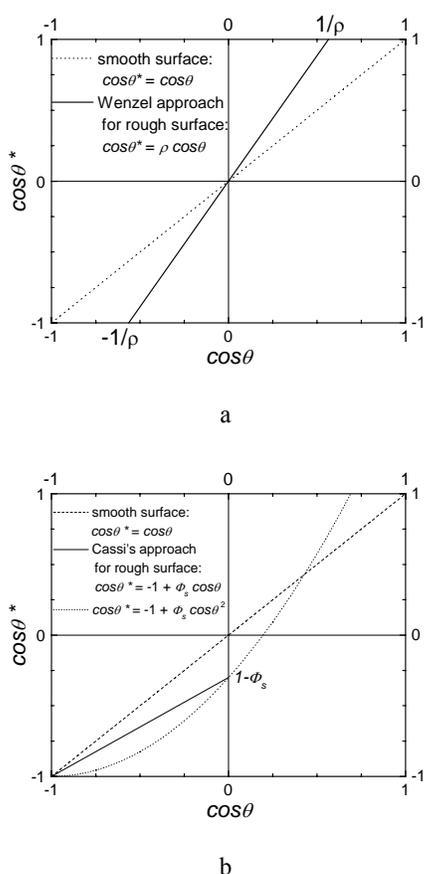


Fig. 2. Comparison of the Wenzel approach (a) and Cassie's approach (b) with the results obtained on smooth surface.  $\theta^*$  is the apparent contact angle,  $\rho$  is the surface roughness parameter.

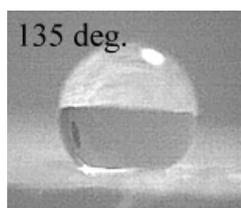


Fig. 3. Water drop on the un-treated PP surface.

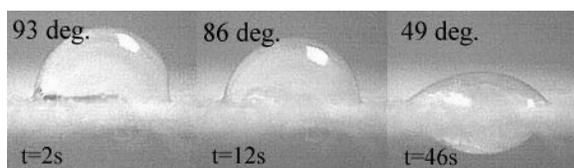


Fig. 4. The dependence of the water contact angle on time due to wetting of the spun-bond PP textile.

In Fig. 3 the high water contact angle with PP is caused by low surface free energy together with high surface roughness. In Fig. 4 the dynamic evolution of the water contact angle and water drop size in time is illustrated. On the basis of the study of the drop behaviour on the PP surface it is possible to distinguish the dynamic wetting from dynamic spreading of the liquid [6].

### 3. Results and discussion

Plasma treatment of PP proceeds by a free-radical mechanism that introduces a wide variety of oxidized functional groups and basic nitrogen containing groups onto the surface of the treated polymer. In Fig. 5 the calculated values of the total surface free energy of PP textile and in Fig. 7 the components of the total free energy depending on the treatment time are depicted. The contact angle measurements were made using four liquids and the surface energy calculations were made according to LW/AB model. The polar part  $\gamma^{AB}$  of the surface energy of the untreated material was almost negligible. The significant increase in surface energy after 1 s treatment was caused mainly by the significant increase of the surface energy component indicating the base character of the studied surface. Approximately after 3s the saturation of all components of the surface free energy was reached. The time dependence (“aging”) of plasma treated samples was studied by measuring the contact angle and permeability measurement up to several days after treatment. After the plasma activation by means of air surface barrier discharge, the samples were stored in air atmosphere at 23 °C. The permeability and contact angle of samples were measured after the subsequent time steps. Fig. 6 gives the dependence of the surface energy of PP textile treated 5 s on the storage time. The decrease of the surface energy of the plasma treated material due to aging (Fig. 6) was caused mainly by rapid decrease of the base (electron-donor) component of the surface energy (Fig. 8).

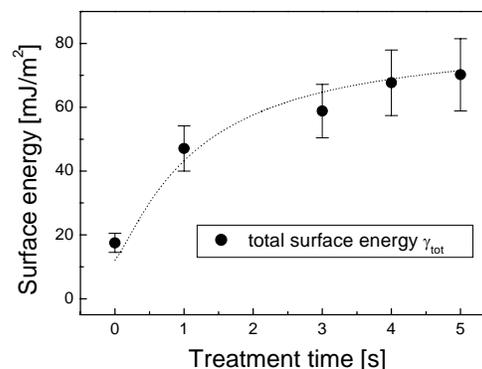


Fig. 5. The dependence of the total surface energy of PP textile on the treatment time. The line connecting the experimental data is only guide for eyes.

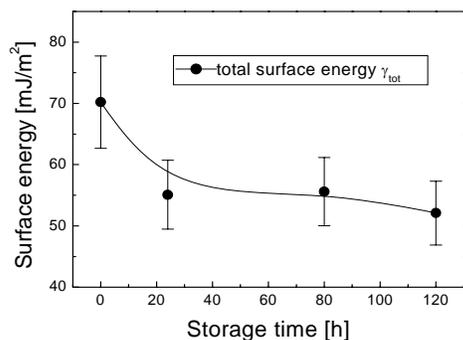


Fig. 6. The dependence of the total surface energy of PP textile on the treatment time. The line connecting the experimental data is only guide for eyes.

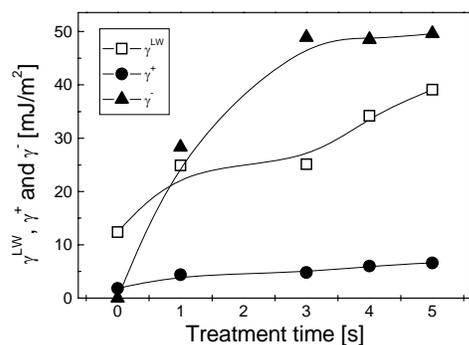


Fig. 7. Dependence of the PP non-woven total surface energy  $\gamma_{tot}$  and its apolar  $\gamma^{LW}$ , polar  $\gamma^{AB}$ , acid  $\gamma^+$  and base  $\gamma^-$  components on the treatment time.

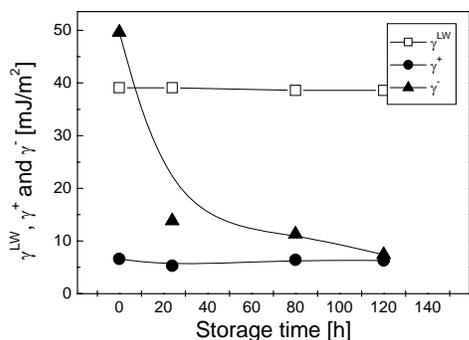


Fig. 8. Dependence of the PP non-woven total surface energy  $\gamma_{tot}$  and its apolar  $\gamma^{LW}$ , polar  $\gamma^{AB}$ , acid  $\gamma^+$  and base  $\gamma^-$  components on the storage time. The lines connecting the experimental data are only guides for eyes.

Fig. 9 shows the dependence of the water contact angle and the water permeability on the treatment time in air surface discharge. In this case the plasma was supplied with 5 kHz sinus signal with amplitude 7 kV and the supplied power was 60 W. Fast increase in permeability was observed during the first 3 s, followed by a slow increase with increasing plasma exposure time. The water contact angle linearly decreases with increasing exposure time.

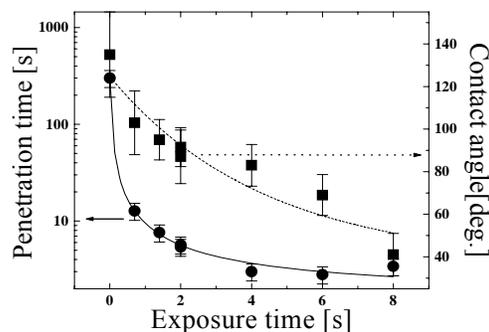


Fig. 9. Dependence of contact angle and water permeability as a function of surface discharge exposure time. Dot and dash lines serve as a guide for eyes.

The results obtained on the contact angle and permeability measurements were completed by XPS analysis of the studied materials. In Fig. 9 the C 1s core level spectra for the air and nitrogen treated and non-woven PP textiles are shown. The untreated PP surface exhibits a narrow peak 285.0 eV, which belongs to C-C and C-H<sub>x</sub> bonds. In the case of the plasma treated surfaces the C 1s signals show a multi-peak structure, however the peaks are rather broad and an accurate determination of the particular contributions is difficult. The main contribution belongs to the C-C and C-H<sub>x</sub> bonds at 285 eV. The asymmetry on the high binding energy side is probably due to bonding states -CH<sub>2</sub>-C=N (286.4 eV), C-O (286.5 eV), C=O (288.0) and O=C-NH at 288.2 eV.

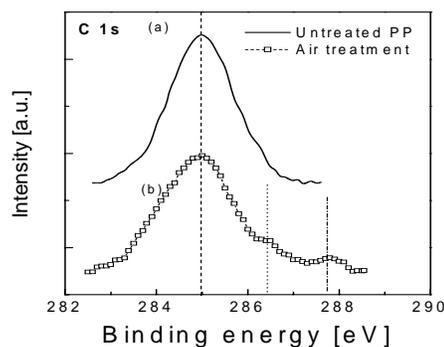


Fig. 10. XPS C 1s core level spectra of the studied surface: (a) untreated PP non-woven textile; (b) plasma treated PP non-woven textile at air.

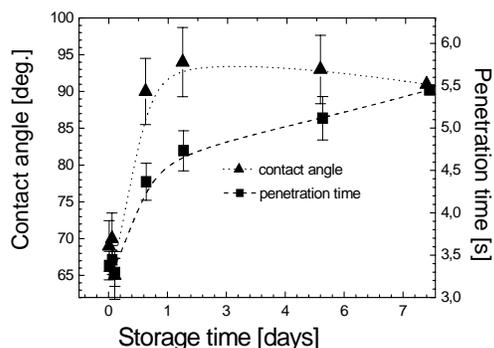


Fig. 11. Dependence of contact angle and water permeability as a function of storage time. The plasma treatment was 3 s in air surface discharge. Dot and dash lines serve as a guide for eyes.

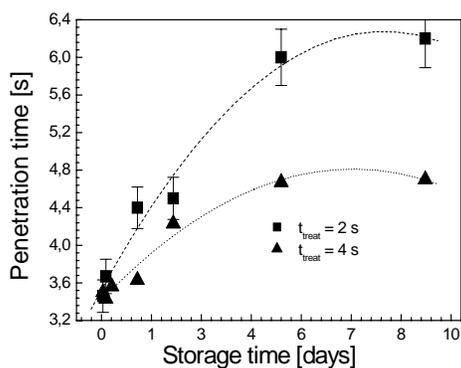


Fig. 12. Dependence of water permeability as a function of storage time. The plasma exposure time was 2 s and 4 s in air surface discharge. Dot and dash lines serve as a guide for eyes.

Fig. 11 shows the kinetics of the permeability and contact angle as a function of storage time. The exponential increase in water contact angle of plasma-activated PP textile with the aging time was observed. The water contact angle reached the saturation after 40 hours of plasma treatment, however there was observed decrease in water permeability of sample even after 40 hours. This discrepancy can be explained with a different sensitivity region of the testing methods. The contact angle is sensitive only to surface properties whereas water permeability is sensitive to both surface and bulk properties. Fig.12 shows the aging of samples treated for 2 s and 4 s at the same plasma conditions. Both samples (treated for 2 s and 4 s) reached the saturation after 10 days of the storing. Moreover, the sample treated for 4 s shows lower degradation than the sample treated for 2 s.

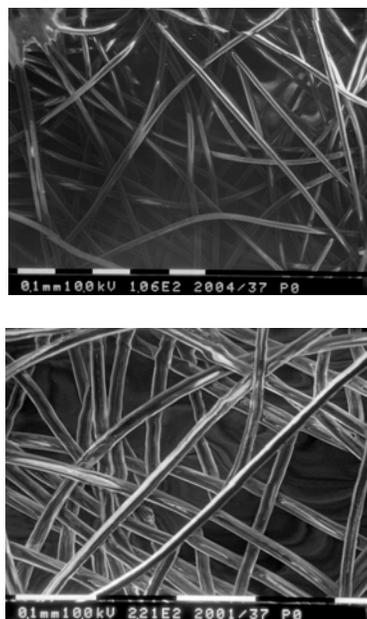


Fig. 13. SEM images of the untreated non-woven PP textile.

An important result is that the plasma treatment of the hydrophobic PP material did not affect the appearance of the PP surface, i.e. we did not observe any substantial change in appearance of the treated material. Moreover the morphology of the PP non-woven textiles did not change significantly during the plasma treatment (see SEM micrographs illustrating the surface morphology of the PP non-woven textiles before and after plasma treatment on the Figs. 13 and 14). The surface structure amplifies to the hydrophobic properties of the non-treated PP textiles.

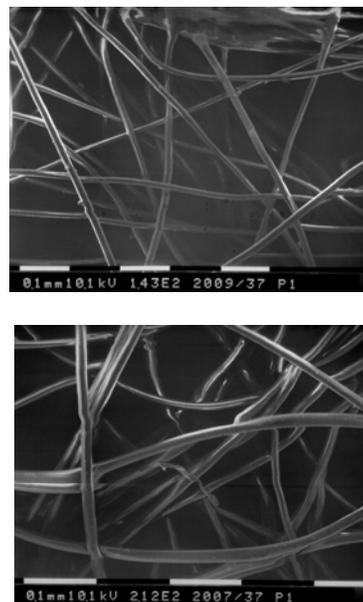


Fig. 14. SEM images of the air plasma-treated non-woven PP textile.

#### 4. Conclusion

The hydrophilisation of non-woven PP textiles in surface barrier discharge was investigated. The dependence of the surface energy on the treatment time and on the storage time was studied by means of contact angle measurements. The obtained results were correlated with the results of permeability tests and XPS analysis. The main contribution to the increase of the surface energy originates from the increase of the apolar and partially of the base part of the surface energy. The aging is caused mainly by the rapid decrease of the base part of the surface energy, which could be related to the non-stable nitrogen-containing surface bonds. The total surface energy of the PP non-wovens after 140 hours of storage was still about 45 mJ/m<sup>2</sup>.

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