

Article

Effect of Low-Pressure Plasma Treatment on the Surface Wettability of Poly(butylene succinate) Films

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Abstract: Poly(butylene succinate) (PBS) films were processed by a radio frequency (RF; 13.56 MHz) low-pressure plasma of oxygen and argon/oxygen, and an oxygen plasma with an argon post-crosslinking plasma to improve their wettability property. Specimens were treated at different times with fixed power processing of 100 W (0.3 W/cm²) and a fixed pressure of 10 Pa. A significant change in hydrophilicity evaluated by the water contact angle was observed. The contact angle of a water drop decreased from 80° for the untreated sample to values lower than 5° for plasma-treated samples. The effect of ageing on the wettability of PBS substrates was also examined, showing a more pronounced trend in the first 4 h and reaching a plateau in the following days. However, partial surface hydrophilicity was maintained for up to 15 days. A practical application of the surface functionalization produced by plasma was obtained via the deposition of SiO_x onto PBS surfaces; the study of films' oxygen permeability demonstrated that the plasma pre-treatment increased the adhesion between PBS and SiO_x, resulting in significantly improved oxygen barrier properties. In order to evaluate the morphology and roughness modification caused by plasma exposure, atomic force microscopy characterization was carried out. Chemical information about treated surfaces, such as an increase in oxygen functional groups during plasma exposure, was measured by Fourier-transform infrared spectroscopy and X-ray photoelectron spectroscopy. Finally, the effects of plasma on crystallinity were investigated by X-ray diffraction.

Keywords: poly(butylene succinate); surface morphology; plasma treatment; surface modification; hydrophilicity



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1. Introduction

The packaging industry nowadays is dominated by non-degradable petroleum-derived polymers, but in recent decades there has been strong focus on the research and development of environmentally friendly, biodegradable polymers. This has motivated scientists to study biodegradable plastics such as poly(butylene succinate) (PBS) for general food packaging or films. PBS is a biodegradable aliphatic polyester that has high flexibility, very good impact strength, and chemical as well as thermal resistance [1]. Nevertheless, PBS also has some disadvantages, limiting its use in different industrial sectors. For instance, PBS surfaces are chemically inert and moderately hydrophobic, resulting in mediocre surface wettability [2]. In order to improve the wettability of PBS or the adhesion between it and a coating, the surface of the polymer needs to be treated. Wet chemical treatments are frequently used, but solvent processes cause substantial volumes of waste. Some solvents can be recycled, but the majority must be discarded via incineration or a disposal

area. In the present study we propose low-pressure plasma technology as an environmentally friendly alternative to conventional methods to increase surface wettability and adhesion properties.

The plasma surface functionalization of polymers is routinely conducted to enhance their wettability, sealability, printability, or adhesion to other polymers or materials without impacting the bulk properties of a polymer. In order to treat the surface of oil-based polymers various plasma gases have been commonly used, especially oxygen-based plasma. A specific characteristic of plasma treatment is that the surface structure of a polymer can be selectively changed by a few nanometers in depth without altering the desired bulk properties of the polymer. Energetic particles produced in the plasma interact with the polymer surface, typically via radical chemistry if pure oxygen plasma is used. The use of gas mixtures, noble gases in particular, can lead to synergistic effects due to the interaction of radicals and ions, which can increase the functional properties of a polymer. Oxygen-based plasmas can introduce a high number of hydrophilic groups [3], such as carboxyl, hydroxyl, and carbonyl, generating strong wettability. The objective of this work is to analyze the wettability property of PBS substrates when they are subjected to three different plasma processes: oxygen only, oxygen/argon mixture, and oxygen with Ar post-crosslinking, and determine the best treatment to keep the polymeric surface hydrophilic for as long as possible without damaging the sample and without requiring long treatment times in order to keep it scalable from an industrial point of view. Under this perspective it is known that the induced surface properties are not stable over time since the surfaces show a tendency to return to the untreated state to the moment of room storage (hydrophobic recovery). Therefore, the durability of the properties obtained via plasma treatment is important for practical application. As such, a study on water contact angle measurements for 15 days after plasma treatment was performed to evaluate the effects of the treatments over time.

Finally, it is important to note that despite plasma functionalization methods being well-established for oil-based polymers there are only a few reports on biodegradable polymers. In particular, in the scientific literature the plasma activation of PBS films through this operating gas mixture has never been reported. There are only few studies about PBS nanofibrous membranes [4] and PBS surface grafting with acrylic acid [5]; therefore, an objective of this experimental activity is to obtain a deeper insight into the plasma functionalization of PBS. In the final section an important industrial food packaging application is proposed. In fact, this kind of surface modification could enhance the adhesion between a plasma-activated substrate and an organic/inorganic thin coating film to avoid interfacial stress and thus maximize the functional properties of the chosen coating. SiO_x thin films (25 nm) were deposited on an untreated and plasma-activated PBS substrate, and a comparison of their oxygen barrier properties was performed.

2. Experimental Details

2.1. Materials

Investigations were evaluated using samples of PBS foil (BioPBS™ FZ91PM/FZ91PB, Bangkok, Thailand) of 30 μm thickness and 4 × 4 cm² size. Before plasma treatments, PBS (1.26 g/cm³) was cleaned by filtered air for 1 min at room temperature. All samples were stored at room temperature and 40% relative humidity. Oxygen (99.998% purity) and argon (99.999% purity) gases were Rivoira products. The hexamethyldisiloxane monomer (HMDSO, 99.9%) was an Aldrich product (Merck Life Science, Milano, Italy).

2.2. Plasma Reactor and Parameters

The device is made up of parallel electrodes in a capacitively coupled plasma system [6]. The plasma is ignited between the upper powered electrode (connected to a 13.56 MHz power source) and the lower grounded electrode (sample holder). The treatments were carried out at a total operating pressure of approximately 10 Pa, kept constant by balancing the inlet flow with the pumping speed of the plant. The working

gases, oxygen and argon, were supplied into the vacuum chamber by a mass flow system. The total gas pressure was determined by capacitive sensors.

Plasma treatments were performed at 100 W (0.3 W/cm^2) as a function of treatment time in the range of 10 to 240 s. Table 1 reports some macroscopic experimental parameters of the processes and plasma parameters, such as plasma density and electron temperature estimated by a Langmuir probe [7]. The neutral atom density, n_n , was evaluated from the operating process pressure (10 Pa) and temperature by applying the ideal gas law ($p_n = n_n k T_g$); it was in the range of 10^{21} m^{-3} for all the treatments. T_g was constant around 300 K, as measured by a K-type thermocouple.

Table 1. Experimental conditions of plasma treatments.

Plasma Gas	Total Gas Flow (Sccm)	Power (W) and Power Density (W/cm^2)	Oxygen %	Electron Density (m^{-3}) in O_2	Electron Density (m^{-3}) in Ar	Electron Temperature (eV)
Oxygen plasma	20	100 (0.3)	/	2×10^{14}	/	≈ 1
Argon/oxygen plasma	20	100 (0.3)	20	1.5×10^{15}	1.5×10^{15}	≈ 1.5
Oxygen plasma with Ar post-crosslinking plasma	20	100 (0.3)	/	2×10^{14}	2.5×10^{15}	$\approx 1 (\text{O}_2)$ $\approx 1.7 (\text{Ar})$

In order to evaluate the oxygen barrier properties, SiO_x barrier coatings were deposited on pristine and functionalized PBS (oxygen plasma with Ar post-crosslinking plasma for 120 s, Table 1). A vaporized source from liquid was used as a precursor of the deposition of SiO_x barrier coatings. SiO_x coating was deposited using oxygen in a ratio of 17:1 with the monomer and with an input power density fixed at 0.6 W/cm^2 . The depositions were performed at a total operating process pressure of about 3 Pa.

2.3. Surface Properties

The chemical characterization of coatings was carried out by means of a Perkin Elmer Spectrum Two FT-IR spectrometer. Samples were placed directly onto the ATR plate. For each sample five measurements in different surface regions were carried out, and the averaged spectrum was reported. The air background spectrum was recorded before each sample scan with a resolution of 4 cm^{-1} . The surface roughness and morphology of coatings were observed by an atomic force microscope (AFM) (CoreAFM, Nanosurf, Liestal, Switzerland) in non-contact mode. A $10 \times 10 \mu\text{m}^2$ scan was performed in various places of the substrates. The measurement on each specimen was repeated three times in different surface areas; an average value and the standard deviation were calculated. The surface chemical characterization was performed using X-ray photoelectron spectroscopy (XPS). The core-level spectra were collected by means of a non-monochromatized Al anode X-ray source ($h\nu = 1486.6 \text{ eV}$) supplied with a single-channel detector. All spectra were assigned to the same energy scale obtained by calibrating the Ag 3d5/2 line at 368.3 eV. The atomic sensitivity factors (ASF) for both the Al and Mg anodes for all the elements, entrance–exit slit combinations, and pass energies were experimentally obtained by means of the transmission factor and Lindau’s cross-sections as described in ref. [8–10] at a take-off angle of 15° . The crystallinity and bulk properties were investigated by an X-ray diffractometer (XRD) with Bragg–Brentano geometry and copper K_α radiation. The X-ray diffraction data were collected in the 2θ range of 10° to 40° with a step size of 0.05° and a velocity of 5 s/step.

2.4. Oxygen Barrier Properties

The oxygen barrier properties of the films were determined by a PermeO₂ device (ExtraSolution, Lucca, Italy) on exposed areas of about 5 cm^2 . Oxygen transmission rate (OTR) ($\text{mL}/(\text{m}^2 \cdot \text{day})$) values were measured at 25°C and 50% relative humidity. All PBS films were measured in triplicate.

2.5. Water Contact Angle Measurements

The analyses of the contact angle were performed using an FKV (Bergamo, Italy) DataPhysics OCA20 goniometer. The surface wettability was obtained by means of the value of the contact angle obtained with a 4 μL drop of distilled water, dropped on the surface of the samples with a 500 μL Hamilton syringe. The variations in the surface wettability were studied for 15 days. At least 3 to 4 replicate measurements were executed for each sample and a mean value was reported.

3. Results and Discussions

3.1. Effects of Plasma on the Hydrophobicity of PBS Samples

The wetting behavior of surface-treated PBS films was evaluated by measuring the water contact angle (WCA) immediately after the application of plasma (Figure 1). Pristine PBS showed a hydrophobic character with a WCA value of $80^\circ \pm 1^\circ$. In all cases, PBS films became hydrophilic when exposed to plasma. In any case, as expected, the hydrophilicity effect was slightly different as a function of the plasma mixture. For O_2 treatments, the results of the WCA indicate that a saturation of the hydrophilic groups was reached on the polymeric surface for a treatment time of 60 s, while for the Ar/O_2 treatment it was reached in 120 s. However, still better results were successively obtained with the O_2 plasma and Ar post-crosslinking process, where the saturation of the hydrophilic groups was reached in 10 s. Regarding this latter process, the Ar ions bombarding the near-surface molecules could produce a branching among the radicals produced on the functionalized surface; therefore, it could minimize the reorientation of the oxidized chemical groups towards the inner surface of polymer which, in turn, preserve a higher surface energy [11] and, consequently, improved surface wettability. An increase in treatment time (over 10 s) of the Ar post-crosslinking process resulted in an unvaried surface wettability or, more specifically, WCAs after the plasma treatments remaining unchanged (Figure 1). In any case, the increase in Ar post-crosslinking treatment time can be very useful for the stability of the surface wettability during the time (see Section 3.3.).

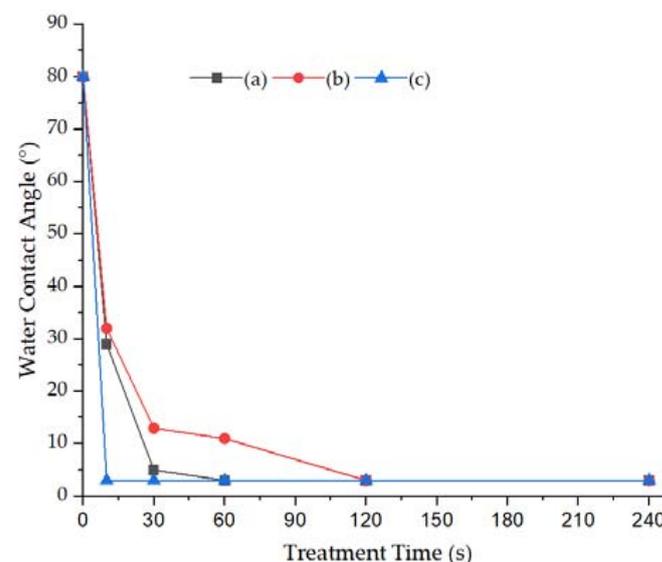


Figure 1. Water contact angle of treated PBS substrates in terms of the treatment time with (a) pure O_2 plasma, (b) Ar/O_2 plasma, and (c) O_2 plasma 30 s + Ar post-crosslinking for 120 s.

3.2. Topographical Changes Induced by Plasma

AFM imaging was performed to study any surface degradation. Before plasma treatment PBS films showed a smooth surface with some pores as well as an average roughness R_a of 30 ± 1 nm (Figure 2a). In terms of both R_a values and visual aspects none of the plasma treatments lasting for 30 s caused important changes in surface topography

(Figure 2b,d,f). On the contrary, when plasma treatments lasted for more than 30 s the surface topography was altered while the roughness showed no significant changes. In the case of O₂ plasma shown in Figure 2c (for reasons of space, only samples treated for the longest times are presented), some topographic characteristics disappeared owing to the etching of plasma, and pores are more evident. In addition, a significant number of structures had been produced on the PBS surface. Additionally, in the case of O₂/Ar plasma a morphological change is evident for process times longer than 30 s (Figure 2e), which is also the case for oxygen plasma with Ar post-crosslinking (Figure 2g). In light of the results obtained, the treatment time was fixed at 30 s in the case of O₂ and O₂/Ar plasmas, while for O₂ plasma with Ar post-crosslinking the activation time was 30 s and the crosslinking was varied in the range of 1 to 4 min (Figure 2f,h,i).

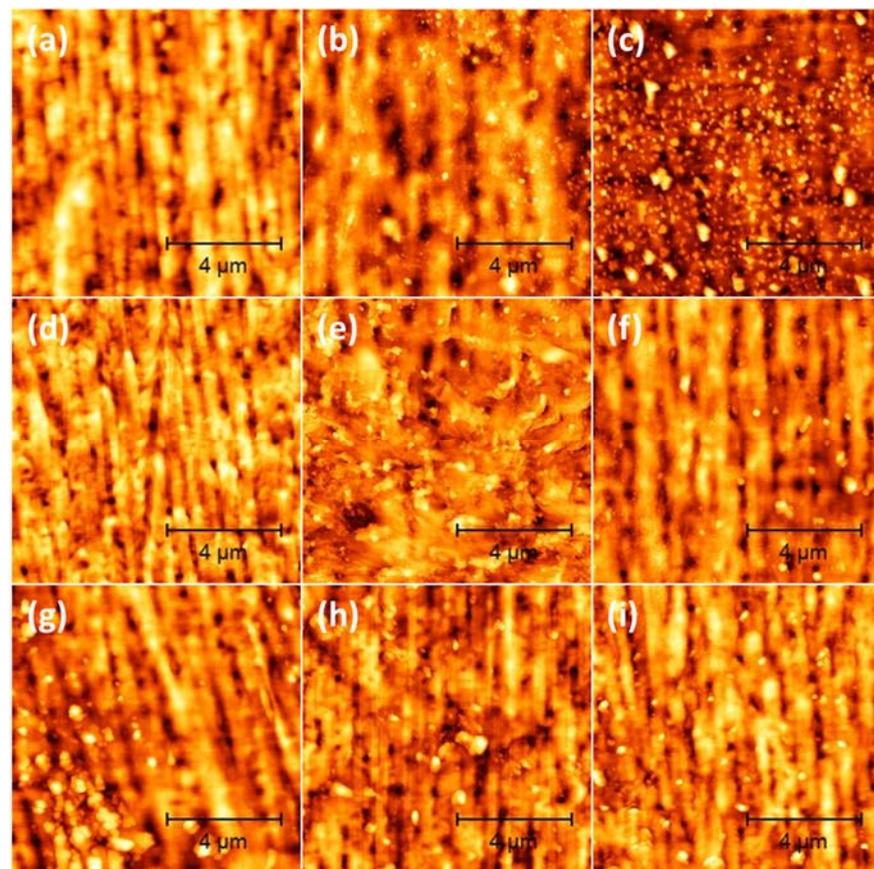


Figure 2. AFM pictures of (a) untreated PBS, (b) O₂-plasma-treated for 30 s, (c) O₂-plasma-treated for 120 s, (d) Ar/O₂-plasma-treated for 30 s, (e) Ar/O₂-plasma-treated for 120 s, (f) O₂ plasma 30 s + Ar plasma 240 s, (g) O₂ plasma 60 s + Ar plasma 240 s, (h) O₂ plasma 30 s + Ar plasma 60 s, and (i) O₂ plasma 30 s + Ar plasma 120 s.

3.3. Stability of Surface-Treated PBS Films

As is well-known in the literature, the effectiveness of the plasma treatment on the wettability property of the films is not stable in terms of time, since the polar groups produced by the action of plasma tend to be reoriented towards the bulk of the film to reduce the high surface energy [12,13]. The ageing phenomenon can be slowed down by stabilizing the surface layer by means of a crosslinking process using noble gas plasma. The effect of this treatment (crosslinked layer) will strongly reduce the diffusion of molecular groups up to the surface, limiting the ageing phenomenon. For this purpose, a two-stage plasma process consisting of O₂ plasma with Ar plasma post-treatment was used. Therefore, the stability of the surface properties was studied in terms of wettability (Figure 3). WCAs changed within the first 4 h for all processes (Figure 3B); the WCA stabilized in the range

of 40° to 30° with a loss of treatment efficiency L (%) in the range of 40% to 33%, estimated according to the mathematical expression formulated by Jacobs et al. [14]. Within 24 h (Figure 3C) the WCA stabilized in the range of 45° to 35° with a loss of treatment efficiency L (%) in the range of 50% to 40%. Over a storage period of 15 days (400 h) (Figure 3D) WCAs raised in the course of time until they reached, in some cases, such as for O_2 and Ar/ O_2 treatments, a value close to 70° . As expected, with the Ar post-crosslinking process PBS retained its hydrophilicity for longer. In particular, for 60 and 120 s of post-argon plasma the WCA stabilized around 60° to the 15th day with a loss of treatment efficiency of approximately 78%–79% (Table 2).

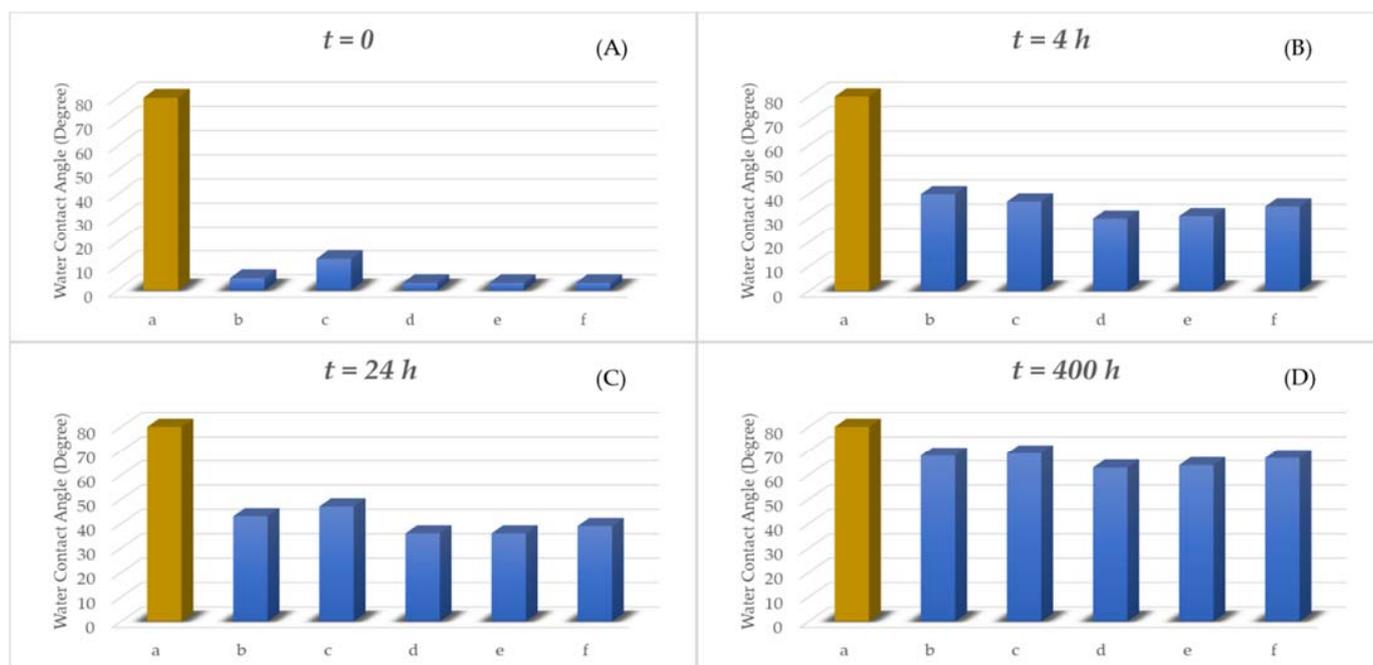


Figure 3. WCA of treated PBS substrates (A) immediately after plasma treatment, (B) after 4 h, (C) after 24 h, and (D) after 400 h. (a) Untreated PBS, (b) O_2 -plasma-treated for 30 s, (c) Ar/ O_2 -plasma-treated for 30 s, (d) O_2 plasma 30 s + Ar plasma 60 s, (e) O_2 plasma 30 s + Ar plasma 120 s, and (f) O_2 plasma 30 s + Ar plasma 240 s.

Table 2. Loss of treatment efficiency after 15 days of ageing.

Plasma Gas	Treatment Time (s)	Ar Post-CrossLinking Time (s)	L %
Oxygen	30	–	84
Argon/oxygen	30	–	83.6
Oxygen plasma with Ar post-crosslinking	30	60	77.9
Oxygen plasma with Ar post-crosslinking	30	120	79.2
Oxygen plasma with Ar post-crosslinking	30	240	83.1

3.4. Chemical Modifications Induced by Plasma

3.4.1. FTIR Analysis

The ATR-FTIR spectra of the PBS plasma-treated surfaces were used to analyze any chemical modifications generated by plasma. The surface of PBS was characterized before and after the plasma treatments. Regarding the pristine PBS (Figure 4a), the peak at 917 cm^{-1} corresponds to the $-C-OH$ bending in the carboxylic acid groups. The vibration bands at about 1041 cm^{-1} were due to $-O-C-C-$ stretching. Peaks in the range of 1140 to

1260 cm^{-1} resulted from the stretching of the $-\text{C}-\text{O}-\text{C}-$ group in the ester bonds. The band at the 1715 cm^{-1} region was assigned to the $\text{C}=\text{O}$ stretching vibrations of ester linkages. The peaks at 1330 and 2945 cm^{-1} were attributed to the symmetric and asymmetric bending vibrations of $-\text{CH}_2-$ groups in the main chains, respectively. $\text{C}-\text{H}$ bending vibration at around 1470 cm^{-1} [15].

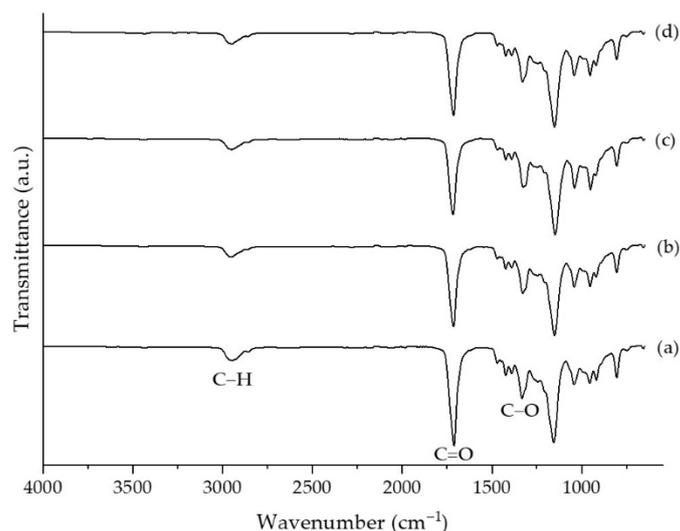


Figure 4. FTIR spectra of (a) untreated PBS, (b) O_2 -plasma-treated for 30 s, (c) Ar/O_2 -plasma-treated for 30 s, and (d) O_2 plasma 60 s more Ar plasma 240 s.

Figure 4b–d display the FTIR spectrum of the PBS samples immediately after the plasma treatments. As can be seen, the vibration peaks are the same for all treatments. On the whole, the results corroborate that no significant chemical modifications occur on the surface of PBS. In any case, although IR did not show the existence of new functional groups on activated PBS the technique can be used for the qualitative determination of the modification of surface chemical structure. A comparison of the spectra obtained before and after the surface modification treatment, via the IR-band ratio method [16], showed (Figure 5) that there was a decrease in the ratio of the signal intensity for the $\text{C}-\text{H}$ vibration at 2945 cm^{-1} to that of the $\text{C}=\text{O}$ at 1715 cm^{-1} and $-\text{C}-\text{O}-\text{C}-$ at 1330 cm^{-1} . This trend could be due to the generation of oxidized species such as carboxyl groups, which explain the increase in the 1710 cm^{-1} and 1330 cm^{-1} intensity after the plasma process.

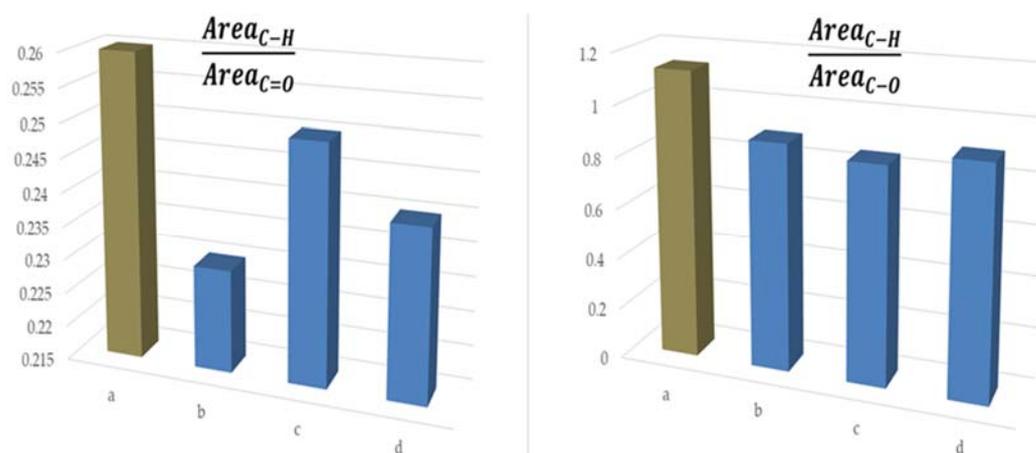


Figure 5. Intensity ratios I_{2945} / I_{1715} and I_{2945} / I_{1330} evaluated as an integrated area for (a) untreated PBS, (b) O_2 -plasma-treated for 30 s, (c) O_2 -plasma-treated for 30 s and Ar post-crosslinking for 60 s, and (d) O_2 -plasma-treated for 30 s and Ar post-crosslinking for 120 s.

3.4.2. XPS Analysis

Given that the best results (also with regard to the ageing) were obtained with the Ar post-crosslinking process, we focused on processes in the O₂ plasma with Ar plasma post-treatment for 60 and 120 s. The surface elemental composition of PBS specimens before and after the plasma process was studied with X-ray photoelectron spectroscopy. As can be seen in Figure 6 (survey spectra), the peaks of C1s and O1s were observed in all samples. Figure 7a shows the C1s high-resolution spectra of pristine PBS (deconvoluted into four different components). The characteristic peaks of the binding energy (BE) at 284.2 eV for the C–C and C–H species, 285.2 eV for the C–O species, 286.7 eV for the C=O and O–C–O species, and 288.9 eV for the O–C=O species were observed. XPS analyses of freshly treated specimens confirm that the functionalization induced on PBS by the plasma treatments is connected to the increase in oxidized groups. This result is consistent with the FTIR spectra (Figure 5). The effect is especially noticeable in the high-resolution C1s peak of the PBS which had undergone the O₂ plasma treatment for 30 s and Ar post-crosslinking for 120 s (Figure 7c). The O/C ratio in the pristine PBS (determined from high-resolution C1s XPS spectra) that was 0.301 rises up to 0.333 for PBS treated in O₂ with Ar plasma post-treatment for 120 s.

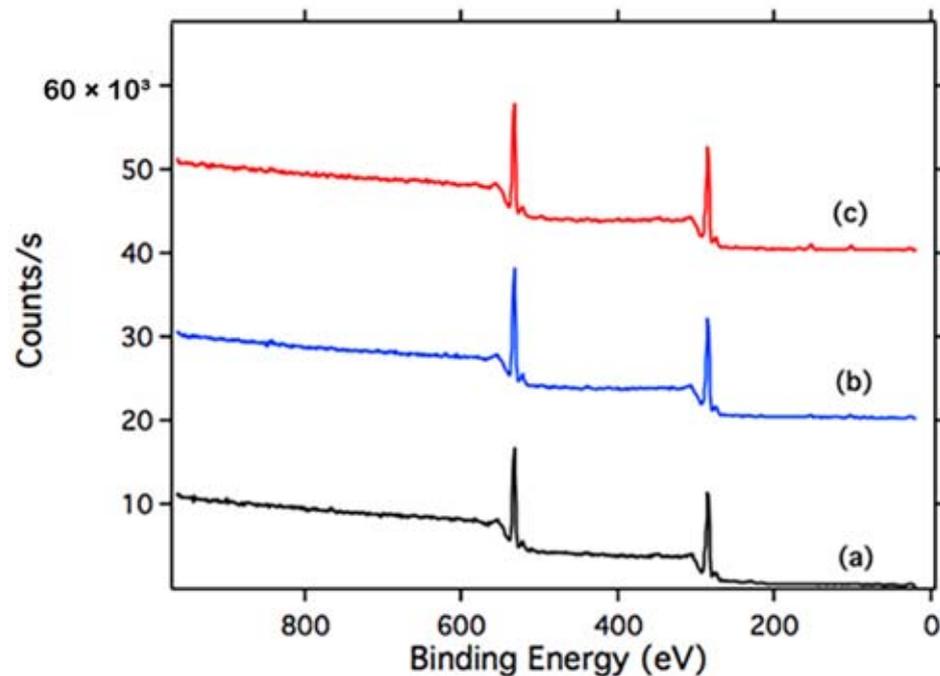


Figure 6. XPS survey scan spectra of surfaces (a) untreated PBS, (b) O₂-plasma-treated for 30 s, and (c) O₂-plasma-treated for 30 s and Ar post-crosslinking for 120 s.

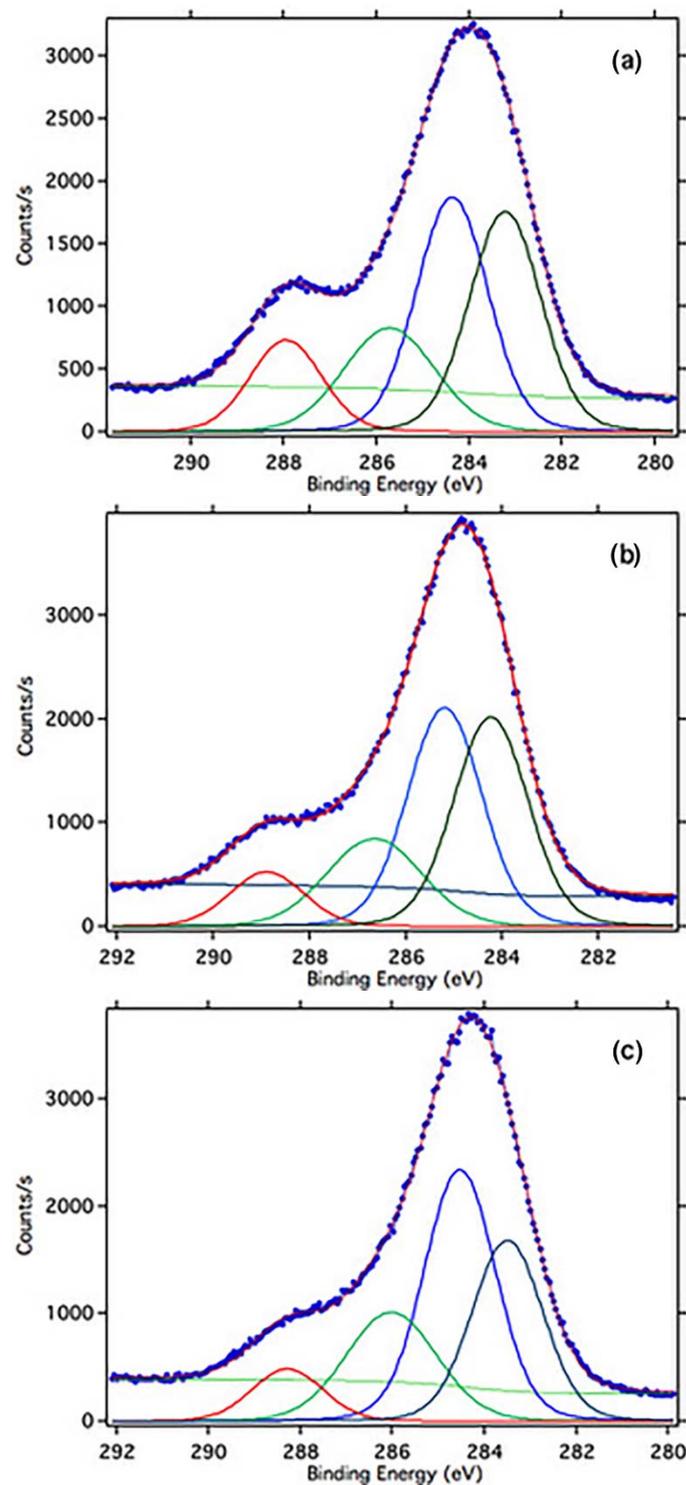


Figure 7. High-resolution C1s peaks of (a) untreated PBS, (b) O₂-plasma-treated for 30 s, and (c) O₂-plasma-treated for 30 s and Ar post-crosslinking for 120 s.

3.4.3. XRD Analysis

In order to underline possible changes in bulk properties X-ray diffraction analysis was performed on untreated and treated samples by collecting and comparing the corresponding XRD spectra. As expected, PBS is a semi-crystalline polymer, as noted in Figure 8a, which shows the X-ray diffraction peaks at $2\theta = 19.7^\circ$, 22.6° , 26.1° , and 28.6° of the PBS [17], corresponding to (020), (110), (121), and (111) reflections, respectively. From the analysis of the other spectra, (b) and (c), in Figure 8, we can say that the plasma treatment did not

result in any significant change in PBS diffraction pattern; consequently, the crystallinity of PBS was not significantly changed.

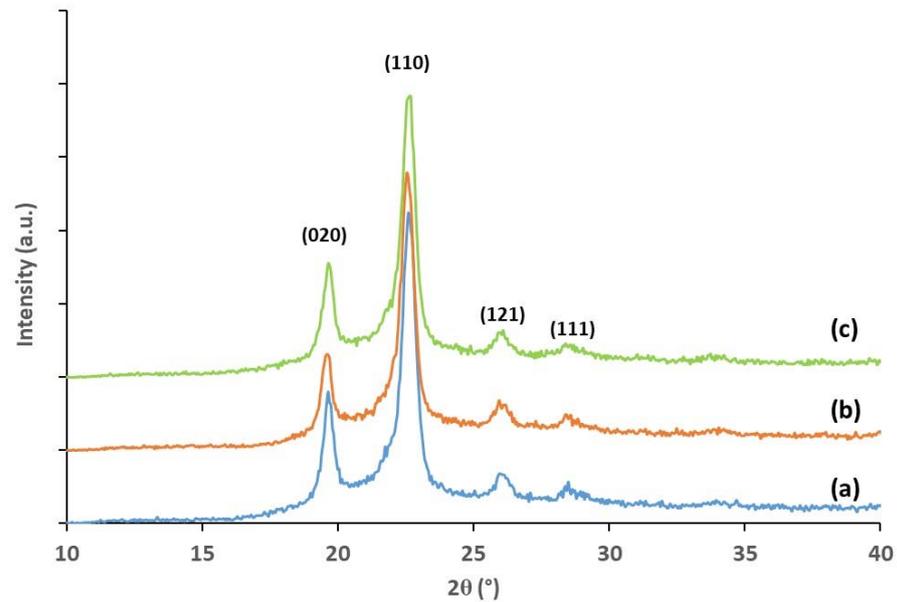


Figure 8. XRD spectra of PBS (a) untreated, (b) O₂-plasma-treated for 30 s, and (c) O₂-plasma-treated for 30 s and Ar post-crosslinking for 120 s.

It is noteworthy that by elaborating the XRD spectra the peculiar peak of the amorphous part was also identified (see example in Figure 9), which contributed about 20% for all three samples, confirming the absence of modifications of the bulk properties.

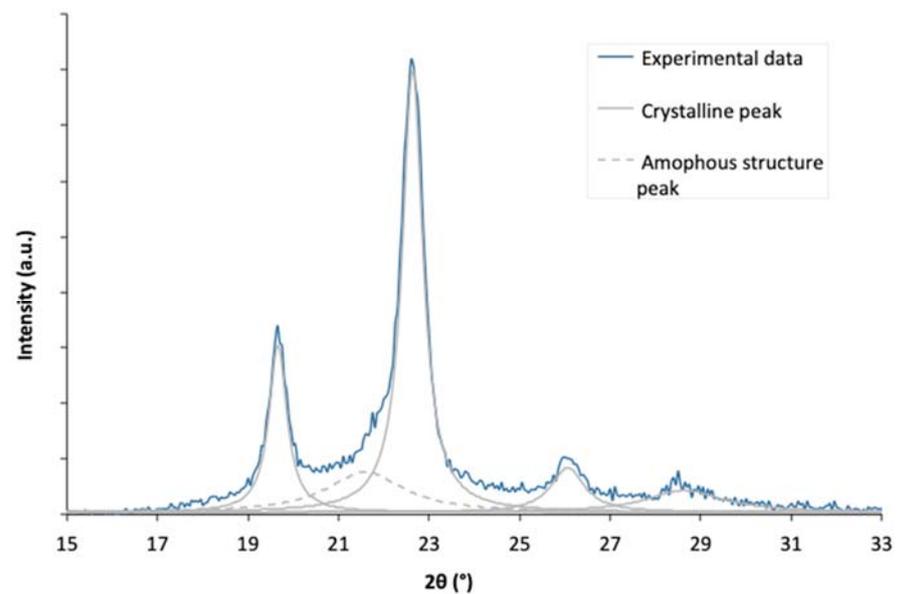


Figure 9. XRD spectrum of PBS sample and identification of the characteristic peaks.

3.5. Oxygen Barrier Property Analysis of PBS

In the scientific literature it is known that the deposition of a SiO_x layer is an excellent way to improve poor barrier functionalities of polymeric food packaging films [18]. However, the enhancement of gas barrier properties is highly dependent on residual stress in the substrate/coating interface [19]. Indeed, since the increase in wettability also involves an increase in the adhesion property [20–23], a practical application of the surface functionalization processes (described in the previous paragraphs) is, for instance, an increase

in the gas barrier property of PBS [24]. For this purpose, SiO_x barrier coatings have been deposited [25] on pristine and functionalized (O_2 plasma with Ar plasma post-treatment for 120 s) PBS samples. As expected, the addition of SiO_x coatings (in this experiment a thickness of 25 nm was deposited) generates a substantial increase in the polymer barrier property (Figure 10); indeed, in the case of pristine PBS coated with SiO_x the oxygen transmission rate (OTR) decreased to about $75 \pm 10 \text{ cc/m}^2\cdot\text{day}$, which corresponds to an OTR reduction of more than 85 % compared to bare PBS, while in functionalized PBS coated with SiO_x the OTR decreased to about $37 \pm 7 \text{ cc/m}^2\cdot\text{day}$ (Figure 10, PBS + act + 25 nm SiO_x), corresponding to a reduction of 95 % compared to bare PBS. This finding could be due to the improved adhesion strength of the SiO_x coating to PBS due to the functionalization treatment [23]. These chemical bonds help the linking of the growing SiO_x coating; overall, a more chemically stable and less porous coating is generated. All this is reflected in improved barrier properties.

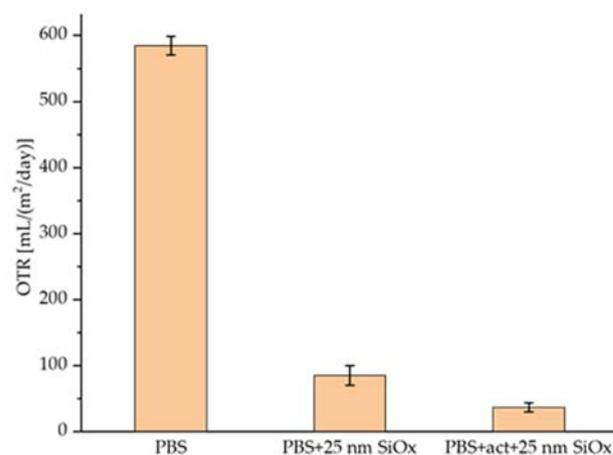


Figure 10. Oxygen transmission rate (OTR) of PBS, PBS coated with 25 nm of SiO_x , and functionalized PBS coated with 25 nm of SiO_x . The tests were performed at 25 °C and 50 % relative humidity (film thickness was 30 μm).

4. Conclusions

The poly(butylene succinate) surface was successfully functionalized by a low-pressure radio frequency plasma under different gas mixtures. The results of the contact angle measurement of PBS films treated by different mixtures showed an increase in hydrophilicity above 90%. AFM was used to investigate the morphology changes in the surface of PBS samples because of the plasma treatments. The oxidation effect due to the plasma treatment was detected by FTIR and XPS analyses. XRD spectroscopy showed that no modification of PBS crystallinity was produced by the plasma treatments, confirming in the substance that the bulk properties had not changed. Ageing for plasma-processed samples stored in air at ambient temperature was studied. Based on the results of wettability, hydrophobic recovery, and AFM measurements, it was established that 30 s of oxygen plasma treatment with Ar post-crosslinking in the range of 1 to 2 min are the optimum parameters for PBS functionalization. The improving of the oxygen barrier property of functionalized PBS covered with a SiO_x coating was also reported as a preliminary result for any practical applications.

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Conflicts of Interest: The authors declare no conflict of interest.

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