Research Article

Beáta Hergelová*, Anna Zahoranová, Dušan Kováčik, Monika Stupavská, Mirko Černák

Polylactic acid surface activation by atmospheric pressure dielectric barrier discharge plasma

Abstract: Polylactic acid (PLA) is suitable for applications in packaging and biomedicine due to its biodegradability. To improve PLA surface adhesion a plasma-chemical treatment using nonthermal plasma generated in ambient air via diffuse coplanar surface barrier discharge (DCSBD) was used. The optimal treatment time and power were investigated. Interaction between active plasma species and the polymer surface, and the resulting surface changes were studied by contact angle measurement, surface energy determination, FTIR, and XPS. The most hydrophilic surface was obtained after only 3–4 s treatment. Treatment up to 10 s did not damage the polymer but longer treatments (30 and 60 s) caused partial degradation. The plasma broke C-C/C-H bonds and formed more C-O, O-C=O and C-O-C bonds. During storage surface oxygen decreased and a negligible amount of nitrogen was adsorbed. The oxygen-containing functional groups probably sank into the PLA volume after treatment.

Keywords: polylactic acid, surface treatment, nonthermal plasma, atmospheric pressure, dielectric barrier discharge

1 Introduction

Renewable, biodegradable polymeric (2S)-2-hydroxypropanoic acid or polylactic acid (PLA) is a promising material, mainly used in packaging and biomedical applications [1,2]. Under elevated humidity and temperature it degrades by hydrolysis [1,2] and waste PLA can decompose in the soil [3,4]. Used as a prosthetic fixative, sutures or for drug encapsulation it is first metabolized to lactic acid then to water and carbon dioxide, so no second surgery is needed for removal [5].

For some applications the PLA surface requires activation. Plasma treatment can avoid wet chemical treatment and consequent degradation. Nonthermal plasma treatment at low or medium pressure is usually used [6-9] at a gas temperature less than the 200°C PLA decomposition temperature.

Atmospheric pressure dielectric barrier discharge with coplanar electrode configuration (Diffuse Coplanar Surface Barrier Discharge – DCSBD) uses two ridge-shaped strip electrodes printed on an Al₂O₃ dielectric plate [10]. Discharge power can be up to 500 W and 10 kV at approximately 18 kHz. The many microdischarges on the ceramic plate form an 0.3–0.5 mm plasma layer with a power density of approximately 3 W cm⁻². The DCSBD plasma has been employed in polymer surface plasma treatment [10-12], removal of surface organic contaminants [13,14] and polymer film deposition [15,16].

2 Experimental Procedure

An 0.5 mm foil of NatureWorks® PLA Polymer 4042D was cut to 2 cm x 5.5 cm and cleaned in ethanol followed by 2 min ultrasonication in 20°C distilled water.

A DCSBD plasma generated at atmospheric pressure in ambient air was used [10]. The sample was held onto the movable cart by vacuum as shown in Fig. 1, and kept 0.3 mm above the DCSBD plate to be most effectively immersed in the plasma. Sample movement through the plasma gives a more homogeneous treatment. Treatment time varied from 2 s to 60 s. The input power

*Corresponding author: Beáta Hergelová: Department of Experimental Physics, Faculty of Mathematics, Physics and Informatics, Comenius University, 842 48 Bratislava, Slovak Republic; Fraunhofer Institute for Surface Engineering and Thin Films, Bienroder Weg 54 E, 38108 Braunschweig, Germany, E-mail: Beata.Hergelova@fmph.uniba.sk
Anna Zahoranová, Dušan Kováčik, Mirko Černák: Department of Experimental Physics, Faculty of Mathematics, Physics and Informatics, Comenius University, 842 48 Bratislava, Slovak Republic
Dušan Kováčik, Monika Stupavská, Mirko Černák: R&D Center for Low-Cost Plasma and Nanotechnology Surface Modifications, Faculty of Science, Masaryk University, 611 37 Brno, Czech Republic

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Actual discharge powers were determined from voltage, current, and waveform measurements (Table 1).

A DSA30 (Krüss GmbH, Hamburg, Germany) was used for contact angle measurements. The droplet volume was 2 μl. For each sample the water contact angle (WCA) was averaged from 20 droplets. Free surface energy was determined using the two-liquid Owens-Wendt (OW) method where the total surface energy $\gamma$ consists of disperse $\gamma_d$ and polar $\gamma_p$ components. Water and diiodomethane were used as test liquids (surface tension values according to Strom). The contact angle of each liquid was averaged from 12 drops.

Untreated and plasma-treated PLA surfaces were examined by ATR-FTIR using a Bruker Optics Vector 22 MIRacle™ spectrometer (PIKE Technologies) and diamond/ZnSe ATR crystals at 45° incidence. Twenty scans per sample were collected from 4000–600 cm$^{-1}$ at 4 cm$^{-1}$ resolution.

The very thin surface layer was examined by XPS measurements on an ESCALAB 250Xi (ThermoFisher Scientific) equipped with a 500 mm radius Roland circle monochromator and a microfocus Al anode X-ray source. Survey spectra were acquired at 50 eV and 1 eV resolution. High-resolution scans were acquired at 50 eV and 0.1 eV resolution. An electron flood gun compensated surface charges. Spectral calibration, processing and fitting routines were done using Avantage software.

Aging was studied after storage for 1, 3 and 7 days in ambient air at 20°C and approximately 40% relative humidity. Changes were investigated via WCA measurements, surface energy determination, ATR-FTIR and XPS.

### 3 Results and Discussion

Treatment at 400 W overheated the sample (especially for longer than 10 s), so treatment was done at 350 W. During first 10 s no visible changes were noted, but after 30 and 60 s treatment the sample was damaged and bent by the heat.

The WCA of cleaned untreated PLA was 70.4 ± 1.18°. Although the average WCA slightly decreased with increased power, the change was less than the error bars (Fig. 2a). Fig. 2b shows the dependence of WCA on treatment time; in the first part it decreases to a local minimum of 53.8 ± 0.85° at 3 s and to 53.8 ± 1.43° at 4 s then increases at longer time up to 10 s. The same effect has been observed in DCSBD treatment of PMMA [11] and PET [12], where the minimum contact angle was achieved at 2-3 s and then at longer time the WCA value increased and become saturated at some value. But at 30 s treatment time of PLA the WCA decreased again to global measured minimum 52.9 ± 1.22°.

Fig. 3a shows the changes in water contact angle after storage in air for 1, 3 and 7 days. A longer treatment time lessened the WCA increase during storage.

The disperse part of the surface energy $\gamma_d$ remained almost constant (41.5–42 mJ m$^{-2}$) and the polar component $\gamma_p$ increased from 6.94 ± 0.09 mJ m$^{-2}$ to 14.19 ± 0.24 mJ m$^{-2}$ after 3 s of treatment and to 14.19 ± 0.19 mJ m$^{-2}$ after 10 s (Fig. 3b). This increase of $\gamma_p$ signifies the formation of new surface polar functional groups. For samples treated for 10 s both components slightly increased after 1 day then decreased slightly after 7 days. Errors in $\gamma_d$ were ± 0.14 - 0.42 mJ m$^{-2}$ and $\gamma_p$ ± 0.09 - 0.24 mJ m$^{-2}$. For better comprehensibility these errors are not shown in Fig. 3b.
Treatment caused no major changes in the PLA surface ATR-FTIR spectra (Fig. 4). There are two sharp peaks. That at 1748 cm$^{-1}$ is assigned to C=O stretching in the –CO–O– group and the second peak at 1181 cm$^{-1}$ is assigned to –CH–O– stretching. A complex triplet at 1128, 1081 and 1044 cm$^{-1}$ corresponds to C–O stretching in –CO–O– groups. The small peaks at 2996 cm$^{-1}$ and 2945 cm$^{-1}$ could be assigned to the C–H stretching vibrations of –CH$_3$. After long treatment (30–60 s) or very high input power (400 W) a very small O–H absorbance from 3650 to 2500 cm$^{-1}$ (Fig. 4b) appeared due to chain depolymerization by reaction with atmospheric water. A peak at 1638 cm$^{-1}$ appeared with increased input power or prolonged treatment (Fig. 5b) which may be due to C=O stretching [17]. During the first half hour after treatment this peak increased slightly then remained at the same intensity but broadened and shifted to longer wavelength (1650 cm$^{-1}$) after 1, 3 and 7 days. We conclude that the C=O mainly formed post-treatment, when oxygen or carbon dioxide is bonded to surface radicals, or the formerly C–O–C bond splits forming C=O. The shift may also be caused by –NH formation (1660 cm$^{-1}$) [17].

Heating a PLA sample to 60°C for 30 min caused absolutely no changes in the ATR-FTIR spectrum, suggesting that the surface changes were not caused by heat.

ATR-FTIR measurements collect information from a depth of several μm and not just the uppermost dozens of nm affected by plasma treatment. The DCSBD plasma treatment did not change the bulk PLA properties.

XPS analysis examined the PLA surface binding states; surface atomic concentrations are summarized in Table 2. Survey spectra of untreated and 30 s plasma-treated samples confirm the presence of carbon, oxygen (and nitrogen for plasma treated samples) as shown in Fig. 5. The most significant result of treatment is the increased O/C ratio. After 5 s treatment the O/C ratio is approximately 4 times that of the untreated sample.
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For longer treatment times (10 and 30 s) the O/C ratios decreased but were still 2–3 times higher than the control. This may be due to degradation, when the chain is cut at the oxygen and cross-linked to a neighboring chain.

The high resolution C 1s peak decomposition is shown in Fig. 6. Table 2 gives the relative areas corresponding to different carbon-containing bonds. The untreated sample showed three components at 285.0 eV, 287.2 eV and 289.08 eV corresponding to C–C/C–H, C–O and O–C=O (Fig. 6a) [17]. Plasma treatment resulted in significant C–O and O–C=O increases, and a new C–O–C peak at 286.5 eV emerged (Fig. 6b).

Ambient air plasma contains reactive species. These can lead to radical formation, cross-linking and double bond formation [9] as well as new polar groups. We attribute the C–C/C–H relative decrease to formation of a C–O bond at the CH₃ side group. This may then transform to an O–C=O bond. It may also be converted to a C–O–C bond, causing chain cross-linking or rearrangement.

Figure 4: ATR-FTIR spectra of PLA samples.

Figure 5: PLA XPS survey spectra: untreated (lower) and treated 30 s (upper).

Figure 6: C1s peak decomposition: a) untreated sample; b) after 30 s treatment.

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XPS composition results are listed in Table 3. After the first day of storage, the O/C ratio rapidly decreased from 7.33 to 0.7, i.e. less than the 2.45 ratio for the untreated sample. The relative areas of C–C/C–H and O–C=O increased and those of C–O and C–O–C decreased.

The ATR-FTIR results suggest that the C–O–C bond splits to shorter chains forming C=O. The two polar ends may disappear from the surface, attracted into the polar bulk. Hence there are more C–C/C–H bonds on the surface. During storage a small amount of nitrogen was adsorbed.

### 4 Conclusions

Plasma treatment of PLA from 3 s up to 30 s caused significant surface change. Treatment up to 10 s did not destroy the surface and considerably increased the surface hydrophilicity. ATR-FTIR measurements showed a small increase in –OH absorbance for longer treatment and higher power due to chain decomposition. New oxygen-containing functional groups form causing the water contact angles to decrease. Hydroxyl-, carboxyl- or carbonyl- groups were created by reaction with the working gas (air).

During aging the water contact angle increased for treatment time up to 5 s and remained constant for times longer than 10 s. The free surface energy and its components did not change with aging. XPS showed significant changes in oxygen content during storage and atmospheric nitrogen adsorption.

Ten seconds of DCSBD plasma causes permanent PLA surface modification. Thus DCSBD, an atmospheric pressure, low-temperature, nonthermal plasma source, is suitable for PLA surface plasma treatment before further polymer processing.

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