X-ray photoelectron spectroscopy studies of laser induced polylactide surface layer modification

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Abstract: The results of the studies of the polylactide surface layer laser induced modification are presented. Various fluence values (E_j) and numbers of laser pulses were applied to modify the surface layer. The method of photoelectron spectroscopy was applied to investigate the chemical composition and the degree of oxidation of the surface layer of the unmodified and modified polylactide. There was found a change in the chemical composition and the degree of oxidation. The alterations depended on the fluence and the number of laser pulses applied.

Keywords: polylactide, laser induced modification, photoelectron spectroscopy.

Badania skutków indukowanej laserem modyfikacji powierzchni polilaktydu za pomocą rentgenowskiej spektroskopii elektronowej

Streszczenie: W pracy przedstawiono wyniki badań warstwy wierzchniej polilaktydu modyfikowanej za pomocą lasera. W procesie modyfikowania stosowano różną jednostkową energię impulsu laserowego (E_j) oraz różną liczbę impulsów. Metodą rentgenowskiej spektroskopii fotoelektronowej badano skład chemiczny oraz stopień utlenienia warstwy wierzchniej pierwotnego i modyfikowanego polilaktydu. Stwierdzono, że na skutek napromieniania zaszły zmiany składu chemicznego oraz stopnia utlenienia, a ich stopień zależał zarówno od wartości E_j, jak i liczby impulsów.

Słowa kluczowe: polilaktyd, modyfikowanie indukowane laserem, rentgenowska spektroskopia fotoelektronowa.

Polylactide is a biodegradable and biocompatible polymer made from renewable materials (*e.g.* corn starch or sugarcane). The polymer is considered to be one of the most promising materials that could be an alternative to polymers derived from petroleum. Polylactide is used in medicine and the production of foodstuffs packaging and textiles [1].

The surface of most polymers is reactive, hydrophobic and demonstrates a low value of surface free energy [2]. Those features make the processes of surface treatment; gluing, printing or metalizing much difficult. In order to reduce these disadvantages there can be applied various methods to modify the surface layer of polymers. The most frequently applied methods of modifying polylactide surface layer are the chemical or corona discharge methods [3, 4].

One of the recent physical methods of modifying the surface of polymer materials is the laser method. Lasers allow to perform precise changes in the properties of surface small fragments without affecting the properties of the deeper layers. The process of laser induced modification is simple, easily controlled and ecologically safe. Depending on the purpose of modification of the surface layer (changes in the geometrical structure or change in the chemical composition), the type of laser applied, conditions of performing the modification and the type of the material modified, the surface layer laser induced modification process can proceed in various ways [5].

Over the recent years there has been recorded a high increase in the number of lasers available, operating in various ranges of the light wavelengths and working in different modes (pulse or continuous). In the processes of surface layer modification of various materials one applies mostly CO_2 gas lasers, excimer lasers as well as solid state lasers (*e.g.* Nd:YAG) [6, 7].

Excimer lasers represent a group of pulse lasers used for the emissions of radiation with the wavelength from 193 to 351 nm, electronic transitions inside the molecules with a short lifespan. They allow for the ablation of inorganic and organic materials. The photon energy of excimer lasers falls within the range from 3.5 to 7.9 eV; as a result a single photon can break most interatomic bonds [8, 9].

In the literature one can find publications describing the use of excimer lasers to modify the surface layer of polylactide [10—12]. Depending on the laser parameters used to modify the polylactide surface a change in the

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chemical composition, the surface roughness and surface free energy of the polymer is observed. In the cited works the fluences up to 20 mJ/cm^2 (ArF laser) or 40 mJ/cm^2 (KrF laser) were used. In the case of KrF laser and fluence up to 15 mJ/cm^2 the increase in the number of pulses led to an increase of modified surface roughness. Exceeding that fluence causes the reverse effect namely decrease of surface roughness with increasing number of pulses. Different effect in the case of ArF laser is observed, where up to 20 mJ/cm^2 with an increase in the number of pulses surface roughness decreases, and then beyond the appropriate number of pulses (depending on the specific fluence), the increase in roughness is observed. Regardless of used laser type, modification of polylactide surface layer causes also changes in the chemical composition of that layer. Besides the typical functional groups present in the surface layer of polylactide, new functional groups containing oxygen are formed, which increases the degree of surface layer oxidation.

Presented in the cited articles results showed that the selected properties of the polylactide surface layer largely depend on the applied laser fluence and the number of pulses. However the results of studies on the changes in polylactide surface layer modified with ArF laser irradiation with fluence over 30 mJ/cm^2 have not been yet published.

As a result of the conducted research selected properties of the laser-modified polylactide surface layer were determined. The aim of the paper was to study the effect of ArF excimer laser on the chemical composition and the degree of oxidation of the polylactide surface layer modified with a higher fluence and to compare obtained results with the results presented in [10, 11].

EXPERIMENTAL PART

Materials and specimen preparation

The study involved the use of polylactide (PLA) 2002 D (Cargill Down LLC, USA), with a mean molecular weight of about 155 500. The specimens to be used for the studies were made with the injection method using the injection molding machine Tederic TRX 80 ECO 60 type (Tederic Machinery Manufacture Co. LTD, Taiwan). Temperatures of the I, II and III cylinder zones of the injection molding machine, head and the mold were: 170, 180, 190, 190 and 30 °C, respectively. The mold was allocated to the manufacture of square plates (60 × 60 × 1 mm) from which smaller specimens for testing (30 × 20 × 1 mm) were cut out.

Testing apparatus and methodology

In the process of laser induced modification of specimens there was applied the ArF LPX 300 excimer laser (Lambda Physik, Germany) of the wavelength of 193 nm (which corresponds to the photon energy equal to 6.4 eV). The specimens were treated with laser pulses at fluence (E_j) values equal to 15 or 60 mJ/cm^2. The size of the modified surface depended on E_j and ranged from 230 to 400 mm^2. An accurate value of the laser pulse energy was determined with the FieldMax II TOP type measuring device (Coherent Inc., US). The specimens were modified with 10 or 1000 pulses. The duration of one pulse was 20 ns. The specimens were marked with symbols PX_Y where X stands for fluence value and Y — the number of pulses.

The study of the photoelectron spectra (XPS) involved the use of photoelectron spectrometer ESCALAB-210 provided by VG Scientific (England). The spectrometer used for the test was equipped with Al anode, which emits X-rays with photons energy of 1486.6 eV. The measurements were taken in the analyser chamber under pressure between 3.0 and $5.0 \cdot 10^{-6}$ Pa, due to desorption of material fragments and gaseous substances of the test samples. The specimens were placed perpendicular to the analyser axis and the source of radiation being placed at the angle of 60°. The size of the analyzed area corresponded to the aperture of the analyzer (large area), of the order of several mm^2, therefore the XPS analysis area was located entirely in the laser modification region. The experimental spectra were deconvoluted applying the Avantage software (ver. 4.84) provided by ThermoElectric. The spectra analysis was performed based on the values of the sensitivity coefficient of respective electron levels determined experimentally by Scofield and measured transmission function. The spectra were fitted using the PLA model structure [13]. Correction of the results was carried out on carbon C-H (285.0 eV).

RESULTS AND DISCUSSION

The results of the quantitative analysis of carbon and oxygen atoms content on the surface layer of the unmodified PLA specimens and modified in extreme conditions are given in Fig. 1.

Carbon atoms content changes with an increase in the fluence and number of pulses. In the case of the specimens modified using 10 pulses with $E_j = 15$ and 60 mJ/cm^2 carbon atoms content decreases from about 80 at. % for the unmodified PLA to 76 and 77 at. %, respectively, for the specimens modified. For the specimens modified by 1000 pulses with $E_j = 15$ and 60 mJ/cm^2 the content of that element atoms decreases to 66 and 72 at. %, respectively. However, as for oxygen atoms content the higher the number of pulses, the higher the content of that element in the surface layer. In the case of the specimens modified using 10 pulses with $E_j = 15$ and 60 mJ/cm^2 oxygen atoms content increases from about 18 at. % (unmodified sample) to 22 and 21 at. %, respectively. For the specimens modified by 1000 pulses with $E_j = 15$ and 60 mJ/cm^2 the content of that element atoms increases to 34 and 28 at. %, respectively.

The obtained results of the oxygen atoms content in the modified PLA surface layer are comparable to the

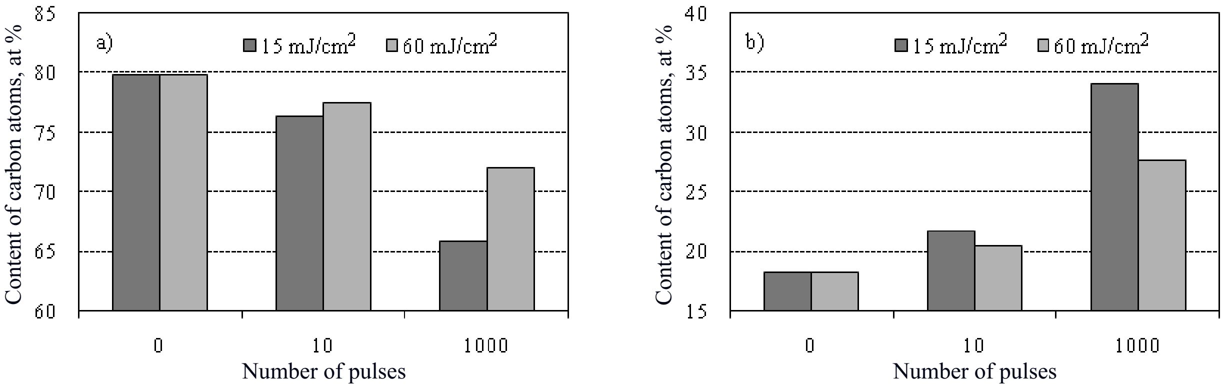

Fig. 1. Effect of the number of pulses on the contents in PLA surface layer of: a) carbon (C_{1s}), b) oxygen (O_{1s})

results presented in [10]. The maximum oxygen atoms content in both cases was approximately 32 at. %. In the cited work this value is reached already at E_i of 5 mJ/cm^2, thus further increase of fluence to 60 mJ/cm^2 does not increase the content of this element in the modified PLA surface layer. Unfortunately the cited work does not contain information regarding the content of carbon atoms, so it is impossible to implement a similar comparison of the content of this element.

For the qualitative analysis of the functional groups of the PLA specimen surface layer, the detailed spectra of C_{1S} and O_{1S} peaks were used. The component peaks from the C_{1S} and O_{1S} bands were defined using the data presented in [14]. The values of the component peaks location, the distance between them and full width at half height of peaks as well as preliminary proportions of their areas, which characterise the specimen of the unmodified PLA, were assumed.

Qualitative analysis of the functional groups present in the surface layer of the unmodified PLA and the specimen modified at the highest fluence (P60_1000) are given in Fig. 2.

Similarly to the results described in [10, 11], in the surface layer of the unmodified and modified PLA typical for that polymer carbon and oxygen functional groups were identified. Those groups are three carbon atom

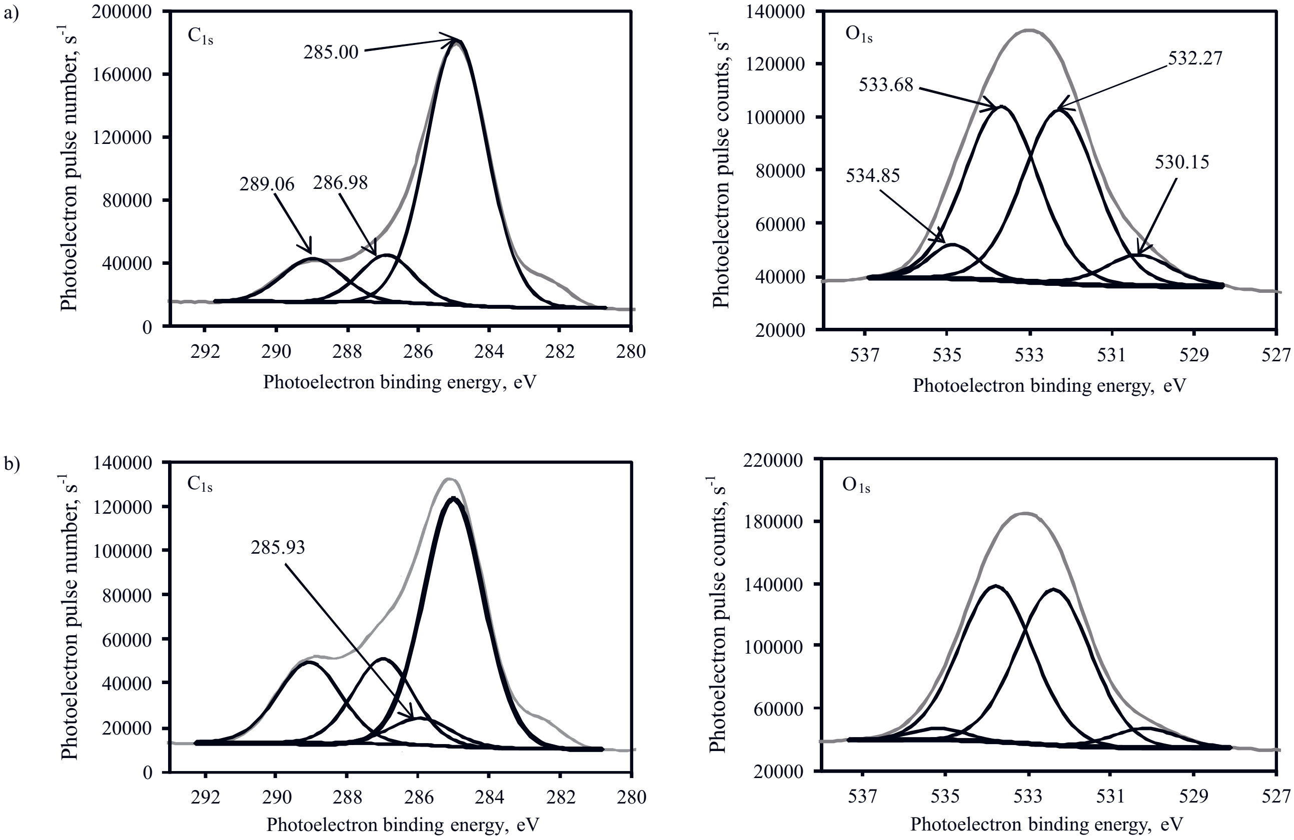

Fig. 2. XPS detailed C_{1S} and O_{1S} spectra of the: a) unmodified PLA, b) P60_1000 specimens

forms in functional groups: C-H (binding energy E_B = 285.00 eV), -CH-CH_3 (E_B = 286.98 eV) and -C-C(O)O (E_B = 289.06 eV). In the C_{1s} spectrum a mismatch in the area of lower E_B can be observed. A peak with the value of E_B = 282.00 eV occurs, which is not found on a typical PLA spectrum. Determination of the origin of this peak requires additional studies. There were also identified four forms of oxygen atoms in functional groups C=O (E_B = 532.27 eV) and C-O (E_B = 533.68 eV) originating from PLA as well as „bulk oxygen" (E_B = 530.15 eV) and oxygen atoms originating from absorbed water (E_B = 534.85 eV). As compared with the standard PLA spectrum in the P15_1000 and P60_1000 specimens an additional functional group -COH (E_B = 285.93 eV) was identified. The same functional groups have also been identified for samples of unmodified and modified PLA with ArF laser with lower values of E_j and the KrF laser up to 40 mJ/cm^2. In addition, in works [10, 11] a carboxyl group -COOH (E_B = 290.30 eV [10] or E_B = 288.80 eV [11]) was also identified which is not present in the samples modified with the parameters applied.

As a result of the laser induced modification in all the specimens the content of methyl groups (-CH_3) gets decreased from about 57 for unmodified PLA down to about 28 at. %, for P15_1000 specimen. This is a greater decrease than in the case of the results presented in [10], where the minimum stated content of -CH_3 groups was about 50 at. %. At the same time the content of the oxygen functional groups (C=O as well as C-O) increases from about 16 at. % for unmodified PLA to about 34 at. %, for P15_1000 specimen.

Decrease in the content of methyl groups and the increase in the content of oxygen functional groups may suggest that as a result of laser induced modification the C-C bonds get broken on account of photodegradation. Based on the presented studies it can be concluded that the process is more intense in the case of larger E_j. The free radicals formed in that process can react with oxygen leading to the formation of new polar groups including oxygen [10] and thus increasing the oxidation degree of surface layer of the modified PLA (Fig. 3) defined as:

$$\text{oxidation degree} = \frac{\text{O atoms content}}{\text{C atoms content}} \cdot 100\ \%$$

As a result of the laser induced specimen modification the degree of the surface layer oxidation increases from about 23 at. %, for unmodified PLA to about 52 and 39 % for P15_1000 and P60_1000 specimen, respectively. Since the above mentioned article does not provide the results of carbon atoms content one cannot perform a direct comparison of the surface layer oxidation. However, based on the difference in the content of -CH_3 groups it can be deduced that in the case of higher E_j (60 mJ/cm^2) the oxidation degree of modified surface layer is higher. It is noted that a greater degree of surface layer oxidation is obtained when lower E_j is applied, which can be due to a greater melting of modified specimens with a greater E_j. As a result of melting, down fractions of unmodified polymer could migrate from deeper layers of the material.

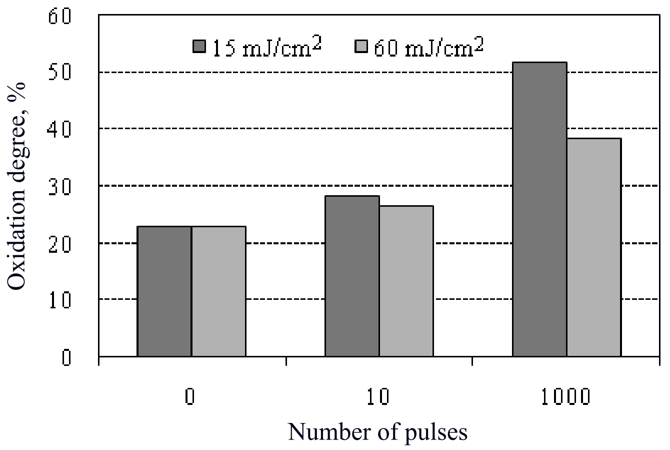

Fig. 3. Effect of the number of pulses on PLA surface layer oxidation

CONCLUSIONS

Based on the present studies one can state that in presented conditions with an increase in E_j and the number of laser pulses the content of carbon atoms decreases and the content of oxygen atoms increases in the surface layer of polylactide. This phenomenon is accompanied by a decrease in the content of methyl groups and an increase in the content of functional groups containing oxygen. Observed effect is similar to the results reported in the literature. However, in the case of higher value of applied E_j, greater decrease of the methyl group content is observed, and hence the degree of oxidation of modified polylactide surface layer increases. An increase in the degree of surface layer oxidation should enhance wettability and adhesion properties of polylactide surface. Further research will cover the analysis of the effect of laser irradiation on the wettability and surface free energy as well as the change in the geometric structure of the surfaces of the polylactide materials modified.

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