

Analysis of the decay of some effects of modification of polylactide surface layers

Magdalena Stepczyńska¹⁾

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Abstract: The results of an investigation into the effects of modifying a surface layer (SL) of polylactide (PLA) as a function of time are presented. The PLA modification was performed by the method of corona discharges (CD) in the air using unit energy values (E_{ii}) equal to 3.5 and 10 kJ/m². The extent of oxidation and contact angle of the SL were determined by the methods of X-ray photoelectron spectroscopy (XPS) and goniometry, respectively. The measurements were carried out immediately after the modification process, as well as 1, 2, and 3 months later.

Keywords: polylactide, surface layer modification, corona discharge, X-ray photoelectron spectroscopy (XPS).

Analiza zaniku wybranych efektów modyfikowania warstwy wierzchniej polilaktydu

Streszczenie: Analizowano zanik w czasie zmian wywołanych modyfikowaniem za pomocą wyładowań koronowych (CD) warstwy wierzchniej (SL) polilaktydu (PLA). Modyfikowanie prowadzono w atmosferze powietrza, z zastosowaniem jednostkowej energii (E_{ii}) modyfikowania o wartości 3,5 i 10 kJ/m². Stopień utlenienia oraz wartość kąta zwilżania SL badano metodą spektroskopii fotoelektronowej (XPS) oraz goniometrii, bezpośrednio po procesie modyfikowania oraz po upływie 1, 2 i 3 miesięcy.

Słowa kluczowe: polilaktyd, modyfikacja warstwy wierzchniej, wyładowania koronowe, spektroskopia fotoelektronowa (XPS).

The method of corona discharges (CD), as applied to the modification of a surface layer (SL) of polymeric materials, and analysis of the state of knowledge in this field have been presented in a number of scientific publications [1–6]. The first descriptions of this method include patents [7–9] while the beginnings of its industrial applications, mostly to modifying polyolefinic films, date back to the 1960s. By now, the scope of applications of the corona discharge technique has significantly broadened and the method is not only applied to flat plastics, like films and plates, but also to products of complex forms, such as tubes and bottles. Therefore, the CD technique becomes a more and more common method for industrial modification of the SL of polymeric materials.

Due to their low price and important functional qualities, polymeric materials attract much interest in the field of the packaging industry [10, 11]. Scientific works on biodegradable materials produced from natural resources are constantly being developed, which enables us to dynamically expand the manufacture of poly(lactic acid) (or polylactide, PLA). Under industrial composting con-

ditions, this polymer decomposes to water, carbon dioxide, and mineral components. Due to its biodegradation properties, PLA is applied in the packaging industry mostly as a disposable material [12–14].

Modification of the SL of polymeric materials is mainly carried out to improve adhesion properties, increase surface purity, and improve wettability [15]. The CD technique as a method for SL modification is commonly applied in the plastic packaging industry in order to prepare the plastic surface to be printed, glued, decorated, or metallized [16].

Corona discharges occur due to a potential difference that is created between two electrodes, *i.e.*, the high-voltage electrode (HVE) and earth electrode (EE). Specifically, the discharges occur in the inter-electrode gap filled with a gas (most commonly air) under atmospheric pressure [17]. Electrons of the kinetic energy of several, or more, eV, created and moving within the inter-electrode gap, hit the polymer chains and cause the breaking of some chemical bonds. As a result, radicals are formed, which initiate chemical reactions (mostly oxidation) that modify the polymer SL. The radicals react with oxygen, ozone, OH groups, and water molecules and form polar compounds, thus causing a change in the surface properties of the products being modified [2, 18]. The oxidation process that occurs during the modification of the SL of

¹⁾ Kazimierz Wielki University, Department of Materials Engineering, Chodkiewicza 30, 85-064 Bydgoszcz, Poland; e-mail: m.stepczynska@ukw.edu.pl

the polymeric materials may be investigated by, *e.g.*, X-ray photoelectron spectroscopy (XPS) [19, 20].

The purpose of the present article is to present the results dealing with the decay of the effects of the corona discharges as the method applied to the modification of the SL of a polylactide film. The CD modification technique was selected as it is a method commonly used in the packaging industry.

EXPERIMENTAL PART

Materials

Polylactide 2002 D (NatureWorks®, USA) was used as the research object. The polymer consisted of L (96.5 %) and D (3.5 %) monomer units, its melt flow index (MFI) was 4.2 g/10 min (2.16 kg, 190 °C) and density 1.24 g/cm³. The form of the polymer was a film *ca.* 70 µm thick.

Sample preparation

The film specimens were prepared with the use of a single-screw extruder type PlastiCorder PLV 151 (Bra-bender, Germany). The characteristic features of the extruder were as follows: screw diameter of 19.5 mm, *L/D* ratio of 25, and flat head with a nozzle of 170 mm width and of an adjustable gap size. The extruder was coupled with a calender consisting of three cylinders, 110 mm in diameter, cooled with water. The temperatures of the cylinder heating zones I, II, III and the extruder head were 180, 190, 200, and 200 °C, respectively. The rotational speed of the extruder screw was 60 min⁻¹ and the temperatures of the upper, middle, and lower rollers were 46, 37, and 27 °C, respectively.

To modify the PLA film, an AF2 film activator (IPTS Metalchem, Toruń, Poland) was used. The main characteristics of the activator include a generator with 2 kW power (Energoelektronika, Bydgoszcz, Poland), discharge frequency of *ca.* 50 kHz, and inter-electrode voltage of 14 kV. The single-tip high-voltage electrode for discharges in the air (0.25 m long) was made of aluminum due to its resistance to the oxidizing effect of ozone. The accuracy of the inter-electrode gap adjustment was 0.1 mm and film feed velocity 0–100 m/min. The width of the inter-electrode gap should not exceed 3 mm [2], thus, in the present research, it was chosen to be 1.8 mm. Due to a definite PLA film thickness, it was the smallest distance possible to carry out a uniform modification process.

The PLA samples were modified by the corona discharges in the air, at ambient temperature (*ca.* 23 °C), and under atmospheric pressure. The unit energies (E_u) applied for the modification were 3.5 and 10 kJ/m². These values were derived from the following equation [21–23]:

$$E_u = \frac{P}{L \cdot v} \quad (1)$$

where: P – the power of the corona discharges occurring in the inter-electrode gap of the activator ($P = \text{const} =$

0.4 kW), L – high-voltage electrode length ($L = \text{const} = 0.25$ m), v – transfer velocity of the modified material.

The above-mentioned values of E_u were chosen while considering previous studies by the author on the effects of modification of the PLA surface layer with the use of the CD technique [21–24]. Velocities (v) of the specimen transfer were calculated from Eq. (1), using the assumed E_u values. They were 27.4 and 9.6 m/min for E_u values equal to 3.5 and 10 kJ/m², respectively. The same CD power was applied in all the experiments, which was advantageous to the operation of the generator. If the generator operates in a single point of its non-linear characteristics, then the error of determining E_u is reduced.

The specimens were designated with the symbols P3.5, P10, P3.5_X, and P10_X. P3.5 and P10 were assigned to the samples examined immediately after the modification while P3.5_X and P10_X, denote samples examined 1, 2, and 3 months later ($X = 1, 2,$ and $3,$ respectively). The unmodified sample was designated P0.

Methods of testing

– The extent of the SL oxidation was determined by XPS, using an X-ray photoelectron spectrometer type Escalab 210 (VG Scientific, UK).

The spectrometer used in the investigations was equipped with an aluminum anode that emitted X-rays of photon energy equal to 1486.6 eV. The measurements were carried out using the power of the radiation source of up to 200 W. The pressure inside the test chamber increased during the measurements from $6 \cdot 10^{-7}$ to $8 \cdot 10^{-6}$ Pa, which was caused by desorption of material fragments and gaseous substances from the specimens. The photoelectron emission angle was 90°, which corresponded to an average thickness of the examined layer equal to 4 nm.

A principle of unity of nature of physical and chemical phenomena of all the investigated samples was assumed, which implies that individual atomic forms of carbon exhibit the same electronic structure and experience the same chemical surroundings. This was a basis for the formation of synthetic peaks attributed to individual functional groups present in various specimens, of exactly or approximately the same shape, similar binding energy, and similar width at half height, but differing in height [25–28].

– The contact angles were measured by a goniometer type DSA100 (Krüss GmbH, Germany) equipped with an automated system for dosing drops of a test liquid.

Measurements of the contact angle (Θ) with the use of water or diiodomethane as test liquids were performed immediately after the modification of a given sample was completed, as well as 1 and 3 months later. The test liquid drops were placed on the central part of the specimen surface. The drop volume was continuously increased while the dynamic contact angle was measured. During the measurements, the volume (V) of the water drop increased from $3 \cdot 10^{-3}$ to $7 \cdot 10^{-3}$ cm³, whereas that of a diiodo-

methane drop, from $1 \cdot 10^{-3}$ to $3 \cdot 10^{-3}$ cm³, both at the rate of $\Delta V = 5 \cdot 10^{-3}$ cm³/min. The time interval (τ) between the successive measurements was 0.5 s. For each sample, 96 and 45 measurements were made to determine the water contact angle and diiodomethane contact angle, respectively. The different measurement numbers resulted from different drop volumes V of the two test liquids and the assumed time interval τ between consecutive measurements of the individual contact angles. Specifically, the smaller number of measurements of the diiodomethane contact angle was due to a smaller range of changes in the drop volume of that liquid. The determination of the contact angle of each sample was made 12 times with the use of each test liquid. Two extreme results of every series were neglected, a mean arithmetic value of the remaining 10 results was calculated, and the standard deviation from the mean value of the contact angle was estimated.

— The extent of oxidation (O/C) of the SL of the examined samples was calculated as well. This quantity was assumed as the ratio of the oxygen atom number to the carbon atom number and expressed as a percentage.

RESULTS AND DISCUSSION

Spectra of the distribution of the photoelectron energies of the investigated samples are shown in Figs. 1–5.

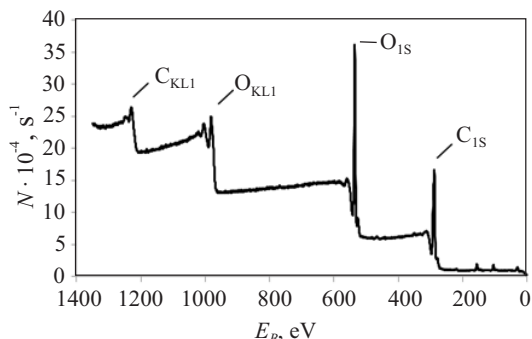


Fig. 1. XPS overview spectrum of the P0 sample; E_B — the binding energy of photoelectrons, N — the number of photoelectron pulses

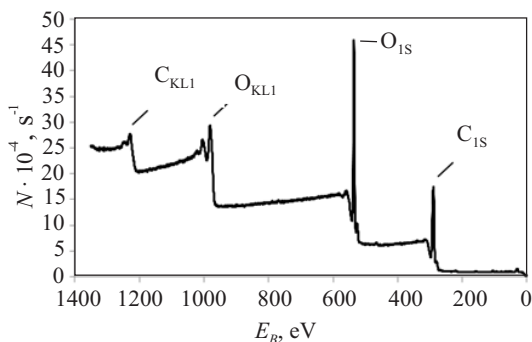


Fig. 2. XPS overview spectrum of the P3.5 sample; E_B and N are the same as in Fig. 1

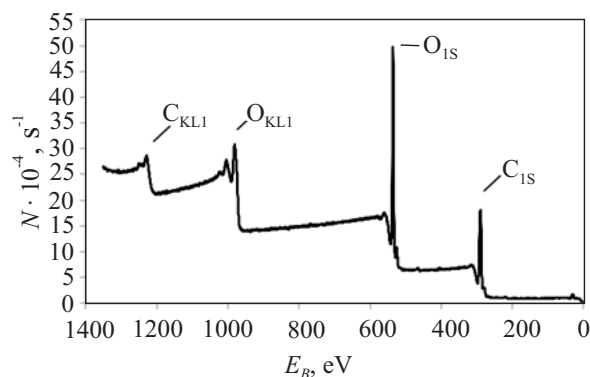


Fig. 3. XPS overview spectrum of the P10 sample; E_B and N are the same as in Fig. 1

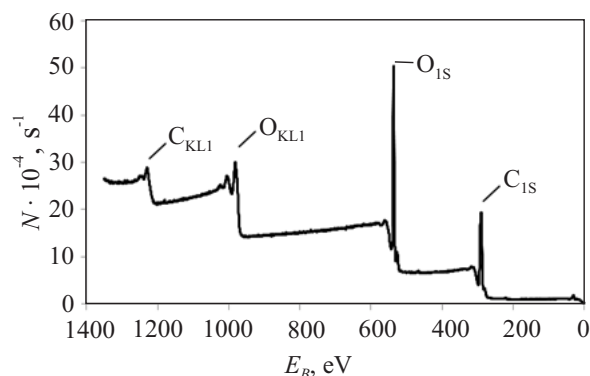


Fig. 4. XPS overview spectrum of the P3.5_3 sample; E_B and N are the same as in Fig. 1

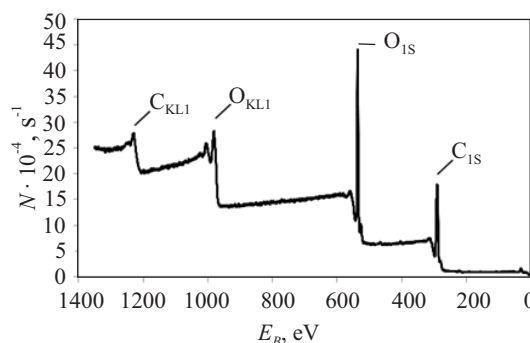


Fig. 5. XPS overview spectrum of the P10_3 sample; E_B and N are the same as in Fig. 1

These are so-called XPS overview spectra. They concern the unmodified (reference), sample (P0) and samples P3.5, P10, P3.5_3, and P10_3. The figures reveal characteristic peaks attributed to photoelectrons originating from the inner orbitals of the carbon (C_{1s}) and oxygen (O_{1s}) atoms. The ordinate axis of each figure relates to the pulse numbers that are a measure of the number of photoelectrons emitted from the specimen and recorded by the spectrometer. The abscissae axis shows the photoelectron binding energies. In addition to the C_{1s} and O_{1s} maxima, the spectra include peaks assigned to the Auger electrons originating from the carbon (C_{KL1}) and oxygen (O_{KL1}) atoms. Contrary to the photoelectron energy, the energy

of the Auger electrons does not depend on the energy of the incident X-rays. Therefore, variation in the X-radiation energy causes a shift of the photoelectron peaks whereas the Auger electron peaks remain in the same positions.

The presented spectra indicate an increase in the number of oxygen atoms in the SL of the modified PLA samples in relation to that of the SL of the unmodified sample, which means an increase in the extent of the SL oxidation immediately after the PLA modification. The number of oxygen atoms in the SL of the investigated samples decreased over the period of 3 months following modification.

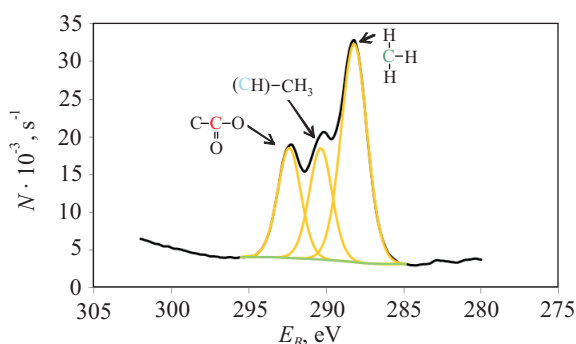


Fig. 6. XPS detailed C1S spectrum of the P0 sample; E_B and N are the same as in Fig. 1

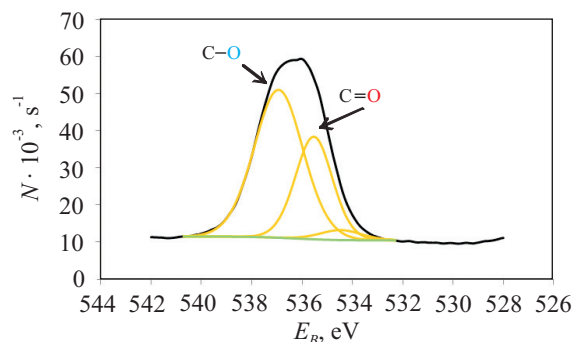


Fig. 7. XPS detailed O1S spectrum of the P0 sample; E_B and N are the same as in Fig. 1

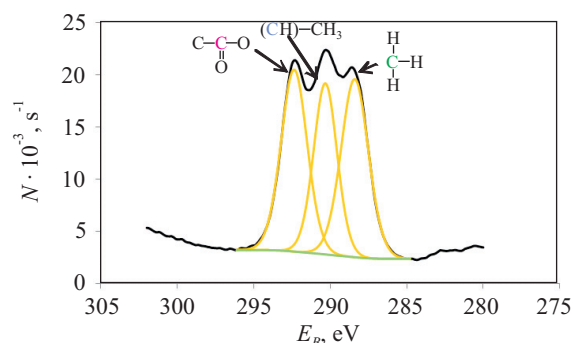


Fig. 8. XPS detailed C1S spectrum of the P10 sample; E_B and N are the same as in Fig. 1

The qualitative analysis of functional groups present in the PLA surface layer was performed by examination of the XPS detailed spectra showing the C_{1s} and O_{1s} peaks. Selected spectra of samples P0, P10, and P10_3, as well as the analyses are shown in Figs. 6–11. Individual peak components corresponding to carbon atoms of different functional groups are marked with colors: green, blue, or red. Analogously, the peaks assigned to oxygen

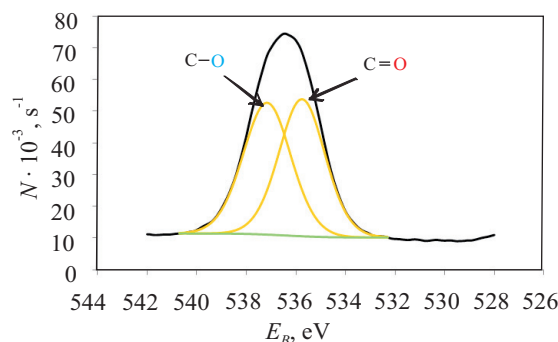


Fig. 9. XPS detailed O1S spectrum of the P10 sample; E_B and N are the same as in Fig. 1

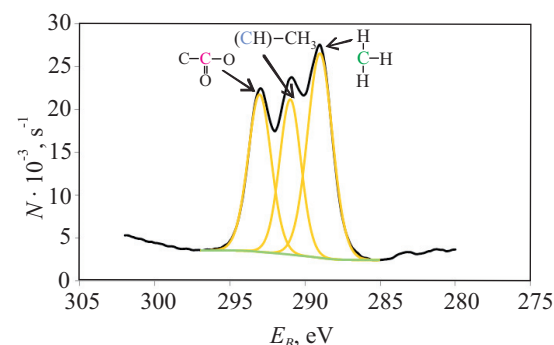


Fig. 10. XPS detailed C1S spectrum of the P10_3 sample; E_B and N are the same as in Fig. 1

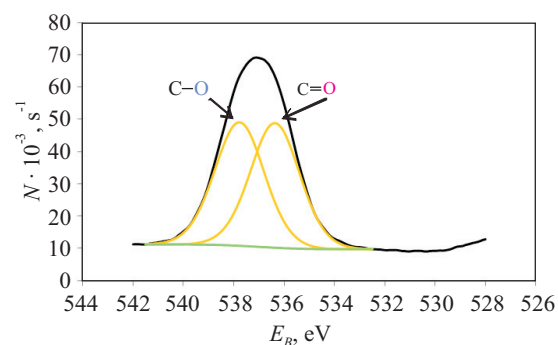
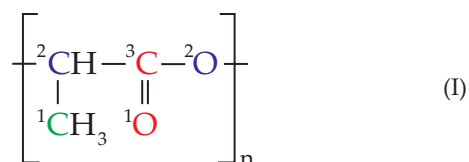


Fig. 11. XPS detailed O1S spectrum of the P10_3 sample; E_B and N are the same as in Fig. 1



atoms of different functional groups are marked with red or blue. The atoms in the structural formula shown in Formula (I) are marked in the same way.

Components of the C_{1s} and O_{1s} peaks were determined using the data presented by Beamson and Briggs [29]. On this basis, the positions of individual lines, distances between them, widths at half height, and preliminary ratios of the areas under the lines were referenced to sample P0.

The spectral analysis showed that the SL of the P0 sample exhibited the largest content of carbon atoms characterized by a binding energy close to 285 eV. This fraction decreased as the CD unit energy (E_u) increased. At the same time, the oxygen fraction in the surface layer of the PLA samples increased. More specifically, the contribution of the carbon atoms diminished from 66.7 % in P0 to 59.7 % in P10, whereas the content of the oxygen atoms rose from 31.2 to 39.3 % in the same samples. Over time,

Introduction of oxygen atoms into the PLA molecular structure causes the formation of dipole moments in fragments of the macromolecules and, thus, an increase in the polarity of the SL. This occurs due to a large difference in electronegativity between the oxygen atoms compared to the carbon and hydrogen atoms. As a result, the density of the cloud of electrons that participate in bonding the oxygen atoms with the carbon or hydrogen atoms is larger in the neighborhood of the oxygen atoms than that in the surroundings of the carbon or hydrogen atoms. Due to the asymmetric distribution of the electric charges, the oxygen functional groups, including the carbon or hydrogen atoms, are of a polar character. Thus, the presence of macromolecules including polar groups changes the surface properties of the PLA while increasing the extent of the SL oxidation.

The determined values of the extent of oxidation (O/C) of the studied samples are summarized in Table 1.

Table 1. The extent of oxidation (O/C) of the PLA samples

Sample	P0	P3.5	P3.5_1	P3.5_2	P3.5_3	P10	P10_1	P10_2	P10_3
O/C, %	46.8	62.6	60.9	60.5	60.0	65.8	62.8	59.9	56.3

the carbon atom content increased from 59.7 % in P10 to 63.4 % in P10_3 while the oxygen atom fraction decreased from 39.3 % in P10 to 35.7 % in P10_3.

Minor amounts of nitrogen and silicon atoms were also identified. However, the fractions of these atoms were negligible. Thus, the presented spectra do not include the peaks corresponding to these chemical elements. The presence of nitrogen and silicon in the surface layer of the PLA samples might be due to lubricants applied during extrusion of the PLA film.

Only the carbon and oxygen functional groups typical of PLA were identified in the surface layer of the investigated unmodified and modified samples. They are indicated by a structural formula in Formula (I).

As to the carbon atoms, the following groups may be mentioned:

-CH₃, to which a line of $E_B = 285$ eV was assigned [the carbon atom of that group is marked with no. 1 and green color in Formula (I)];

-CH-CH₃, to which a line of $E_B = 286$ eV was assigned [the carbon atom of that group is marked with no. 2 and blue color in Formula (I)];

-C-C(O)O, to which a line of $E_B = 289$ eV was assigned [the carbon atom of that group is marked with no. 3 and red color in Formula (I)]

In the case of the oxygen atoms, the groups below may be considered:

C=O, to which a line of $E_B = 532$ eV was assigned [the oxygen atom of that group is marked with no. 1 and red color in Formula (I)];

C-O, to which a line of $E_B = 533$ eV was assigned [the oxygen atom of that group is marked with no. 2 and blue color in Formula (I)].

The results presented in Table 1 proved that the higher the value of E_u , the larger the increase in the extent of oxidation: the O/C of 46.8 % in P0 increased to 62.6 % in P3.5 and to 65.8 % in P10. This means that the O/C rose in relation to P0 by 33.8 % in P3.5 and by 40.6 % in P10. This increase in the O/C was caused by formation of oxygen functional groups in the PLA samples, which was initiated by free radicals generated due to the energy of electrons hitting the PLA macromolecules and reacting with oxygen. One may also note that the extent of oxidation decreased over time, namely from 62.6 % in P3.5 to 60.0 % in P3.5_3 and from 65.8 % in P10 to 56.3 % in P10_3, *i.e.*, when 3 months had elapsed. In other words, the O/C decreased by 4.2 % in P3.5_3 compared to P3.5 and by 14.4 % in P10_3 in relation to P10. This reduction in the O/C resulted presumably due to the decay of the effects of the corona discharges.

In order to confirm the statement that the polarity of the surface layer of the PLA increased with the rising extent of oxidation, measurements of PLA wettability were carried out. The measurements were performed immediately after the PLA modification (samples P3.5 and P10), 1 month later (samples P3.5_1w and P10_1w), 2 months later (samples P3.5_2w and P10_2w), and 3 months later (samples P3.5_3w and P10_3w). As found, the water (Θ_w) and diiodomethane (Θ_d) contact angles decreased as E_u increased. The reduction in Θ_w was greater than that in Θ_d because polar forces play a major role in intermolecular interactions. The interaction of the dispersive character is less significant. The modification of PLA resulted in the formation of polar groups in the polymer surface layer, which strongly interacted with water molecules. Therefore, water as a polar test liquid interac-

Table 2. The water contact angles (Θ_w) of the PLA samples

Sample	P0	P3.5	P3.5_1w	P3.5_2w	P3.5_3w	P10	P10_1w	P10_2w	P10_3w
Θ_w , deg	74.5	61.7	62.3	66.4	68.8	58.2	64.1	65.7	68.4

ted with the modified PLA film more strongly than the dispersion test liquid. The values of the contact angles increased over time, probably because of a decay in the effects of the corona discharges. The results of the contact angle determination are listed in Table 2. The data on Θ_d are omitted since, as mentioned earlier, the dispersion interaction is of much less importance.

One may note that the water contact angle of the modified samples increased over 3-months by *ca.* 10 deg, probably due to a decay in the effects of the corona discharges.

CONCLUSIONS

Corona discharges cause changes in the surface layer of PLA samples being modified, including an increase in the extent of oxidation, exceeding even 40 % in relation to the O/C of an unmodified sample, and improvement in wettability. The polarity of the SL of these samples increases with rising O/C, which is caused by the formation of polar functional groups. The increase in the extent of oxidation and improvement in wettability of the PLA surface layer are desired effects of the modification due to the enhancement of adhesion properties of PLA.

Investigation of the PLA samples, performed 1, 2, and 3 months after the modification, indicates that the effects of the corona discharges decay over time. This is because the extent of oxidation of the SL of these samples decreases by more than even 14 % in relation to the O/C of the samples examined immediately after the modification. The same conclusion results from the measurements of the contact angle: the values of the water contact angle increase over 3-months by *ca.* 10 deg when compared to Θ_w of the samples investigated immediately after the modification.

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