PLASMA POLYMERIZATION OF ACRYLIC ACID AT MEDIUM PRESSURE

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Abstract

Plasma polymerization of acrylic acid has become an interesting research subject, since these coatings are expected to be beneficial for biomedical applications due to their high surface density of carboxylic acid functions. However, the application of these deposits is counteracted by their low stability in humid environments, which is a required characteristic for almost any biological application. The present work investigates whether it is possible to obtain stable deposits with a high retention of carboxylic acid functions by performing plasma polymerization with a dielectric barrier discharge operating at medium pressure. The chemical properties of the deposited films are studied using contact angle measurements and FTIR. Moreover, to determine whether the obtained deposits are soluble in water, the coatings are once again analyzed after rinsing in water. This paper will clearly show that stable COOH-rich surfaces can be obtained at high discharge power and close to the monomer inlet, which might open perspectives for future biomedical applications.

1. Introduction

Since a few decades, plasma polymerization of organic compounds to produce thin polymeric coatings has been an active area of research [1,2]. This great interest in plasma deposition can be ascribed to the unique properties of the obtained coatings: these films are generally amorphous, free from pinholes, highly cross-linked, highly resistant to heat and corrosion and very adhesive to a variety of substrates such as polymer, glass and metal surfaces [3-6]. Due to these excellent properties, plasma polymers are applicable in many technological fields as barrier coatings, protective coatings, selective permeation membranes, dielectric layers in microelectronics,… [7] Besides these well-known examples, state-of-the-art applications are continuously being developed, especially in the biomedical domain [8-10]. In the framework of these biomedical applications, plasma polymerization of acrylic acid has been extensively studied in order to obtain coatings with a high density of carboxylic acid (-COOH) groups [1,3,11-17]. Such COOH-dense surfaces can be employed for covalent immobilization of biomolecules and as cell adhesion promoters. Plasma-polymerized acrylic acid coatings are expected to be beneficial for these above mentioned applications, since they show a high retention of carboxylic acid groups, however, their application is hindered by their low stability in humid environments, which is a required characteristic for almost any biological application [13-15]. As a result, the stability of the plasma-polymerized acrylic acid coatings should be increased without loosing the high surface density of carboxylic acid groups. Different studies have shown that COOH-rich surfaces can be successfully obtained by plasma polymerization of acrylic acid [3,12,14,17], however, only few papers [1,11,13,15] deal with the stability of the deposited coatings. Moreover, it is low pressure technology that is nowadays the most widespread tool for acrylic acid plasma deposition [18]. However, the use of low pressure plasma...
polymerization techniques has important limitations for industrial applications. Some of the disadvantages include the requirement for expensive vacuum pumping systems, the restriction to the use of vacuum compatible materials, low deposition rates and the difficulty to develop continuous processing systems. Therefore, in recent years, a lot of effort has been put into the development of non-thermal plasma reactors working at (or near) atmospheric pressure [19-22]. In between vacuum and atmospheric pressure plasma technology lies a wide -almost unexplored- pressure range (so-called medium pressure) which might combine the advantages of both vacuum and atmospheric pressure technologies [23-25]. The present work tries to contribute to the understanding of plasma deposition processes at medium pressure by studying plasma polymerization of acrylic acid at 9.5 kPa (medium pressure). The polymerization process is performed using a dielectric barrier discharge (DBD), a discharge which has received a lot of attention due to the easy formation of a stable regime and due to its scalability. In this paper, plasma-polymerized acrylic acid coatings are deposited on polypropylene (PP) substrates using helium as carrier gas. The effect of discharge power and location in the plasma reactor on the retention of carboxylic acid groups will be studied in detail using contact angle measurements and Fourier transform infrared spectroscopy (FTIR). In contrast to most of the existing literature on plasma polymerization of acrylic acid, not only the chemical structure of the deposits will be studied, but also their stability in water, which is an important aspect when applying the obtained coatings for biomedical applications [15].

2. Experimental details

2.1. DBD set-up

The medium pressure dielectric barrier discharge plasma reactor was built in the lab and is schematically shown in Figure 1. The plasma reactor contains two circular parallel plate copper electrodes with a diameter of 55 mm, each covered by a glass dielectric of 2 mm thickness and an area of 70 mm x 80 mm. The distance between the two glass plates is kept constant during plasma deposition at 4 mm. The upper electrode is connected to a high frequency (50 kHz) AC power source, while the lower electrode is connected to earth through a resistor R (50 Ω) or a capacitor C (10 nF).

Before starting the thin film deposition, a polypropylene (PP) film (Goodfellow, UK, thickness 0.075 mm) with an area of 60 mm x 60 mm is placed on the lower glass plate. After introduction of the substrate sample into the plasma reactor, the discharge chamber is pumped down below 0.3 kPa using a rotary vane pump and afterwards filled with the discharge gas helium (Air Liquide, Alphagaz 1, purity 99.999%) until atmospheric pressure (101 kPa) is reached. This step is performed in order to reduce the amount of oxygen contamination in the plasma chamber. Once atmospheric pressure is obtained, the discharge chamber is pumped down to 9.5 kPa, while maintaining a helium gas flow between the electrodes. This helium gas flow is controlled using a Bronkhorst El-Flow® mass flow controller and is kept constant at 3 slm (standard liters per minute), while the operating pressure is kept constant at 9.5 kPa by the use of a valve placed in front of the rotary vane pump.
the plasma reactor and is believed to be more reliable and stable compared to the more commonly used bubbler systems [26]. During plasma deposition, the monomer concentration is kept constant at 0.1 g/h and the deposition time is maintained at 20 minutes. To study the influence of discharge power on the plasma polymerization processes, the plasma power (obtained from Lissajous figures) is varied between 0.6 and 5.0 W. As stated before, also the effect of the location of the substrate in the plasma reactor will be studied: for that purpose, the electrode area is subdivided into 4 regions, as shown in Figure 2, and every region will be examined in detail using contact angle and FTIR measurements. In order to study the water stability of the deposited plasma polymers, the samples are washed in 150 ml of distilled water during 5 minutes and are dried in atmospheric air at room temperature before surface characterization.

The contact angle values, shown in this work, are obtained using Laplace-Young curve fitting and are the average of 7 values measured over an extended area of the deposited plasma polymers.

2.3 Fourier-transform infrared spectroscopy (FTIR)

FTIR can be used to gather information on the chemical structure of the obtained plasma polymers. A commercial Bruker Vertex 70 spectrometer, purged with dry, CO$_2$ free air is used to collect infrared absorption spectra of coatings deposited on PP samples. The spectrometer is equipped with a single reflection ATR accessory (MIRacle™, Pike Technologies) using a germanium (Ge) crystal as internal reflection element. The FTIR spectra are recorded using a liquid nitrogen cooled MCT (mercury-cadmium-telluride) detector with a resolution of 4 cm$^{-1}$. The spectra shown in this paper are corrected for the wavelength dependence of the penetration depth and are the result of 32 scans.

3. Results & Discussion

3.1 Contact angle measurements

The surfaces of the plasma-polymers are first studied using contact angle measurements, since these measurements represent the easiest and quickest method to examining surface properties. Water contact angles on acrylic acid plasma-polymerized films can provide information on the hydrophilicity of the samples and consequently give an indication on the chemical composition of the plasma polymers. Tab. 1 shows the water contact angle values of the plasma polymers for different discharge powers and different locations in the plasma reactor, measured immediately after the deposition process. The presented contact angle values are the average of 7 independent measurements and the standard deviation on these average values is smaller than 0.9°. Tab. 1 clearly shows that the water contact angle of the plasma polymers varies both with discharge power and substrate location, resulting into contact angles ranging from highly hydrophilic (8.7°) to only moderate hydrophilic (43°). For similar regions, the water contact angle increases with increasing discharge power, suggesting that the hydrophilicity of the samples decreases with increasing power. These results could suggest that the retention of the (hydrophilic) carboxylic acid groups is lower at higher discharge powers, a statement which will be
further examined using FTIR measurements. Tab. 1 also shows that the hydrophilicity of the deposited films is not equal at different locations in the discharge area: as the distance from the monomer inlet increases (region 1 → 2 → 3 → 4), the deposited films tend to be less hydrophilic. This last mentioned result might suggest that the retention of carboxylic acid groups depends on the substrate location, however, further investigation is necessary to back-up this assertion.

Tab. 1. Water contact angles of the plasma-polymerized acrylic acid films for various discharge powers and different locations in the discharge chamber

<table>
<thead>
<tr>
<th>Power</th>
<th>Region 1</th>
<th>Region 2</th>
<th>Region 3</th>
<th>Region 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.6 W</td>
<td>8.7°</td>
<td>11.4°</td>
<td>13.1°</td>
<td>17.4°</td>
</tr>
<tr>
<td>1.3 W</td>
<td>15.1°</td>
<td>15.6°</td>
<td>21.9°</td>
<td>39.3°</td>
</tr>
<tr>
<td>2.2 W</td>
<td>16.2°</td>
<td>18.1°</td>
<td>24.5°</td>
<td>40.6°</td>
</tr>
<tr>
<td>3.0 W</td>
<td>18.4°</td>
<td>20.6°</td>
<td>27.5°</td>
<td>41.4°</td>
</tr>
<tr>
<td>4.3 W</td>
<td>19.4°</td>
<td>21.1°</td>
<td>39.9°</td>
<td>42.5°</td>
</tr>
<tr>
<td>5.0 W</td>
<td>20.3°</td>
<td>38.9°</td>
<td>41.3°</td>
<td>43.0°</td>
</tr>
</tbody>
</table>

3.2 FTIR results

As stated before, FTIR can be used to gather information on the chemical structure of the plasma-polymerized acrylic acid films. Fig. 3 represents the FTIR spectra of coatings deposited at low discharge power (0.6 W) for different regions in the discharge chamber. Fig. 3 clearly shows that the FTIR spectra of the deposited films show a very strong absorption band at 1710 cm\(^{-1}\) which can be assigned to C=O stretching vibrations of carboxylic acids. The FTIR spectra also contain a very broad absorption band in the region 3600-2400 cm\(^{-1}\), which can be attributed to OH stretching vibrations in carboxylic acids [27]. Superimposed on this broad peak, one can see a smaller peak in the wave number region 3000-2900 cm\(^{-1}\) due to C-H stretching vibrations [27]. At lower wave numbers, a broad peak between 1330 and 1130 cm\(^{-1}\) can be observed: this peak can be assigned to C-O stretching vibrations [27]. The FTIR spectra of the plasma-polymerized acrylic acid films also show two smaller absorption peaks at 1450 and 1410 cm\(^{-1}\), which are likely due to the combination of C-O stretching and OH deformation vibrations [27]. Based on these above mentioned absorption peaks, one can conclude that the deposited films contain a significant amount of carboxylic acid groups.

Fig. 4 shows the FTIR spectra of coatings deposited at high discharge power (5.0 W) for different distances from the monomer inlet. These deposited films show similar absorption peaks and consequently also contain a large amount of carboxylic acid groups. An indication of the amount of carboxylic acid groups present in the deposited thin films can be obtained by calculating the ratio of the area of the C=O stretching band at 1710 cm\(^{-1}\) to that of the C-H stretching bands in the region 3000-2900 cm\(^{-1}\) [28]. These calculated ratios are reported in Tab. 2 for non-washed and washed samples as a function of discharge power and distance to the monomer inlet. Tab. 2 clearly shows that for the unwashed samples, the C=O/C-H ratio decreases with increasing discharge power, suggesting that the retention of the monomer structure decreases by increasing input power. This phenomenon can be explained as follows: increasing the discharge power leads to a higher energy input per monomer molecule and consequently to a higher monomer
fragmentation and thus less carboxylic acid functions. Tab. 2 also shows that the C=O/C-H ratio decreases with increasing distance to the monomer inlet. Close to the gas inlet (region 1), the residence time of acrylic acid in the plasma phase is short leading to less monomer fragmentation and thus a large amount of carboxylic acid groups. In contrast, the residence time of the monomer increases far from the gas inlet leading to a more pronounced monomer fragmentation and less carboxylic acid functions on the surface of the deposited films.

Tab. 2. C=O/C-H ratio for non-washed and washed samples as a function of input power and distance to the monomer inlet

<table>
<thead>
<tr>
<th>Power (W)</th>
<th>0.6</th>
<th>1.3</th>
<th>2.2</th>
<th>3.0</th>
<th>4.3</th>
<th>5.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Region 1-unwashed</td>
<td>6.81</td>
<td>5.95</td>
<td>5.82</td>
<td>5.61</td>
<td>5.53</td>
<td>5.24</td>
</tr>
<tr>
<td>Region 2-unwashed</td>
<td>6.76</td>
<td>5.90</td>
<td>5.63</td>
<td>5.49</td>
<td>5.39</td>
<td>4.92</td>
</tr>
<tr>
<td>Region 3-unwashed</td>
<td>6.40</td>
<td>5.39</td>
<td>4.81</td>
<td>4.35</td>
<td>3.28</td>
<td>3.24</td>
</tr>
<tr>
<td>Region 4-unwashed</td>
<td>5.73</td>
<td>3.53</td>
<td>2.89</td>
<td>2.52</td>
<td>1.80</td>
<td>1.63</td>
</tr>
<tr>
<td>Region 1-washed</td>
<td>0.03</td>
<td>0.38</td>
<td>0.75</td>
<td>2.35</td>
<td>4.45</td>
<td>5.33</td>
</tr>
<tr>
<td>Region 2-washed</td>
<td>0.04</td>
<td>0.61</td>
<td>0.90</td>
<td>4.50</td>
<td>5.28</td>
<td>5.00</td>
</tr>
<tr>
<td>Region 3-washed</td>
<td>0.04</td>
<td>0.62</td>
<td>4.55</td>
<td>4.39</td>
<td>3.17</td>
<td>3.54</td>
</tr>
<tr>
<td>Region 4-washed</td>
<td>0.07</td>
<td>2.48</td>
<td>2.88</td>
<td>2.67</td>
<td>1.98</td>
<td>1.63</td>
</tr>
</tbody>
</table>

By comparing the C=O/C-H ratios before and after washing in water, it is possible to evaluate the stability of the differently prepared plasma-polymerized coatings in water. Tab. 2 shows that coatings prepared at low power inputs are easily washed off from the PP substrate, since the C=O/C-H ratio falls close to zero after washing. Based on this result, one can conclude that the stability of the deposited films at small input powers is rather low, since a large part of the deposited coating is dissolved. Tab. 2 also shows that the stability of the plasma-polymerized films can be increased by increasing the discharge power and at a power of 5.0 W, the plasma-polymerized thin films are found to be totally stable. Higher input powers lead to an increased monomer fragmentation: the greater monomer fragmentation results in an increase in reaction pathways available which manifests itself as a deposit containing a higher cross-linking degree [3]. As a result of this high cross-linking degree, the deposited thin films tend to be less soluble in water. Tab. 2 also shows that the stability of the plasma-polymerized acrylic acid films increases with increasing distance to the monomer inlet. As previously mentioned, monomer fragmentation is more pronounced far from the monomer inlet, leading to highly cross-linked and stable deposits at a large distance from the monomer inlet.

4. Conclusions

In this work, acrylic acid has been plasma-polymerized to form coatings with a high retention of carboxylic acid groups and a high stability in humid environments, two properties which are crucial when applying the plasma-polymerized coatings for biomedical applications. In order to obtain the desired chemical and physical properties of the deposited films, it is very important to optimize the deposition parameters. Hence, the influence of discharge power and location in the discharge reactor has been examined in this paper. Results have shown that low plasma power deposits (0.6 W) exhibit a high amount of carboxylic acid functions (high C=O/C-H ratio). However, the resultant coatings tend to be of low molecular weight with insufficient cross-linking to prevent dissolution in water. In contrast, high plasma power deposits (5.0 W) are characterized by a lower, but still significant amount of carboxylic acid functions (lower C=O/C-H ratio). Moreover, these deposits are stable in water due to a higher cross-linking degree. At optimal plasma deposition conditions, stable coatings with a high amount of carboxylic acid functions can be obtained and these coatings might offer interesting perspectives for the use in biomedical applications.

References


