SURFACE MODIFICATION OF NON-FABRICATED POLYPROPYLENE TEXTILE IN LOW-TEMPERATURE PLASMA AT ATMOSPHERIC PRESSURE

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Abstract: The plasma activation of polypropylene (PP) non-fabricated textile in low temperature plasma at atmospheric pressure has been studied. The aim of the present work was the study of the surface modification of non-fabricated textiles in order to improve their hydrophilic properties. The surface treatment has been provided by nonequilibrium discharges as barrier discharge and surface discharge. The surface properties have been characterized by measuring the contact angle of PP textiles with liquid, standard industrial permeability measurements and absorption tests. The degradation of treated PP samples has also been studied.

1. INTRODUCTION

Polypropylene has a very low value of the surface free energy (approximately 20-25 mJ/m^2) [1]. Due to low surface energy polypropylene has very weak hy[1]drophilic properties. In many industrial applications there is a need to modify the polymer surface with keeping their desired unchanged bulk properties. Chemical activation of the surfaces is the most often used method for their activation, however the ecological requirements force the industry to search alternative environmental safety methods. The surface modification of polymers in low-temperature plasma appears as one of the most prospective and cheap solutions.

The aim of the present work is to investigate the surface modification of non-fabricated polypropylene textiles by means of plasma treatment at atmospheric pressure to improve their hydrophilic properties. Many plasma applications in the surface modification field were made at reduced pressures in the order of 1 – 10 Pa [1, 2]. A significant increase in the hydrophilicity of low-pressure plasma treated materials was observed but the application in industry has many disadvantages, mainly problems with the need of vacuum system, long processing times and high energy consumption. This study is focused on the plasma surface activation of polypropylene non-fabricated textiles at atmospheric pressures. Interesting results were obtained using the surface discharges (SD) as well as by the application of barrier discharge (DBD). Some studies have been focused on the stabilization of surfactants [3, 4].

2. EXPERIMENTAL

In this study the plasma activation of polypropylene non-fabricated textiles were investigated. The textiles are produced by Pegas a.s. Bučovice, the main applications of these textiles are in medical, sanitary and hygienic industries. The surface weight of PP textiles varied from 20 to 50 g/m^2 in the case of spun-bond samples (in application used as a liquid transporting layer) and melt-blown type samples with surface weight varying from 50 to 200 g/m^2 (in application used as an absorption stratum). The surface activation was provided by barrier discharge (DBD) and/or surface discharges (SD) [5] at atmospheric pressure where the operation frequency varied from 50Hz to 10 kHz. The surface properties of treated and untreated samples were characterized by means of the contact angle measurement, the industrial absorption test and the water permeability measurement.

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Dielectric barrier discharges (DBD) were created between two metal electrodes covered with insulating layers (glass, ceramic and polycarbonate). AC driving voltage with the amplitude of approximately 7-10 kV was used to create the discharge in DBD where the gap spacing was in the order of a few mm [8]. Many separate microdischarges are observed in DBD at these conditions. Thanks to the special shape of the metal electrodes, the microdischarges can be observed with the same density around the barrier surface. A significant disadvantage is that the DBD homogeneity considerably depends on the operating frequency and the gas mixture composition [6, 7]. Under certain specific conditions, the DBD discharge can produce so-called atmospheric pressure glow (APG) discharge [8, 9, 10], which can also be effectively used for the surface treatment [9].

Surface discharge SD was revived on the surface of the insulating plate (glass, ceramic and polycarbonate). The insulating layer was from one side fully covered with metal electrode. On the other side of the insulating plate the metal electrode consisted of 18 strips (10 cm long and 1 mm wide) with a 3 mm distance between them and connected together. The discharge appears along the insulator surface in a decreasing initial electric field from the side of the thin strips.

Dry air and partially nitrogen were used as the buffer gases. Plasma induced changes of PP textiles were indicated by the contact angle measurement and liquid permeability tests. The contact angle of liquid on solid is closely related to surface free energy and this parameter is useful in the discussion of hydrophilicity, absorbency of sample and adhesivity. The contact angle was measured directly from the observation of the solid-liquid meniscus. For the determination of total surface energy from contact angle measurement Wu's equation [11] and Owens-Wendt-Kaeble equation [12,13] can be used. Water permeability of samples before and after plasma treatment was determined measuring the time necessary for the penetration of 5 ml of the testing liquid across the sample. The absorption properties of sample were measured as a difference of the weights of the sample before and after the dipping in the testing liquid. The industrial absorption tests were measured at the Testing Textile Institute at Brno.

3. RESULTS AND DISCUSSION

The first part of our study is devoted to activation of the spun bond non-fabricated textiles with surface weight 20 g/m^2, in the second part the results of activation of melt-blown textiles are shown. The PP textiles were exposed to surface discharge and DBD in air. The degradation of spun-bond textiles is presented in the third part.

3.1. Activation of the spun-bond textiles

Plasma treatment of PP proceeds by a free-radical mechanism that introduces a wide variety of oxidized functional groups onto the surface of the treated polymer. These oxidized functional groups may include C-OH, C=O, COOH, C-O-C, epoxy, ester, or hydroperoxide [14, 15], and they are responsible for the change in the polymer surface properties.

Figure 1 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 5kHz sinus signal with amplitude 7 kV. The area of each electrode was 200 cm^2 and the power supply was 60 W. Fast increase in permeability was observed during the first 3 s, followed by a slow increase with increasing plasma exposure time. However the water contact angle linearly decreases with increasing exposure time. Figure 2 shows the dependence of the permeability on the contact angle. The permeability t_p can be described with a stretch exponential course $t_p = t_s+(t_i-t_s)*\exp(-\cos\Theta-\cos\Theta_i)/\beta$. Where t_i and Θ_i represent permeability and contact angle in initial (untreated) state, respectively t_s is permeability in (degraded) study state, and β represents dispersion parameter.

The effect of the power supply on the water contact angle and water permeability was tested and the results are shown in Figure 3. The treatment time was fixed to 2 s and the power supply was varied

The area of each electrode was 200 cm^2 and the frequency was 3 kHz. Strong influence of the power supply to hydrophilic properties of PP textiles was observed. The permeability exponentially increases with increasing supplied power, however the water contact angle decreases linearly.

The plasma treatment of spun bond PP textiles in DBD operated at 3 kHz in air was studied (see Figure 4). The space between electrodes was 2 mm and the surface of the each electrode was 200cm^2.

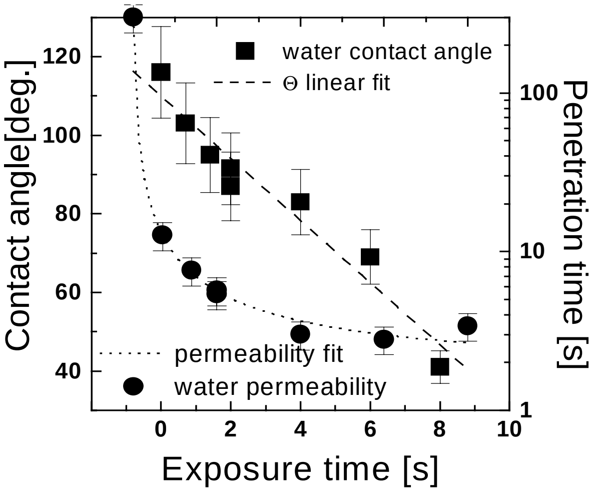

FIGURE 1. Dependence of contact angle and water permeability as a function of surface discharge exposure time.

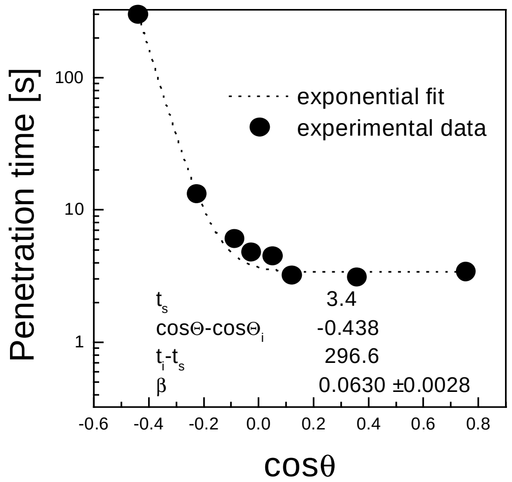

FIGURE 2. Dependence of the water permeability as a function of the cosΘ of PP sample.

The power supply was fixed to 100 W. The contact angle decreased linearly with increasing plasma treatment time. The permeability increases exponentially. The plasma treatment longer than 2 s can cause the hydrophilisation of surface of PP textile. Due to this result, the optimal plasma treatment time at this condition is 2 s. The influence of the operating frequency in range 1 kHz to 10 kHz was not registered. The higher frequency was not tested due to undesirable plasma perforations of treated material.

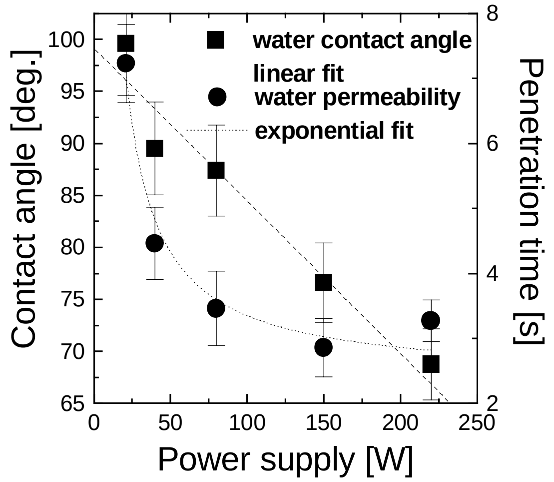

FIGURE 3. Dependence of contact angle and water permeability as a function of supplied power

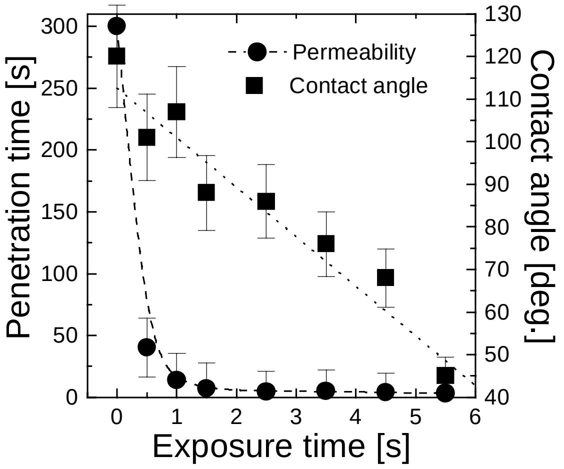

FIGURE 4. Dependence of contact angle and water permeability as a function of DBD exposure time. Dot and dash line serves as a guide of eyes.

3.2. Activation of the melt-blown textiles

In the case of melt-blown PP textiles the aim of our work was to increase the absorption capacity of the material. For the plasma surface activation, the air surface discharge operated at 5 kHz was used. For the activation of melt-blown textiles it was necessary to use higher exposure time than for spun-bond textiles. With plasma activation it is possible to reach 500% absorption improvement of polypropylene textiles with surface weight 75gm^{-2} as is shown on Figure 5. The water contact angle decreased to 70°. However the samples with higher surface weight (200 gm^{-2}) treated at the same plasma conditions show only small improvement of the absorption. The plasma treatment acted only on the surface of the PP material i.e. the water contact angle decreased to 80°, however the absorption increased only up to 90 % (see Figure 6).

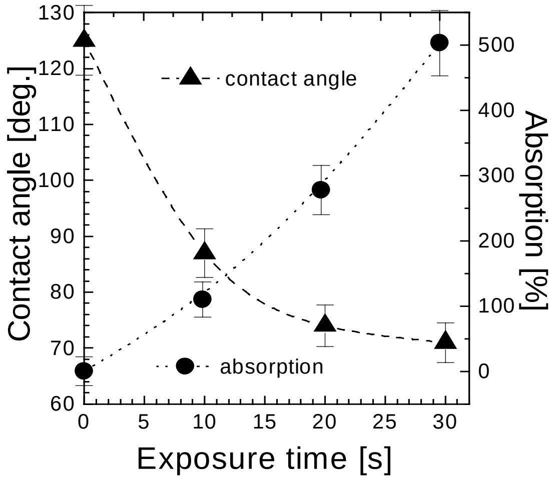

FIGURE 5. Dependence of contact angle and absorption as a function of surface discharge exposure time. Dot and dash lines serve as a guide of eyes.

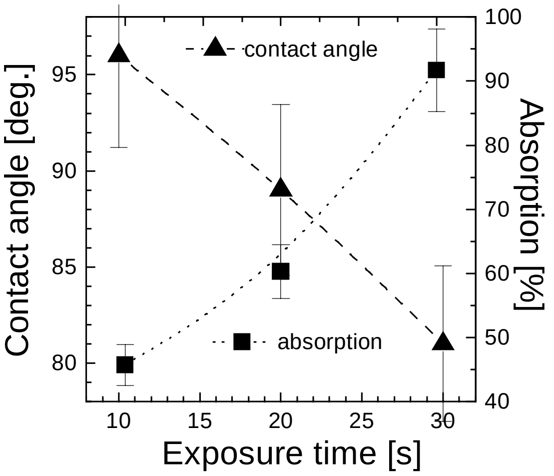

FIGURE 6. Dependence of contact angle and absorption as a function of surface discharge exposure time. Dot and dash lines serve as a guide of eyes.

3.3. Aging of spun-bond textiles

The degradation of the modified properties was studied. The metastability of the PP properties can be attributed to four effects [16]:

1. thermodynamically driven reorientation of polar species away from the surface into the subsurface
2. diffusion of mobile additives or bloomers from the polymer bulk to the surface
3. formation of low molecular weight species in subsurface during the plasma treatment and their subsequent migration to the surface
4. reaction of the residual free radicals with ambient

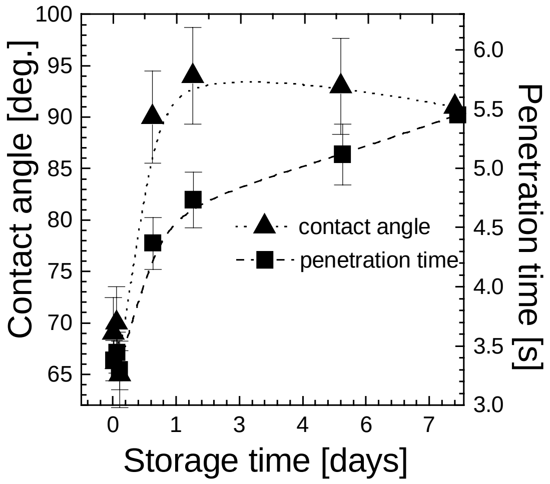

FIGURE 7. Dependence of contact angle and water permeability as a function of storage time. The plasma treatment was 3 s in air surface discharge. Dot and dash lines serve as a guide of eyes

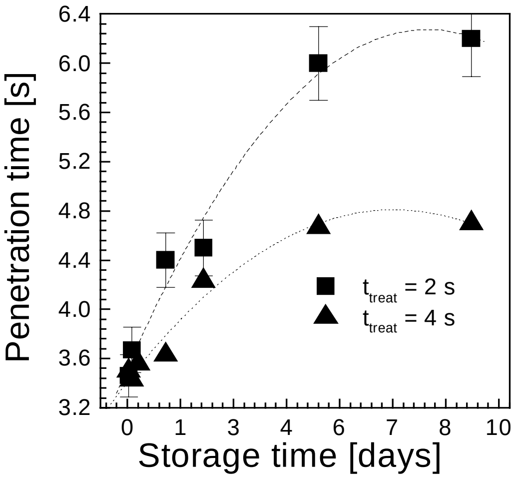

FIGURE 8. Dependence of water permeability as a function of storage time. The plasma exposure time was 2s and 4s in air surface discharge. Dot and dash lines serve as a guide of eyes.

After the plasma activation the spun-bond samples were stored in air atmosphere at 23°C. The PP samples were activated in air surface discharge. Surface area of the each electrode was 200 cm^2, power supply 60 W. The permeability and contact angle of sample were measured after the subsequent logarithmical time steps.

Figure 7 shows the kinetics of the permeability and contact angle as a function of storage time. The stretch exponential increase in water contact angle of plasma activated PP textile in the aging time was observed. The water contact angle reached the saturation 40 hours after the 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 however water permeability is sensitive to surface and bulk properties.

Figure 8 shows the degradation 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.

4. CONCLUSIONS

We made the first experiments with the plasma treatment of PP non-fabricated textiles to increase their hydrophilicity. The surface discharge was found to be more effective tool for the treatment of this type of material than the dielectric barrier discharge DBD. The barrier discharges were used at atmospheric pressure and at various operating frequencies in air. We observed that the frequency of the supplied power has no significant effect on the treatment. On the other hand, large effect of the supplied power was observed.

The plasma treatment of the PP non-fabricated textiles was characterized by different techniques. The technological and construction points of view were taken into account. The experimental results of the used techniques correspond with results obtained with other authors.

The aim of further experiments will be the optimization of the discharge conditions in order to reach the lower plasma exposure time and to increase the stability. Special attention of our work will be devoted to stabilization of surfactants namely due to grafting.

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