

Article

Aging of Polylactide Films Exposed to Plasma—Hydrophobic Recovery and Selected Application Properties

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Abstract: In this study, the effect of polylactide (PLA) material on the susceptibility to hydrophobic recovery due to storage was examined, the effectiveness of plasma activation of the film, defined as improving the hydrophilicity of the material, was studied, and the selected film properties that are important from an application point of view were investigated. The study was conducted on three films using oxygen and argon plasma. Contact angles of water, diiodomethane, and ethylene glycol were investigated, and the values of surface free energy (SFE) and its polar and dispersive components were determined immediately after activation, as well as after a specified storage time (after 1, 7, 14, 30, and 60 days). The effects of film activation on its roughness, weight loss, tensile strength, color changes, and gloss were also determined. Based on the results, it was concluded that the type of film influences the course of hydrophobic recovery. At the same time, the trend of changes depends on the type of gas used for activation, while the magnitude of changes depends on the film. Moreover, it was observed that the type of PLA film had a significant effect on the changes in the polar and dispersion components of SFE, as well as on roughness and mass loss due to plasma activation. Furthermore, these parameters also depended on the type of gas used for plasma activation.

Keywords: aging; hydrophobic recovery; storage time; biodegradable polymers; PLA films; plasma activation; argon plasma; oxygen plasma

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1. Introduction

Aging of polymeric materials is an undesirable but inevitable process. It can be spontaneous (natural aging) or forced (accelerated aging). Moreover, aging can be caused by external and internal factors. As a result of the aging processes, polymers undergo thermal, oxidative, chemical, radiation, mechanical, and biological degradation. Furthermore, it should be noted that spontaneous aging of the material is a process that occurs in all plastics, both conventional and biodegradable. The nature of its course is usually very slow, but irreversible and impossible to stop [1–3]. Since it cannot be stopped, it is important to know its course and take into account changes in polymer properties when processing and applying materials.

Aging of polymer films can be manifested by changes in their mechanical properties (including a decrease in tensile strength), chemical properties (the appearance of functional groups indicating degradation of the material), or changes in appearance (a change in color or gloss, and, as a result of long-term storage or in extreme weather conditions, even surface cracking associated with a change in the brittleness of the material). The course of the aging process and the intensity of the changes occurring in the material depend on the time and conditions under which it takes place. Properties of materials depend on such factors as temperature, humidity, and light, especially in the UV region, as well as the type of gas used [3–11].

Materials with a plasma-modified top layer are subjected to short but nevertheless intense UV radiation resulting from the plasma process [12] and the interaction of ions, electrons, and other reactive molecules, which can lead not only to the desired changes in the properties of the film—its functionalization—but also its aging, i.e., degradation [13–18]. Another important issue is the disappearance of properties obtained by plasma activation; with storage time, the chemical changes introduced in the surface layer of the material are altered [19–24]. Therefore, in this article, two aspects of aging are distinguished and studied:

1. aging in the context of changing the properties of the modified layer—hydrophobic recovery,
2. additionally, aging (change in mechanical and optical properties) of the film as a result of plasma modification of its surface layer.

Hydrophobic recovery is essential from an application perspective. Hydrophilicity, and by extension the process of its loss during storage, is a fundamental parameter determining the printability and processability of the material. The second point complements the first, allowing a more complete evaluation of the impact of the activation process, determining that plasma activation does not lead to a significant change in the material's properties and its degradation, thus preventing its proper application.

The study was conducted for biodegradable films, which are an environmentally friendly alternative to films made of traditional plastics. Their similar mechanical and optical properties, as well as analogous processing, make it feasible to use them in the packaging industry, which is one of the main areas of application for plastics [25–27], and represents a significant environmental problem in the form of packaging waste [28]. One of the most relevant biodegradable polymers with wide applications in packaging, but also used in other areas such as medicine, textiles, and 3D printing, is polylactide (PLA) [29–33].

Polymer films, as non-absorbent materials, require surface preparation before the printing and finishing process [34,35]. In industrial settings, this is commonly done using in-line corona activation during the printing process [36] or, alternatively, chemically modified materials at the film production stage are used in printing houses. However, according to previous publications [19,20,37–48], a favorable alternative to these modification processes is low-temperature plasma activation.

Preparing the surface for printing involves improving the wettability of the polymer substrate and cleaning it, which is reflected by a decrease in the water contact angle and an increase in the surface free energy value of the material and the unfolding of its surface. This also translates into improved adhesion of the printing ink to the substrate [35–37]. It is generally recognized that the higher the SFE values, the better the wettability and adhesion should be, and thus the quality of the print [49].

Prior to the printing process, materials in printing houses should be stored under constant conditions (usually temperature 20–25 °C, relative humidity (RH) 50–55%) close to standard conditions (23 ± 0.5 °C, RH 50 ± 1.5%) in accordance with ISO 187:1990. Changing these conditions will lead to problems during the printing process, such as the accumulation of static electricity on the material and improper drying of the print. It is known that during storage the SFE of films modified at the production stage changes; that is, it decreases, while the water contact angle increases toward the pre-modification value. This is related to the fact that during storage the polar functionalities present at the polymer surface disappear at different rates [50]. Moreover, the rate of change occurring over time depends on storage conditions and the type of material [51,52]. Hence, this article investigates how the type of PLA film affects hydrophobic recovery.

The results presented in the article focus on the aspects of aging of PLA film connected to application relevant properties only. The aspect of chemical changes occurring on the surface layer of the material was omitted, as there is continuing research in the field of plasma chemistry for identification of reactive species generated in the plasma [13,17,19,20,50], and this is beyond the scope of this article. From the point of view of printing and its quality, the main effects of aging of printed films are the changes in the hydrophilicity of the material and its strength after short and long storage periods. However, storage time is usually quite short due to the high turnover of materials in printing houses.

We have previously conducted studies on the aging of plasma-modified PLA films [19,20], but these were carried out for different films while considering only one type of film in each study. By comparison, Moraczewski et al. [22] showed that the type of polymer has a significant effect on the persistence of plasma activation effects. Due to the complexity of plasma activation processes and the complexity of the physicochemical changes that occur, it can be suspected that not only will the type of gas used and the varying activation time have a significant impact on the disappearance of hydrophilic properties of the plasma-modified film, but also the type of substrate (film produced on the basis of polylactide with various additives used at the production stage). Moreover, thermal, thermo-oxidative, or thermo-mechanical degradation of the polymer may occur at the PLA processing stage, which will translate into different properties of the produced material [53]. Therefore, this paper aims to determine the efficiency of the plasma activation process depending on the material, demonstrate whether plasma activation itself leads to the appearance of signs of film aging by examining selected parameters such as color change, gloss, and tensile strength, and determine the effect of storage on the plasma activation durability of the various PLA-based films tested. The results of the study can be useful for better understanding of plasma activation processes, and have application significance, allowing possible prediction of changes occurring in plasma-modified materials.

2. Materials and Methods

2.1. Materials

Three biodegradable, commercially available PLA-based films were used for the study: Nativia BOPLA NTSS (Taghleef Industries GmbH, Holzhausen an der Haide, Germany), EarthFirst PLA BCP (Plastic Suppliers, Inc. EarthFirst, Ghent, Belgium), and EarthFirst PLA TCL (Plastic Suppliers, Inc. EarthFirst, Ghent, Belgium). All the films selected for the study are transparent, high-gloss materials dedicated to packaging applications for both food and non-food products. They can be used instead of petroleum-based plastics such as polypropylene, polyester, or polyethylene, using the same processing and packaging technologies. In addition to being biodegradable, all materials are also compostable according to the EN13432 norm and made from raw materials from renewable sources. The films were supplied for testing by the manufacturers in the form of A4 sheets. Detailed film characteristics are included in Table 1.

Table 1. The characteristics of the films used for the research (data provided by film manufacturers).

Film Name	Nativia BOPLA NTSS	EarthFirst PLA BCP	EarthFirst PLA TCL
Abbreviation used	NTSS	BCP	TCL
Thickness (μm)	20	50	50
Surface free energy (mJ/m^2)	37	38	38
Gloss (GU)	80 (45°)	125 (60°)	115 (60°)
Haze (%)	1.5	7.0	3.0
Tensile strength MD/TD (N/mm^2)	105/205	55/55	98/182

The film samples were conditioned in an air-conditioned laboratory room under standard ambient conditions (ISO 187:1990) (temp. 23 ± 0.5 °C, RH $50 \pm 1.5\%$) before and after plasma treatment, and were stored at all times under the same environmental conditions.

2.2. Preparing Materials for Testing—Plasma Activation of Samples

Both tested films were plasma-activated using a half-automated vacuum chamber with a Diener Nano low-pressure plasma system basic unit type D (Diener Electronic, Altensteig, Germany). A5 sheets were plasma-activated using 2 different gases: oxygen (100% O_2) and argon (100% Ar). The device operated at the settings identified in earlier work [19,20,37]

as optimal, namely: radio frequency 40 kHz, power 1000 W, plasma process pressure 0.4–0.5 mbar (40–50 Pa), gas supply process pressure 0.3 mbar (30 Pa), pumping off pressure 0.2 mbar (20 Pa), control pressure via gas, venting time 1 min, gas supply time 2 min, and plasma activation time 2 min. The temperature of plasma was close to room temperature, as in this process the temperature of the plasma is practically not increased compared to that of the non-excited gas. This means that the operating temperature was well below the glass transition temperature of PLA [54]. In consequence, it can be considered that the process should have only minimal to non-existent impact on the degradation of the material from temperature perspective.

2.3. Testing of Film Properties

2.3.1. Changes in Contact Angle and Surface Free Energy

The contact angles (CAs) of distilled water, diiodomethane 99% CH₂I₂ (Sigma-Aldrich, Taufkirchen, Germany), and ethylene glycol HOCH₂CH₂OH (Sigma-Aldrich, Germany) were measured according to the procedure specified in [20], using a DSA 100 drop shape analysis system (Krüss, Hamburg, Germany) with Tangent method 2. The contact angle measurements were assessed for the films before treatment, immediately after plasma activation, and after the specified sample storage times. The results presented are the average of five measurements.

The surface free energy (SFE) of the film, as well as its polar and dispersion components, were calculated with the Owens–Wendt method [55,56] according to Equations (1)–(3). This is one of the most commonly used methods, where CA measurements are made with two measuring fluids (polar and non-polar) to determine SFE, where water and diiodomethane, respectively, are commonly used as these fluids [57].

$$\gamma_s = \gamma_s^d + \gamma_s^p \quad (1)$$

$$(\gamma_s^d)^{0.5} = \frac{\gamma_d(\cos\Theta_d + 1) - \sqrt{(\gamma_d^p/\gamma_w^p)}\gamma_w(\cos\Theta_w + 1)}{2\left(\sqrt{\gamma_d^d} - \sqrt{\gamma_d^p(\gamma_w^d/\gamma_w^p)}\right)} \quad (2)$$

$$(\gamma_s^p)^{0.5} = \frac{\gamma_w(\cos\Theta_w + 1) - 2\sqrt{\gamma_s^d\gamma_w^d}}{2\sqrt{\gamma_w^p}} \quad (3)$$

where γ_s^d is the dispersive component of SFE of the examined films, γ_s^p is the polar component of SFE of the films, γ_d is the SFE of diiodomethane, γ_d^d is the dispersive component of diiodomethane SFE (=48.5 mJ/m²), γ_d^p is the polar component of diiodomethane SFE (=2.3 mJ/m²), γ_w is the SFE of water, γ_w^d is the dispersive component of water SFE (=21.8 mJ/m²), γ_w^p is the polar component of water SFE (=51 mJ/m²), Θ_d is the contact angle of diiodomethane, and Θ_w is the water contact angle.

2.3.2. Changes in Mechanical, Typographic, and Weight Properties of Samples

Determination of tensile properties of films before and after plasma activation was carried out according to the procedure specified in [37], using a static testing machine Roell (ZwickRoell GmbH & Co. KG, Ulm, Germany) and testXpert II software (V.5.61). Tensile testing with measurements of ultimate tensile strength were performed. Stress–strain analysis was conducted for the machine direction (MD) of the film. The reported results are the average for the five tested samples of each film.

Surface roughness was analyzed according to the procedure specified in [19], using a Sensofar Plμ Neox microscope (Sensofar Metrology, Terrasa, Spain). The analysis was performed on the surface in three areas and the average value is reported as the result.

Weight change analysis of the samples was performed according to the procedure specified in [19], using a Sartorius LE 225DOCE semimicrobalance (Sartorius, Göttingen,

Germany). Samples were weighed immediately before and after plasma activation, and the average of four determinations is reported as the mass change value.

2.3.3. Changes in Color and Gloss of the Sample

The changes in color and gloss of the film due to activation were determined according to the procedure specified in [37], using a spectrophotometer SpectroEye (GratagMacbeth/X-Rite GmbH, Neu-Isenburg, Germany) and triple angle gloss meter PicoGloss 503 (Erichsen GmbH & Co. KG, Hemer, Germany), respectively. CIELab measurements and the parameters light source D65, observation angle 2° , and no filter were used in the spectrophotometric measurements. Measurement angle of 20° was used for gloss measurements, as all films tested were high gloss materials exceeding 70 GU when measured for 60° geometry according to the EN ISO 2813 standard. The final values were calculated as the arithmetic means of 5 and 6 results, respectively.

2.4. Aging of Samples Due to Storage

Samples for hydrophobic recovery analysis were stored under standard conditions. The samples' storage time after plasma treatment was 1, 7, 14, 30, and 60 days. After each storage time, the contact angles of the 3 measuring liquids were measured and the surface free energy and its components were calculated using the Owens–Wendt method.

3. Results and Discussion

3.1. Changes in Film Wettability and Surface Free Energy—Effectiveness of Activation

The water contact angle (WCA) is the basic parameter used to characterize plasma-activated materials, determining their wettability. Although PLA is a relatively hydrophobic polymer with a static water contact angle of about 80° [58], all the films tested were hydrophilic substrates even before the plasma activation process (Figure 1), as the WCA value was less than 90° . Obviously, the smaller the WCA, the better the wettability [56], so it can be concluded based on the results obtained that NTSS film would potentially produce good quality prints even without modification, while BCP film would be more difficult and TCL film the most difficult for printing and finishing processes. Nevertheless, printing inks would also have a significant impact [37].

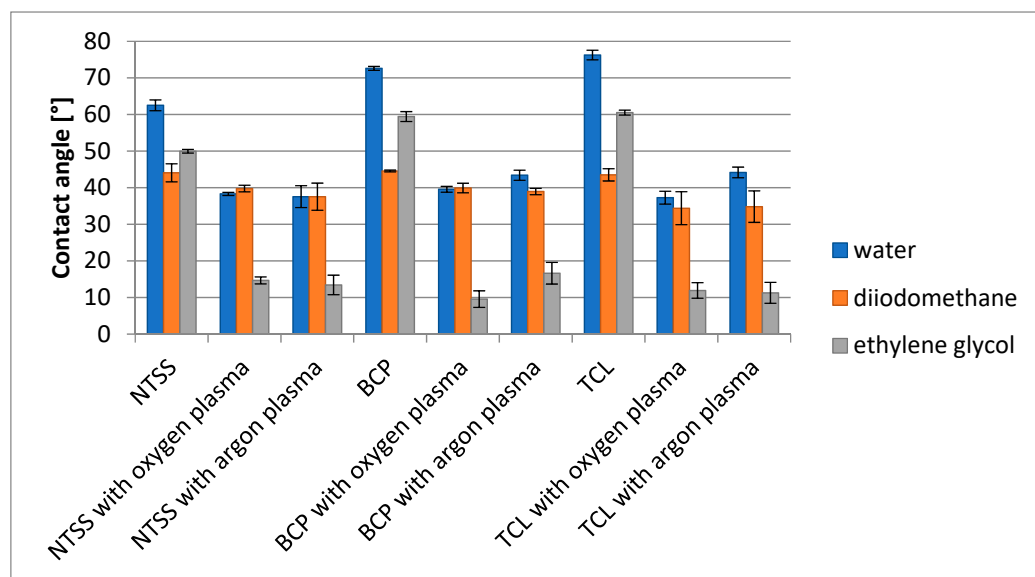


Figure 1. Contact angle of PLA film with water, diiodomethane, and ethylene glycol before and after plasma activation.

The type of material had no significant effect on the WCA value obtained by plasma modification of the films (Figure 1). As a result of both oxygen and argon plasma activation

for all the polylactide films tested, the WCA decreased significantly (from a value of 62.5–76.2 before activation to a value of 37.3–44.2), with the largest changes occurring for the TCL film (WCA reduction of up to about 50%) characterized by the initially largest contact angle, and the smallest for the NTSS film with the initially smallest contact angle (WCA reduction of 40%). A slightly higher efficiency of oxygen plasma compared to argon plasma was observed for all films. This may be due to the fact that the water contact angle depends primarily on the chemical structure and morphology of the polymer surface, and it was with oxygen plasma activation that the surface became more polar (Figure 2). Nevertheless, larger changes in roughness occurred with argon activation (Figure 3). Considering that the tested films are well-wettable materials, the roughness may have a noticeable effect on their water contact angle. With argon activation, physical etching occurs, rather than reactive etching as with oxygen activation, which may lead to increased surface roughness.

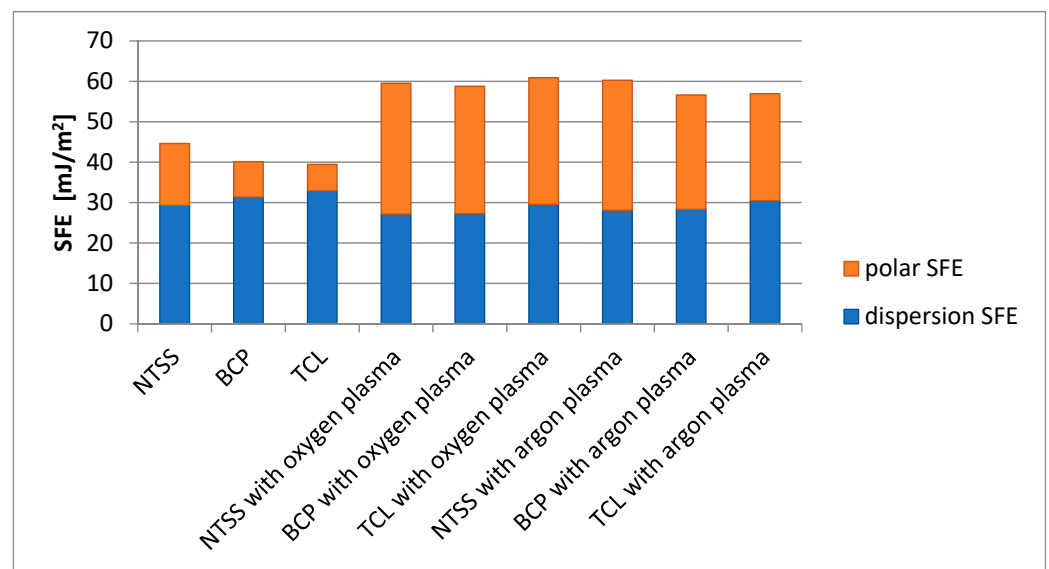


Figure 2. Changes in surface free energy of the film and its components due to plasma activation of the material.

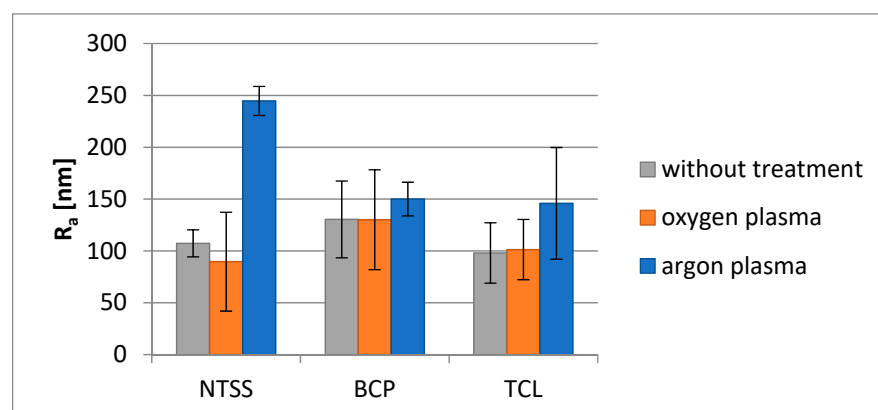


Figure 3. Film roughness before and after plasma activation.

Contact angle with diiodomethane is commonly determined alongside WCA, since knowledge of these two values makes it possible to calculate the value of surface free energy (SFE) and its polar and dispersion components [57]. There is a correlation between the components of SFE and the printability of materials, namely, the higher the polar component and the lower the dispersion component, the better the print quality [59]. In

contrast to WCA (40–51% reduction), diiodomethane CA did not decrease as significantly (10–20% reduction). In contrast, ethylene glycol CA had values reduced by up to 70–84% as a result of plasma activation. Such a large reduction in contact angle with ethylene glycol is due to the fact that it is a polar liquid like water, for which a significant improvement in substrate wetting was also observed as a result of its plasma activation, but with a lower surface tension (48.8 mN/m). Moreover, due to its much lower vapor pressure than water, the contact angle can be monitored for 30 min without the effect of evaporation, which can be a problem in WCA measurements [60]. Changes in the contact angle with diiodomethane, despite the fact that its surface tension (50.8 mN/m) is only slightly different from that of glycolic ethylene, are much smaller, due to the fact that it is a non-polar liquid with completely different wetting properties.

The type of material and SFE values of non-activated films had no significant effect on the SFE values of oxygen plasma-modified films (Figure 2). In the case of argon plasma activation for NTSS films, slightly better results were obtained. Moreover, for all materials regardless of the type of gas used for activation, the polar component of SFE increased significantly (110–378%), while the dispersion component of SFE decreased (4–13%). At the same time, regardless of the type of gas used, the largest change in the dispersive component of SFE was observed for BCP films, while the polar component of SFE was observed for TCL films. In addition, a significant change in surface polarity was observed for all films as a result of activation—the polar component of SFE was increased at least twofold (NTSS) and at most fourfold (TCL with oxygen plasma).

3.2. Changes in Selected Film Properties as a Result of Plasma Modification

Surface roughness and the degree of surface development have a significant impact on surface wettability and printability. An increase in roughness indicates that the surface of the substrate has developed, which should translate into better wettability and adhesion of ink or adhesive to the material [61]. However, significant changes in roughness can also indicate material degradation. Significant roughness changes (exceeding 100 nm) were observed only for films modified with argon plasma (Figure 3), which can be explained by slightly higher water contact angle values for such activated materials. The increase in roughness can be explained by the peculiarities of the argon plasma mechanism leading to significant etching of the surface during plasma interaction with the material [62]. Particular changes in this regard were observed for NTSS film (Figure 4), for which the mass loss is the highest (Figure 5). However, the results may also be influenced by the much smaller thickness of the material compared to the other two films. The effect of oxygen activation on roughness was negligible, which is consistent with the results obtained by Moraczewski et al. [22] and Więcek et al. [63]. This is due to the fact that during both oxygen and ambient air activation, the improvement in material wettability is due to the resulting polar functional groups containing oxygen, which interact strongly with water molecules, and not due to physical etching of the material surface as is the case during argon activation (Figure 4).

Another parameter to determine material degradation that is easy to measure, besides roughness, is the change in sample weight. A change in the mass of a sample can indicate the removal of contaminants from the surface of the material, oxidation of the material, and etching of the material [64]. In general, the mass is reduced as a result of defragmentation of the polymer and removal of degradation products to the environment. For all films, greater weight loss was observed as a result of oxygen activation than argon activation (Figure 5). This may be related to the fact that during oxygen plasma activation, products weakly bound to the sample surface are formed on the surface of the modified PLA [3,19]. Moreover, the largest weight changes were observed for NTSS film. This may be due to its much smaller thickness compared to the other films. For BCP and TCL films, the changes were at a similar level.

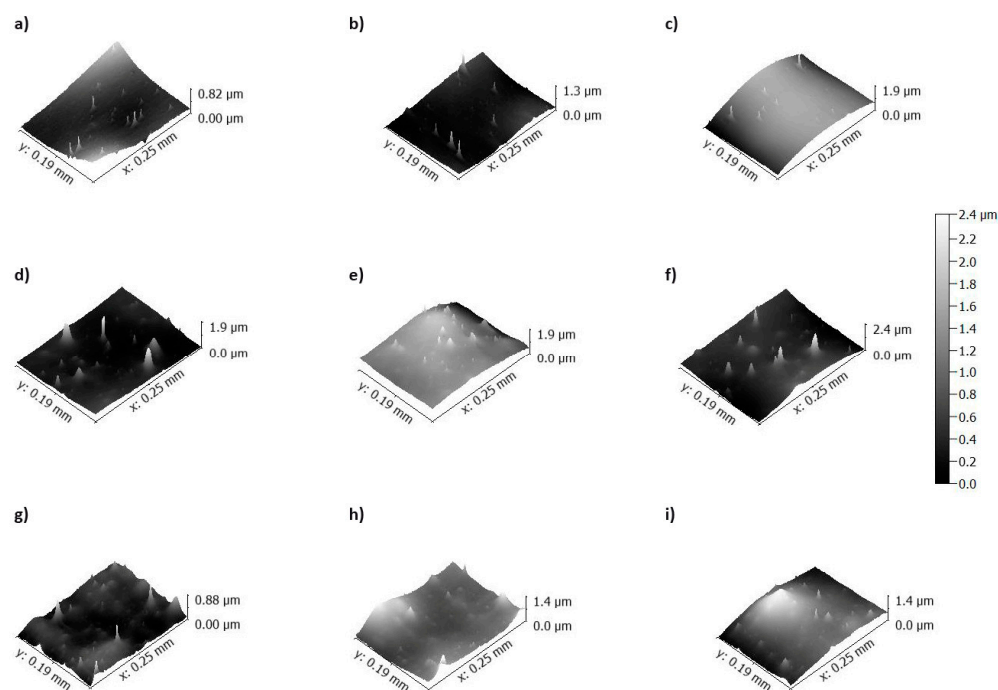


Figure 4. Surface topology of PLA films: (a) NTSS before plasma activation, (b) NTSS after oxygen plasma activation, (c) NTSS after argon plasma activation, (d) BCP before plasma activation, (e) BCP after oxygen plasma activation, (f) BCP after argon plasma activation, (g) TCL before plasma activation, (h) TCL after oxygen plasma activation, (i) TCL after argon plasma activation.

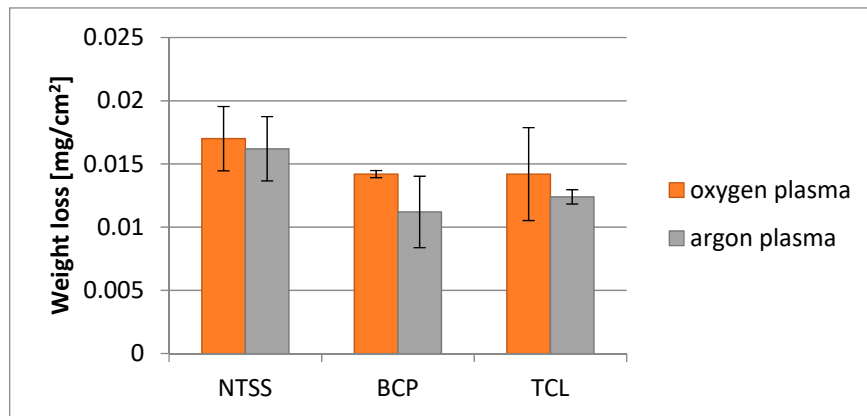


Figure 5. Weight change in samples due to plasma activation.

Another parameter indicative of material aging and degradation is the strength of plastics, most often determined by measuring tensile strength. The reduction in strength is a consequence of the tearing of polymer chains. It is known that chain crosslinking and chain rupture can occur simultaneously during plasma activation. Strong chain-break reactions cause etching of the polymer surface, while crosslinking inhibits this process [13].

Plasma activation caused a reduction in the tensile strength of all the oxygen-plasma-activated films (Figure 6). Considering the weight loss of the activated samples, it can be concluded that material degradation has occurred, translating into lower tensile strength values. However, it should be emphasized that the observed changes are not significant enough to affect the application of the materials. Moreover, it is worth noting that argon plasma has no significant effect on the tensile strength of the material. This is due to the fact that during argon activation there is crosslinking of polymer chains, while with oxygen activation the main mechanisms are surface oxidation accompanied by chain scission rather than crosslinking.

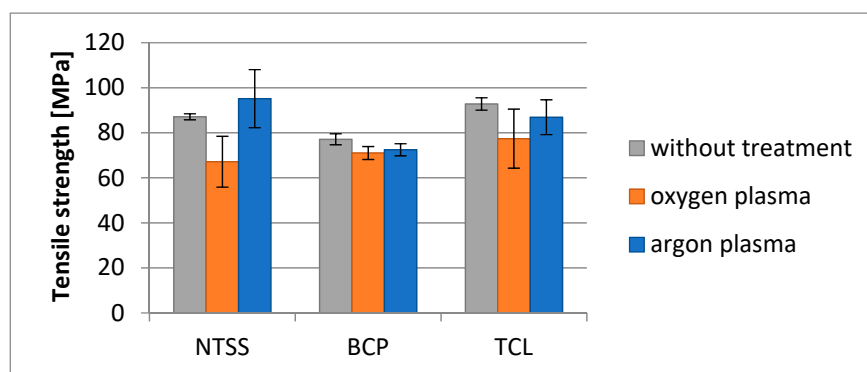


Figure 6. Changes in tensile strength in MD of the film due to plasma activation.

The higher tensile strength values of films activated by argon plasma compared to those modified by oxygen plasma can be explained by the changes that these gases cause in the material. Namely, if the plasma comes from an inert gas such as argon, it generally leads to crosslinking. With reactive gases such as oxygen, on the other hand, chemical changes on the surface predominate, such as the formation of peroxide, hydroperoxide, carboxyl, or hydroxyl groups [41]. A higher number of hydrophilic end groups is one of the factors accelerating degradation [58]. A previous study that also included XPS analysis [20] found that oxygen plasma activation led to the formation of a significant number of carboxyl groups, with an increase in activation time resulting in a higher proportion of hydroxyl groups. Determination of the detailed chemical changes taking place in the material is, however, beyond the scope of this paper.

Color change is another parameter showing the aging of plastics. Yellowing or browning of the sample is a natural reaction of polymers to both thermal and UV aging [65]. Nevertheless, none of the films tested showed significant color changes (Figure 7).

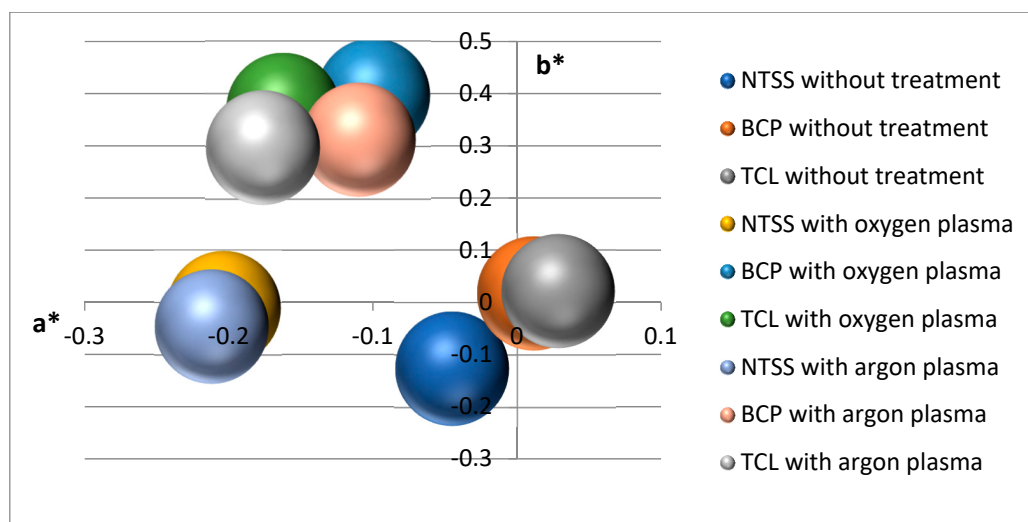


Figure 7. Color changes of the film due to plasma activation (the axes a^* and b^* describe the green-red and blue-yellow opponent colors, respectively).

The observed differences in film lightness (L^*) were within the range of measurement error. Moreover, as a result of plasma activation with both oxygen and argon plasma, the lightness did not change significantly for any of the materials tested. The color changes that were observed for all of the samples were not significant or noticeable to the naked eye, as evidenced by the very low values of the color difference ΔE of the non-activated and plasma-activated films. The highest ΔE values of 0.7 and 0.6 were recorded for BCP film activated with oxygen and argon plasma, respectively. For the other substrates, the ΔE

value was below 0.5, with similar slightly greater color changes occurring due to oxygen activation than due to argon activation. This can be justified by the fact that the color change is the result of a radical oxidation reaction [65,66].

In addition to color, gloss is an important parameter characterizing quality. All of the tested films are materials with very high gloss, although for NTSS film, much lower values were recorded for measurements obtained with a measurement geometry of 20° (Figure 8). Moreover, for this material, quite large differences were observed for the measured values in the transverse and longitudinal directions, both for non-activated samples and those subjected to different types of activation. NTSS films, unlike BCP and TCL films, gained luster as a result of activation. Nevertheless, for the latter, no negative effect of activation can be concluded based on the obtained results, as the recorded changes are considered insignificant and are invisible to the observer.

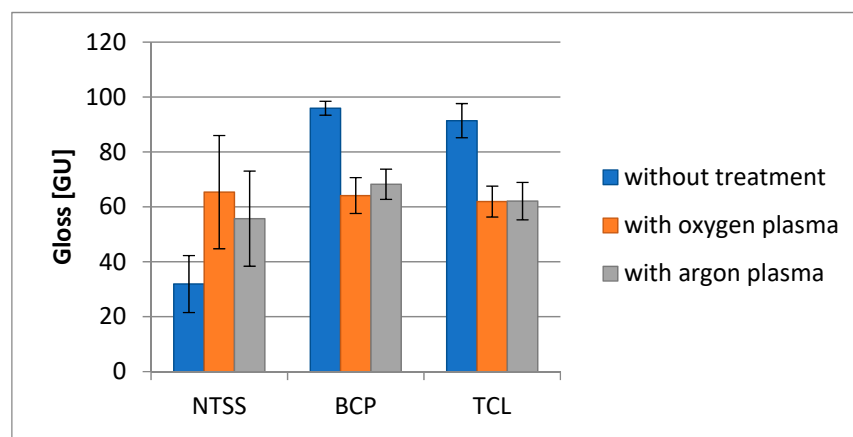


Figure 8. Changes in film gloss due to plasma activation.

The mechanism of film degradation depends on a number of interrelated factors [58], whereby additives used in film production and plasticizers can affect the degradation of the material, as confirmed by the results obtained in this study. Moreover, the degradation rate of PLA depends on its crystallinity, molecular weight and its distribution, morphology, rate of water diffusion into the polymer, and stereoisomer content [67]. When analyzing the ageing of the PLA films studied, we limited ourselves to only selected studies, choosing them based on the influence of a given parameter on the application aspects of the material and its relevance to wettability. However, the scope of material ageing studies could be significantly extended to include, for example, XRD, FTIR, XPS, or DSC analysis, which would be particularly relevant for, for example, medical applications of PLA, while this work focuses on applications related to further processing (printing, bonding, etc.). A particularly important parameter seems to be the change in PLA crystallinity and the chemical changes that occur as a result of plasma activation, both of which have a significant impact on degradation. Lower crystallinity, a more hydrophilic monomer, more hydrophilic end groups, and a more reactive hydrolytic group in the backbone will lead to an acceleration in polymer degradation [65]. Research in this area can be continued in future work on PLA ageing.

3.3. Aging of Samples Due to Storage

Ageing and hydrophobic recovery of PLA-activated samples were analyzed by evaluation of CA (Table 2) and SFE changes (Figures 9 and 10).

The course of changes in the water contact angle of the tested films depends on the type of plasma activation. For argon plasma activation, the changes are close to linear, with WCA increasing with storage time. At the same time, WCA values for BCP and TCL films are close to each other, while for NTSS films they are lower (Table 2). However, for oxygen plasma-activated films, changes are non-monotonic in nature; as a result of storage

for 14 days, after an initial slow increase in WCA, suddenly the WCA value increases very significantly, then decreases again. Such a course of changes is less frequently observed, but is consistent with observations made by other researchers [24,68–70]. The aging of the surface and the disappearance of hydrophilic properties of films modified with argon plasma are probably caused by the reorientation of the polar groups into the bulk polymer. By comparison, for oxygen-modified materials, it can be expected that, in addition to the aforementioned process of the reorientation of the polar groups, the mobility of small polymer chain segments into the matrix also occurs. Intense oxidation leads to the formation of small fragments loosely bound to the surface, and such a surface is more susceptible to aging precisely because of the migration of small fragments into the bulk. In addition to post-plasma rearrangement processes, storage can lead to migration and diffusion of low molecular weight additives that were introduced into the polymer, from the bulk towards the surface, creating a weak boundary layer [20]. It can be speculated that such processes are responsible for the changes in the form of a significant increase and subsequent decrease in the water contact angle between the 14th and 30th days of sample storage. Moreover, it can be speculated that the non-polar environment in which the samples were stored and the average ambient humidity (RH 50%) further induced rather than inhibited the aging processes taking place [71]. Analyzing the obtained data, it can be concluded that the type of film has a significant effect on the course of hydrophobic recovery. Moreover, for NTSS and TCL films, the value of WCA after storage for 60 days was almost the same for samples activated with different types of plasma, despite previous significant changes in these values.

Analyzing CA with diiodomethane, it can be seen that as the storage time increases (for periods of 30 and 60 days), the values, regardless of the type of film and gas used for plasma activation, begin to become increasingly similar to each other (Table 2). In addition, the smallest changes in CA with diiodomethane during storage are observed for BCP film, while the largest changes are observed for TCL film.

Table 2. Contact angle values for water, diiodomethane, and ethylene glycol of samples after plasma activation and during storage.

	After Treatment	After 1 Day	After 7 Days	After 14 Days	After 30 Days	After 60 Days
water contact angle [°]						
NTSS with oxygen plasma	38.3 ± 0.4	38.8 ± 2.4	41.8 ± 0.7	56.0 ± 1.1	51.3 ± 2.0	48.7 ± 0.6
BCP with oxygen plasma	39.6 ± 0.8	42.6 ± 0.6	43.4 ± 0.8	64.8 ± 1.7	54.4 ± 2.4	58.0 ± 2.2
TCL with oxygen plasma	37.3 ± 1.7	42.3 ± 0.4	43.1 ± 1.5	63.3 ± 1.2	53.2 ± 3.1	56.7 ± 2.5
NTSS with argon plasma	37.6 ± 3.0	42.5 ± 2.5	45.3 ± 1.7	42.7 ± 0.9	46.5 ± 0.8	48.2 ± 0.9
BCP with argon plasma	43.4 ± 1.4	47.7 ± 2.3	48.2 ± 0.9	48.5 ± 2.3	51.5 ± 1.7	53.4 ± 1.9
TCL with argon plasma	44.2 ± 1.5	46.1 ± 1.1	48.2 ± 0.7	49.1 ± 1.0	48.8 ± 0.5	55.5 ± 2.9
diiodomethane contact angle [°]						
NTSS with oxygen plasma	39.8 ± 0.9	40.7 ± 1.6	40.3 ± 0.1	42.7 ± 2.4	37.9 ± 1.9	44.4 ± 1.3
BCP with oxygen plasma	39.9 ± 1.3	40.2 ± 0.9	41.6 ± 0.9	42.6 ± 0.6	40.7 ± 0.6	42.2 ± 0.6
TCL with oxygen plasma	34.4 ± 4.5	39.9 ± 1.3	42.6 ± 0.5	40.6 ± 0.9	41.8 ± 0.4	43.8 ± 1.1
NTSS with argon plasma	37.6 ± 3.7	37.2 ± 4.9	41.4 ± 1.2	40.7 ± 0.9	41.6 ± 0.6	43.0 ± 0.5
BCP with argon plasma	39.0 ± 0.9	40.5 ± 2.6	39.3 ± 0.7	39.6 ± 1.3	41.8 ± 0.5	42.2 ± 0.5
TCL with argon plasma	34.8 ± 4.3	37.9 ± 2.2	41.5 ± 0.5	39.6 ± 0.7	41.3 ± 0.6	44.9 ± 0.2
ethylene glycol contact angle [°]						
NTSS with oxygen plasma	14.7 ± 1.0	15.5 ± 0.5	16.0 ± 1.0	34.5 ± 0.4	23.8 ± 2.8	25.2 ± 1.3
BCP with oxygen plasma	9.6 ± 2.3	11.1 ± 1.3	14.2 ± 1.1	32.2 ± 1.5	23.5 ± 1.6	29.4 ± 1.5
TCL with oxygen plasma	11.9 ± 2.1	13.7 ± 1.3	17.7 ± 1.4	33.9 ± 1.6	23.6 ± 2.6	33.8 ± 1.6
NTSS with argon plasma	13.4 ± 2.7	10.5 ± 2.0	12.5 ± 1.5	18.1 ± 1.8	22.7 ± 2.3	20.8 ± 1.8
BCP with argon plasma	16.6 ± 3.0	16.3 ± 3.2	19.4 ± 1.0	21.3 ± 2.2	24.5 ± 2.4	26.2 ± 1.0
TCL with argon plasma	11.3 ± 2.9	13.9 ± 2.1	22.3 ± 1.3	23.0 ± 1.5	27.2 ± 0.8	31.5 ± 1.7

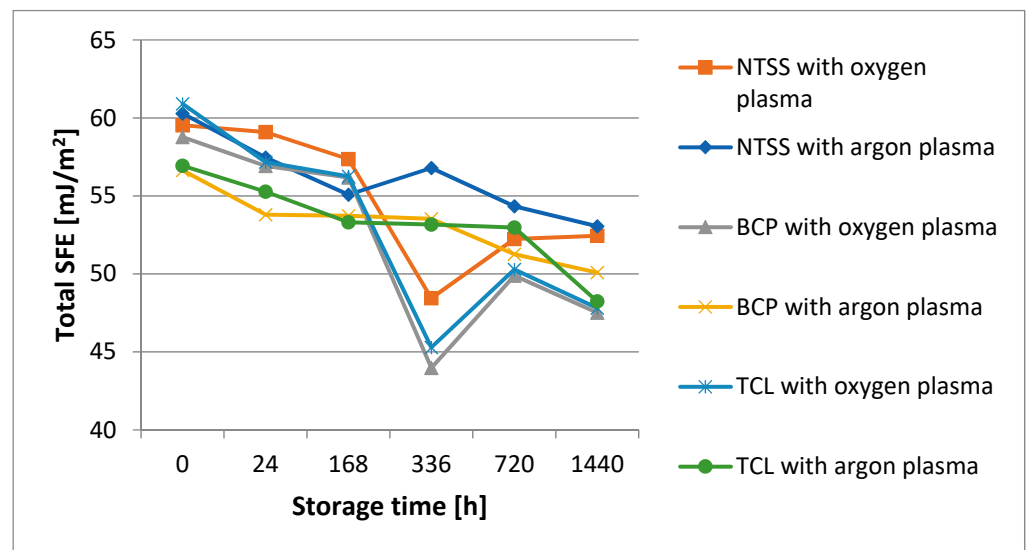


Figure 9. SFE changes due to storage.

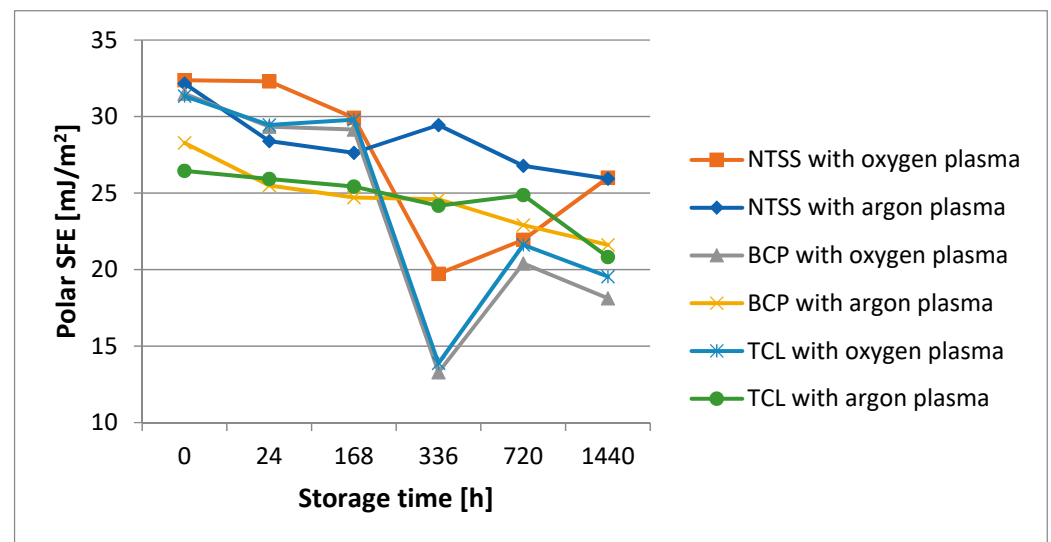


Figure 10. Changes in the polar component of SFE due to storage.

The course of changes in the contact angle with ethylene glycol is similar to that observed for water, but with significantly lower values (Table 2). It is worth noting that the changes significantly depend on the type of gas used for plasma activation, regardless of the type of liquid used for contact angle measurements. In the case of oxygen plasma-activated samples, a sharp decrease in wettability was observed on day 14 and its subsequent improvement on day 30 of storage, as assessed by both ethylene glycol and water contact angles. In contrast, the changes occurring for samples modified with argon plasma have a completely different course, i.e., close to a linear increase in values. In conclusion, it can be said that the type of gas and the type of film have a significant effect on the obtained ethylene glycol CA values, although in this case it is not possible to indicate the film for which the values would be clearly lower, as in the case of water.

Analysis of the course of aging of plasma activation effects based on the SFE value confirms the conclusions drawn from the contact angle analysis. Namely, the type of gas used for plasma activation has a significant effect on the course of changes, while the type of film has a slight effect, although the NTSS film is more resistant to aging than the other films tested (Figure 9).

In addition, for all oxygen plasma-activated films, the lowest SFE values were recorded after 14 days of storage, and increased with longer storage time. This is closely related to the previously discussed changes in WCA with polar liquids, where a sudden peak in values was observed after 14 days, and is also consistent with the changes in the polar component of SFE (Figure 10). It is noteworthy that the reduction in SFE after 14 days is so significant that it is only slightly higher than the SFE of unmodified films (higher by 3.82, 3.85, and 5.84 mJ/m² for NTSS, BCP, and TCL films, respectively). By comparison, after 30 days it already increases to a value of about 50 mJ/m² for all the films tested, which again should be satisfactory from the point of view of further applications of the materials (e.g., bonding and printing).

4. Conclusions

The study determined the effect of the type of material, or more precisely, the effect of the manufacturing process and the additives used to produce PLA-based films, on the plasma activation efficiency of the film assessed by improved wettability, and on selected properties of the film that may indicate its aging and susceptibility to hydrophobic recovery as a result of storage.

The type of material was found to have a significant effect on the water contact angle of unmodified films, while it did not significantly affect the WCA value after plasma modification. For all polylactide films, a significant reduction in WCA was observed following plasma activation with both oxygen and argon plasma.

Activation for all films resulted in the conversion of weakly polar surfaces into polar surfaces, with changes in the values of the polar and dispersion components of SFE depending on the type of film. For oxygen activation, similar total SFE values were obtained for all films, while they were slightly different from film to film when using argon plasma activation.

Aging effects due to plasma activation were presented for all films tested, and no negative impact of the activation on film properties was observed. Plasma activation—by either oxygen nor argon—did not lead to significant changes in color or gloss that lowered the quality of the films, nor to a significant reduction in tensile strength that further affected refining or printing processes. Conversely, the observed changes in sample weight and roughness are closely related to the type of film and the type of gas used for activation, and are consistent with the specific nature of a given plasma.

Based on the results, the type of film was found to affect the course of hydrophilic recovery, which was confirmed by the analysis of contact angle, as well as SFE results and those of its components. The aging course of modified films depends on the type of gas used for activation. The changes—an increase in the water contact angle, as well as a decrease in the SFE and its polar component—for films modified with argon plasma typically have a monotonic course, while those for films modified with oxygen plasma are non-monotonic with a sudden peak or decline, respectively, observed at 14 days of storage. Such a course of hydrophobic recovery of PLA films modified by oxygen plasma can be a subject of further detailed studies in this area to explain the processes occurring during this phenomenon. However, from an application perspective, it is important to note that storage shorter than or equal to 7 days does not cause significant hydrophobic recovery, regardless of the type of plasma activation. Although the trend of changes depends on the type of gas used for activation, the magnitude of changes depends on the film.

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