Highly hydrophilic and stable polylactic acid surface achieved by argon plasma treatment

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Abstract. The effect of modifying additives such as low molecular weight polylactide (PLA) and benzyl alcohol (BA) on the degree of hydrophilicity of high molecular weight PLA before and after plasma treatment with low density and specific power per area was investigated. The lowest water contact angle (WCA) after modification was about 17°. A comparative evaluation of the formed functional groups amount, the hydrophilicity and stability of the plasma modification was carried out. WCA measurements of ageing of modified samples over time up to one year was carried out. It was found that plasma treated PLA films, obtained from tetrahydrofuran solution of high-molecular weight PLA and BA, demonstrated one of the highest ageing stability at high hydrophilicity. At the same time, the increase of the oxygen-containing functional groups amount on the modified PLA surface (about 40%, estimated by XPS) is close to the critical value in point of view of ensuring both high hydrophilicity and stability of the PLA surface after the modification.

1. Introduction

Poly(lactic acid) (PLA) based polymers have a high potential for orthopaedics and dentistry application as biocompatible coatings that improves osteointegration [1] and as the base material of bioresorbable implants [2]. Low hydrophilicity is one of the PLA disadvantages that reduces cell adhesion, growth and therefore osteointegration [3]. PLA surface can be hydrophilized by addition of oxygen-containing polar functional groups by plasma treatment. High dose of plasma exposure allows to obtain a large density of functional groups, however, leads to a significant degradation of the surface with a molecular weight decrease. Exceeding a maximum dose specific for each polymer significantly changes the molecular structure that leads to surface instability to rinsing with a polymer nonsolvent removing of measurable amounts of surface layer [4, 5]. Such processing is unacceptable from the point of view of aging stability and resistance to biological mediums.

Moreover it leads to unacceptable modification for cells cultivation especially in the case when the hydrophilicity that is acceptable for cell adhesion and spreading significantly and rapidly degrades in several hours or first days of cultivation [3]. An optimal ratio of hydrophilicity, stability and morphology has to be achieved for better cells fixation and grow on the PLA surface. These properties can be adjusted by optimization the film composition and plasma treatment parameters both at once.

This work is devoted to the study of influence of the polymer composition and plasma treatment parameters, such as power density and treatment time, on the hydrophilicity of the PLA surface that can improve cells fixation and growth [3].
2. Materials and methods
High molecular weight PLA (high-$M_n$ PLA, $M_n \sim 80$ kDa) was dissolved in tetrahydrofuran or dichloromethane (THF or DM). Concentration of PLA was 45 mg/ml. Benzyl alcohol as a low evaporation rate modifying additive, as well as low molecular weight PLA (low-$M_n$ PLA, $M_n \sim 5$ kDa) were added to the solution in selected experiments in the amount of 1.5-3 volume % relative to solvent volume and 15 weight % relative to the high-$M_n$ PLA weight respectively.

The PLA films were dip-coated (figure 1) at low drawing rate in nitrogen atmosphere on the cover glasses covered with 20 nm titanium layer.

![Illustration of the process of PLA film obtaining and modifying.](image)

Obtained samples were annealed at 60 °C in atmosphere after deposition. The amount of residual solvent as well as benzyl alcohol was reduced to the value that is not detectable by Raman spectroscopy. Relatively little change of the water contact angle (WCA) of the obtained PLA surface was the only evidence of residual solvents and modifying additive. The different solvents used are also slightly affect the WCA of PLA surface as was previously reported [6].

PLA films were modified by RF argon plasma treatment for 100 s at low plasma and power density (less than 50 mW/cm²). Samples were analysed by x-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM) before and after modification.

The obtained XPS spectra were fitted with Gauss-Lorentz curves by specialised software. To estimate the amount of functional groups the area under the peaks corresponding to R-C-O and R-C=O bonds (about 287 eV and 289 eV, respectively) was calculated and normalized to the C-C bonds peak (285 eV). The ratio of the values obtained before and after plasma treatment was used as estimation of the functional groups amount increase. To investigate the stability of the modification the WCAs of initial, plasma treated and aged (for several days) surfaces were measured. AFM and WCA measurements were carried out as described previously [6].

3. Results and discussion
According to the results of WCA measurement the most hydrophilic films were obtained by plasma treatment of dip-coated PLA samples containing a low-$M_n$ PLA (26°) or BA (17°) (figure 2a). The best of obtained values of WCA are significantly less than those described in the literature [3].
The high hydrophilicity obtained is due not only to the composition of the material, but also to the used plasma treatment parameters. Plasma treatment was carried out with low power density (2-5 times less compared to literature sources [7, 8]), that significantly increased modification stability over a long period (figure 2a, figure 3). However, the presence of both low-Mₘ PLA and BA reduced hydrophilicity measured immediately after modification and demonstrated lowest stability of modification over time (figure 2a, figure 3). The observed decrease of the modification stability when both components were used can be explained by a decrease in the average molecular weight of the main component of the film material, which is similar to the effect of plasma with high power density and treatment time reported in the literature [5, 8].

Additionally, we demonstrate that when we use a high-Mₘ PLA with a BA additive, WCA decreases after sequential rinsing with ethyl alcohol and water and film wettability degradation slows down (figure 2b). At the same time, in the case of low-Mₘ PLA and BA, the effect of additional degradation with rinsing is observed, which is consistent with the literature data [8]. It indicates that the low molecular weight component accelerates wettability degradation over time, therefore the formation of too short PLA molecules is unacceptable as a result of plasma treatment, which imposes restrictions on the plasma treatment parameters.

A similar effect of a low-Mₘ PLA or BA addition was observed for THF samples: WCA reduced to 37° and 38°, respectively, while samples that hadn't containing additives demonstrated significantly higher WCA - about of 45-50° after similar plasma treatment (figure 3). However, the presence of both modifying components at the same time leads to the relatively high WCAs similar to theirs absence. It indicates that the presence of both additives doesn't additionally increase functional groups amount on the surface (figure 3). It should be noted that addition of a low-Mₘ PLA doesn't change the chemical structure of polymer and only reduces the average molecular weight of the polymer molecules that cannot change the mechanisms of functional groups formation on the surface during plasma treatment. Functionalization by plasma treatment is always accompanied by etching.
Therefore, the effect observed in the experiment apparently due to increased contribution of the etching process in plasma modification. Taking into account that fact, etching process apparently start to play a significant role in case of the simultaneous presence of both modifying additives due to increase of etching rate of polymer with lower molecular weight together BA content. So the effect of plasma treatment was reduced (figure 2).

![Figure 3](image)

**Figure 3.** The degradation of WCA of the PLA films with different molecular weights and from various solvents over time after plasma treatment. The filled markers correspond to the experimental points of high-Mₘ PLA, empty markers - low-Mₘ PLA. The dashed line corresponds to WCA of the PLA without plasma treatment.

A similar effect of reducing the hydrophilicity of the surface is observed in another work [3]. Slepićka et al. used a different power plasma (3 W and 8 W), while the etching rate remained rather high. When plasma power decreased from 8 W to 3 W (approximately 2.67 times), the thickness of the etched material changed from 140 nm to 80 nm with a process time of 240 s, which corresponds to a change in the etching rate from 0.58 nm/s to 0.33 nm/s (decreasing only 1.75 times) [3]. A smaller change in the etching rate of the material compared to a change in plasma power indicates an increase the contribution of the etching process in plasma treatment process with a decrease in plasma power to 3 W. This leads to a greater hydrophilicity of the material with increasing plasma power due to the formation of a larger amount of functional groups per unit time. Therefore, probable reason of that effect in the case of using low-Mₘ PLA and BA simultaneously is also relative increase of etching rate with equal or lower efficiency of functional groups forming at surface by plasma treatment. According to the results of the measurements of the film thickness obtained by AFM before and after plasma treatment with increased treatment time to 420 seconds, the etching rate was about 0.07 nm/s. No more than 7 nm of PLA film was etched at 100 seconds of plasma treatment. Etching effect was
investigated also by AFM. All pores, initially closed with a thin layer of PLA and formed during film coating process with subsequent heat treatment, lost this layer and became open (figure 4).

![Figure 4 (a, b, c). AFM-images of PLA film surfaces obtained with THF and BA solution with low-Mₗ PLA additive before (a) and after plasma treatment (b) and also with THF and BA only in solution (c).](image)

At the same time, the number of pores per surface area unit significantly increases and their size significantly decreases when a low molecular weight polylactide in the composition of the solution was used. It is similar to BA usage as an additive to the solution [6], that can be seen by comparison of AFM images of high-Mₗ PLA in THF without BA (figure 1), containing both BA and low-Mₗ PLA, and high-Mₗ PLA containing BA only (figure 4). In addition, anomalously high hydrophobicity of the as deposited films was observed when both at once low-Mₗ PLA and BA were added (figure 2a). That in conjunction with the changed pore size and their amount per area on the surface, indicates the difference in mechanisms of solvents evaporation from film layer and their residual amount, which inevitably affects the achieved value of surface hydrophilicity and its stability over time.

To assess the effectiveness of the formation of functional groups in the surface layer by plasma treatment XPS was carried out. XPS data (figure 5) demonstrated an appreciable increase in the intensity of the peaks corresponded to the formation of functional groups, although several times lower than achieved in the literature [7].

![Figure 5. XPS spectra of C1s peaks of PLA film obtained with solution with low-Mₗ PLA before and after plasma treatment.](image)

The achieved increase of functional groups percent in the surface layer was up to 47 % (compared to 225% in literature [7]). At the same time, the achieved WCA stability over time under normal conditions is 0.34° per day for the high-Mₗ PLA with BA sample (figure 3), while it was at least 1.5°
per day in the analysed literature [7] (determined by the ratio of WCA change to the time when the WCA degradation rate reduce to less than 0.2° per day). Taking into account the obtained low WCA and its stability, concentration of functional groups on the surface that was achieved is close to a limit, at which the modification is still stable for a long time. Obtained results are extremely significant, since culturing cells on the surface or in vivo implantation are accompanied by the polymer surface exposure to elevated temperatures, grow medium or intercellular fluids, causing degradation of the surface and its hydrophilicity. High rate of degradation of modified surface may result in decrease of cells grow rate on the surface after a long period (about 5-7 days) [3], that is unsuitable for implant material. Demonstrated high stability of modification is a good prerequisite for suppression mentioned effect.

4. Conclusion
Addition of low-molecular weight PLA as well as BA in the composition of PLA films can significantly improve the hydrophilicity of the surface modified by plasma treatment. Additionally, the low molecular weight polylactide and BA reduce the diameter of pores that are forming in the polylactide film during deposition. Plasma-modified high-molecular PLA containing BA as an additive demonstrates sufficiently high hydrophilicity in conjunction with great stability over time and resistance to rinsing in ethyl alcohol and water. Achieved ageing and rinsing stability is extremely important for implants fabrication application, since the cell detachment due to significant degradation of the PLA surface and its hydrophilicity reduction during the first few days is undesirable and can nullify the benefits of surface modification. Comparison of the WCA stability over time with XPS data, as well as literature data, allows to conclude that the treatment with low plasma density and low power density per area that was used, provides sufficiently high hydrophilicity even without high density of formed functional groups in opposition to other works. The density of functional groups obtained is close to optimal to ensure both high hydrophilicity and stability over time and can be implemented to implants modification.

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