Comparison of NPIII and DBD Plasma Treatment in Terms of Wettability of PTFE and PA6

Z. Károlyi, Sz. Kléberti, H. Al-Malikii, T. Pataki

Abstract: We compared the effect of nitrogen plasma immersion ion implantation and dielectric barrier discharge surface treatment on the wettability of two engineering polymers: PTFE and PA6. We found that NPIII is capable to make the surface either hydrophilic or superhydrophobic depending on the operating parameters (fluence and voltage). DBD plasma treatment effectively decreased the water contact angle of both types of polymer. However, while the lowest value of water contact angle was reached within a few seconds for PA6, it took more than 5 minutes for PTFE.

Keywords: wettability, surface, plasma, DBD, N PIII, polymer

1 INTRODUCTION

Wettability is one of the most important characteristics of solid surfaces. Polymers usually have hydrophobic surface even though there could be a great difference in their surface energy. In many applications, however, hydrophilic surface is required to attain adequate adhesion to other material types or to graft the surface with various chemical agents for the adhesion and proliferation of living cells. In contrast, in certain applications super hydrophobic surface is required. By now several methods have been developed for polymer modification, such as chemical vapor deposition, soft-lithographic imprinting, sol–gel method, etc. to modify the wettability by changing physical and chemical properties of surface. However, plasma treatment is becoming the primary method in changing the surface wettability of polymers [1]. Since plasmas contain different active species such as ions, radicals, and electrons its ability to change the wettability of a surface is promising because it has etching and activation effects [2]. Among low pressure plasma techniques plasma immersion ion implantation has been extensively studied and successfully applied for surface modification of various polymers [3-5]. Recently, atmospheric-pressure plasma has been of rising interest from viewpoints of both academic research and industrial applications, and is widely used for surface modification of polymeric materials instead of low-pressure plasma, because it does not need vacuum system as it is operated under atmospheric pressure. In addition atmospheric pressure plasma is characterized by high concentration of activated species generated by plasma, short mean-free path of electrons and high concentration of working gases. As a result, three-body collisions of activated species occur more easily in atmospheric-pressure plasma than in low-pressure plasma. In this study we compared the effect of a low pressure and an atmospheric cold plasma treatment for the wettability of Poly(tetrafluoroethylene) (PTFE) and Polyamide 6 (PA6). These two polymers greatly differ in their chemical composition and as a consequence in their surface properties, too.

2 EXPERIMENTAL

2.1 Material applied and sample preparation

Commercial pristine grade PTFE and extruded PA6 manufactured by GAPI Group and Ensinger GmbH, respectively, was used. Disc-shaped samples with a diameter of 10 mm and thickness of 2 mm were prepared. The samples were polished with wet SiC papers (grit numbers P1200 and P4000) and with wet felt sheet. Subsequently, they were rinsed in distilled water and in 96% ethanol then dried in pure nitrogen flow.

2.2 PIII-treatment

The samples were treated in a single run by N PIII. The base pressure in the stainless steel chamber was 4×10⁻⁸ Pa. A 27.13MHz RF plasma generator was applied (Dressler, Germany). The basic parameters were as follows: high purity (99.995%) N₂ (Messer Ltd.), flow rate = 25 cm³ min⁻¹ (STP), pressure = about 4×10⁻¹ Pa, RF power = 150 W. The PIII-treatment of the samples was performed by a high voltage pulsar (ANSTO, Australia). Accelerating voltages (U) between 15 and 30 kV, particle fluences (F) between 1×10¹³ and 3×10¹⁷ cm⁻² and fluence rates (FR) between 3×10¹³ and 7×10¹⁵ cm⁻² s⁻¹ were varied. Pulse duration was 5 µs, the pulse frequency was varied between 42 and 140 Hz to adjust the desired fluence rate.

2.3 Dielectric barrier discharge

The atmospheric pressure ambient air plasma was generated by DCSBD plasma source. The principle of DCSBD plasma is based on a coplanar DBD where comb-shape electrodes are embedded in a dielectric. The diffuse plasma is generated in thin 0.3 mm thick flat layer on alumina ceramic which designates the DCSBD to be used especially for treatment of flat surfaces. The DCSBD electrode system was powered by AC HV source of frequency approx. 14 kHz and voltage approx. 20 kV peak-to-peak and the total power in plasma during the experiments was 400 W. The area of generated plasma of DCSBD is 170 cm², thus the surface energy
density and volume energy density at power of 400 W are approximately 2 W cm\(^2\) and 80 W cm\(^3\), respectively. The DCSBD plasma is described in detail [6]. The plasma treatment was performed in dynamic treatment mode and the distance between the treated polymer surface and DCSBD ceramic was 0.3 mm.

2.4 Contact angle measurements

Contact angle measurements were done by the static sessile drop method at 23 °C, with double distilled water and diiodomethane (Sigma–Aldrich, Reagent Plus 99% grade), applying the SEE System apparatus (Advex Instruments, Czech Republic). A Hamilton syringe was used to inject 2 µl droplets. Each result of contact angle is an average of 5 measurements, performed always on previously non-wetted parts of the samples.

3 RESULTS AND DISCUSSION

3.1 Wettability

Table 1 collects the corresponding values of contact angles and the calculated values of the total surface free energy (\(\gamma_{\text{total}}\)) and its polar (\(\gamma_{\text{polar}}\)) and dispersive (\(\gamma_{\text{disp}}\)) components. Even though there is a considerable difference in the water contact angle of the two pristine polymers, both of them are considered hydrophobic. It can be seen that after N PIII treatment, the contact angles significantly decreased for PA6, whilst the total surface energy, as well as its polar and dispersive components increased. In particular, the polar component tripled and the dispersive component increased by about 10%. The decrease of water contact angle is in line with the literature and is reasoned by the formation new chemical bonds on the surface layer. The increase of wettability can be attributed essentially to the formation of N-containing new polar functionalities [7], considering that the surface concentration of oxygen even decreased slightly upon treatment.

Upon N PIII treatment of PTFE experimental parameters such as voltage and fluence had considerable effect on the water contact angle. Fig. 1 demonstrates its evolution versus fluence and voltage (the U axis is reversed for clarity of presentation). It is remarkable that at the lowest voltage (15 kV) and highest fluence (3\(\times\)10\(^{13}\) cm\(^{-2}\)) the water contact angle reaches its highest value (122°), being substantially higher than that of the untreated sample. By contrast, at the highest voltage (30 kV) and lowest fluence (1\(\times\)10\(^{12}\) cm\(^{-2}\)) \(\Theta_w\) reaches its smallest value (77°), which is much smaller than the corresponding value of the untreated sample. The object of PTFE plasma treatment, however, is not invariably to transform its surface to hydrophilic but also to achieve superhydrophobic surface properties [8-9]. In general, the wettability of a surface can be changed by altering the surface chemical functionalities and/or the surface roughness [10-11]. Accordingly, the dependence observed in Fig. 1 can be explained by the competition of two factors: increase of roughness and change in surface chemical composition. The chemical change and the physical topological change in the PTFE surface induced by PIII have the opposite contribution to the wettability. PTFE is basically hydrophobic material in nature because of the –CF\(_2\) – repeat element. The increase of wettability can be attributed essentially to a defluorination effect of the plasma along with the formation of various oxygen and nitrogen containing polar groups [12]. High fluence, however, results in greater roughness and water contact angle as a consequence.

![Fig. 1. Water contact angle of PTFE after N PIII treatment versus fluence and voltage](image)

Fig. 2 shows the changes of water contact angles upon atmospheric air DBD plasma treatment. The treatment decreased the contact angle for both polymers but the rate of decrease was different. The water contact angle dropped almost immediately after treatment for PA6 and longer treatment time resulted in only minor decrease. In contrast, PTFE needed a more prolonged treatment time up to 5 min to reach a steady value for the water contact angle. There is another huge difference in the attained wettability. While DBD treatment of PA6 resulted in a complete hydrophilic behavior and significantly lower contact angle as compared to N PIII treatment, the lowest value of water contact angle for PTFE (after 10 min) remained much higher (65°) that still cannot really be considered as hydrophilic. The atmospheric air DBD contributed to hydrophilic modification but was not effective to achieve complete wettability. This is in accordance with general findings that PTFE is very difficult to transform hydrophilic by nitrogen or air plasmas [13]. During DBD treatment the basic processes that led to lower water contact angle is similar to low pressure plasmas: CF\(_2\) components are diminished in part and C-H, C-O, C-N, C=O and CF groups are formed on the modified PTFE surface [14]. It is noteworthy, however, that longer DBD treatment resulted in a significantly greater drop in water contact.
angle than N PIII. This contradicts to Norhiro findings [13] that atmospheric plasma treatment was less effective in defluorination comparing with low pressure plasmas, although treatment time was not clearly defined.

**Table 1.** Contact angle, surface energy and its components for untreated, NPIII treated and DBD treated PTFE and PA6 polymers

<table>
<thead>
<tr>
<th></th>
<th>( \Theta_w ) (deg)</th>
<th>( \Theta_{DBD} ) (deg)</th>
<th>( \gamma_p ) (mJ m(^{-2}))</th>
<th>( \gamma_d ) (mJ m(^{-2}))</th>
<th>( \gamma_{tot} ) (mJ m(^{-2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTFE, untreated</td>
<td>108±1.5</td>
<td>73±3.2</td>
<td>0.2</td>
<td>21.2</td>
<td>21.5</td>
</tr>
<tr>
<td>PA6, untreated</td>
<td>70±7.2</td>
<td>32±2.1</td>
<td>6.3</td>
<td>43.6</td>
<td>50.0</td>
</tr>
<tr>
<td>PA6, ( \text{N}_2 )</td>
<td>36</td>
<td>24</td>
<td>23</td>
<td>47</td>
<td>70</td>
</tr>
<tr>
<td>PA6, DBD</td>
<td>21±0.5</td>
<td>26±1.5</td>
<td>29.1</td>
<td>45.8</td>
<td>74.9</td>
</tr>
<tr>
<td>PTFE, DBD</td>
<td>75±1</td>
<td>56±1</td>
<td>7.5</td>
<td>30.9</td>
<td>38.4</td>
</tr>
</tbody>
</table>

**Fig. 2.** Water contact angle of PTFE and PA6 after DBD treatment versus duration of treatment

**4 CONCLUSIONS**

We compared the effect of nitrogen plasma immersion ion implantation and dielectric barrier discharge surface treatment on the wettability of PTFE and PA6. Our findings were that N PIII is capable to make the surface either hydrophilic or superhydrophobic depending on the operating parameters (fluence and voltage. Atmospheric air DBD plasma is capable of modifying polymeric surfaces from hydrophobic to hydrophilic. However, while the lowest value of water contact angle was reached within a few seconds for PA6, it took more than 5 minutes for PTFE. The results suggest that atmospheric DBD is more effectively applied to transform the surface hydrophilic, while N PIII may be applied to form superhydrophobic surfaces, too.

**ACKNOWLEDGEMENT**

This research work is supported by OTKA K 113039.

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