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Effect of plasma treatment on the surface properties of polylactic acid films

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ABSTRACT

Plasma treatment is one of the methods currently used to obtain polymeric materials with surface properties appropriate to the functionality for which they were designed. However, the effects achieved after surface modification are not always long lasting and involve chemical and physical changes in the outermost layer. In this context, the effects of both argon and oxygen plasma on polylactic acid (PLA) films deposited on titanium were studied to determine which physical and chemical processes occur at the surface, and their duration. Regarding physical surface changes, there were scarcely any differences between both plasmas: roughness was very similar after treatments, root mean square height (Sq) being 10 times higher than the control, without plasma. Water contact angle (WCA) showed that the surface became more hydrophilic after application of the plasma, although hydrophilization was longer lasting in the case of argon treatment.

With regard to chemical changes, it was observed that the argon plasma treatment caused greater fragmentation of the polymer chains, and increased crosslinking between them. ToF-SIMS analysis made it possible to propose mechanisms to explain the formation of the fragments observed.

1. Introduction

Polymer materials are widely used today with a multitude of applications: prostheses [1,2], medical devices [3,4], food packaging [5,6], textile industry [7,8], 3D printing [9,10], etc. In addition to bulk properties of a material, surface properties such as hydrophobicity, surface tension and roughness are decisive for the successful performance of any item manufactured from that material. This explains why science and technology today focus not only on the preparation of new materials, but also on the surface modification of existing ones. Modification of the surface layer of polymers is one of the ways to achieve the desired surface properties [11]. This outermost layer is the critical zone of the material, since the oligomers that predominate in it are weakly bonded to the macromolecules of the bulk [12]. This makes it easier to create new functional groups (usually polar groups) and/or to alter the surface topography.

Polylactic acid (PLA) is one of the polymers used for biomedical purposes. It is hydrophobic [13,14] (its water contact angle (WCA) ranges from 70° to 80°), and therefore its surface is prone to non-specific protein adsorption, which promotes bacterial adhesion [15]. It is important to modify these surface properties in order to improve their biocompatibility and antibacterial properties, because these play a fundamental role in the control of the biological processes that occur at the interface [16,17].

An existing method to modify the surface layer of polymers is the application of plasma [18–23]. Plasma is a confined ionized gas obtained from the dissociation of gas-forming plasma when an electric field is applied in the reactor. Plasma can be of high or low temperature and high or low pressure [17].

The effects of plasma occur only on the surface of the material, at the nano- and micrometric scale, without altering the properties of the bulk [24]. Moreover, it is a process that modifies the surface in a controlled, reproducible and homogeneous way, and so it can be used even in cases where the surface has an irregular geometry [25].

Generally, the effects of plasma are as follows [17]:

- Surface cleansing, removal of organic contaminants.
- Surface degradation (etching).
- Crosslinking of polymer chains.
- Modification of the functional groups present on the surface.

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The changes that occur depend on the gas used to generate the plasma, and give rise to different physical and chemical properties [26, 27]. In general, when reactive gases such as oxygen, fluorine or ammonia are applied, chemical changes occur; in the case of oxygen, for example, new peroxide, hydroperoxide, carboxyl or hydroxyl groups are formed at the surface which result in the immobilization of other compounds of interest [28]. When the plasma comes from an inert gas, such as helium or argon, crosslinking generally predominates [29]. In any case, the application of plasma involves the generation of numerous reactive species, such as ions, radicals, electrons, photons and other excited species [30], so other secondary reactions can be expected.

The aim of this work is to study the surface properties of PLA films when they are subjected to plasma treatments, both of a reactive gas (oxygen) and of an inert gas (argon), and to determine which chemical and physical changes are responsible for the modification in each case, and to establish the duration of the effects of the two treatments.

2. Materials and methods

2.1. Sample preparation

PLA particles (PURASORB®, PDL 04, Corbion, Amsterdam, The Netherlands) were dissolved in chloroform (20% w/v) using a rotator stirrer (JP Selecta, Abrera, Barcelona, Spain). Then, 150 μL of the solution was deposited on cp-Ti supports with a diameter of 12 mm and a thickness of 1 mm (Ticare, Mozo Grau S.A., Valladolid, Spain), and left to dry at room temperature for 1 h. Later, samples were dried in an oven for 48 h at 70 °C to completely remove any remaining solvent.

2.2. Low pressure plasma treatment

Plasma treatments (oxygen and argon) were carried out on Yocto III equipment (Diener Electronic GmbH, Ebhausen, Germany). Reactor parameters were as follows: power (0–24 W), frequency (100 kHz), treatment time (10 min) and gas pressure 0.5 bar. Samples (5 each time) were located at the middle of the chamber.

2.3. Fourier transform IR (FTIR) spectroscopy

FTIR spectra were recorded on a VERTEX 70 spectrophotometer (Bruker, Billerica, Massachusetts, USA), working in DRIFT mode. The spectral resolution was 0.4 cm^{-1} and the detector was DLaTGS.

2.4. Time of flight secondary ion mass spectrometry

Secondary ion mass spectrometry was performed using a ToF-SIMS[5] (ION-TOF, Muenster, Germany) instrument equipped with a Bi_3^+ primary ion source operated at 25 kV. Negative ion spectra were taken on two sample replicates for each group ($n = 2$). The total ion dose used to acquire each spectrum was $\sim 1 \times 10^{12}$ ions/cm^2 with an analyzed area of 50×50 μm^2. Depth profile was recorded with a sputtering gun of 0.25 kV of Cs^+ for an acquisition time of 900 s. A pulsed low energy electron flood gun was used for charge neutralization. Calibration of mass spectra in the negative mass mode was based on H^-, C^-, CH^-, O^-, OH^-, C_2^-, C_3^-, C_4^-, C_5^-, C_6^-, C_7^-. In order to analyse the changes provoked by plasma, after treatment the samples were immediately inserted in the vacuum pump of the TOF-SIMS device, and data recording was started about 1 h after the plasma treatment.

2.5. Contact angle measurements

WCA of the samples was measured with a Krüss goniometer (Krüss, Hamburg, Germany) by sessile drop method. Determination of contact angle was performed with Drop Shape Analyser image analysis software (Krüss GmbH). The contact angle values are the average of at least four drops on different points of three samples and reported with standard deviation. Contact angles were measured as a function of time, starting immediately after plasma treatment.

2.6. Topographic characterization

An atomic force microscope (Agilent AFM 5500, Agilent Technologies, California, CA, USA) was used to evaluate surface topography and to quantify roughness of the samples before and after plasma treatments. Measurements were carried out at room temperature, with rectangular reflective aluminium cantilevers with a nominal spring constant of 0.2 N m^{-1} and a specified tip radius of ~8 nm (ESPA-V2, Bruker, Billerica, Massachusetts, USA).

3. Results and discussion

3.1. Chemical changes induced by plasma

The surface of the thin PLA films was completely characterized before and after the application of the plasma treatments. FTIR spectroscopy confirmed the presence of the polymer on the support substrata, since the characteristic bands of its functional groups appeared, as shown in Fig. 1. The bands corresponding to C–H stretching are at 3001 and 2949 cm^{-1}. C=O stretching appears at 1788 cm^{-1}, while the bending band corresponding to the methyl group is located at 1466 cm^{-1}. At 1392 and 1286 cm^{-1} the bands for C–H deformation and bending appear. At 1231 cm^{-1} the bands of the asymmetric vibrations of C–O–C and $-CH_3$ are seen; the C–O stretching and the C–COO stretching bands appear at 1146 cm^{-1} and 876 cm^{-1}, respectively. Fig. 1 also shows the FTIR spectrum of the PLA sample immediately after the application of oxygen plasma. As it can be seen, the bands are the same, only with lower intensity.

However, argon plasma treatment does induce noticeable changes in the FTIR spectrum of PLA. Fig. 2 shows these spectra immediately following application of plasma, after 2 min and after 20 min. As can be seen, initially only the bands corresponding to the functional groups of the polymer appear, but after 2 min a band located at 2362 cm^{-1} is assigned to carbon monoxide and carbon dioxide. After 20 min, this band disappears, and the initial spectrum is recovered.

These results confirm that chemical changes occur on the surface of the polymer coating, especially in the case of argon plasma. As postulated by Inagaki et al. [31], the treatment of argon plasma causes the rupture of the C–C and C–H bonds of the polymer chain giving rise to carbon radicals. As these species are extremely unstable, they react with each other, causing crosslinking of the polymer chains. This is further enhanced by vacuum ultraviolet (VUV), and some authors suggest that this is the main reason for the polymeric crosslinking [32,33]. Also, these species react residually with air as soon as the samples are taken from the plasma chamber, oxidizing to C–OH, C=O and COOH. In any case, the predominant reactions when applying argon plasma are those of degradation, and not of surface modification. Generation of these radicals can be inferred from FTIR detection of the band corresponding to CO_2 when PLA samples are subjected to argon plasma treatment. CO_2, CO and other small molecules such as ethylene, are some of the degradation by-products of PLA [31,34]. Oxygen plasma, being a reactive species, reacts either with the active sites of the polymer chain or with the radicals generated during treatment, giving rise to other species containing oxygen atoms. For this reason, neither CO nor CO_2 are detected by FTIR, as the new species generated still maintain functional groups already found in PLA, such as carbonyl, carboxyl and hydroxyl groups.

To complete the chemical characterization of the PLA films after plasma application, a depth profile was carried out using ToF-SIMS to determine which functional groups are exposed on the surface and their distribution. Differences in distribution of the studied ions are observed in the depth profiles carried out for the different treatments in each sample. For the $C_4H_7O_2^-$ and $C_4H_7O^-$ ions (Fig. 3a and b), in the control

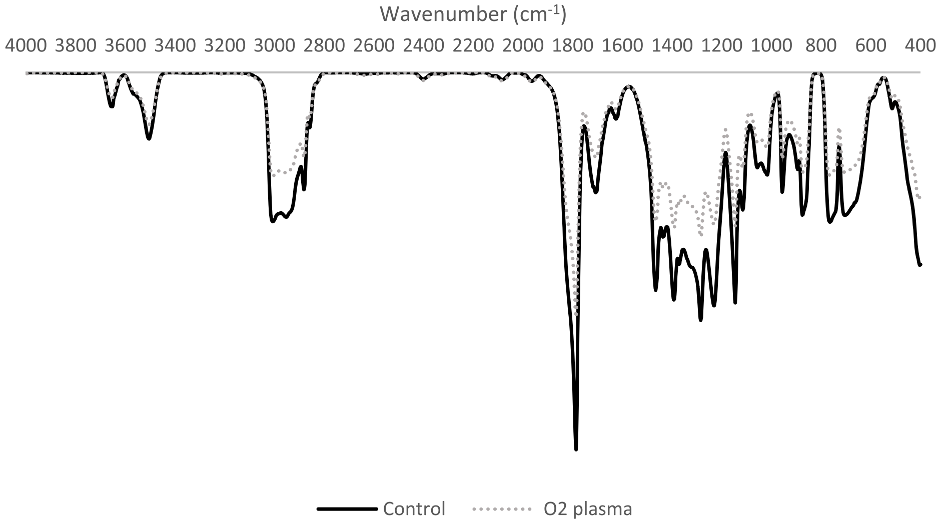


Fig. 1. FTIR spectra of PLA samples before (control) and after application of O_2 plasma.

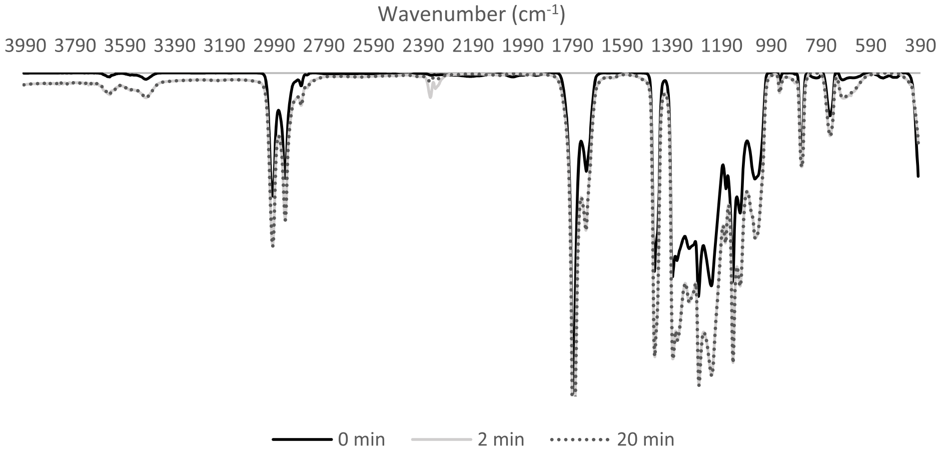


Fig. 2. FTIR spectra of PLA samples recorded immediately following Ar plasma treatment (0 min), after 2 min and after 20 min.

sample, it can be seen that these are in a high proportion in the outermost layer, and become zero in the first seconds of sputtering. In the samples treated with plasma; however, these ions are still present at up to 200 or 400 s of sputtering (argon and oxygen plasma, respectively) (Fig. 3a and b). Differences in the behaviour of the OH^- ions are highlighted for the control samples and with different treatments (Fig. 3c). In the control sample, an accumulation of OH^- ions can be seen in a layer that is situated immediately after the outermost layer composed of the $C_4H_7O_2^-$ and $C_4H_7O^-$ ions. However, this behaviour was not observed for any of the samples treated with plasma, in which the amount of OH^- ions increased as the $C_4H_7O_2^-$ and $C_4H_7O^-$ ions decreased. With regard to CO^- (Fig. 3d), both plasmas eliminate it completely from the surface, and then it increases as it goes deeper into the bulk.

Based on our results, it is clear that both types of plasma follow a similar pattern. Suganya et al. [24] observed in their research that when plasma is applied for a long time, the incorporation of polar groups becomes saturated and these can recombine with each other and degrade, so this may be the reason why the differences between the two gases are minimal.

However, when the mass spectra obtained by ToF-SIMS are analyzed, interesting conclusions can be drawn about both types of plasma. Firstly, the peak corresponding to the monomer ($m/z = 144$) is much more intense in the control than in the plasma-treated samples and, furthermore, fragmentation is greater in the argon plasma than in the oxygen plasma. The application of plasma induces the following radical fragmentations [31] (Fig. 4): in blue is fragment $C_3H_4O_2$, with $m/z = 72$. In green are the fragments C_2H_4 and CO_2, of m/z 28 and 44, respectively, and in red the fragments C_3H_4O and $C_3H_4O_3$, of m/z 56 and 88, respectively.

To determine whether the fragments obtained in the mass spectrum correspond to the action of the plasma or to the technique itself, the intensity of each peak after plasma was divided by the intensity of that peak obtained in the control (Fig. 5). This also permitted us to evaluate the action of each plasma. Some of the fragments obtained had already been proposed by Inagaki et al. [31], and either come from inside the polymer chain or they correspond to its extreme end: PLA ends in ester groups, so the fragments that end in the methoxy group ($-OCH_3$) are also obtained. Fragments of $m/z = 70$ and $m/z = 88$ were obtained by aldolic condensation of acetaldehyde (Scheme 1):

The other fragments are obtained when the reactions of Schemes 2 and 3 occur. In the first reaction of Scheme 2, the hydroxyl radical and that generated in PLA radical fragmentations are recombined to become an alcohol. This secondary alcohol can be dehydrated after protonation of the –OH group, resulting finally in alkene of $m/z = 72$. In the second reaction, the same occurs, although it is at the end of the polymer chain and it ends up as a methyl ester.

In Scheme 3, the reaction between a hydroxyl radical and one generated from the species in Scheme 2 is shown, and the corresponding enol obtained. From here, the reaction pathways are separated. On the one hand, the enol tautomerizes rapidly to generate the corresponding

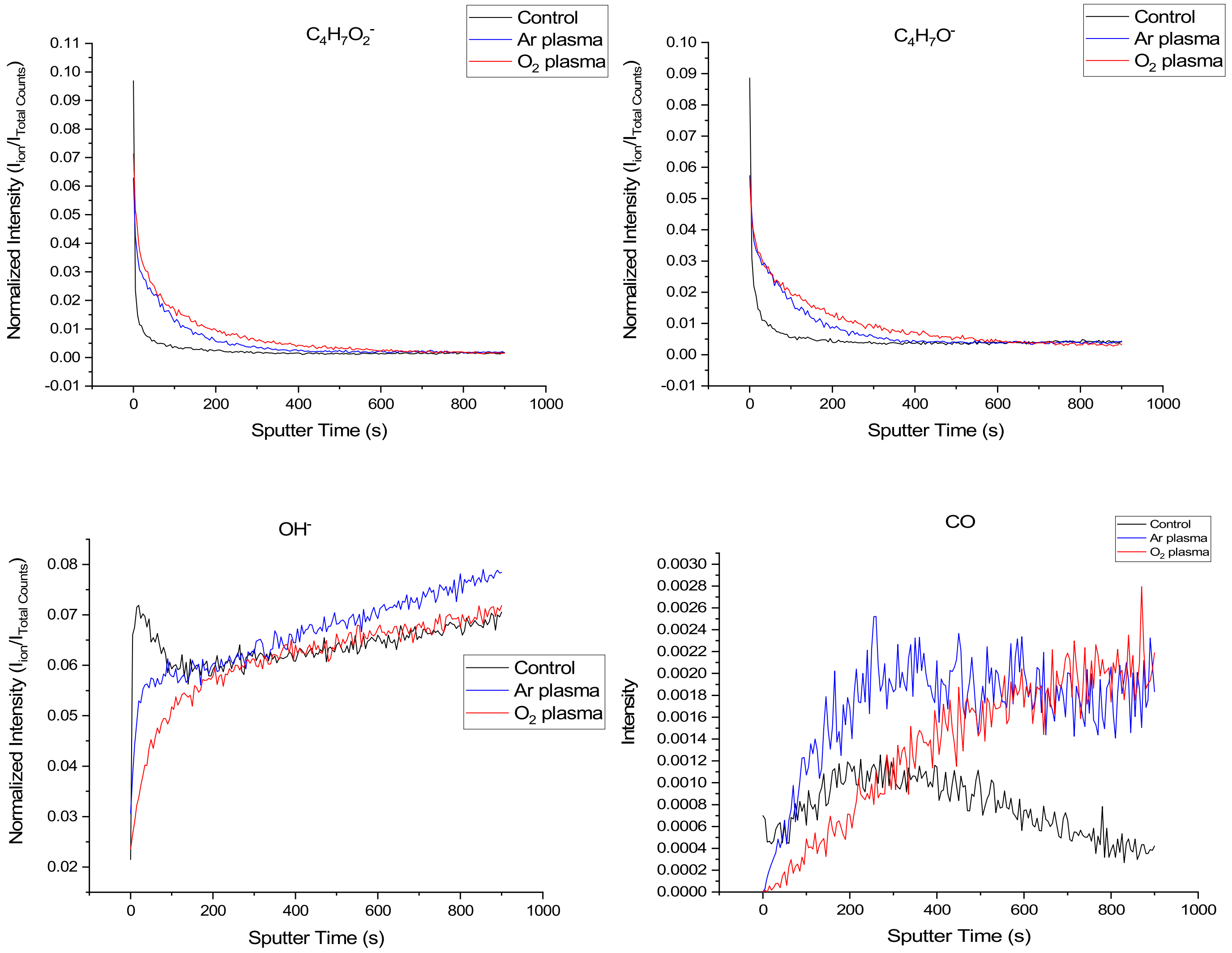


Fig. 3. ToF-SIMS depth profiles of Ti-PLA samples: control, after oxygen plasma and after argon plasma: a) $C_4H_7O_2^-$, b) $C_4H_7O^-$, c) OH^- and d) CO^-.

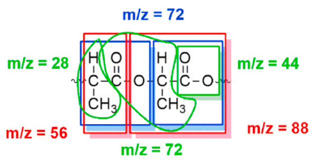


Fig. 4. Fragments of PLA that may be produced after plasma treatment.

ketone. As it maintains the ester group, it can undergo an acylic nucleophilic substitution reaction of a hydroxide ion to the ester carbonyl carbon, thus giving rise to the corresponding oxocarboxylic acid ($m/z = 88$). On the other hand, although the tautomerization equilibrium is very much displaced towards the formation of the keto form, it is possible that a small proportion of the enolic form reacts. Since the local pressure and temperature conditions generated by the plasma are extreme, the dehydration reaction of the enol could occur to obtain alkine ($m/z = 84$). This alkyl ester can fragment radically, generating a methoxy radical and the radical of $m/z = 53$. This latter radical can react with the radical anion CO_2 to generate the compound of $m/z = 97$.

This reaction path may not be the only one that leads to these species, but it can be reached by recombination of radicals with a much smaller m/z ratio. As can be seen, the formation of some of these fragments requires the participation of reactive species containing oxygen, mainly the OH ion or radical and the carbon dioxide radical anion. The fact that they appear in both plasmas indicates that the argon plasma probably contains some impurities such as traces of O_2, and it is of special significance the fact that some of these species are found in a higher proportion in that plasma compared with the oxygen plasma. These impurities are very unlikely to come from the plasma chamber itself, because before the samples are subjected to plasma treatment, the atmosphere is removed from the chamber by an argon cycle. Finally, it should be noted that some of these reactions would not take place under normal conditions of pressure and temperature or in the absence of catalysts, but the high-energy conditions generated by the plasma have been taken into account. Some of the compounds generated are not sufficiently stable, so they tend to recombine and/or continue evolving into compounds which are stable.

According to Fig. 5, fragments with m/z ratios of 87, 88, 97 and 102 are more abundant in oxygen plasma than in argon plasma. This corroborates the reaction path proposed in Scheme 3: the presence of the anion or the radical OH is necessary, as well as the radical anion carbon dioxide (the formation of this species is energetically expensive, but it can be formed in the conditions of the plasma), which are in a much higher proportion in the oxygen plasma. In addition, the lower abundance of the CO_2 radical anion in this plasma is justified by its reaction with the rest of the radical species formed. The species with a ratio of m/z 71, 72, 85 and 89 are more abundant in argon plasma, since, with the exception of $m/z = 89$, they are formed by the radical rupture of the polymer chain.

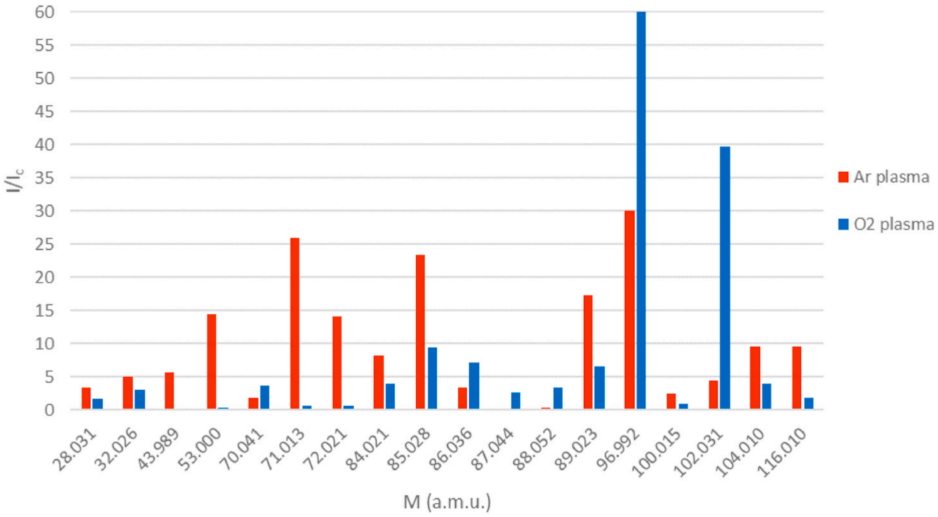
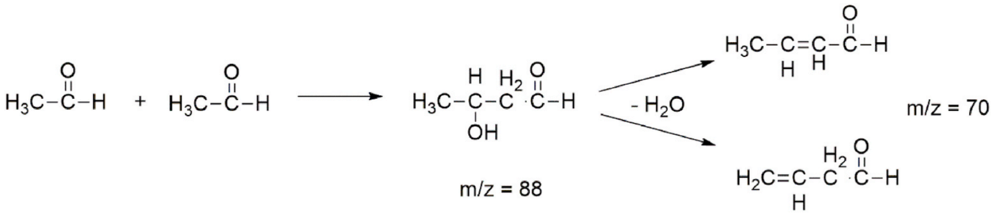
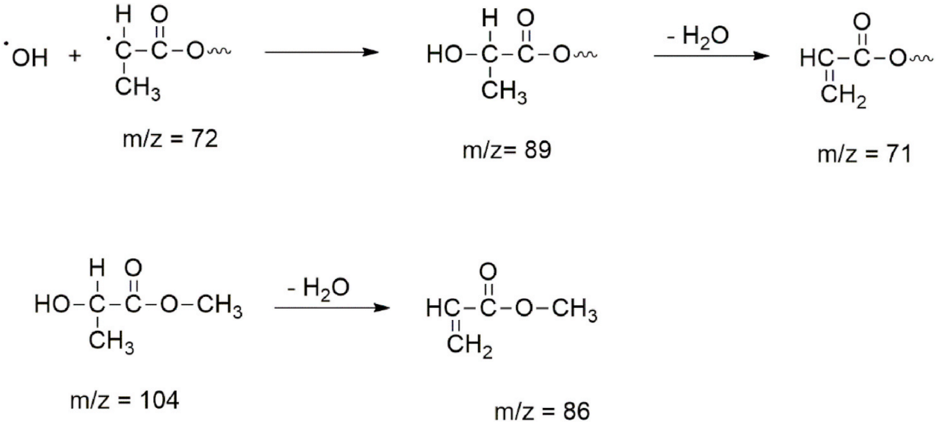


Fig. 5. Relative intensities of the most representative mass fragments of oxygen and argon respect to control.



Scheme 1. Aldolic condensation of acetaldehyde.



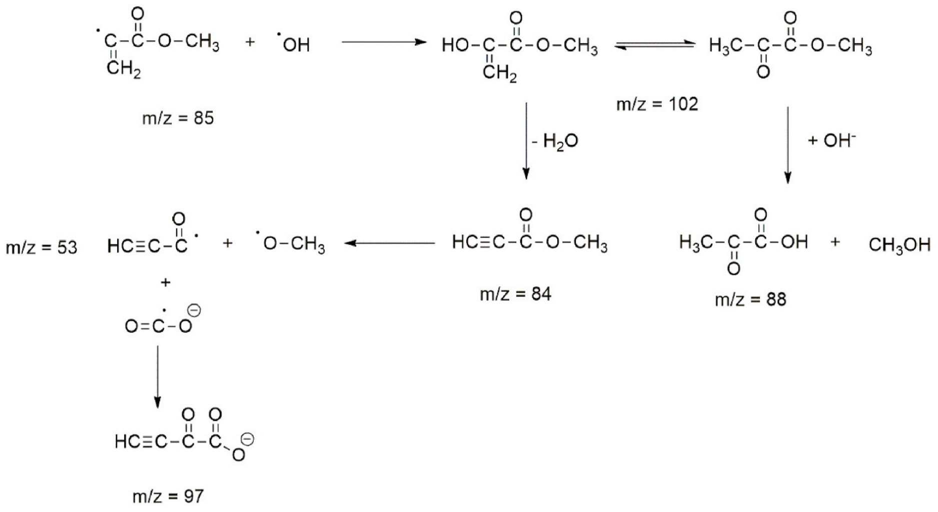
Scheme 2. Recombination of radicals and dehydration of the generated alcohols.

3.2. *Effects of plasma on the hydrophobicity of Ti-PLA samples*

In addition to the chemical changes that the PLA surface undergoes when exposed to argon and oxygen plasma there are changes in the wettability of the films. Hydrophobicity was evaluated by measuring the WCA over them. The surface of the titanium supports was also measured before and after plasma application. The results are summarized in Table 1.

The WCA of the Ti and the PLA are practically the same, both being hydrophobic surfaces. However, they behave differently when subjected to plasma treatment: Ti becomes completely hydrophilic, while in the case of PLA the variation is smaller: the WCA decreases by almost 30% (oxygen plasma) and 37% (argon plasma). Although it is difficult to set a threshold for hydrophobicity, in both cases, the PLA surface becomes hydrophilic when exposed to plasma. These values are very similar to those obtained by Morent et al. [35] after treating PLA films with argon and air plasma (WCA = 60° and 59° respectively), and also to those obtained by Inagaki et al. [31] and Hirotsu et al. [36] after treating PLA films with oxygen plasma (WCA = 55°) and argon (WCA = 50°), respectively. This hydrophilicity was to be expected according to the chemical changes observed at the surface. It is interesting to point out that, although the final effect of the application of both types of plasma is the same, the cause is different in each case: in the oxygen plasma surface functionalization reactions predominate, while in the argon plasma surface degradation predominates.

However, the effect of the plasma on the wettability of the films is not permanent, since the polar groups generated by the action of plasma tend to be reoriented towards the bulk of the film or to migrate by



Scheme 3. Set of reactions that can lead to alkynes and oxoacids.

Table 1
WCA of Ti supports and PLA films, before and after application of O_2 and Ar plasma.

	$WCA_{control}$ [°]	$WCA_{O2\ plasma}$ [°]	$WCA_{Ar\ plasma}$ [°]
Ti	80 ± 2	<10	<10
PLA	81 ± 3	57 ± 2	51 ± 3

Table 2
Loss of plasma treatment efficiency (L) over time in PLA.

t (weeks)	L (%)$_{O2\ plasma}$	L (%)$_{Ar\ plasma}$
0	–	–
1	8	23
2	25	37
3	42	23
4	42	27
6	46	47
7	58	43
8	63	47
12	67	40

diffusion towards the polymeric matrix to reduce the high surface energy [35,37]. Therefore, the temporal evolution of the plasma treatments was followed by measuring the WCAs of the samples at different times (Fig. 6).

Fig. 6 shows that the initial value of the WCA of the PLA (81°) is not recovered in either case. Recovery of hydrophobicity is faster during the first two weeks for both plasmas. After this time, the WCA of the sample treated with argon plasma decreases and then increases again until it reaches a plateau and stabilizes around 63°. This behaviour had already been observed by Izdebska-Podsiadly and Dörsam [37]. In the case of oxygen plasma, the WCA tends to increase steadily until 8 weeks, after which it stabilizes, reaching a value of 73°.

Loss of treatment efficiency (L) was calculated according to the formula (equation (1)) proposed by Jacobs et al. [38]; data are summarized in Table 2. $WCA_{treated}$ and $WCA_{untreated}$ refer to samples with and without plasma treatment, respectively, and WCA_{stock} refers to samples with plasma treatment and stored for different times.

$$L\,[\%] = 100 \times \frac{WCA_{treated} - WCA_{stock}}{WCA_{treated} - WCA_{untreated}} \qquad \text{Eq. (1)}$$

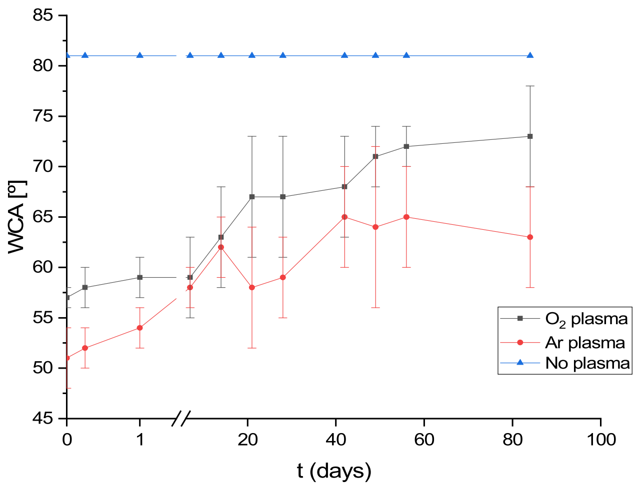


Fig. 6. WCA variation with aging of PLA films after O_2 and Ar plasma.

It has already been noted that the effect of the plasma is lost due to the reorientation of the polar groups on the surface. However, as can be deduced from the data in Table 2, the recovery of the initial WCA value is different for each treatment. In the case of oxygen plasma, the free radicals generated by the treatment react with the oxygen itself (and other oxygen-containing species) of the plasma, resulting in new polar groups that have to be reoriented to minimize the surface energy. However, in the case of argon plasma, as it is an inert gas, the radicals have to react with the neighboring polymer chains, creating a cross-linked and oxidized polymer network, which hinders the mobility of the chains [35,39]. For this reason, PLA treated with argon plasma retains its hydrophilicity for longer.

3.3. Topographical changes induced by plasma: AFM results

In the AFM images (Fig. 7) it can be seen that the PLA control surface, before being treated, is very smooth (look at the scale of the vertical axis of Fig. 7a and b). When scanning very small areas (2 × 2 μm), it is possible to see the polymer chains, perfectly defined and aligned, as in a nanostructure configuration. However, the plasma treatment causes this structure to be lost: in this case the surface is granular-like and rougher than in the control case. In Table 3 the root mean square height (Sq) values of PLA films (untreated and Ar plasma treated) are shown; preliminary studies determined that there was no significant difference between argon and oxygen plasma in terms of roughness, so only the argon plasma data are included. The increase of an order of magnitude (from units of nm to tens of nm) in the surface roughness demonstrates

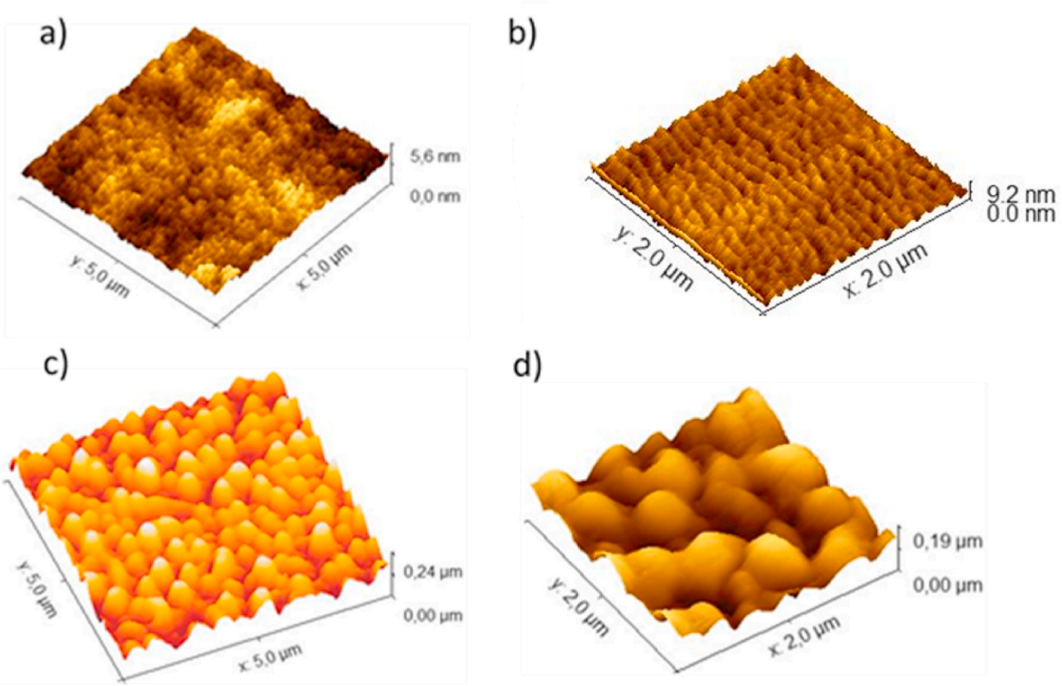


Fig. 7. AFM images of untreated Ti-PLA a) 5 × 5 μm and b) 2 × 2 μm and Ar plasma treated Ti-PLA c) 5 × 5 μm and d) 2 x 2 μm.

Table 3
Sq values of untreated and plasma-treated PLA surfaces. Data are the average of 10 measurements.

Sample	Area	Sq (nm)	σ Sq (nm)
Ti_PLA$_{untreated}$	10 x 10	2.1	0.4
	5 x 5	3.4	0.5
Ti_PLA$_{Ar\ plasma}$	10 x 10	24.7	1.8
	5 x 5	27.4	0.5

that the plasma not only functionalizes the surface, but also etches it.

The Sq data obtained are of the same order as those found in the literature: there is always an increase in roughness when plasma treatment is applied, mainly because material is removed from the surface. De Geyter et al. [40] obtained an Sq value of around 20 nm when they applied argon plasma to PLA, but the roughness of the PLA control was 11.7 nm. Jordá-Vilaplana et al. [41] reported a similar roughness for pristine PLA (12.1 nm), which doubled and even quadrupled when air plasma was applied. In our case, the variation is more pronounced, since the Sq value is multiplied by 10 (from 2.4 to 27.4 nm), probably because the frequency of plasma treatment is higher.

4. Conclusions

Argon plasma favours the crosslinking of polymer chains, as well as the fragmentation into low molecular weight moieties, as can be deduced from data obtained by ToF-SIMS. However, oxygen plasma reacts with the free radicals generated in the treatment, leading to new oxygen-rich, higher molecular weight species.

The analysis of the fragments obtained in the ToF-SIMS has also allowed us to propose possible reaction paths to explain the formation of these species, and to confirm the presence of traces of O_2 in the argon plasma.

Although the nature of the chemical modifications is different, similar physical changes are observed for both plasmas: increase in surface roughness and decrease in hydrophobicity. However, the latter is more durable in the case of argon plasma, due to the lower mobility of the chains.

Author statement

V. Luque-Agudo: Conceptualization, Formal Analysis, Investigation, Data Curation, Writing-Original Draft **M. Hierro-Oliva:** Conceptualization, Investigation, Data Curation, Writing-Original Draft **A. M. Gallardo-Moreno:** Conceptualization, Writing-Review and Editing, Supervision, Funding acquisition **M. L. González-Martín:** Conceptualization, Writing-Review and Editing, Supervision, Funding acquisition.

Data availability

The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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