Glass surface modification using diffusion coplanar surface barrier discharge (DCSBD)

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Abstract. The paper deals with the surface modification of the glass substrates using diffuse coplanar surface barrier discharge (DCSBD). The changes of surface properties after modification with plasma discharge were observed in time. During eight days, contact angles were measured by the method of sessile drop, using distilled water and diiodomethane as testing liquids. The surface free energy and its polar and dispersion component were calculated using Fowkes method. The morphology and \( \text{rms} \)-roughness of modified substrates were evaluated, using atomic force microscopy. The effect of modification by plasma discharge on the observed surface properties is the most noticeable immediately after modification. After 3 days, the observed surface properties of the modified surface are comparable to the unmodified surface.

1. Introduction
At present, the economic aspect is a very important factor in the choice of material and its properties. It is not always necessary and advantageous to create new materials. From an economic point of view, it is very useful when we can achieve the desired properties only by modifying an existing material.

Diffuse Coplanar Surface Barrier Discharge (DSCBD) is the latest plasma source that has tremendous potential in the surface treatment industry. DCSBD discharge has unique properties that distinguish it from other plasma sources for surface treatment. It generates a diffuse type of plasma at atmospheric pressure in the air, but also in many other working gases without adding noble gas. Very high plasma power densities of up to 100 W.cm\(^{-3}\) allow short plasma exposure times and hence high machining speeds [1].

Due to affordability and high industrial usability, modification of glass surface by DCSBD plasma discharge is a method with increasing interest and use in industry. Its great advantage is to maintain the original advantageous properties of the material and the possibility of major changes in the surface properties of the material. Significant changes in the surface of the material include an increase in the surface energy of the material and thus an increase in wettability. This change in surface properties is important, for example, when applying additional coatings [2].

The contact angle (CA) is one of the few solid-liquid-gas interface properties that can be measured directly. It is the angle that the tangent line to the surface of the drop, passing through the drop point and interface. Particularly important parameter in this method is the high sensitivity to the chemical structure of the top layer of molecules and is a relatively simple, inexpensive and widely used technique for characterizing different types of surfaces as a tool to calculate the surface energy of these surfaces [3, 4].
Atomic force microscopy (AFM) is a complex instrument used to investigate the surface at the micro- and nanometer scale [5, 6]. The pictorial representations of the surfaces can be similar to those seen from scanning electron microscope (SEM) measurements, but AFM provides much more information in the z-direction than SEM [7].

To our knowledge, there is no paper about effectiveness of glass surface modification using DCSBD. The aim of this paper is to determine the effectiveness of glass surface modification by DCSBD on the basis of monitoring changes in surface properties – hydrophobicity, surface free energy, rms-roughness.

2. Experiment

2.1. Preparation of samples
Microscope slides with dimensions 76 × 26 mm and thickness 1–1.2 mm were used for experiments. The samples were washed with water, detergent, rinsed with distilled water and isopropyl alcohol. The cleaned slides were dried at 100 °C for 10 minutes and placed in a container in which they were protected from light and air humidity.

2.2. Plasma treatment
The cleaned slides were placed to the KPR 200 plasma reactor electrodes and treated after 60 seconds at 375 W (figure 1). The distance between the electrode and the sample was 0.16 mm. We carefully put the treated slides into a container that was protected from light and air humidity.

2.3. Measurement of contact angles
Contact angles (CA) were measured at 0, 1, 2, 3, 4, 7 and 8 days after surface modification of the DCSBD by plasma discharge. The contact angle values of distilled water and diiodomethane of the modified surfaces were determined by the sessile drop method. 10 drops of 10 µl test liquid were placed on the modified surface to be examined by means of a micropipette so that they were evenly distributed over the surface. The contact angles of distilled water and diiodomethane were calculated from the scanned drop profiles. The results were statistically processed [8].

2.4. Determination of surface free energy
From the calculated contact angles of distilled water and diiodomethane, the surface free energy ($\gamma_s$) values of the modified surfaces and their polar ($\gamma_s^p$) and dispersive ($\gamma_s^d$) components were calculated using the Fowkes method [9]. First, the contact angle $\theta$ for the solid surface was determined using a nonpolar liquid. Then the value of $\gamma_s^d$ was calculated from the equation (1):

$$\gamma_s^d = 0.25\gamma_l(1 + \cos\theta)^2$$

where $\gamma_l$ is the surface energy for the non-polar liquid to which $\gamma_l = \gamma_l^d$ is valid. The value of the contact angle $\theta_p$ determined for the polar liquid where $\gamma_l = \gamma_l^d + \gamma_l^p$ and the calculated value of $\gamma_s^d$ was used to calculate the value of $\gamma_s^p$ according to equation (2):
\[ \gamma_s^P = \left\{ 0.5\gamma_l \left( 1 + \cos \theta_p \right) - \left( \gamma_s^d - \gamma_l^d \right)^{0.5} \right\}^2 / \gamma_l^P \]  

(2)

Diiodomethane was chosen as a non-polar liquid \( (\gamma_l = \gamma_l^d = 50.8 \text{ mJ m}^{-2}) \) and distilled water as the polar liquid \( (\gamma_s^d = 21.8 \text{ mJ m}^{-2}, \gamma_l^P = 51.0 \text{ mJ m}^{-2}) \).

2.5 Measurement on AFM

Atomic force microscopy (AFM) images were measured by NT-206 (Micro test Machines Belarus) device with probe head operated in contact regime. Si$_3$N$_4$ tip (Micro Masch NSC 11/AIBS) with the toughness \( k = 3 \text{ N m}^{-1} \) was used. Dimension of analysed area were \( 10 \times 10 \mu\text{m} \). The surface topography was measured under room temperature and ambient atmosphere. AFM images were analysed using Surface Xplorer software. AFM was used as method for observing the surface quality.

During topography evaluation, using AFM method, height irregularity values at certain points of the surface were determined. A set of height values was obtained, on the basis of adjustment where the obtained height values were based on the plane passing through the three lowest values for the given image and it lead to the measurement output. A similar adjustment was also used in the fast scan direction where the obtained height values were related to the line assigned to the two lowest values for given scan. With these adjustments, the most relevant surface image to reality is obtained. From the obtained set of height values \( (z_{ij}) \), the values of the mean square deviation of the measured values \( z_{ij} \) around - so-called \( \text{rms} \) - roughness of surface were calculated using the following equation \([10]\):

\[ \text{rms} = \frac{1}{n \times m} \sum_{i=1}^{n} \sum_{j=1}^{m} (z_{ij} - \bar{z})^2 \]  

(3)

where \( n \) is the number of rows and \( m \) is the number of columns corresponding to the AFM raster image, and \( z_{ij} \) is the height for point \( ij \) and \( \bar{z} \) is the average of measured height values of \( z_{ij} \). Parameters of \( \text{rms} \) were used to quantify the surface roughness.

3. Results and discussion

3.1. Contact angle and surface free energy

Figure 2 and 3 show the dependence of the contact angle (CA) of distilled water and diiodomethane on the time of surface modification by diffuse coplanar surface barrier discharge (DCSBD).

\[ \text{Figure 2. Average values of the contact angle (CA) of distilled water (--- unmodified surface).} \]

\[ \text{Figure 3. Average values of the diiodomethane contact angle (CA) (--- unmodified surface).} \]

Figure 2 shows that the average values of the contact angle of distilled water gradually increased and approached the value of the unmodified surface indicated by the broken line in the figure and this result refers to the 8th day from the surface modification. The contact angle of distilled water was changed by \( 23^\circ \) over 8 days. A similar trend can be seen in figure 3, where the contact angle of diiodomethane with
time of surface modification by plasma discharge is shown. The contact angle values of diiodomethane were changed by 12° over 8 days.

The graphical dependence (figure 4) of the calculated surface free energy versus the time of surface modification by diffuse coplanar surface barrier discharge (DCSBD) shows a gradual decrease in the surface free energy value. During the day of surface modification, surface free energy value was highest and gradually decreased over time. After 8 days, its value was close to the surface free energy of the surface without modification. Based on this, we can conclude that surface modification is most effective in the shortest possible time after treatment, and its effects gradually disappear. Relating to polar component is similar to the trend for surface free energy dependence on time, including all samples (figure 5). During the day of surface modification, the polar component had the highest value. Over the time, the given value dropped to the same value which was observed for the sample without surface modification. The values of the dispersion component of surface free energy (figure 6) showed similar behaviour in comparison with the polar component of the surface free energy.

![Figure 4. Average values of surface free energy (γ_s) (-- unmodified surface).](image1)

![Figure 5. Average values of the polar component of surface free energy (γ_s^p) (-- unmodified surface).](image2)

![Figure 6. Average values of the dispersion component of surface free energy (γ_s^d) (-- unmodified surface).](image3)

3.2. AFM

Figure 7 shows 2D AFM images of the surface of glass samples from the time of surface modification by DCSBD.

The surface of the plasma-untreated glass has scratches that disappear after the modification by DCSBD of the plasma discharge and the bumps are uniformly distributed on the surface. The uniform distribution of the bumps is observed even during the 2nd day after the modification, during the 3rd day, there is a partial disappearance of the bumps further days after the plasma was applied to the glass surface, the bumps on the glass surface gradually disappeared.
unmodified surface
during the day of modification
the 1st day after modification
during the 2nd day after modification
the 3rd day after modification
during the 4th day after modification
the 7th day after modification
during the 8th day after modification

**Figure 7.** 2D AFM images of glass sample surface based on diffusion coplanar surface barrier discharge (DCSBD) modification.

From the 2D AFM images we can see that the surface morphology after the plasma modification is almost the same for 3 day after the treatment and subsequently, its morphology is changed and it is partially similar to the untreated or unmodified glass surface.

**Table 1.** Mean *rms*-roughness values after the DCSBD modification.

| time (day) | *rms*-roughness (nm) |
|------------|----------------------|
| unmodified surface | 8.65 ± 0.27 |
| 0 | 5.00 ± 0.36 |
| 1 | 3.80 ± 0.25 |
| 2 | 5.11 ± 0.69 |
| 3 | 6.07 ± 1.24 |
| 4 | 7.62 ± 0.78 |
| 7 | 9.99 ± 1.52 |
| 8 | 7.33 ± 1.32 |
From the results of the $rms$-roughness of the plasma-treated glass surfaces (table 1), it can be seen that the application of plasma to the surface of the microscopic glass reduced the $rms$-roughness values, i.e., smoothed the glass surface. This trend is observed up to 3 days after plasma treatment. Then, the roughness values approach and are higher than the $rms$-roughness values of the untreated glass.

4. Conclusion
The material surface was modified for 60 seconds at a plasma reactor power of 375 watts. By processing of the measured and calculated values, we found out that the plasma surface modification effect is greatest immediately after irradiation and decreases with time. On average, it takes about eight or more days for the modification to disappear completely and the surface free energy and its given polar and dispersive component reach the surface value comparable to values without modification. In relation to the AFM images, the morphology of the glass surface after plasma application is similar for 3 days after application and then it changes. A similar trend is observed for $rms$-roughness.

Resulting from the given findings, we can conclude that the recommended way is to perform any further treatment of the plasma-treated glass as soon as possible after irradiation or up to 3 days, because after this time there are significant changes in properties – hydrophobicity, surface free energy, $rms$-roughness.

5. References
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