Wettability and aging of polylactide films as a function of AC-discharge plasma treatment conditions

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Abstract. Plasma treatment is among the most versatile and promising tools for modifying the properties of polymeric surfaces. It is mainly used to control the hydrophilic-hydrophobic balance of a surface and to optimize its adhesion properties, including material/cell interactions. From this point of view, a wide set of variable plasma processing conditions and their effect on surface wettability, as well as the tendency of plasma-treated surfaces to restore their initial characteristics after storage, require preliminary optimization of the treatment conditions. This work is aiming to study the effect of AC-discharge plasma treatment conditions (duration, power, frequency) on the wettability contact angle of poly(L,L-lactide) film and to evaluate the aging of this effect in time as a function of the plasma treatment parameters.

1. Introduction

Low-temperature plasma treatment is becoming one of the most popular tools for modifying the characteristics of polymer surfaces for a wide range of applications. A particularly interesting and intensively developing area of plasma industry is related to the treatment of polymeric materials tailored for biomedical application [1–3]. Among the number of advantages of plasma technologies, its flexibility in terms of treatment conditions, i.e. various discharge types, gases, pressure and duration of treatment, etc., is particularly attractive. From another point of view, this flexibility requires optimization of the treatment conditions to achieve the desired surface properties of a given material.

Materials based on synthetic polyester – polylactide – possess a number of favorable properties, but their surface hydrophobicity limits significantly their application, including those related to medicine [4, 5]. Various methods of polylactide-based material modification are used to optimize its bulk and surface characteristics, which could be controlled during the material fabrication process [6, 7], however, post-treatment is still the main approach. Among the large number of methods of surface modification, plasma treatment is particularly attractive due to the above-mentioned flexibility, ecological benefits and relative simplicity. Plasma-chemical modification of polylactide-based materials is widely studied using various discharge types and plasma treatment conditions [8, 9]. Besides some specially targeted applications, plasma treatment of polylactide materials is mainly

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accessed as a fast and easy way to increase their surface hydrophilicity. However, this effect is not permanent and has a tendency to age in time at different rates as a function of a variety of parameters [10–13].

This work was aimed to study the effect of the AC-discharge plasma treatment conditions (i.e. frequency, power, time) of poly(L,L-lactide) films on their surface wettability and its aging.

2. Materials and methods

Poly(L,L-lactide) (PLLA) films with a thickness of ~100 μm were prepared by casting a 5 wt % solution of commercially available PLLA (Sigma-Aldrich, Germany) with an average Mw of 160 kDa in CH₂Cl₂ on a glass Petri dish. The films were dried in a dust-free chamber at RT, and finally dried in vacuum. The film side generated on the solution/glass interface was used for further investigation.

The plasma treatment was realized using a CUTE-1MPR set-up (Femto Science Inc., Korea). The plasma chamber was evacuated to a pressure of 20 mTorr before introducing the working gas – synthetic air – at a flow rate of 20 sccm. The treatment conditions, i.e. duration (1 – 30 sec), power (10 – 100 W) and frequency (20 – 100 kHz), were varied and their effect on the contact angles of sessile drops of distilled water (mQ) was evaluated using an Acam-MSC01 device (Apex Instruments, India). The contact angles measurements were carried out at least in triplicate and presented as a mean value (±1°) for each experimental point.

The samples (PLLA film pieces with a size of 10×25 mm) were weighed before and immediately after the plasma treatment by a WXTS3DU (Mettler Toledo, Switzerland) microbalance. The difference in the weight of the treated and untreated film are presented as a mean ± standard deviation calculated from three experiments.

3. Results and discussion

3.1. Sample mass changes

The plasma treatment effect consists mainly in changes in the surface characteristics due to functionalization and etching of the surface layer. These two processes affect oppositely a sample’s weight. According to literature data, a mass loss (0.05 – 0.8 wt %) as a function of the plasma treatment conditions could be observed after a relatively long exposure time (several minutes) under a rather aggressive conditions [9, 10].

![Figure 1. Mass change of PLLA films as a function of AC (40 kHz) discharge plasma treatment conditions.](image-url)
The analysis of the sample mass change under the mild conditions of this study after several seconds of plasma treatment showed a slight mass loss (0.01 – 0.03 wt %) only for a treatment duration of 1 sec. As can be seen in figure 1, the prolonged plasma activation, especially at higher powers, led to an opposite effect, i.e. an increase of the sample mass. This effect could be caused by the formation of functional groups within the surface layer. According to the X-ray photoelectron spectroscopy data, the plasma treatment of PLLA films at 40 kHz, 50 W during 60 s led to the formation of nitrogen-contained groups (0.6 wt %) and an increase of oxygen-containing ones (from 33.0% at % to 33.2 at %). However, changes in the surface morphology were observed as well. Thus, atomic-force microscopy measurements showed an increase in the surface roughness from 0.26 nm (non-modified PLLA film) to 2.37 nm (40 kHz, 50 W, 60 sec). Apparently, for the short treatment time applied (1 – 30 s), the contribution of surface functionalization was the predominant process in terms of sample mass changes.

Interestingly, the study of the mass changes after plasma treatment at 50 W for 30 s as a function of the discharge frequency (20 – 100 kHz) showed that the treatment at 40 kHz led to the highest increase in the sample mass (0.03 ± 0.003 wt %) compared to effect at the other frequencies (~ 0.005 ± 0.001 wt %).

3.2. Effect of treatment conditions on the PLLA surface wettability and its aging

The measurement of the wettability contact angle of water carried out immediately after plasma treatment using frequency of 40 kHz showed that the plasma treatment increased the surface hydrophilicity even after only several seconds of treatment. The wettability contact angle of water drops changed from 78° (non-treated PLLA film) to 50° (figure 2). The main changes occurred within the first 1 – 10 s of treatment, while a prolonged treatment (up to 30 – 60 s) led to a minor modification of the surface hydrophilicity. Varying the power (from 10 – 100 W) affected the surface hydrophilization kinetic. The fastest contact angle decrease was observed at 50 W, while treatment of polylactide films at 10 W and 100 W required a longer time of treatment to achieve surface hydrophilization.

Interestingly, an AC-discharge provided a decrease of the contact angle to 50° only, while under the same conditions (working gas, pressure, treatment duration) a DC-discharge led to a full spreading of the drops [14].

The hydrophilization effect achieved by plasma treatment decreased with the increase of the storage time of the plasma-treated films under ambient conditions. As can be seen in figure 3, this aging occurred mainly within 24 hours of storage and reached a change of 25 % in the contact angle value. Storage of the PLLA film treated at 10 W for 1 sec led to a full restoration of the contact angle after one day. Raising the treatment time and power slowed down the aging of the plasma treatment effect. The films treated using a higher power were less sensitive to the plasma treatment duration in terms of ability to keep the hydrophilization effect. The aging of the plasma-treated samples is likely caused by a re-arrangement of the polar groups generated on the surface to the bulk phase of the polymer [15]. Increasing the treatment time and power could lead to a more intensive formation of these groups within the surface layer and a deeper functionalization of the sample surface, which, afterwards, slows down the aging process.

Thus, AC-discharge plasma treatment allows one to achieve a significant hydrophilization of PLLA films after several seconds of treatment, but this effect has a tendency to “age” at different rates depending on the treatment time and conditions.

Figure 2. Dependence of the wettability contact angle on the treatment time using AC (40 kHz)-discharge at various powers.
Figure 3. Dependence of the wettability contact angle on the storage time of films treated at 40 kHz at a power of 10 W (a) and 100 W (b).

4. Conclusions
AC-discharge plasma treatment of poly(L,L-lactide) films allows one to increase their surface hydrophilicity even after only several seconds of treatment. Increasing the plasma treatment time leads to a decrease of the contact angle of wettability by water, while varying the discharge power produces a more complex effect. The fastest contact angle decrease (from 78° to 50°) is observed at 50 W, while treatment of polylactide films at 10 W or 100 W requires a longer duration of treatment to achieve this value. This difference could be related to the different contribution of surface etching and functionalization, which are opposite processes taking place during plasma treatment. We monitored the superposition of these processes by measuring the samples’ mass change. The hydrophilization effect’s tendency of aging can be offset by increasing the treatment time and power.

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References
[1] Poncin-Epaillard F and Legeay G 2003 J. Biomater. Sci. Polym. Ed. 14 1005
[2] Petlina D G, Tverdokhlebov S I and Anissimov Y G 2017 J. Control. Release 266 57
[3] Yoshida S, Hagiwara K, Hasebe T and Hotta A 2013 Surf. Coat. Technol. 233 99
[4] Namboothiri K M, Nair N R and John R P 2010 Bioresour. Technol. 2010 101 8493
[5] Farah S, Anderson D G and Langer R 2016 Adv. Drug. Deliv. Rev. 107 367
[6] Demina T S, Akopova T A, Vladimirov L V, Zelenetskii A N, Markvicheva E A and Grandfils C 2016 Mater. Sci. Eng. C 59 333
[7] Demina T S, Sevrin C, Kapchiekue C, Akopova T A and Grandfils C 2019 Macromol Mater. Eng. doi.org/10.1002/mame.201900203
[8] Demina T S, Gilman A B and Zelenetskii A N 2017 High Energy Chem. 51 302
[9] Jordá-Vilaplana A, Fombuena V, García-García D, Samper M D and Sánchez-Nácher L 2014 Eur. Polym. J. 58 23
[10] Izdebska-Podsiadly J and Dorsam E 2017 Vacuum 145 278
[11] Moraczewski K, Stepczynska M, Malinowski R, Rytlewska P, Jagodzinski B and Zenkiewicz M 2016 Appl. Surf. Sci. 377 228
[12] Morent R, De Geyter N, Trentesaux M, Gengembre L, Dubruel P, Leys C and Payen E 2010 Plasma Chem. Plasma Process 30 525
[13] Vesel A and Mozetic M 2017 J. Phys. D: Appl. Phys. 50 293001
[14] Demina T, Zaytseva-Zotova D, Yablokov M, Gilman A, Akopova T, Markvicheva E and Zelenetskii A 2012 Surf. Coat. Technol. 207 508

[15] Nakamatsu J, Delgado-Aparicio L F, Da Silva R and Soberon F 1999 J. Adhes. Sci. Technol. 13 753