Durability studies of modifications effects of polyhydroxybutyrate surface layers

Magdalena Stepczyńska[1), *)], Krzysztof Moraczewski[1)], Bartłomiej Jagodziński[1)], Marian Żenkiewicz[1)]

DOI: dx.doi.org/10.14314/polimery.2018.4.4

Abstract: The results of an investigation on the stability of low-temperature plasma and corona discharge modification effects on polyhydroxybutyrate (PHB) surface layers (SL) are presented. The changes in geometrical structure and chemical composition were examined using atomic force microscopy (AFM) and Fourier-transform infrared spectroscopy (FT-IR), respectively. The measurements were carried out immediately after the modification process, as well as 3, 6, and 9 weeks later.

Keywords: plasma, polyhydroxybutyrate, modification, surface layer.

Badania trwałości efektów modyfikowania warstwy wierzchniej polihydroksymaślanu

Streszczenie: Oceniano efekty modyfikowania warstwy wierzchniej (ang. SL) polihydroksymaślanu (PHB) za pomocą plazmy niskotemperaturowej oraz wyładowań koronowych po upływie 3, 6 i 9 tygodni od zakończenia procesu. Metodami mikroskopii sił atomowych (AFM) oraz spektroskopii w podczerwieni z transformacją Fouriera (FT-IR) wykazano, że modyfikowanie warstwy wierzchniej PHB powoduje trwałe zmiany struktury geometrycznej i składu chemicznego badanych powierzchni.

Słowa kluczowe: plazma, polihydroksymaślan, modyfikacja, warstwa wierzchnia.

Due to the numerous applications of polymeric materials, including biodegradable materials, in packaging, medical, pharmaceutical, electronics, automotive and construction industries, an increased interest in the surface engineering of these materials has been observed. By using appropriate methods to modify the surface layer (SL) of polymer materials, new or improved surface properties can be obtained. Surface layer modifications of polymeric materials are carried out mainly in order to improve their adhesion properties, increase the surface roughness and improve the wettability [1–3].

Surface modification of biomaterials by low-temperature plasma or corona discharge are economical and effective methods of modifying their surface properties [4] in which biofunctionality and biocompatibility can be achieved while maintaining the favorable properties of biomaterials, such as strength and physiological inertness.

A low-temperature plasma modification has been intensively studied since the 1950s [5–7]. This method is used in industry in many different areas where there is a need to change the chemical or physical structure of the SL. It is also used in the sterilization process of food packaging or medical equipment [8]. The method of corona discharge (CD), which was developed in the US in the 1960s [9–11], is a popular SL modification method of industrial plastics [12]. It is widely used in the packaging industry to convert the surface properties of plastic films, as well as in sterilization processes [13].

As in the case of polymers derived from oil, one of the requirements of the application of biodegradable polymers, such as polylactide (PLA), polycaprolactone (PCL) or polyhydroxybutyrate (PHB), is the need to modify the surface layer to facilitate printing, bonding or decorating processes. The modification is especially needed when paints or adhesives with aqueous solvents, preferred because of the requirements of environmental protection, are used. Fading of modification effects after the modification of polymeric materials (in particular polyolefins) by various methods can result in the deterioration of the wettability and adhesion properties of these materials [14–19].

Low-temperature plasma is formed during an electrical discharge in a gas atmosphere. It has a temperature of less than 10^4 K, therefore it is also called cold plasma. This plasma is formed due to partial discharges generated by the rapidly changing electromagnetic field in the gaseous medium, which constitutes oxygen, nitrogen, helium, argon, chlorine or air. The electromagnetic field is generated between two electrodes located in the vacuum chamber, also called a discharge chamber, in which the

---

1) Kazimierz Wielki University, Chodkiewicza 30, 85-064 Bydgoszcz, Poland.

*) Author for correspondence:
e-mail: m.stepczynska@ukw.edu.pl

gas pressure ranges from 0.05 to 5 hPa. A high frequency electric voltage, which is generated in the generator, is transmitted to the electrodes [20–22].

The corona discharges occur due to the difference in the potentials in the inter-electrode space filled with gas (most often with air) under atmospheric pressure. The generated electrons, moving in the inter-electrode space with kinetic energies ranging from a few to a dozen or so eV, hit the polymer chains, thus breaking some chemical bonds. The radicals generated during the breaking of bonds initiate chemical reactions with oxygen, ozone, OH groups or water molecules. As a result of ongoing reactions, polar compounds or functional groups are formed, causing a modification of the material surface properties. These processes are generally accompanied by an increase in surface roughness of the modified material [23–26].

The purpose of the presented work was to determine the durability of modification effects of low-temperature plasma and corona discharge used as the methods to modify the surface layer of a biodegradable material. The test results can be used in industrial practice, as part of the preparation technology of packaging materials before printing, gluing, laminating, or decoration. The obtained results can be useful in the determination of the recommended storage time of modified PHB before further processing operations.

EXPERIMENTAL PART

Materials

Polyhydroxybutyrate (PHB), SoGreen 2001 (Tianjin Greenbio Material Co. Ltd, China).

Apparatus

Injection molding machine Tederic TRX 80 ECO 60 (Tederic Machinery Manufacture Co. Ltd, Taiwan). The injection process parameters were as follows: the temperature distribution along the cylinder of the injection molding press 155, 165 and 165 °C, the head temperature 150 °C, the mold temperature 35 °C.

Single screw extruder W25-30D (Metalchem, Toruń, Poland). The extrusion process parameters were as follows: the temperature distribution along the cylinder of the extruder 160, 165 and 170 °C, the head temperature 170 °C, screw rotation speed 50 rpm, barrel temperature from 45 to 50 °C.

The plasma modification was performed using a Femto plasma generator (Diener electronic GmbH, Germany), with nominal power of 100 W.

The corona discharge modification was performed using the AF2 film activator (IPTS Metalchem, Toruń, Poland). The main characteristics of the activator includes a generator with the power of 2 kW, discharge frequency of 50 kHz, inter-electrode voltage of 15 kV, accuracy of the inter-electrode gap adjustment of 0.1 mm, single-tip high-voltage electrode for discharges in air (0.25 m long) and film feed velocity of 0–100 m/min.

Methodology

Samples of PHB, in the form of a plate (30 mm × 20 mm × 1 mm), were placed in a metal plasma generator chamber on a metal slab and exposed to the effect of a plasma discharge generated in oxygen under lowered pressure (20 Pa). The samples were modified for 5, 10 or 25 min with a plasma power of 35 or 75 W.

Samples of PHB were modified by CD in air at ambient temperature (approx. 23 °C) and atmospheric pressure. Based on several searches by the authors on the CD modification effects of biodegradable materials surface layers to test the sustainability of modification effects, a specific energy (E_j) of 3.5 or 10 kJ/m^2 was used. The E_j values were determined from the following Formula (1):

$$E_j = \frac{P}{L \cdot v} \tag{1}$$

where: P – power of the corona discharges occurring in the inter-electrode gap of the activator (P = const = 0.4 kW); L – high-voltage electrode length (L = const = 0.25 m); v – transfer velocity of the modified sample.

The transfer velocity of the modified samples (v) for selected E_j values were calculated by solving Formula (1) (E_j = 3.5 kJ/m^2 → v = 27.4 m/min, E_j = 10 kJ/m^2 → v = 9.6 m/min). The constant-power value of CD has the advantage of enabling the generator to work at a single point of its nonlinear characteristic, which reduces the error of determining the value of E_j.

The modified samples were aged for 3, 6 or 9 weeks under free access to air at a temperature of about 23 °C and relative humidity of about 60 %. The aging time was based on the analysis of the literature concerning the aging of polymeric materials [27, 28].

Samples of unmodified PHB are symbolized by P. Plasma modified samples are symbolized by P(X, Y, Z), where X denotes the plasma power (35 or 75 W), Y denotes the modification time (5, 10 or 25 minutes) and Z denotes aging time (0, 3, 6 or 9 weeks).

Corona discharge modified samples are symbolized by C(X, Y), where X denotes specific energy (3.5 or 10 kJ/m^2) and Y denotes aging time (0, 3, 6 or 9 weeks).

Methods of testing

– Fourier transform infrared spectra were obtained with a Nicolet iS10 (Thermo Scientific, USA) spectrometer by the attenuated total reflection method (ATR). Each analyzed spectrum was an average of 16 measurements recorded in the wave number range from 4000 to 650 cm^{-1}.

– To investigate the geometrical structure of the surface, an atomic force microscope Nanoscope IIIa (Digital Instruments, USA) was used. The geometrical structure of the PHB surface was studied using the tapping mode. In AFM studies, silicon rectangular cantilevers with approximately 10 nm radius blades were used. All samples were studied in an air atmosphere with a scanning frequency from 1 to 1.7 Hz. Images at a resolution of 512 × 512 lines were recorded. Images of sample surface area were recorded in the computer memory and displayed on the monitor thanks to a CCD camera coupled to the optical magnification system of the AFM. The root-mean-square (*RMS*) roughness was calculated from AFM images according to ISO 4287:1997 [29].

RESULTS AND DISCUSSION

Surface images and values of *RMS* of individual PHB samples as derived by AFM are shown in Figs. 1–3 and Table 1. The surface morphology of PHB film is well documented in [4].

With increasing modification times, the *RMS* increased for samples modified with low-temperature plasma with a power of 35 W. The *RMS* also increased with longer aging times.

The increase in surface roughness of PHB samples occurred due to the formation of new functional groups on the surface layer of samples formed during plasma modification and as a result of ablation processes occurring during direct contact of plasma particles with the surface of modified samples. As a result of the ablation processes, impurities situated on the surface of the samples were removed, as well as fragments of weakly bound material consisting of additional components contained in the PHB.

The influence of ablation on the surface structure of biodegradable polymers modified by different methods has been examined by our team [30, 31]. An increase of roughness occurred over time after modification of samples that could be related to the progressive degradation of PHB.

Similarly to the samples modified with a power of 35 W, samples modified with a power of 75 W, we found that longer modification times resulted in increased *RMS* values. The *RMS* values increased with longer aging times. The reasons for these changes have been discussed above.

With the increase in the E_j value, the surface roughness of the tested samples increased. However, the greatest changes occurred in the sample modified with the lowest E_j value. Probably, in the case of samples modified with $E_j = 3.5$ kJ/m^2, oxidation of the PHB surface layer was the main effect of modification, while in the case of the

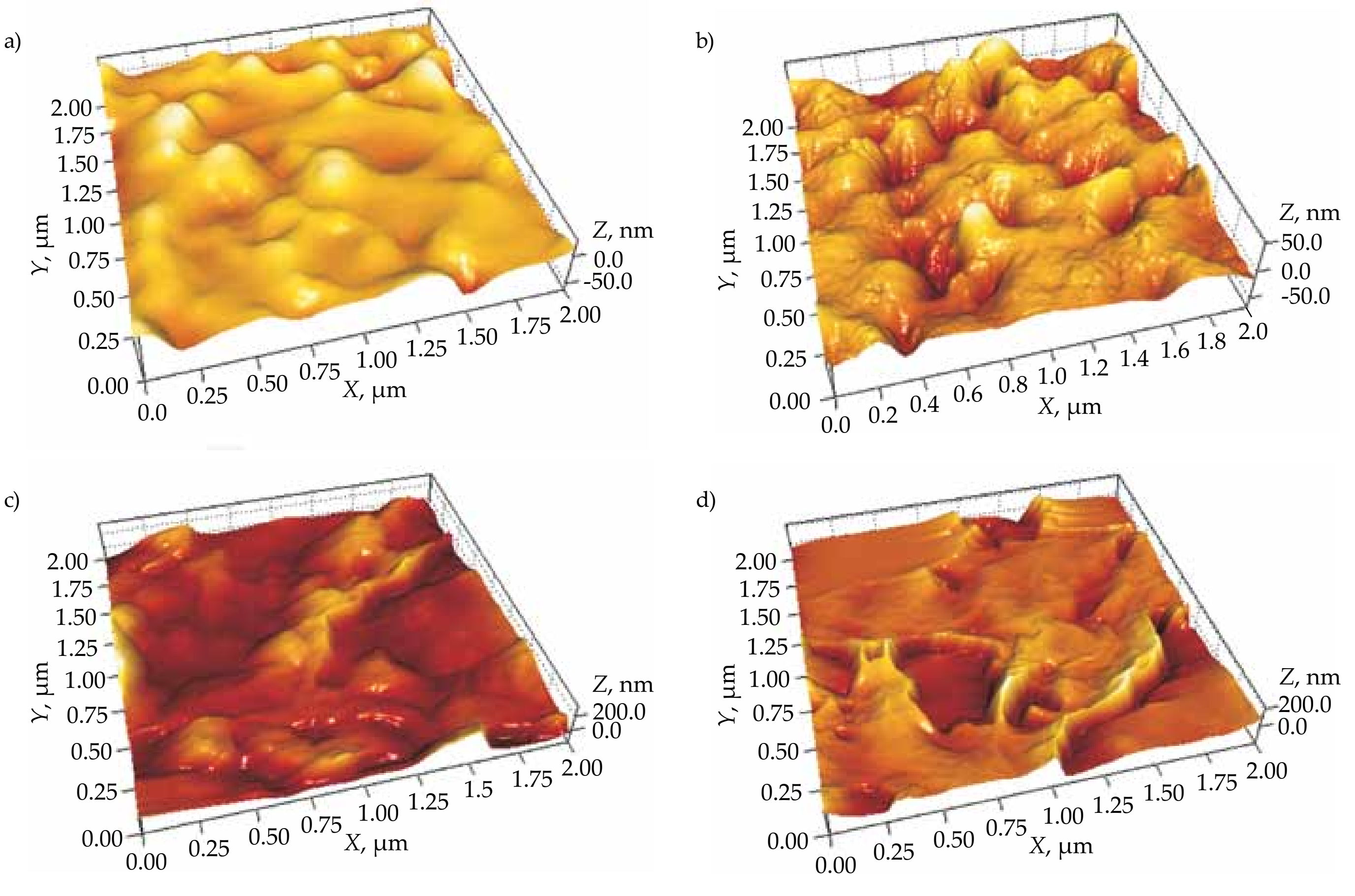

Fig. 1. AFM surface images of PHB samples modified with low-temperature plasma: a) P(35, 5, 0), b) P(35, 5, 9), c) P(35, 25, 0), d) P(35, 25, 9)

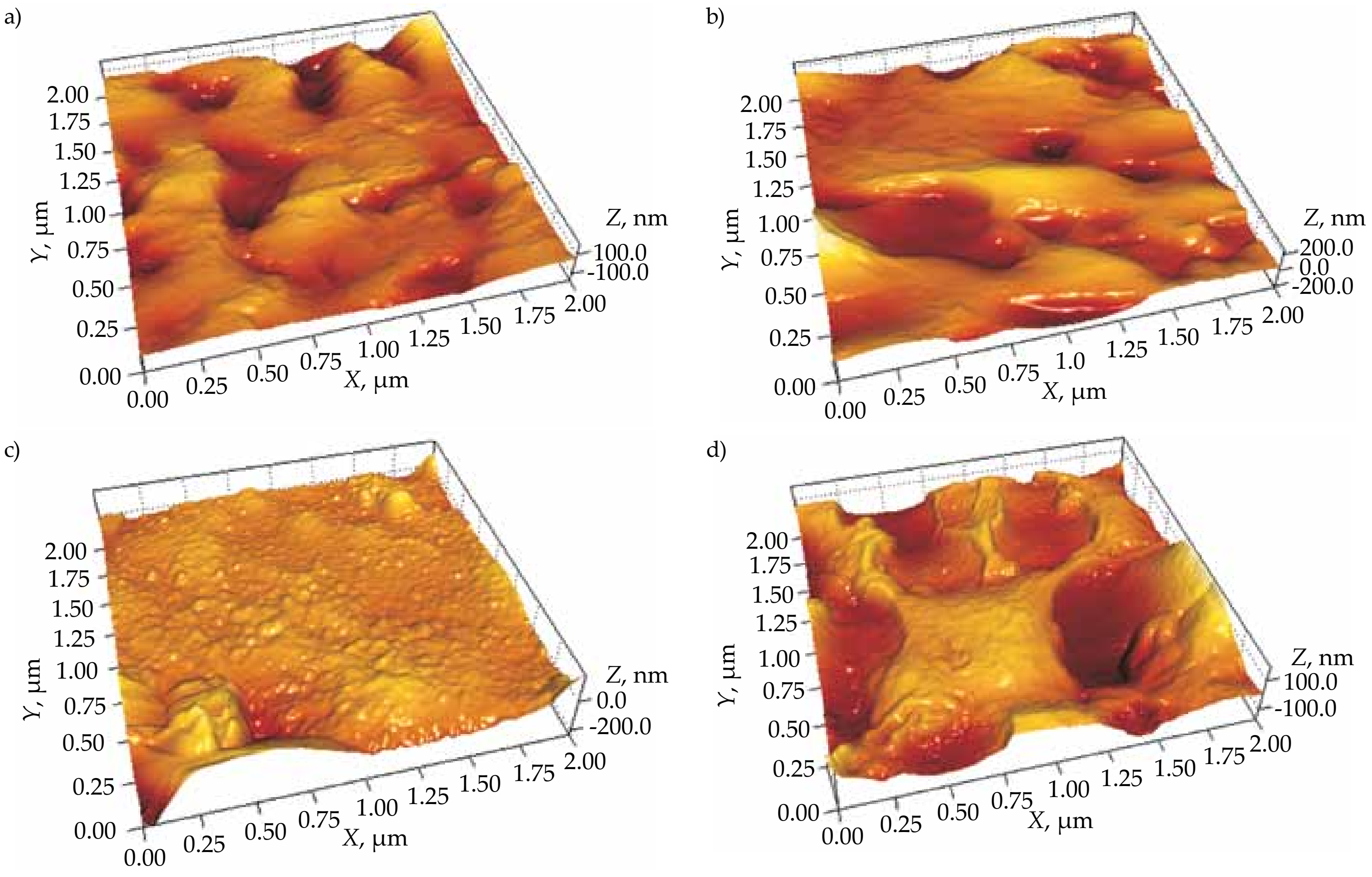

Fig. 2. AFM surface images of PHB samples modified with low-temperature plasma: a) P(75, 5, 0), b) P(75, 5, 9), c) P(75, 25, 0), d) P(75, 25, 9)

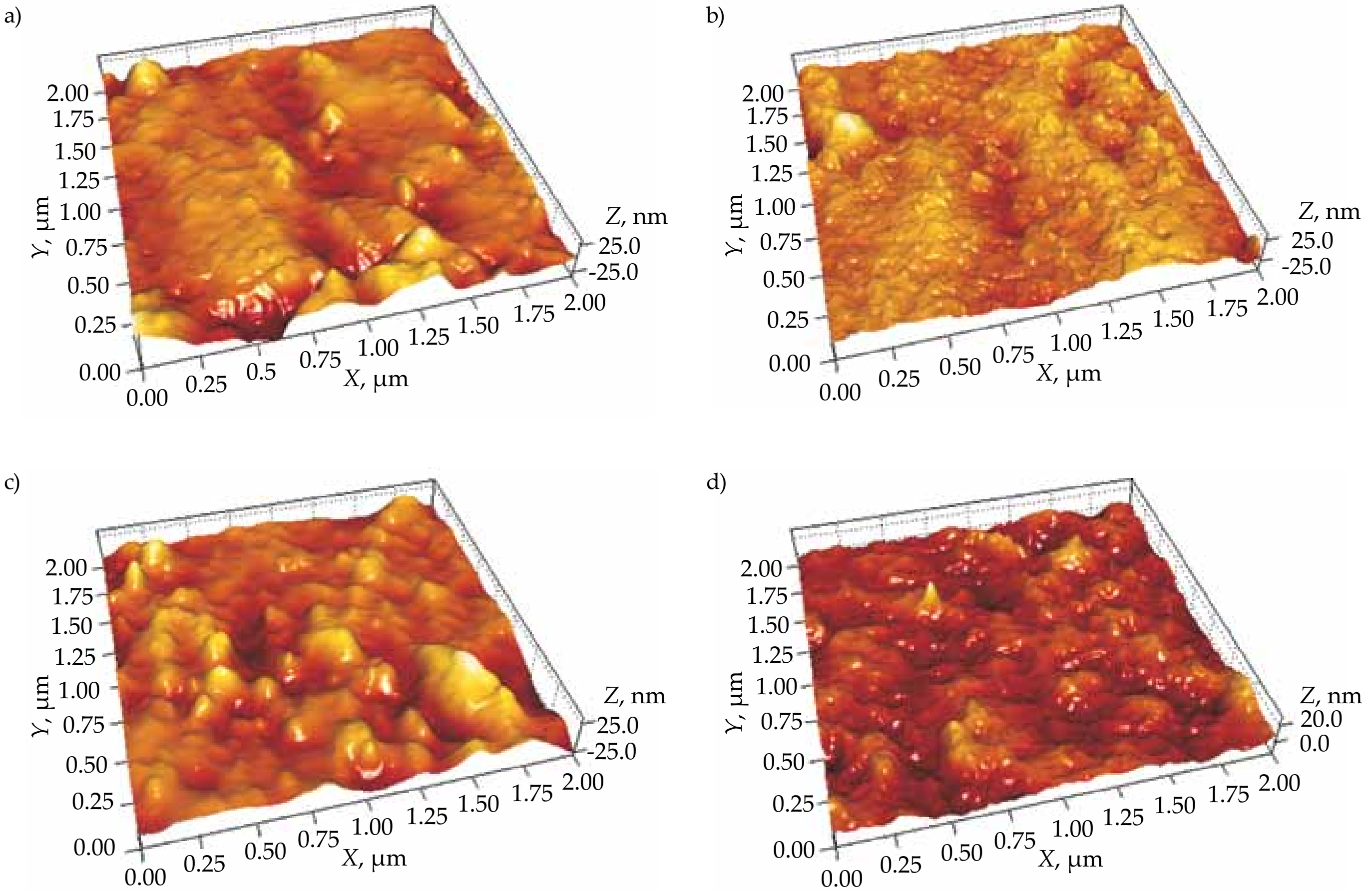

Fig. 3. AFM surface images of PHB samples modified with CD: a) C(3.5, 0), b) C(3.5, 9), c) C(10, 0), d) C(10, 9)

T a b l e 1. The *RMS* values of modified samples (based on AFM results)

Sample	*RMS*
P	0.30
P(35, 5, 0) P(35, 5, 3) P(35, 5, 9)	5.70 8.49 19.30
P(35, 25, 0) P(35, 25, 3) P(35, 25, 9)	8.46 42.90 43.30
P(75, 5, 0) P(75, 5, 3) P(75, 5, 9)	2.94 11.50 11.00
P(75, 25, 0) P(75, 25, 3) P(75, 25, 9)	7.69 12.10 15.90
C(3.5, 0) C(3.5, 3) C(3.5, 9)	3.08 3.14 8.11
C(10, 0) C(10, 3) C(10, 9)	1.90 6.20 6.23

sample modified with E_j = 10 kJ/m², the process of polymer degradation predominated. As for samples modified with low-temperature plasma, the *RMS* increased with aging time.

Table 1 shows the *RMS* values of samples modified with low-temperature plasma or corona discharge.

Figure 4 shows the spectrum of neat PHB sample.

The IR bands of the PHB sample at 2980 cm^{-1} and 2944 cm^{-1} were assigned to the C–H stretching region [$CH_{3(asym)}$ and $CH_{3(sym)}$]. The peaks that appeared at 2921 cm^{-1} and 1755 cm^{-1} correspond to the stretching (valence) vibrations of the carbonyl groups C=O. The CH_3 groups are responsible for the appearance of the band at 1454 cm^{-1}. The C–H deformation and asymmetric bands appear at 1383 cm^{-1} and 1360 cm^{-1}. The C–O stretching mode of the ester groups appears at 1262 cm^{-1} and 1183 cm^{-1}, and the C–O asymmetric mode appears at 1088 cm^{-1}.

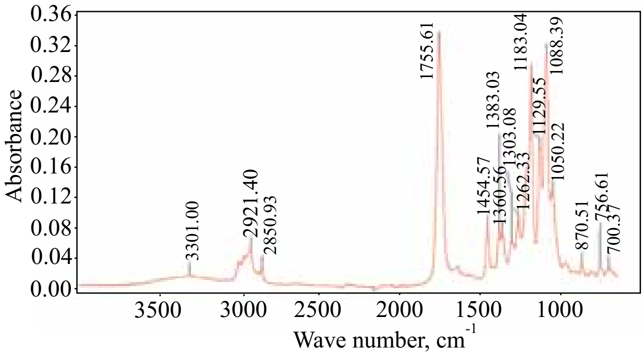

Fig. 4. FT-IR spectrum of neat PHB sample

The selected peaks of samples modified by low-temperature plasma and corona discharge are shown in Fig. 5 and Fig. 6, respectively.

Modification by low-temperature plasma mainly caused changes in the absorbance peaks corresponding to oxygen-containing functional groups, *i.e.*, 1755 cm^{-1} and 1300–1000 cm^{-1} peaks. Major changes in the absorbance of the 3000–2800 cm^{-1} peaks occurred only after applying the highest parameters of modification. Based on the analysis of the obtained results, it can be concluded that the largest increase of oxidation of the surface layer was obtained using short-time (5 min) modification with a power of 35 or 75 W. An increase in the modification time caused a significant drop in the value of the analyzed absorbance peaks, and the results obtained after modification were similar to those for unmodified PHB. In the case of the sample modified for 25 minutes with power of 75 W, a large increase in absorbance of the 3000–2800 cm^{-1} peaks also occurred, which may indicate a degradation process occurring in the surface layer during modification.

Modification by corona discharge caused a significant change in peak intensity in the 3000–2800 cm^{-1} (C–H, CH_2, CH_3 functional groups) and 1300–1000 cm^{-1} (C–O functional groups) range. There were also slight changes in the absorbance of the 1755 cm^{-1} peak. Surface modification with E_j = 3.5 kJ/m² resulted in a significant decrease in the absorbance of the 3000–2800 cm^{-1} peaks and a large increase in the absorbance peaks from the range of 1300–1000 cm^{-1}. Modification also resulted in a slight increase in the absorbance of the 1755 cm^{-1} peak.

In the case of samples modified with E_j = 10 kJ/m², different effects of surface modification were observed. Modification resulted in a large increase in the absorbance of the 3000–2800 cm^{-1} peaks, as well as in a decrease in the absorbance of peaks from the 1300–1000 cm^{-1} range and the 1755 cm^{-1} peak.

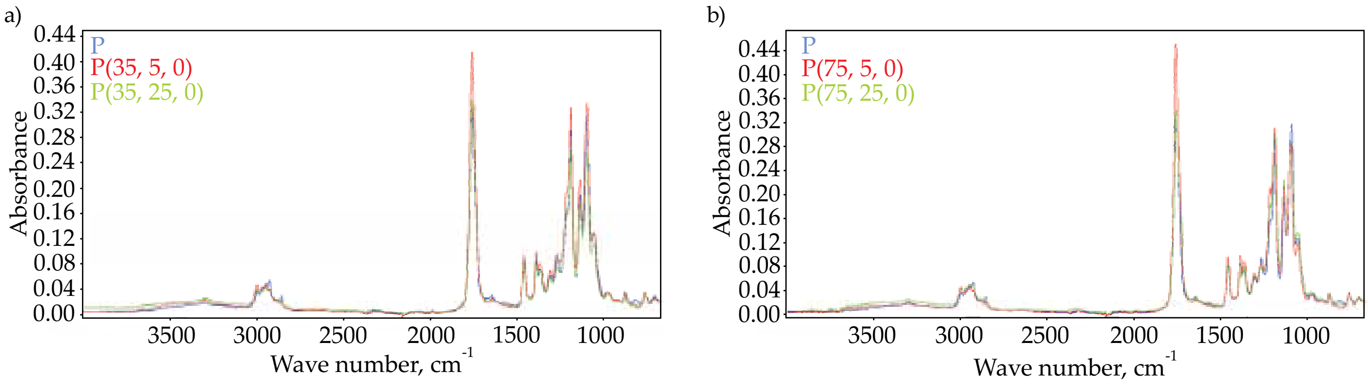

Fig. 5. FT-IR spectra of PHB samples modified with plasma at a) 35 W, b) 75 W

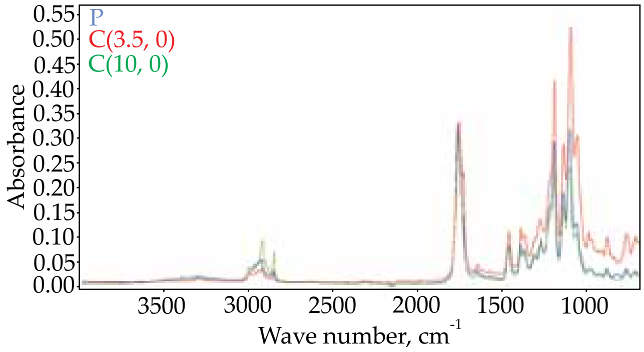

Fig. 6. FT-IR spectra of PHB samples modified with CD

On the basis of the observed changes, it can be concluded that modifying the surface layer of PHB with a smaller value of E_j increased the oxidation of this layer. As a result of modification, the content of oxygen atoms increased due to the generation of more functional groups containing oxygen (C=O and C–O). While the application of higher values of E_j caused an increase in the content of the CH, CH_2 and CH_3 functional groups, which might suggest that the result of modification of the degradation process occurs rather than oxidation.

Changes in the FT-IR spectra obtained during aging of the samples modified with low-temperature plasma depended on the power of the generated plasma and time of modification. For samples modified with a power of 35 W for 5 minutes, the absorbance of the 3000–2800 cm^{-1} peaks did not change significantly, and for samples modified for 25 minutes the absorbance increased with longer aging times. The absorbance of the 1755 cm^{-1} peak initially increased with aging time regardless of the modification time. In the case of the samples modified for 5 minutes, this increase is maintained until six weeks after the modification, followed by a slight decrease in the value. In contrast, in the case of samples modified for 25 minutes a large increase in absorbance occurred after 3 weeks of aging, followed by a decrease to a value lower than the unmodified PHB sample (Fig. 7). Also, the absorbance of 1300–1000 cm^{-1} peaks initially increased with longer aging times. Later, however, the absorbance value decreased, which can be associated with the reorganization of the macromolecules in the surface layer of the polymer. For samples modified for 5 minutes, the decrease occurred after 3 weeks of aging, while for the sample modified for 25 minutes, after 6 weeks of aging. In both cases, the absorbance of peaks after aging was lower than for unmodified PHB.

In the case of samples modified with a power of 75 W, the absorbance of the 3000–2800 cm^{-1} peaks neither changed significantly for the sample modified for 5 minutes, nor increased with the aging time for the samples modified for 25 minutes. The absorbance of the 1755 cm^{-1} peak decreased with longer aging times for the sample modified for 5 minutes, however, the value after aging was still greater than the value of the unmodified PHB. Initially, an increase in absorbance of the 1755 cm^{-1} peak was observed for samples modified for 25 minutes. This value increased during six weeks of aging, subsequently decreasing to a value lower than value of unmodified PHB. The absor-

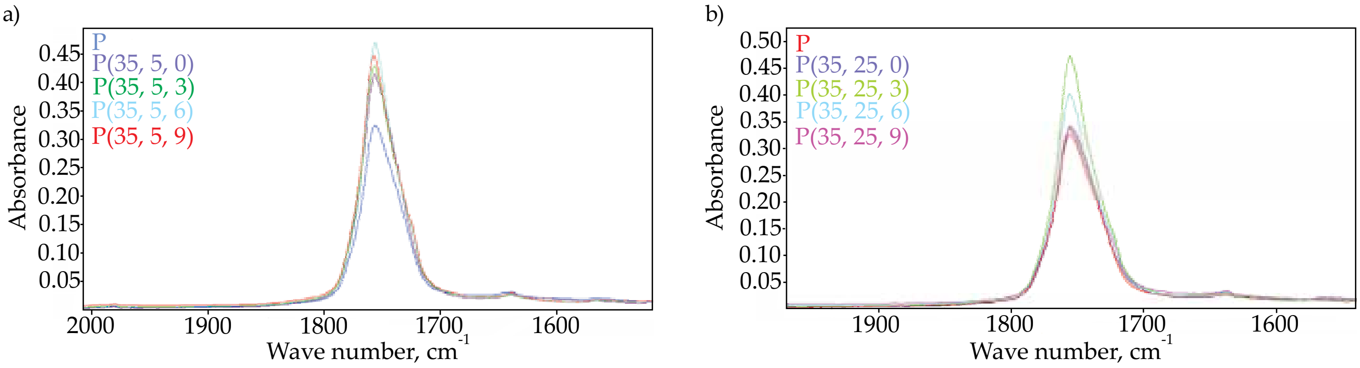

Fig. 7. Absorbance of 1755 cm^{-1} peak of aged PHB samples modified with plasma at 35 W for: a) 5 min, b) 25 min

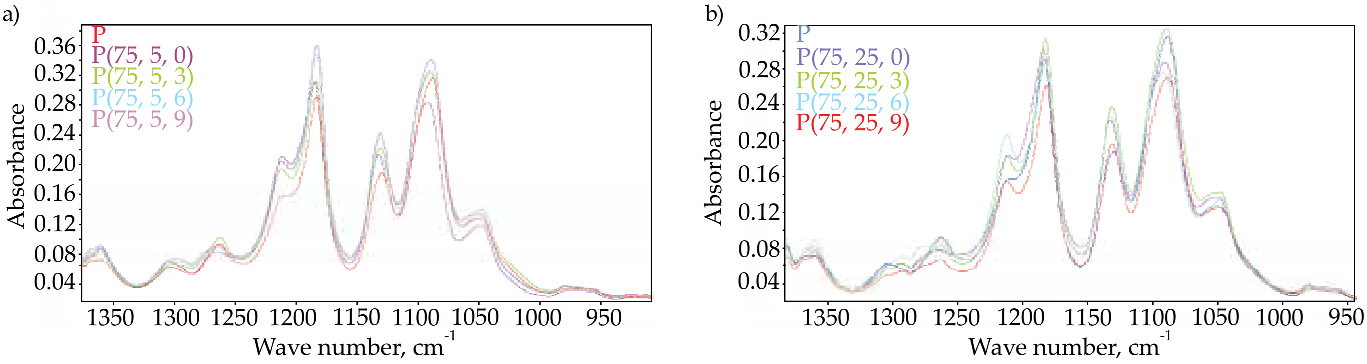

Fig. 8. Absorbance of 1300–1000 cm^{-1} peaks of aged PHB samples modified with low-temperature plasma at 75 W for: a) 5 min, b) 25 min

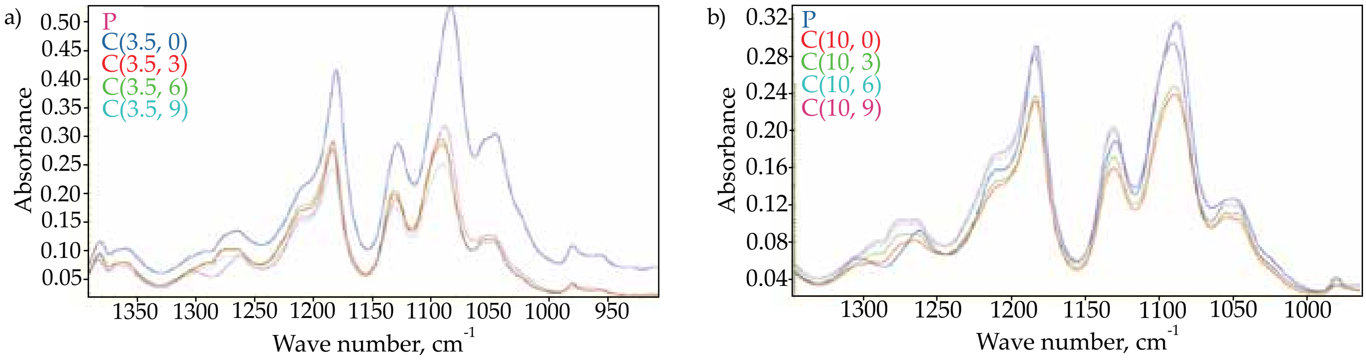

Fig. 9. Absorbance of 1300–1000 cm^{-1} peaks of aged PHB samples CD modified with E_j of: a) 3.5 kJ/m^2, b) 10 kJ/m^2

bance of the 1300–1000 cm^{-1} peaks increased with longer aging times for samples modified for 5 minutes reaching a value greater than the value of the unmodified sample. For the sample modified for 25 minutes, an increase in the absorbance was observed only during three weeks of aging, followed by a decrease in absorbance to a value lower than for the unmodified sample (Fig. 8).

The aging process resulted in significant changes in the FT-IR spectra of the tested samples. Over time, and after CD modification with E_j = 3.5 kJ/m^2, an increase in the absorbance of the 3000–2800 cm^{-1} peaks were observed to a value greater than for unmodified PHB. Initially, the absorbance of the 1755 cm^{-1} peak also increased reaching its' highest value after 6 weeks of aging. Longer aging resulted in a decrease in the absorbance value to the level measured for unmodified PHB. The absorbance of the 1300–1000 cm^{-1} peaks decreased approximately linearly with aging time. After 3 weeks of aging, the measured value was lower than the absorbance value of PHB, further decreasing up to 9 weeks of aging (Fig. 9a).

The use of CD with a higher E_j of 10 kJ/m^2 resulted in different changes in the FT-IR spectra. In contrast to the lower E_j value, longer aging times resulted in a decrease in the absorbance of the 3000–2800 cm^{-1} peaks and increase in the absorbance of the 1300–100 cm^{-1} peaks (Fig. 9b). There was, however a similar increase in the absorbance of the 1755 cm^{-1} peak but in the case of modification with higher E_j values this growth was maintained up to 9 weeks of aging.

CONCLUSIONS

Modification of the surface layer of PHB with low-temperature plasma or corona discharge caused changes in the geometrical structure and chemical composition of the tested surfaces.

The *RMS* values of samples modified with low-temperature plasma increased with longer aging times. Changes in FT-IR spectra occurred as a result of aging and mainly depended on the power of the generated plasma and modification time. In the case of CD modification, an *RMS* increase with aging time was also observed. The *RMS* values were higher in the samples modified with a smaller E_j where mainly the oxidation of PHB surface occurred while in the samples modified with higher E_j mainly the degradation of PHB occurred.

REFERENCE

[1] "Polymer Surface Modification: Relevance to Adhesion" Vol. 2, (Ed. Mittal K.L.), VSP, Zeist 2000.
[2] Lee J., Hwang S., Cho D.H. *et al.*: *Applied Surface Science* **2017**, *394*, 543. http://dx.doi.org/10.1016/j.apsusc.2016.10.113
[3] Cardoso M.R., Tribuzi V., Balogh D.T. *et al.*: *Applied Surface Science* **2011**, *257*, 3281. http://dx.doi.org/10.1016/j.apsusc.2010.10.156
[4] Stepczyńska M.: „Studium plazmowego modyfikowania warstwy wierzchniej oraz metod sterylizacji materiałów biodegradowalnych", Wydawnictwo Uniwersytetu Kazimierza Wielkiego, Bydgoszcz 2017.
[5] Kramer A., Bekeschus S., Matthes R. *et al.*: *Plasma Process and Polymers* **2015**, *12*, 1410. http://dx.doi.org/10.1002/ppap.201500170
[6] Hegemann D., Michliček M., Blanchard N.E. *et al.*: *Plasma Process and Polymers* **2016**, *13*, 279. http://dx.doi.org/10.1002/ppap.201500078
[7] Hegemann D., Nisol B., Watson S., Wertheimer M.R.: *Plasma Process and Polymers* **2016**, *13*, 834. http://dx.doi.org/10.1002/ppap.201500224
[8] Stepczyńska M.: *Plasma Process and Polymers* **2016**, *13*, 1078. http://dx.doi.org/10.1002/ppap.201600051
[9] *US Pat.* 3 018 189 (1962).
[10] *US Pat.* 3 640 733 (1962).
[11] *US Pat.* 3 113 208 (1963).
[12] Lieberman M.A., Lichtenberg A.J.: "Principles of Plasma Discharges and Materials Processing" Second Edition, Wiley & Sons, Inc., New York 2005.
[13] Stepczyńska M.: *Journal of Food Engineering* **2014**, *126*, 56. http://dx.doi.org/10.1016/j.jfoodeng.2013.10.038
[14] Żenkiewicz M.: *Polimery* **2005**, *50*, 429.
[15] Żenkiewicz M.: *Polimery* **2007**, *52*, 760.
[16] Żenkiewicz M.: *International Journal of Adhesion and Adhesives* **2005**, *25*, 61. http://dx.doi.org/10.1016/j.ijadhadh.2004.03.004
[17] Olewnik E., Richert J.: *Polymer Composites* **2015**, *36*, 17. http://dx.doi.org/10.1002/pc.22906
[18] Stepczyńska M.: *Polimery* **2015**, *60*, 385.

http://dx.doi.org/10.14314/polimery.2015.385

[19] Moraczewski K., Stepczyńska M., Malinowski R. *et al.*: *Applied Surface Science* **2016**, *377*, 228. http://dx.doi.org/10.1016/j.apsusc.2016.03.171

[20] Żenkiewicz M.: "Adhesion and modification of the surface layer of macromolecular materials", WNT, Warsaw 2000.

[21] Keidar M., Beilis I.: "Plasma Engineering" 1st Edition, Elsevier Academic Press 2013.

[22] Stevens J.E.: "Plasma Fundamentals for Materials Processing" in "Handbook of Advanced Plasma Processing Techniques" (Eds. Shul R.J., Pearton S.J.), Springer, Berlin Heidelberg 2000.

[23] Napartovich A.P.: *Plasmas and Polymers* **2001**, *6*, 1. http://dx.doi.org/10.1023/A:1011313322430

[24] Belevtsev A.A., Biberman L.M.: *Beiträge aus der Plasmaphysik* **1983**, *23*, 313. http://dx.doi.org/10.1002/ctpp.19830230310

[25] O'Hare L.A., Smith J.A., Leadley S.R. *et al.*: *Surface and Interface Analysis* **2002**, *33*, 617. http://dx.doi.org/10.1002/sia.1429

[26] O'Hare L.A., Leadley S., Parbhoo B.: *Surface and Interface Analysis* **2002**, *33*, 335. http://dx.doi.org/10.1002/sia.1217

[27] Slepička P., Trostová S., Slepičková Kasálková N. *et al.*: *Plasma Process and Polymers* **2012**, *9*, 197. http://dx.doi.org/10.1002/ppap.201100126

[28] Stepczyńska M., Żenkiewicz M., Tracz A.: *Przemysł Chemiczny* **2015**, *94*, 62.

[29] Myshkin N.K., Grigoriev A.Ya., Chizhik S.A. *et al.*: *Wear* **2003**, *254*, 1001. http://dx.doi.org/10.1016/S0043-1648(03)00306-5

[30] Rytlewski P., Mróz W., Żenkiewicz M. *et al.*: *Journal of Materials Processing Technology* **2012**, *212*, 1700. http://dx.doi.org/10.1016/j.jmatprotec.2012.03.019

[31] Moraczewski K., Rytlewski P., Malinowski R., Żenkiewicz M.: *Applied Surface Science* **2015**, *346*, 11. http://dx.doi.org/10.1016/j.apsusc.2015.03.202

Received 28 VI 2017.