# Storage stability of the oxygen plasma-modified PLA film

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**Abstract.** Polylactide (PLA) is the second most popular biodegradable plastic in the world currently and is a growing alternative to traditional plastics. Similar to most of the polymers, PLA requires surface activation before further processing, among others plasma activation. Hydrophobic recovery is a major problem of plasma-treated polymer; therefore, authors performed extensive research on the storage stability of the oxygen plasma-treated PLA film. For that purpose the low-temperature plasma with oxygen was applied on PLA film and its influence on surface-free energy (SFE) and contact angle (CA) with water, diiodomethane and ethylene glycol was analysed together with their subsequent hydrophobic recovery during storage. In addition, chemical changes were measured with X-ray photoelectron spectroscopy (XPS), mass loss was determined by weight measurement and the surface topography was measured by means of confocal microscopy. The best wettability of the substrate was observed after 2 and 10 min activation time, which was confirmed by the lowest CA, as well as the highest values of SFE. The degree of hydrophobic recovery depends on treatment time and is most stable for 6 min treatment. The PLA hydrophobic recovery reached its peak after a storage period of 14 days, after which the hydrophilic properties improved again, regardless of the activation time.

**Keywords.** Ageing; hydrophobic recovery; polylactide; plasma treatment; wettability.

## 1. Introduction

Plastics are the most commonly used packaging material [1]. Despite its many packaging advantages, plastic waste is a major worldwide problem [2]. Polylactide (PLA) is one of the most popular biodegradable plastics with both medical and industrial applications, and its consumption is still increasing [3–10]. PLA is not only a biodegradable material, but also compostable, obtained from natural raw materials (e.g., corn starch, sugarcane, potatoes, beetroots), and can be 'green' alternative to conventional plastics [11]. PLA, like most other biodegradable and synthetic plastics, requires modification of the surface layer before further processing (coating, gluing, metallization, printing, etc.) [12–15]. Due to the lack of reactive groups of chain branches, as a chemically inert material it is quite difficult to modify [16,17], although all the techniques available for plastics can be used: corona treatment, flame, laser, ultraviolet light, γ-ray, ion-beam techniques or chemical modification [13,14].

Plasma activation is widely used due to high repeatability and process stability, as well as the possibility of achieving differential effects due to proper selection of gas composition, pressure and feeding system parameters. Moreover, plasma treatment is environmentally friendly, contrary to traditional wet chemistry modification [18–22]. Due to the thermal properties of the polymers, lack of resistance to high temperatures, their modification is mainly carried out using cold plasma [23–25]. Modification of the top layer of polymers is performed in order to: produce on its surface functional groups, change the surface-free energy (SFE), improve the surface hydrophilicity or obtain hydrophobicity, modify the surface morphology and the crosslinking of the surface, remove impurities, increase biocompatibility [14,26–28].

Plasma activation is carried out in different environments [21,23,29]. A significant number of publications refer to atmospheric or low pressure air plasma on PLA [3,13,29–36]; however, other gases such as carbon dioxide [37], sulphur hexafluoride [38], helium [32,33,36,39–41], nitrogen [32,39–41], argon [32,36,41,42] and oxygen [39,40,43,44] are also used for PLA modification and have been widely studied.

Due to the increasing use of PLA in the packaging industry and its ever-increasing consumption, further research seems necessary. In this study, oxygen has been used, as it is a cheap, commonly available gas and one of the most widely used in plasma cleaning technology [45]. Moreover, the oxygen plasma allows the surface to be cleaned and effectively increases the SFE of the material.

The oxygen plasma treatment was studied by others [39,40,43] and all of them have shown that it gives good results for PLA film modifications, it has significant impact on the geometric structure and chemical composition of the surface, wettability and SFE of tested PLA. However, the activation times used in the research were usually very long (3, 10 and 30 min [39], 10, 20, 30 and 40 min [40] and 40 min [43], respectively). What is more, other process parameters influencing the effect of modification were also different from those used by us, which causes that the results presented in the article significantly supplement the available knowledge on plasma activation. Moreover, according to our knowledge, there are no other such extensive studies on the influence of storage time on changes in CA and SFE of modified PLA films.

During oxygen activation, multiple different groups of oxygen atoms are formed on the surface of modified material, leading to improvement of hydrophilicity of the material or even to change of its properties from hydrophobic to hydrophilic [46,47]. Plasma activation in the oxygen and air environment has a significant impact on wettability of the surface, as a result of polar functional groups containing oxygen, which interact strongly with water molecules. The introduction of oxygen groups is accompanied by simultaneous surface digestion [25,26]. However, it should be emphasized that in many works only a slight influence of aerobic plasma on roughness was observed [39,48,49].

Excessive activation is not necessary or advisable, it can even lead to material destruction and significant deterioration of properties. Moreover, it is not economically justified. For example, excessive oxidation on the polymer surface causes oxidative chain-scissions, which generate low-molecular weight fragments that may weaken the strength of adhesive bond [27,50]. Another important reason for optimization of this process is to reduce weight loss associated with surface oxidation or digestion [51,52]. Therefore, it is important to optimally select the activation process parameters for given material type in order to eliminate too long activation times and high power levels. Previous studies [53,54] identified an optimal pressure level for an aerobic plasma of 50 Pa, while the present study will examine in detail the influence of activation time on modified material properties and the selection of optimal conditions to obtain the highest possible improvement in material hydrophilicity while reducing processing time.

Additionally, extended activation time may result in a higher tendency towards ageing of the surface due to migration of small particles into the interior [50,55]. Generally, during ageing the materials subject to plasma activation undergo a process of disappearance of the hydrophilic properties acquired as a result of modification. This phenomenon is referred to as hydrophobic recovery and is a result of recombination of active groups, diffusion and chains relaxation, and reorientation of polar chemical groups into the bulk [18,56–59]. On some polymers activation may last for weeks, while on others the activation effect will disappear after a few days or even several hours [23,46,60]. The course of changes may also vary depending on the type of material and plasma used [20,43,61]. The ageing factors during storage are: type of plasma treated polymers (its chemical structure, crystallinity, thickness, surface morphology), kind of plasma gas, the treatment level, the storage environment (water, air) and conditions (temperature and humidity) [3,6,20,27,39,46,50,56,59,60,62–67]. The course of the changes depends on the type of material, the type of activation used and other mentioned factors and is still not fully known. Therefore, it seems important to determine the course of hydrophobic recovery for PLA studied by us, where the activation level of the material is taken into account as a variable factor influencing ageing.

In this study we investigated the influence of activation time on the change of hydrophilic properties, morphology and topography of samples and surface chemistry in order to obtain the optimal modification time of PLA. Hydrophilic properties were determined by CA for three different fluids (water, diiodomethane, ethylene glycol) and SFE with its polar and dispersional components. Morphology and typography of samples were investigated using microscopic and surface chemistry tests evaluated with X-ray photoelectron spectroscopy (XPS). In addition, we have studied in detail the effect of the activation time on the ageing of modified material and the return of hydrophobicity. The analysis of our own results refers to the results obtained for other plasma activation types and compares their effectiveness with each other. In addition, the results of the tests allowed identification of optimal activation time, which will enable the greatest possible change of hydrophobic film properties into hydrophilic ones, while minimizing sample failure and maintaining high resistance to hydrophobic recovery, knowledge useful in production processes.

## 2.  Materials and methods

### 2.1  *Materials*

Commercially available PLA film Nativia BOPLA NTSS (Taghleef Industries) was used, as it is a biaxially oriented, biodegradable and compostable film. The samples were prepared from A4 sheets 20 μm thick and were cut to dimension of $105 \times 148$ mm, and their properties were following as provided by the manufacturer: SFE of untreated films 37 mJ m$^{-2}$, gloss 80 gloss units (G.U., 45°), haze 1.5%, water vapour permeability 440 cm$^3$ m$^{-2}$ per day, oxygen permeability 1100 cm$^3$ m$^{-2}$ per day, tensile strength machine direction (MD) = 105 N mm$^{-2}$ and transverse direction (TD) = 205 N mm$^{-2}$, elongation at break MD = 185%, TD = 85%. The film samples were conditioned in standard ambient conditions (ISO 187:1990)

(temp. 23 ± 0.5°C, HR 50 ± 1.5%) before treatment and were stored after treatment in the same way. The samples storage time after treatment was 24 h, 7, 30 and 60 days. The wettability was investigated after storage time, as well as before and immediately after treatment.

## 2.2 Plasma treatment

Cold, low pressure oxygen plasma (100% $O_2$) was applied to PLA films in a vacuum chamber with Diener Nano System (Diener Electronic, Germany). The device was working with the following settings: pressure 50 Pa, radio frequency (RF) 40 kHz. The control pressure was set to 'via gas' and constant gas supply time was 2 min. The exposure time was variable—settings of 2, 4, 6, 8 and 10 min were used.

## 2.3 Analysis of CA and SFE

The CA of three liquids: distilled water, diiodomethane 99% $CH_2I_2$ (Sigma–Aldrich, Germany) and ethylene glycol $HOCH_2CH_2OH$ (Sigma–Aldrich, Germany) were measured. These fluids are characterized by different surface tension values (at 20°C) equal to 72.8, 50.8, 47.7, respectively [68]. DSA 100 (Krüss, Germany) was used for drop shape analysis and measurement before modification, immediately after modification and after subsequent storage. For unmodified samples, the test was limited to one measurement, since according to the published results [59,65,69] the CA of unmodified material does not change over time. The needles of 0.5 mm diameter were used to deposit the sessile liquid drops on PLA film. The CA was measured on static drops using Tangent method in constant environmental conditions and temperature 23 ± 1°C. The measurements of CAs were repeated in five different locations of each sample and the reported values are their mean [42,70]. The SFE of PLA film was calculated by Owens–Wendt method [3,71,72].

## 2.4 Surface chemistry and morphology investigation

The study of chemical changes after plasma treatment was performed for untreated and 2 and 10 min treated samples using XPS method with 100 SSX ESCA Spectrometer (Surface Science Laboratories Inc., USA). The following settings were used: monochromatic Al Kα radiation, X-ray emission at 9 kV and 19 mA, measuring spot sizes 0.25 × 1.0 mm, 0.15 × 0.8 mm and 0.15 × 0.1 mm. In the spectrum obtained, only carbon and oxygen signals were found. The results were analysed using CASA software.

For all PLA films in this study, both treated and untreated, the surface topology and roughness were measured using Sensofar Plµ Neox microscope (Sensofar

Metrology, Spain). The 50 × 0.95 N lens was used to obtain surface topography images using white light, threshold 15% and layer thickness of 15.2 µm. The topographic image resolution was 768 × 576 pixels (area of 254.64 × 190.90 µm$^2$). The results were calculated as an average of measurements in three different spots.

Additionally some sample weight changes analysis was done. Sartorius LE 225D-OCE (Sartorius, Germany) semi-microbalance was used to measure the weight of samples before plasma treatment and immediately after. The samples in size 50 × 50 mm were weighed. The reported values present the weight loss and are calculated as an average for four samples.

## 3. Results

### 3.1 Analysis of CA and SFE

One of the basic tasks of activation is to improve wettability of the material and change its hydrophobic properties into hydrophilic ones. Hydrophilicity is a feature that is required for coating, metalizing, laminating, gluing or printing. The basic parameters used to assess the change of wettability are the measurement of CA with different polar and non-polar fluids and the measurement of SFE. The results of CA change in water, diiodomethane and ethylene glycol are shown in figure 1, while figure 2 presents the changes of SFE and its components: dispersive and polar.

PLA film before plasma treatment exhibits a water CA of 62.5°, which is quite low compared to values of untreated PLA reported in the literature (quite hydrophobic material with CA app. 70–80°) [29,39]. However, even lower value (60.4) was previously reported [6]. Initial high CA values indicate the non-polar character of the PLA surface. After plasma treatment CA value decreased and amounted to 37.0–46.3°, depending on treatment time. It indicates that a
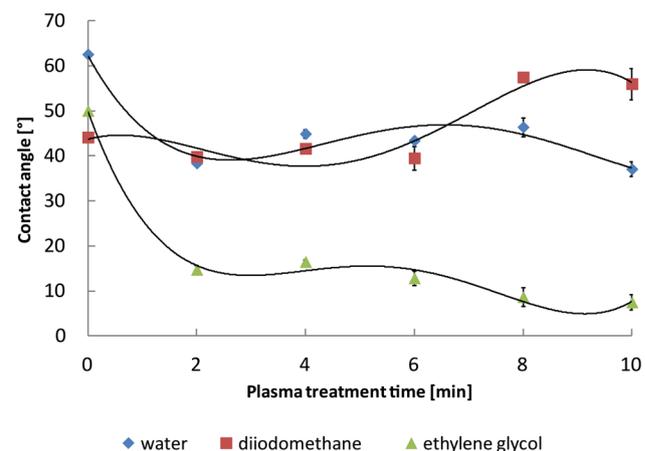


**Figure 1.** Changes in contact angle values as a function of plasma treatment time for water, diiodomethane and ethylene glycol.
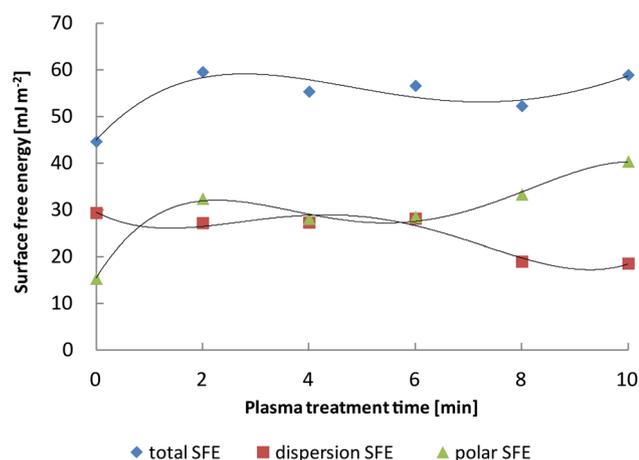
**Figure 2.** SFE and value of its components (polar and dispersive) as a function of plasma treatment time.

substantial modification of the PLA surface occurs during the plasma process, regardless of the activation time. The smallest values were obtained for activation lasting 10 ($37.0 \pm 1.61$) and 2 min ($38.3 \pm 0.44$). The lowest value obtained for an extended activation time may result from the change in topography and the highest roughness of this sample, and the case of 2 min activation may be explained by the functionalization of the surface (increased proportion of carboxyl groups).

The CA was reduced from 26% to over 40% as a result of PLA modification with oxygen plasma. Referring to the results obtained for the same material by means of corona activation, the CA of water was reduced by only a dozen percent [6], which proves that the plasma method is much more effective in relation to the corona method. Referring to the results for other gases and other plasma types, it can be stated that the results obtained for the oxygen activation used by us are comparable or even better than those obtained for the plasma with such gases as air, argon, helium, nitrogen and carbon dioxide [3,32,33,35,39,42]. However, at this point it should be noted that the results obtained are determined by the conditions of modification, for example, the results of air dielectric barrier discharge plasma can be either better, worse or comparable to ours [3,33], another example is the results for oxygen plasma [39]. Good results for oxygen activation can be explained by the fact that when activating with oxygen, different groups containing oxygen atoms are formed on the surface of the modified material. The created polar functional groups containing oxygen interact strongly with water molecules, which has a positive effect on the wettability of the surface with polar liquids, such as water.

Oxygen plasma activation caused a significant decrease not only in the water CA but also in the CA of ethylene glycol (figure 1). It was reduced by approximately 70–85%, while the longer modification time resulted in a further decrease of its value for polar liquid. For non-polar liquids (diiodomethane), the CA decreased for 2–6 min treatments.

The increase in the activation time, on the other hand, resulted in an increase in this value in relation to the initially measured value for the inactivated sample. This indicates an increase in the dispersive nature of substrate due to longer activation. Plasma treatment for 10 min made PLA surface more hydrophilic and more oleophobic [73].

Moreover, oxygen plasma treatment caused a significant increase in wettability, which was manifested also by an increase of SFE. The results of the tests showed the highest SFE value with activation lasting 2 min (SFE = 59.5 mJ m$^{-2}$) and only slightly lower at activation of 10 min (figure 2). The values obtained are high and should ensure good wettability and adhesion in finishing processes [45]. Moreover, the obtained values are slightly higher than those recorded in the literature for PLA plasma activation using other gases or other plasma activation parameters [3,29,37,42]. Only the use of much extended activation times (30 min) or very aggressive conditions of spot activation allows to obtain better results [3,29,39]. In addition, plasma allowed a significant increase in SFE compared to corona activation, where the value increased only slightly from 32.5 to 39.2 mJ m$^{-2}$ [6] and was still lower than the value for our material before modification.

It should also be emphasized that the observed changes in SFE result from the decrease in its dispersion component and increase of its polar component (figure 2). Moreover, for 10 min treatment the polar component value was more than twice higher than the dispersion component. As a result of treatment, the strongly non-polar surface was changed into a polar surface [72]. The material obtained this way is characterized by very good wettability, high hydrophilicity and usefulness for further processing, such as coating, gluing, printing, etc.

### 3.2 *Surface chemistry, topography analyses and weight changes*

One of the aims of plasma activation is chemical functionalization of its surface. Table 1 presents changes occurring in the surface layer of the polymer for untreated and oxygen plasma-treated PLA films with treatment times that allowed to obtain the best surface wettability results—two different treatment times met the criteria: 2 and 10 min.

**Table 1.** Concentration of the different chemical bonds on the surface of PLA films untreated and treated with oxygen plasma.

|  | C1s components (%) | | |
| --- | --- | --- | --- |
|  | C–C/C–H 285.0 eV | C–O 286.5 eV | O–C=O 289.0 eV |
| PLA untreated | 48.06 | 31.57 | 20.38 |
| PLA treated 2 min | 37.19 | 24.44 | 38.37 |
| PLA treated 10 min | 27.74 | 34.77 | 37.49 |

Large differences were observed between C1s core-level spectra of untreated and treated PLA films. Through XPS peak fitting it was shown that the concentration of C–C and C–H functional groups is decreased from 48.06% before treatment to 37.19% and to 27.74% after plasma treatment for treatment time 2 and 10 min, respectively. Moreover, the main group that contributed to the increase of oxygen contents was carboxyl group in the case of 2 min exposure time. In the case of plasma activation lasting 10 min, a large number of carboxyl groups appear on the surface and the number of hydroxyl groups increases. It was found that the exposure time had a significant influence on the concentration of oxygen groups in the top surface layer. The obtained differences in the number of carboxyl and hydroxyl groups are represented by the components of SFE. Although the total SFE values for samples activated for 2 and 10 min are similar, a sample with a longer activation time has a significantly higher polar component of SFE.

As a result of oxygen plasma activation, surface etching occurs leading to chain breakage, volatile products and degradation of the material [28], which is associated with weight loss. The results of mass loss tests are presented in table 2. As a result of an increase in the activation time an increase in sample weight loss was observed, which indicates higher material degradation. The course of changes is linear and well described in equation: $y = 0.63x - 0.247$ ($R^2 = 0.9834$). However, regardless of the activation time, the weight loss was large. Even at the shortest time it amounted to 0.6–0.8% of the mass of the untreated sample, while at the longest time it increased to 4.8–5.1%. Moraczewski *et al* [39] likewise observed a large loss of sample thickness, which increased with the increase of activation time up to 220 nm. Our results are even higher (120–950 nm depending on the activation time, assuming PLA density is 1.25 g cm$^{-3}$). Such a large depth of oxidative degradation (etching) may be due to the thickness of the material, which is much smaller, making the sample more sensitive to modification and material changes. Oxygen is a reactive gas that leads to the occurrence of significant ablative processes on the material surface [39,50]. For comparison, air atmospheric plasma on PLA led to relatively low weight loss,

smaller than 0.05% [3]. It is well known that during oxygen plasma activation, products weakly bound to the surface of the sample are formed on the modified surface of PLA. What is more, with increasing modification time, larger amount of degradation products appear on the material [39]. It is therefore important to find the shortest possible time to achieve a significant improvement in wetting without unduly altering the surface morphology.

Plasma activation leads to changes in surface topography. They can be a result of both chemical erosion by atoms as well as physical erosion by ions. The changes occurring on the surface as a result of plasma activation are presented in the form of roughness measurement results in table 2. The roughness initially decreases (for an activation time of 2 min), which may be the effect of removing contaminants from the material surface as a result of activation. Then the roughness increases with longer treatment time in relation to the value obtained for unmodified material. Higher roughness and corrugation of the samples indicate greater etching. The observed increase in roughness values (above 100 nm) may influence the CA value [35,71,74]. Increased roughness leads to an increased CA with water, as we observed for activation time such as 4, 6 and 8 min compared to 2 min treatment.

## 3.3 *Ageing and hydrophobic recovery*

Hydrophobic recovery and ageing of PLA-activated samples under various conditions were analysed by evaluation of CA and SFE changes. The results are shown in figures 3–5. As a result of storage, the plasma-activated PLA gradually lost its hydrophilic properties, with the course of changes depending on the activation time (figure 3). Such hydrophobic recovery results from the removal of polar groups from the surface or their movement into the bulk of the polymer [26,45,56,72]. As a result of oxygen activation, bond breaking and chain scission occurs, which lead to the formation of low-molecular-weight oxidized material on the surface of the material. This low-molecular-weight oxidized material can more readily diffuse into the bulk

**Table 2.** Mass changes and surface roughness ($R_a$) depending on plasma treatment time.

| Plasma treatment time (min) | Mass loss (mg cm$^{-2}$) | | Surface roughness (nm) | |
|---|---|---|---|---|
| | Average | Deviation | Average | Deviation |
| 0 | — | — | 107.32 | 13.07 |
| 2 | 0.0170 | 0.0025 | 89.64 | 47.64 |
| 4 | 0.0394 | 0.0020 | 158.74 | 45.36 |
| 6 | 0.0682 | 0.0048 | 145.28 | 63.55 |
| 8 | 0.0826 | 0.0008 | 116.42 | 54.38 |
| 10 | 0.1214 | 0.0042 | 148.67 | 75.56 |

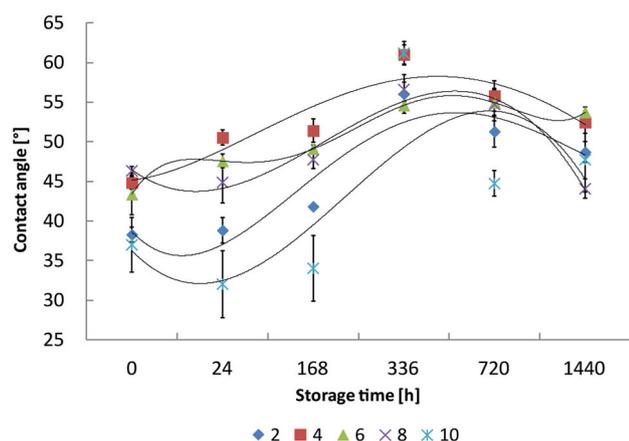*Bull. Mater. Sci.*    (2021) 44:79



**Figure 3.** Changes in water contact angle as a function of the treatment and storage time.

of treated polymer [20,58]. At much longer modification times, low-molecular-weight oxidized material is removed [39].

The smallest and mildest effect of storage time on the water CA was observed for a 6-min activated sample, although it was not the most hydrophilic material. The smallest increase in the CA with the longest storage time was observed for the activated sample of 8 min, even the value after 60 days was lower than immediately after activation. Regardless of the activation time, the CA was observed to increase within 14 days of sample ageing, after which the value decreased. In addition, the changes occurring during the first 24 h significantly depended on the activation time, for the longest periods (8 and 10 min) a further decrease in the CA was observed initially, even larger for the sample modified longer. The initial decrease in the CA value of water seems to be quite characteristic for longer exposure times in case of the oxygen plasma [39]. Further oxidation after activation (post-treatment oxidation) occurs during storage. This may be due to reactions between the groups on the surface of the material and oxygen or water in the air, which causes further modification of the material [18,75]. Moreover, longer modification may lead to thicker plasma-induced cross-linked layer, and thicker layer may reduce or even prevent the migration of functional groups into the material [27,75]. In the case of the shortest modification, the change was insignificant, within the limits of the measurement error. However, it should be noted that regardless of the storage time of the sample, they have retained their partially improved hydrophilic properties. The lack of full hydrophobic recovery may be explained by the change in morphology of the sample during modification [58].

It can be concluded that the smallest variation of hydrophilicity during storage was observed to occur for the sample with shorter activation time. Moraczewski *et al* [39] reached the same conclusions, where ageing times used by him were much longer than ours.

The changes in the CA for diiodomethane (figure 4) as a result of storage are significantly smaller than for water. The

course of changes observed for samples activated at 2, 4 and 6 min is of similar character. Values changed only slightly during storage, increased and decreased irregularly. A completely different course of changes was observed for 8 and 10 min of the samples activated, also their value differed from other samples immediately after activation—it was much higher (56–57°). The 8-min activated sample was characterized by a significant decrease in the diiodomethane wetting angle during 14 days of ageing, and later the value started to rise slowly. For the activated sample of 10 min, however, after 7 days of storage, very dynamic changes in CA, its reductions and growths were observed.

For ethylene glycol (figure 5), CAs for samples stored for 7 days reached similar values regardless of their activation time. The biggest increase of the angle occurred after 14 days, where the material lost its polar properties. However, longer ageing of the material caused a significant decrease in CA.

Plasma activation is performed in order to improve SFE of the polymeric material, however, these changes are not permanent (figures 6–8). Moraczewski *et al* [39] found a return to the premodification value after 9 weeks of sample storage time. In our case, with ageing only 3 days shorter, despite the visible partial return to preactivation state and the recorded hydrophobic recovery process, the values of SFE are higher than the initial ones even after 60 days of storage. The changes result from postplasma oxidation reactions.

With 2 min oxygen activation, even after doubling the storage time from 30 to 60 days, the SFE values stay almost unchanged and are still relatively high (53.6 and 52.2 mJ m$^{-2}$, respectively). In addition, it has been observed that with longer activation times further increases in SFE values can occur during sample storage. Samples are further oxidized and polar groups are formed on their surface. As a result of sample storage extension from 24 h to 7 days, for films activated with plasma for 8 and 10 min, the SFE value increased by up to 4–5%. However, for an activation time of 10 min, the
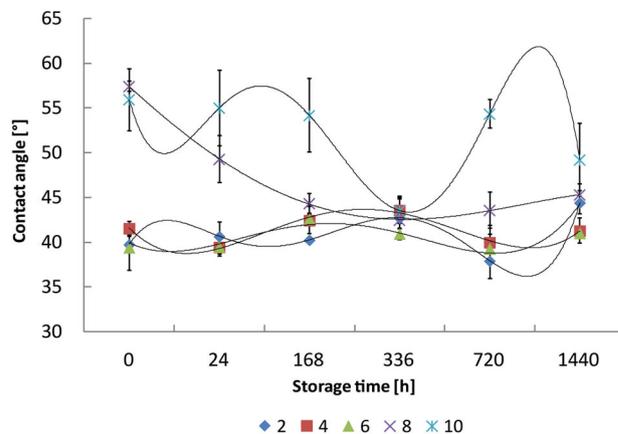


**Figure 4.** Changes in diiodomethane contact angle values due to treatment and storage time.
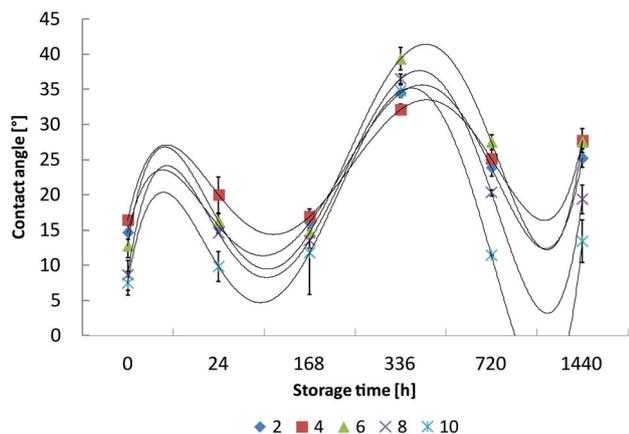
**Figure 5.** Changes in ethylene glycol contact angle values due to treatment and storage time.
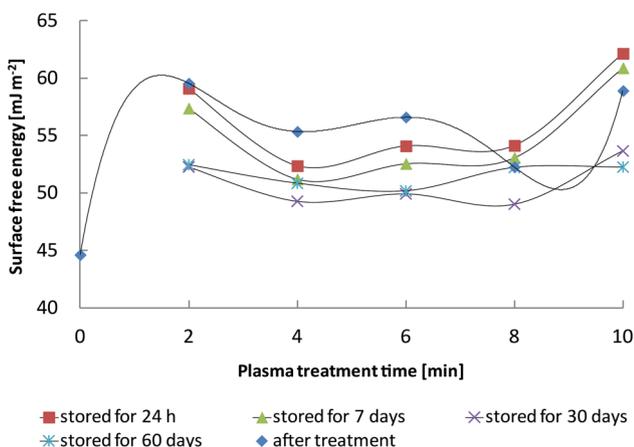


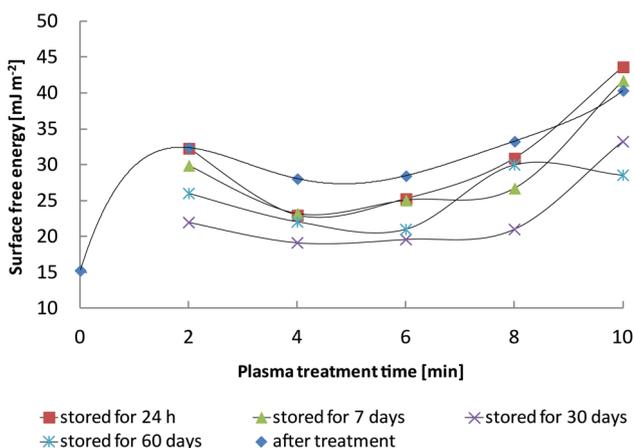**Figure 6.** Changes in total SFE values as a function of treatment and storage time.



**Figure 7.** Changes in polar components of SFE as a function of treatment and storage time.

increase in the SFE value was associated with an increase in the polar component rather than dispersion component in case of 8 min activation. This will translate into better wettability
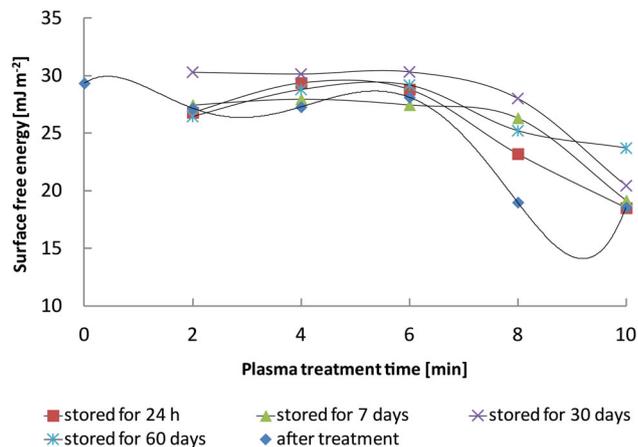


**Figure 8.** Changes in dispersive components of SFE as a function of treatment and storage time.

of the substrate and suitability for further processing. The improvement of wetting properties are also confirmed by water CA results. The changes in the dispersion component of the SFE are in line with the changes observed for the wetting angle of diiodomethane. The biggest changes, regardless of the activation time, occur after 14 days of storage, therefore it seems optimal to carry out further material refining processes within a week of modification, when the SFE of the material is only relatively slightly reduced or even may be increased.

## 4. Conclusions

As a result of oxygen plasma activation, no matter the exposure time, the hydrophilicity of PLA was significantly improved. The SFE increased by more than 30% and reached a maximum value of 60 mJ m$^{-2}$, while the wetting angle was reduced by more than 40% to a minimum of 37°. The best results for improvement of wettability and hydrophilicity were obtained for activation lasting 2 and 10 min. However, the samples were characterized by a slightly more rapid changes during ageing. Nevertheless, plasma activation lasting 10 min makes the polymer surface more hydrophilic and more polar than 2 min treatment. It should be noted, though, that the material degradation with prolonged exposure time was much stronger, and from economic perspective the increased time leads to additional costs. Taking into account the economic aspects, the smallest sample degradation, very good CA and SFE values, relatively good stability of the achieved surface functionality of the activated film during its storage and only small changes of SFE even after 60 days, our results show the validity of the shortest 2-min activation time for PLA film.

All samples during storage were subject to ageing, but the hydrophobic recovery process was dependent on the activation time. It was found that the optimal use of samples is possible if not directly after activation, then within 7 days from the date of its execution. In that case the surface

changes are minimal. The most balanced course of changes was characteristic for PLA activated for 6 min. However, the improvement of hydrophilicity achieved in this case was not the best. The significant increase in the ageing time (30, 60 days) of activated materials had a positive effect on the change of SFE and CA. This can be explained by reactions occurring between groups on the surface of the material and oxygen or water in the air, leading to further oxidation of the surface.

## Acknowledgements

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