

# Autocatalytic metallization of polylactide

Krzysztof Moraczewski<sup>1),\*)</sup>, Rafał Malinowski<sup>2)</sup>, Piotr Rytlewski<sup>1)</sup>, Marian Żenkiewicz<sup>2)</sup>

DOI: dx.doi.org/10.14314/polimery.2015.492

**Abstract:** In this work experimental results of a research aimed to provide the assessment of the ability of chemical modification to prepare polylactide (PLA) surface for autocatalytic metallization are presented. Chemical modification of PLA was performed using two solutions (1 and 2). Analysis of PLA samples was performed by means of goniometry, atomic force microscopy (AFM), scanning electron microscopy (SEM) and photoelectron spectroscopy (XPS). Results of contact angle measurements and surface energy calculations were presented. Qualitative and quantitative analysis of elemental composition of PLA surface layer was performed. Based on the experimental results, it was found that the proposed method can be successfully applied to prepare PLA surface for metallization. Autocatalytically deposited copper layer exhibited good adhesion to PLA and electrical conductivity.

**Keywords:** polylactide, chemical modification, autocatalytic metallization.

## Autokatalityczne metalizowanie polilaktydu

**Streszczenie:** Zbadano możliwość wykorzystania modyfikacji chemicznej w procesie przygotowania powierzchni polilaktydu (PLA) do procesu autokatalitycznego metalizowania. Modyfikację chemiczną PLA przeprowadzono za pomocą dwóch roztworów (1 i 2). Próbkę PLA zbadano metodami: goniometrii, mikroskopii sił atomowych (AFM), elektronowej mikroskopii skaningowej (SEM) i spektroskopii fotoelektronowej (XPS). Wykonano też pomiary kątów zwilżania oraz obliczenia swobodnej energii powierzchniowej, a także przeprowadzono jakościową i ilościową analizę składu chemicznego warstwy wierzchniej PLA. Wyniki badań wskazują, że zaproponowana metoda może być wykorzystana w procesie przygotowania powierzchni polilaktydu PLA do metalizowania. Uzyskana warstwa metaliczna charakteryzuje się dobrą wytrzymałością adhezyjną i dobrymi właściwościami elektrycznymi.

**Słowa kluczowe:** polilaktyd, modyfikacja chemiczne, metalizowanie autokatalityczne.

In metallization process of polymeric materials a metal layer is usually deposited by chemical reactions between metal ions and a reducer compound present in metallization bath. This process occurs in the presence of a catalyst. If the catalyst is the deposited metal, autocatalytic process occurs, and the deposited layer may have theoretically unlimited thickness. This is crucial in practical application of electroless metallization, which under these conditions is termed as autocatalytic metallization [1].

Properties of the surface layer (SL) of polymeric materials, such as chemical composition, molecular structure, surface geometrical structure, wettability and surface energy significantly affect the metallization process, adhesion of deposited metal to the polymer substrate, as well as the material structure and its electric conductivity [2]. Most of polymer materials are unreactive, hydropho-

bic and have low surface energy [3]. These features substantially hinder metallization process. Thus, adhesion strength can vary within a relatively wide range depending on the types of materials forming polymer/metal interface. In the metallization process of polymeric materials a necessary step of SL modification is required in order to deposit catalyst and to improve adhesion of the deposited metal layer to the polymer substrate [4]. This modification causes chemical and/or physical alterations improving chemisorption of catalyst and adhesion strength of the metal/polymer interface [5–7].

Chemical, corona discharge, flame, plasma, ozone, electron and laser surface treatments are the most well-known methods of SL modifications. In the case of polymers, chemical, plasma or laser surface treatments are most commonly applied to prepare the surface for metallization [8–12]. Generally, chemical modification methods consist in treatments of polymer SL with strong oxidizing compounds, acids or solvents. Solutions of sodium dichromate(VI) or potassium dichromate(VI), and potassium manganate(VII) in diluted sulfuric(VI) acid are most commonly used for that purpose [9, 13, 14], however, phenol, sodium hydroxide, sodium chlorate(I) and sodium metal are also used [1, 11]. SL of polymer

<sup>1)</sup> The Kazimierz Wielki University, ul. Chodkiewicza 30, 85-064 Bydgoszcz, Poland.

<sup>2)</sup> Institute for Engineering of Polymer Materials and Dyes, ul. Marii Skłodowskiej-Curie 55, 87-100 Toruń, Poland.

<sup>\*)</sup> Author for correspondence; e-mail: kmm@ukw.edu.pl

material is cleaned, partially etched and chemically altered as a result of chemical treatment.

New polymeric materials derived from renewable resources as an alternative for polymers derived from petroleum are increasingly wanted. Polylactide is an important example of such a polymer [15], being a subject of numerous investigations and applications. It is considered to be one of the most promising polymers able to replace polymers of petroleum origin. Two main branches of its application can be distinguished. The first encompasses medical applications such as sutures, implants and drug carriers, while the second relates to consumer products, mainly in the form of packaging materials and disposable products. An increasing interest in application of PLA to manufacture electronic printed circuit boards and carriers was recently noticed [16].

Development of new autocatalytic metallization technologies for PLA would broaden the applicability of this polymer. It would also reduce consumption of petroleum and the burden on the natural environment. It is expected that an increase in production of PLA would also lower the price of this polymer, thus making it competitive with regard to the polymers derived from petroleum.

With this aim in mind, studies on chemical and plasma modifications of PLA in order to prepare its surface for autocatalytic metallization were undertaken in this work. This paper presents the results of chemical modification of PLA surface layer. It was found that chemical treatment was the most effective method in preparation of the surface to be metallized. Selected properties of the copper layer deposited on PLA were also presented.

## EXPERIMENTAL PART

### Materials

The study involved application of the following materials:

- polylactide (PLA) type 2002 D (Cargill Down LLC, USA) with weight-average molecular weight of about 155 500, containing 3.5 % of structural units D and 96.5 % of structural units L;
- distilled water Aqua purificata (Maggie Co., Poland);
- sodium hydroxide (pure p.a., POCh, Poland);
- ethanol 96 % retail (PPS Polmos Warszawa, Poland);
- potassium manganate(VII) (pure p.a., POCh, Poland),
- nitric acid (65 % pure p.a., POCh, Poland) with density 1.40 g/dm<sup>3</sup>;
- palladium(II) chloride (pure p.a., POCh, Poland);
- tin(II) chloride (pure, Chempur, Poland);
- hydrochloric acid (35–38 % pure p.a., Chempur, Poland) with density 1.19 g/dm<sup>3</sup>;
- autocatalytic copper plating bath M-Copper 85 (MacDermid, USA);
- formaldehyde (36 % pure, POCh, Poland);

- diiodomethane (99 % pure p.a., Sigma-Aldrich, Germany).

### Preparation of samples

Samples were manufactured using the injection molding machine type Tederic TRX 80 ECO 60 (Tederic Machinery Manufacture Co. Ltd., Taiwan). Temperatures of I, II and III zone of the injection molding machine cylinder, head and mold were: 170, 180, 190, 190 and 30 °C, respectively.

Chemical modification of PLA surface was performed using two solutions. The first was the solution containing 0.17 mol/dm<sup>3</sup> of KMnO<sub>4</sub> and 1.24 mol/dm<sup>3</sup> of HNO<sub>3</sub> (herein referred to as solution 1). Modification with this solution was carried out at the room temperature for 30, 40, 50 or 60 min [17]. The second solution was prepared by mixing the water solution containing 0.25 mol/dm<sup>3</sup> of NaOH and ethyl alcohol with volume ratio of 1:1 (herein referred to as solution 2). Modification with this solution was carried out at 50 °C for 1, 2, 2.5, 5, 7.5 or 10 min [18]. Samples were designated as PXY, where X denotes the type of the solution (M – solution 1, N – solution 2) and Y denotes the time of modification.

Autocatalytic copper plating was carried out in a multistep process including activation, rinsing, acceleration, autocatalytic metallization, rinsing and drying. Surface activation was conducted in a single-step process, by immersing the samples in an aqueous solution containing 0.25 g/dm<sup>3</sup> PdCl<sub>2</sub>, 12 g/dm<sup>3</sup> SnCl<sub>2</sub> and 60 cm<sup>3</sup>/dm<sup>3</sup> of 38 % solution of HCl at 25 °C for 5 min. The specimens were subsequently immersed in an accelerating solution containing 32 cm<sup>3</sup>/dm<sup>3</sup> 38 % solution of HCl at 25 °C for 5 min. After the acceleration process the samples were rinsed with deionized water to prevent contamination of the plating bath. Activated samples were consequently immersed in autocatalytic copper plating bath at 46 °C for 5 min. The pH value of the bath at the temperature of 46 °C was 12.8. Following the recommendations of the manufacturer, the bath was continuously aerated during the metallization. Samples were metallized for 1, 2.5 or 5 min. In the post-treatment stage, the samples were dried in a laboratory oven.

### Methods of testing

Atomic force microscope (AFM) Nanoscope IIIa (Digital Instruments, USA) was used to investigate surface geometrical structure. The studies were performed in the oscillation mode, using scanner „J” and probes RTSEP (Veeco, USA), in air with the scanning frequency of 1 Hz. The images at the resolution of 512 × 512 lines were recorded.

The images of modified and metallized PLA surface were made with the Hitachi SU8010 scanning electron microscope (Hitachi High-Technologies Co., Japan). The studies were made at the accelerating voltage of 2 kV, cur-

rent from 6 to 10  $\mu\text{A}$  (depending on the type of sample), with the working distance of 4 mm. Prior to testing, the samples were sprayed with a gold layer about 3 nm thick.

To measure the contact angle, DSA 100 goniometer (Krüss GmbH, Germany) was applied. The apparatus was equipped with the automatic liquid drop dosing system. Contact angle measurements were taken immediately after modification of samples, applying water (polar liquid) and diiodomethane (dispersive liquid). The drops of the liquids were placed onto the surface of samples, while their volume was continuously increasing and simultaneously dynamic contact angle was measured. Twelve measurements of the contact angle were taken for each sample and the lowest and highest values were rejected. For the other 10 values arithmetic mean was calculated and applied for the calculations of surface energy (*SE*) according to the Owens-Wendt method [19].

To investigate the photoelectron spectra (XPS), photoelectron spectrometer ESCALAB-210 manufactured by VG Scientific (UK) was used. The tests were made applying non-monochromatic X-ray irradiation Al  $K\alpha$  (energy of 1486.6 eV), with the lamp working parameters of 14.5 kV and 20 mA, respectively. The measurements were taken in the analyzer chamber keeping its pressure between  $3.0 \cdot 10^{-6}$  and  $5.0 \cdot 10^{-6}$  Pa. The specimens were

Measurements of volume and surface resistivity were performed using an electrometer of type 6517 and a set of electrodes of type 8009 (Keithley Instruments, USA). Measuring volume and surface resistivity voltage and polarization time were set to 500 V and 30 s, respectively. An average values from 15 measurements of the electric current were taken for calculations of the volume or surface resistivity.

## RESULTS AND DISCUSSION

Preparation of surface is one of the most important steps in autocatalytic metallization of polymer materials. This process significantly affects the quality of deposited metallic layer. The adhesion strength is a key parameter in assessment of the quality of the deposited metallic layer. It can be improved by increasing surface roughness of the material. By increasing the roughness, not only an increase in surface area but also in the number of grooves is observed. These grooves can serve as sites for anchoring the deposited metal layer to the polymer substrate, thus increasing the adhesion strength. As it is shown in Fig. 1, on the untreated PLA surface one can perceive scratches about 100 nm deep, which probably reproduced the surface structure of the mold. Relatively

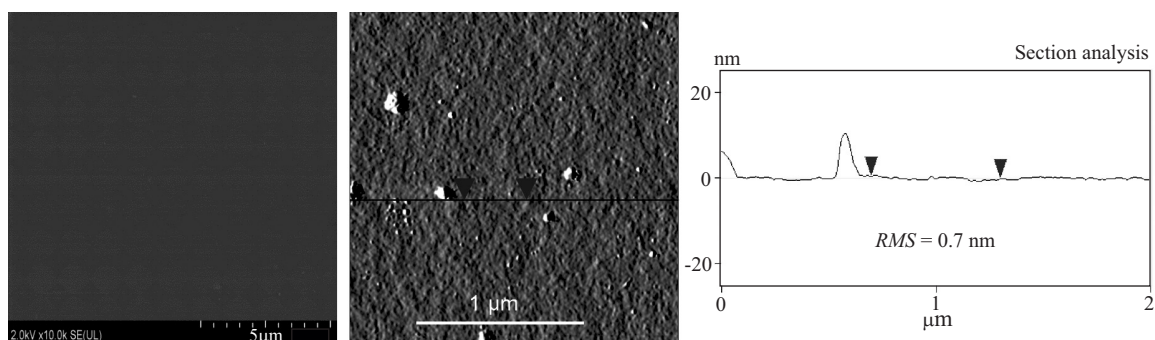


Fig. 1. SEM and AFM images with the roughness profile of unmodified PLA surface

placed perpendicular to the analyzer axis and the source of irradiation was placed at the angle of  $60^\circ$ . The surface of the specimens analyzed corresponded to the size of the analyzer aperture, about a dozen  $\text{mm}^2$ . The experimental spectra were deconvoluted using the AVANTAGE software (version 4.84, Thermo Electric). Spectral analysis was performed based on the values of sensitivity coefficients for respective electron levels resulting from the PLA structure [20].

Adhesion strength was determined by pull-off method using adhesion tester PosiTest 03810 (DeFelsko, USA). The measurements were performed with testing fixture of the diameter 6.30 mm, adhesively bonded to the copper layer covering the polymer sample. Two-component epoxy adhesive Araldite 2011 (Huntsman, Switzerland) with drying time up to 48 h was applied.

smooth surface was detected in-between the scratches. The average deviation from the roughness profile (*RMS*) was about 0.7 nm.

Chemical modification resulted in significant changes in the surface geometrical structure of PLA. However, depending on the solution type, the nature of these changes was different. In the case of solution 1, results presented in Fig. 2 show surface irregularities formed, with size depending on the modification time. Modification for 30 and 60 min caused an increase in *RMS* values to 1.7 and 4.4 nm, respectively. The increase in surface roughness resulted probably from chemical etching of PLA.

Surface of the samples modified with solution 2 was too rough for reliable and artefacts-free AFM imaging. *RMS* values obtained for these samples ranged from 300 to 700 nm and could contribute to a higher level of mea-

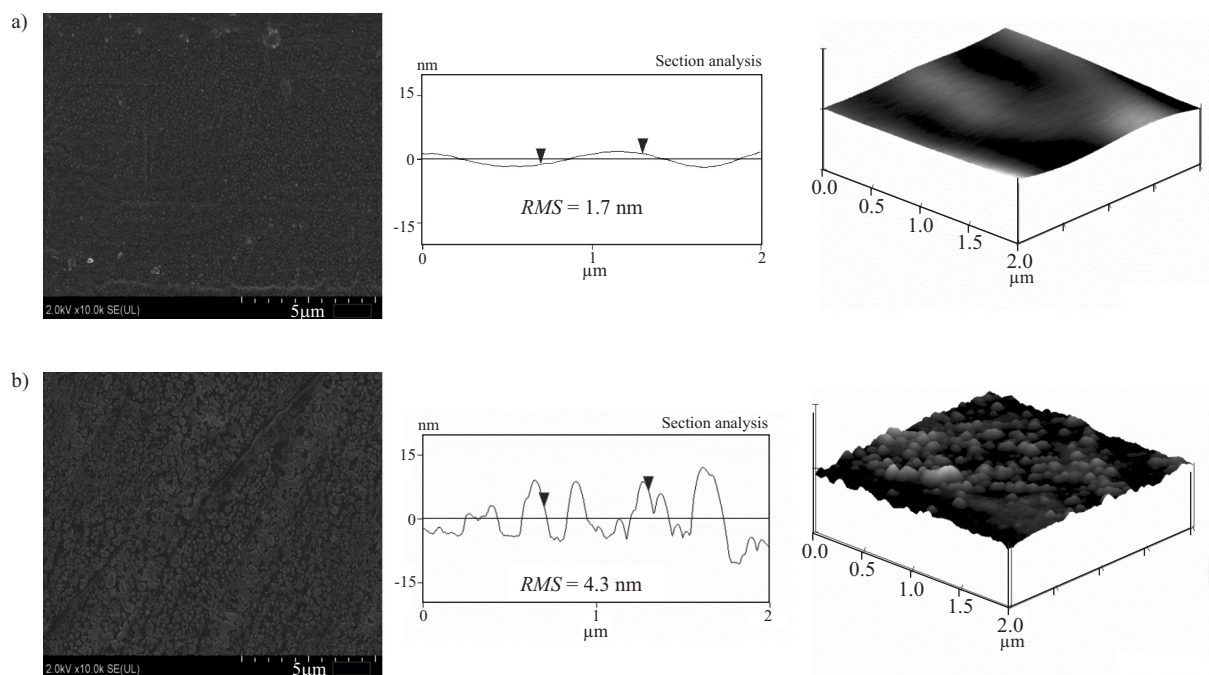


Fig. 2. SEM and AFM images with the surface roughness profile of the samples: a) PM30, b) PM60

surement error. For that reason it is recommended to characterize the samples with SEM technique. The SEM images are shown in Fig. 3.

Chemical modification with solution 2 caused significant changes in the surface of the studied samples. After 1 min of modification, deep fractures were formed in the surface layer (Fig. 3a). Between these fractures the surface structure was similar to that for unmodified PLA. The surface became rough after 5 min of modification (Fig. 3b). Numerous small fractures were visible although unmodified areas could be still perceived. The whole surface was covered with numerous small fractures and grooves after 10 min of modification. The thickness of the modified surface layer was about 15  $\mu\text{m}$  (Fig. 3d).

Surface alterations induced by chemical modification resulted from hydrolytic degradation of PLA. This polymer is one of the aliphatic polyesters whose ester groups undergo hydrolytic degradation in the presence of water [15]. This process depends on the pH value of the solution. In an alkaline solution degradation occurs by backbiting to form a lactyl dimer (lactide) unit, which is further hydrolyzed to give lactoyl lactic acid [21]. Hydro-

lytic degradation is catalyzed by hydroxyl ions present in the solution of NaOH. A high concentration of hydroxide ions in an alkaline solution significantly accelerates the process of hydrolytic degradation of PLA [22, 23].

In the case of alkaline solutions, the degradation process occurs by surface etching, as presented in Fig. 3. During the hydrolytic degradation water-soluble, low molecular weight oligomers and monomers are formed, and then washed away leaving fractures and grooves on the polymer surface [15]. Changes in the surface topography indicated that better results were obtained for the samples modified with solution 2. Numerous fractures and grooves resulting from modification can suggest that after metallization process the deposited metal layer would have high adhesion strength. However, similar effect was not obtained using solution 1, where only a small increase in RMS values was noticed. The modified PLA had no apparent new surface features able to anchor the metal layer to its surface.

Metallization of polymeric materials is possible only after deposition of the catalyst atoms on the surface [24, 25]. This process, called surface activation, is essential for

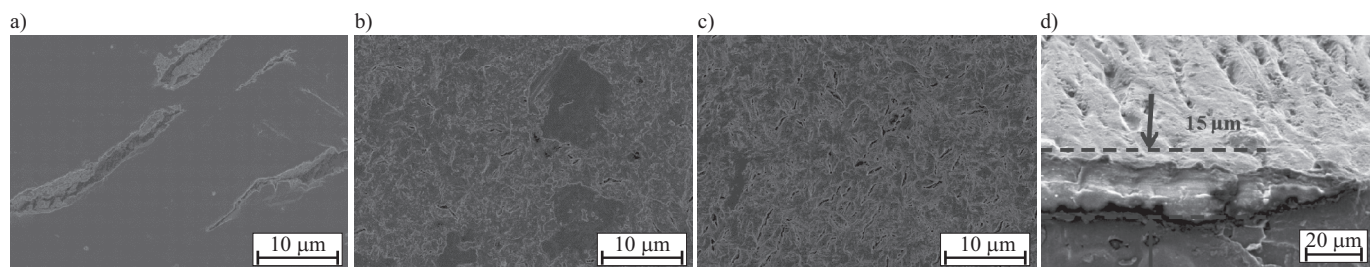


Fig. 3. SEM image of the samples: a) PN1, b) PN5, c) PN10, d) the cross-section of the sample PN10

the quality of the deposited metal layer. The main problem associated with this process is effective chemisorption of catalyst atoms [26]. Therefore, formation of suitable functional groups containing oxygen which adsorb catalyst atoms is necessary.

Contact angle measurements, surface energy ( $SE$ ) calculations and photoelectron spectroscopy (XPS) were performed in order to determine the change in elemental composition of the PLA surface layer after chemical modification. Surface energy is one of the parameters characterizing the ability of a surface to be metallized. Calculations of  $SE$  were carried out based on measured contact angle values. The results are presented in Fig. 4.

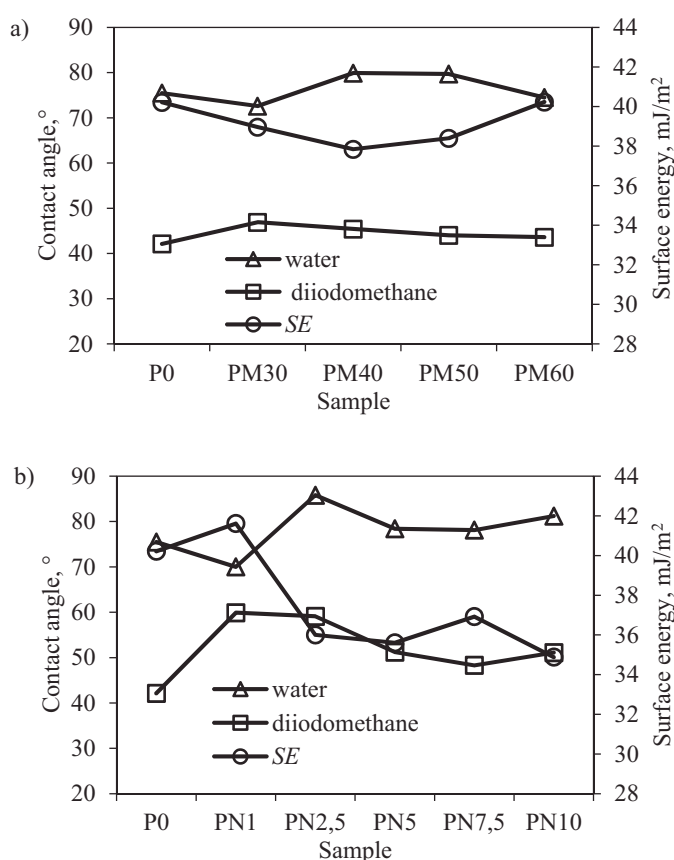


Fig. 4. Effects of the modification time on water and diiodomethane contact angles and surface energy ( $SE$ ) of the samples modified with: a) solution 1, b) solution 2

The values of water ( $\Theta_W$ ) and diiodomethane ( $\Theta_D$ ) contact angles for unmodified PLA (P0) were 75.5° and 42.1°, respectively. Modifications with both solutions caused a slight change in the values of  $\Theta_W$  and  $\Theta_D$ . It should be noted, however, that these changes were more significant when solution 2 was applied. In both cases, the changes were similar. Initially, a decrease in  $\Theta_W$  and increase in  $\Theta_D$  values were observed. However, more extensive modification caused an increase in  $\Theta_W$  and decrease in  $\Theta_D$  values.

Initial change in the contact angle (decrease of  $\Theta_W$  and increase of  $\Theta_D$ ) could result from formation of polar functional groups with incorporated oxygen atoms and from depletion of non-polar functional groups such as C-C and C-H [27, 28]. Further change in contact angles (increase of  $\Theta_W$  and decrease of  $\Theta_D$ ) could be affected by an increase in surface roughness (especially in the case of solution 2).

It was proved elsewhere [29], that increasing roughness leads to an increase in the contact angle of non-wetting liquids (water) and to a decrease in the contact angle of wetting liquids (diiodomethane). These changes affecting contact angle values are in accordance with the results of SEM, AFM and XPS measurements presented in this article.

In the case of the treatment with solution 1, calculated values of the surface energy varied slightly. Initially, during up to 40 min of modification (sample PM40) a slight decrease in  $SE$  (from 40 to 38 mJ/cm²) was observed, then the value for unmodified PLA was reached again. More significant changes were noticed for the samples modified with solution 2. After one minute treatment  $SE$  decreased to about 35 mJ/m² for sample PN1. Further modification did not result in significant change in  $SE$ .

In the most common surface modification techniques (e.g. using other chemical solutions, corona discharge, or plasma treatment) with increasing time or energy doses an increase in  $SE$  of PLA was observed. However, in the case of results presented in this article  $SE$  values did not change or decreased slightly. This phenomenon requires further investigations, although it did not affect the process of autocatalytic metallization presented in this article.

Quantitative analysis of chemical composition of PLA surface layer was performed in order to determine the degree of oxidation. It was calculated as the ratio of the number of oxygen atoms (O1s), and the number of carbon atoms (C1s). The effect of modification conditions on the degree of oxidation is shown in Fig. 5. The degree of oxidation for unmodified PLA was about 23%. Chemical modification resulted in a significant change in the

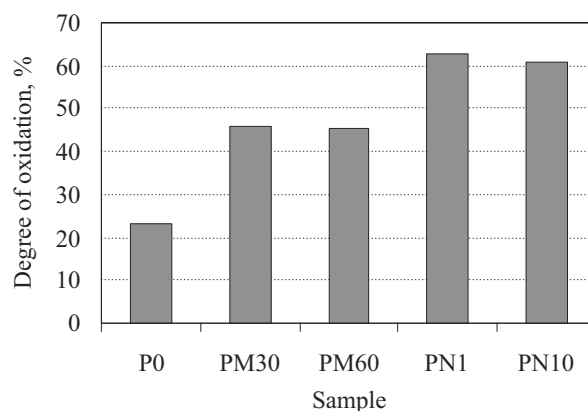


Fig. 5. Effects of the modification time on the degree of oxidation for the samples modified with solution 1 (PM30, PM60) and solution 2 (PN1, PN10)

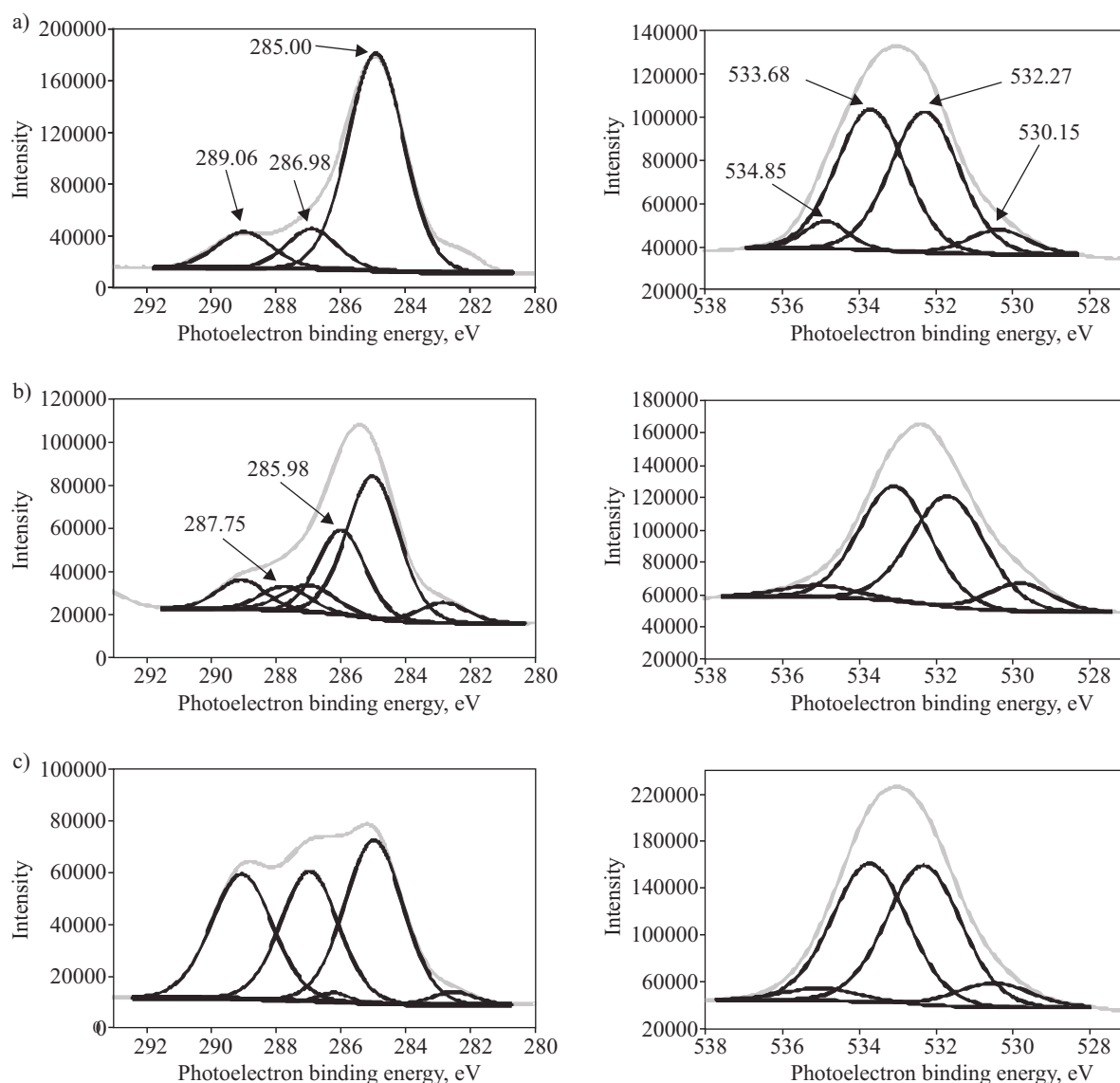


Fig. 6. XPS spectra for C1s and O1s of the samples: a) unmodified, b) PM60, c) PN10

degree of oxidation. The results show that these changes were more significant in the case of solution 2.

Modification with solution 1 caused an increase in the degree of oxidation to about 46 %, whereas with solution 2 to about 63 %. These high values were reached after modification for a very short time. Therefore, the increase in the degree of oxidation can be explained by the initial decrease in  $\Theta_w$  as shown in Fig. 4. Further modification did not cause significant change in the degree of oxidation of PLA surface layer.

An increase in the degree of oxidation can suggest a large quantity of oxygen functional groups, which could significantly improve chemisorption of the catalyst on the surface, thus improving the autocatalytic process and the quality of the deposited metallic layer.

Qualitative analysis of the chemical composition of the PLA surface layer was performed. The XPS spectra for selected samples are shown in Fig. 6. The spectra for the samples modified with different solutions were similar and varied only in intensities of individual peaks.

Functional groups of PLA were identified in unmodified surface layer. There were three functional groups containing carbon,  $-\text{CH}_3$  (with binding energy  $E_B = 285$  eV),  $-\text{CH}-\text{CH}_3$  ( $E_B = 286.98$  eV),  $-\text{C}-\text{C}(\text{O})\text{O}$  ( $E_B = 289.06$  eV), and two functional groups containing oxygen groups  $\text{C}=\text{O}$  ( $E_B = 532.27$  eV) and  $\text{C}-\text{O}$  ( $E_B = 533.68$  eV). In the O1s spectrum bulk oxygen was also identified ( $E_B = 530.15$  eV) and it is assumed that it came from absorbed water ( $E_B = 534.85$  eV).

In both cases of applied solutions changes in carbon and oxygen contents and in the type of functional groups in the PLA surface layer were detected. Carbon content decreased from about 80 at. % for unmodified PLA to about 60 at. % for modified PLA. This decrease was mainly due to the decrease in methyl groups. The content of these groups in the unmodified PLA was about 57 at. % and after modification with solutions 1 or 2 it decreased to about 27 and 23 at. %, respectively. Simultaneously, an increase in the content of oxygen atoms was detected. In the surface layer of unmodified PLA the oxygen content

was about 18 at. %. After modification with solutions 1 and 2 it increased to about 27 or 37 at. %, respectively.

The nature of changes in the elemental composition of the surface layer varied depending on the applied solution. Modification with solution 1 resulted in the formation of new functional groups of  $-C-OH$  ( $E_B = 285.95$  eV) and  $-N-C-O$  ( $E_B = 287.5$  eV), which contributed to the increase in oxygen. Modification with solution 2 did not cause formation of any new functional groups. In this case, the increase in the degree of oxidation of the surface layer was caused by an increase in the content of  $C=O$  ( $E_B = 532.27$  eV) and  $CO$  ( $E_B = 533.68$  eV) functional groups.

Metallization of modified and activated PLA surfaces was performed in order to evaluate the effectiveness of solutions to prepare the surface. Metallized samples are shown in Fig. 7.

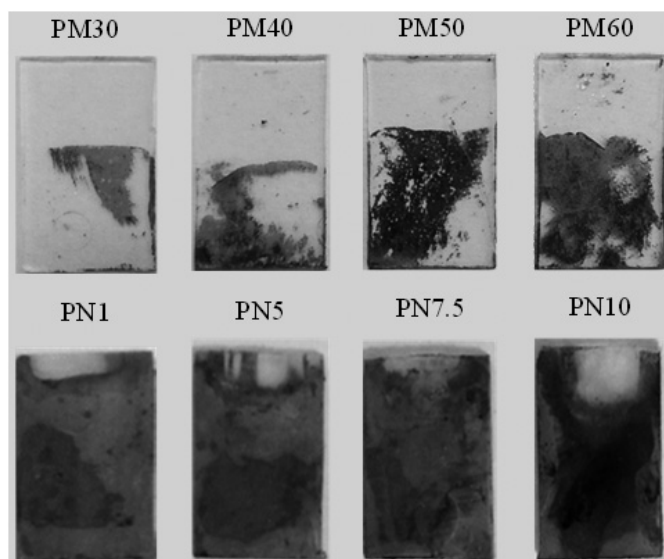


Fig. 7. Effects of metallization for chemically modified samples of PLA

Despite small area of the deposited copper layer, one can conclude that with increasing modification time the surface covered with copper increased. Better efficiency of metallization was achieved for the samples modified with solution 2. Unlike in the case of samples modified with solution 1, copper was found on the entire surface of the sample (copper free area resulted only from sample holder) modified with solution 2. It can be seen that with increasing time of modification with solution 2 copper layer became darker. According to [29], the higher the surface roughness of deposited metallic copper, the darker its layer is. Samples modified with solution 2 were selected for further testing based on the results of the metallization process and visual quality of deposited copper layers.

Properties and structure of the deposited copper layer depend on the structure of substrate surface [8]. Metal

layers deposited on a non-conductive material on which the catalyst is present are characterized mostly by grain structure. These grains tend to form larger structures with increasing thickness of the deposited layer. Grain structure is obtained when the catalyst is dispersed on the metallized surface. Initially, metallization starts on the surface of the catalyst, then with increasing metallization time the dimension of individual grains increases until merging and forming a continuous metal layer.

The copper layer deposited on the samples was characterized by grain structure, as it is shown in Fig. 8.

The particle size depends on the metallization time. With increasing metallization time, the grains became

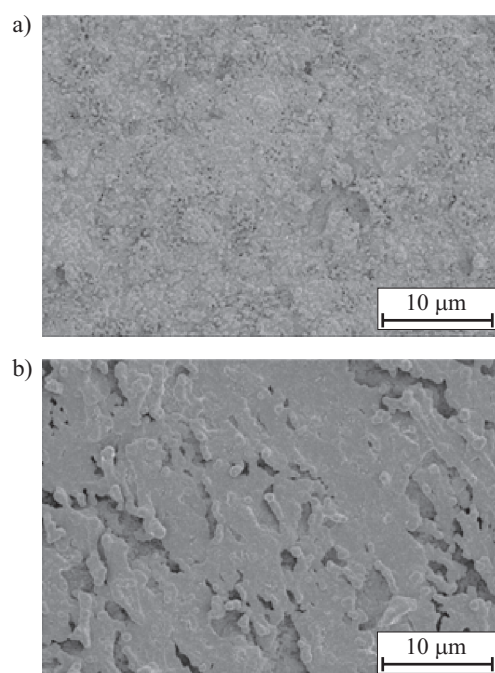


Fig. 8. SEM images of metallized samples PN10 modified for: a) 1 min, b) 5 min

larger and finally merged. The copper layer was deposited on the entire surface covering the grooves and fractures resulted from chemical modification. It can suggest that deposited copper layer penetrates into the grooves and fractures, thus improving its adhesion strength to the PLA surface.

The dependence of adhesion strength of the deposited copper layer is related to the modification and metallization time. It is presented in Fig. 9. It was found that with increasing modification time adhesion strength increased. This can be associated with higher surface roughness and with formation of the sites for anchoring the copper layer to the PLA substrate. The maximum adhesion strength was about 1.2 MPa. This value was obtained for the sample PN10 metallized for 1 min. This sample characterized with the largest surface roughness. The minimum adhesion strength (0.4 MPa) was obtained

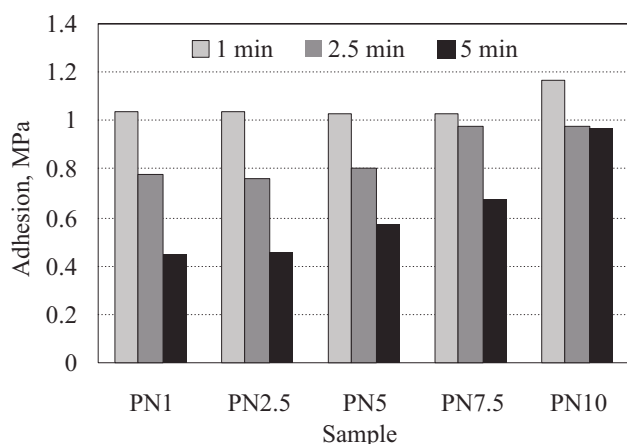


Fig. 9. Effects of modification and metallization time on the adhesion strength of the deposited copper layer

for the sample PN1 metallized for 1 min and characterized with the smallest surface roughness.

Initially, the longer metallization time the larger the differences in adhesion strength were noticed. With in-

- all the samples metallized for 1 min,
- the sample PN7.5 metallized for 2.5 min,
- the sample PN10 regardless of the metallization time.

Most preferred are short times of modification and metallization due to the efficiency of the process.

Values of volume ( $\rho_v$ ) and surface ( $\rho_s$ ) resistivity for metallized samples are listed in Table 1. The values of  $\rho_v$  and  $\rho_s$  for unmodified PLA were  $4.7 \cdot 10^{16} \Omega \cdot \text{cm}$  and  $6.3 \cdot 10^{16} \Omega/\text{cm}^2$ , respectively. The obtained order of magnitude is characteristic for the non-conductive polymers. Shorter metallization time (1 min) caused a decrease in  $\rho_v$  and  $\rho_s$  to  $10^{12} \Omega \cdot \text{cm}$  and  $10^{11} \Omega/\text{cm}^2$ , respectively. Therefore, these materials can be classified as dielectrics. In the case of the samples metallized for longer times (2.5 or 5 min), this process resulted in further decrease in  $\rho_v$  and  $\rho_s$  values to about  $10^8 \Omega \cdot \text{cm}$  and  $10^7 \Omega/\text{cm}^2$ , respectively. It classifies these materials as semiconductors [34].

The results of  $\rho_v$  and  $\rho_s$  resistivity measurements for the deposited layers of copper indicate that the samples can be further processed with galvanic technique. Based

Table 1. Values of volume ( $\rho_v$ ) and surface ( $\rho_s$ ) resistivity of the metallized PLA samples

Sample	$\rho_v$ ( $\Omega \cdot \text{m}$ ) of samples metallized for			$\rho_s$ ( $\Omega/\text{cm}^2$ ) of samples metallized for		
	1 min	2.5 min	5 min	1 min	2.5 min	5 min
Nonmetallized PLA		$4.7 \cdot 10^{16}$			$6.3 \cdot 10^{17}$	
PN1	$1.9 \cdot 10^{12}$	$4.4 \cdot 10^8$	$2.4 \cdot 10^8$	$5.1 \cdot 10^{11}$	$3.6 \cdot 10^7$	$2.6 \cdot 10^7$
PN2.5	$2.6 \cdot 10^{12}$	$6.2 \cdot 10^8$	$4.4 \cdot 10^8$	$1.9 \cdot 10^{11}$	$1.0 \cdot 10^7$	$4.6 \cdot 10^7$
PN5	$1.1 \cdot 10^{12}$	$3.0 \cdot 10^8$	$1.3 \cdot 10^8$	$1.9 \cdot 10^{11}$	$5.2 \cdot 10^7$	$3.9 \cdot 10^7$
PN7.5	$2.2 \cdot 10^{12}$	$2.98 \cdot 10^8$	$3.4 \cdot 10^8$	$2.3 \cdot 10^{11}$	$1.1 \cdot 10^7$	$3.6 \cdot 10^7$
PN10	$1.1 \cdot 10^{12}$	$1.87 \cdot 10^8$	$2.4 \cdot 10^8$	$2.7 \cdot 10^{11}$	$9.5 \cdot 10^7$	$4.1 \cdot 10^7$

creasing modification time of the samples, these differences became smaller. This effect resulted from the structure of the metallized surface. In the case of the samples modified for a short time no significant number of grooves was formed on the surface. This caused rapid growth of the copper layer thickness as compared with the samples modified for longer time. In the case of the latter samples, copper was deposited in a large number of cavities present on the PLA surface. Only after filling of these cavities, an increase in the thickness of the deposited metal layer was noticed, thus resulting in lower overall thickness of this layer.

Breaking of adhesion joint can occur not only at the interface of polymer/metal layers, but also inside of the metal layer, thus reducing the adhesion strength of the joint. Adhesion strength of the deposited metal layers for common autocatalytic processes of polymers ranges from 0.1 to 2 MPa [31–33] depending on the type of deposited metal as well as metallized polymer. However, it is required that the value for a high quality layer should be about 1 MPa. Modification with solution 2 enabled to obtain such a value. This was achieved for:

on experimental results concerning the quality of deposited copper layers, it can be concluded that metallized PLA can be successfully applied in many branches of industry.

## CONCLUSIONS

Chemical modification caused significant changes in the structure of the PLA surface. The nature of these changes was different, depending on the type of applied solution. It was concluded that more efficient metallization process was obtained for the samples modified with solution of NaOH ( $0.25 \text{ mol}/\text{dm}^3$ ) in water and ethyl alcohol. Numerous grooves and fractures resulting from the surface modification with this solution constituted active sites for anchoring the copper layer to the PLA substrate, thus improving adhesive strength. Modification with this solution was associated with a larger increase in the degree of oxidation of the PLA surface layer. In the surface layer of PLA, changes in carbon and oxygen contents and in their functional groups were detected after modifications with both types of solutions. Larger degree of oxi-



dation can suggest formation of larger quantity of oxygen functional groups, which significantly improve chemisorption of the catalyst on the surface, thus improving autocatalytic metallization and quality of the deposited metal layer as well. The deposited copper layer had high adhesion strength and good electrical properties, enabling wide industrial applications of metallized PLA.

*The project has been financed from the funds of the National Science Centre allocated upon decision number DEC-2011/01/N/ST8/04397.*

## REFERENCES

- [1] Vakelis A.: "Electroless plating" in "Coatings Technology Handbook" (Ed. Tracton A.A.), CRC Press, Boca Raton 2006, p. 27-1.
- [2] Siau S., Vervaeke A., Schacht E., Demeter U., Van Calster A.: *Thin Solid Films* **2006**, 495, 348.  
<http://dx.doi.org/10.1016/j.tsf.2005.08.355>
- [3] Paunovic M., Schleinger M.: "Fundamentals of electrochemical deposition", Wiley Interscience, Hoboken 2006.
- [4] Kim G.G., Kang J.A., Kim J.H. *et al.*: *Surface and Coating Technology* **2006**, 201, 3761.  
<http://dx.doi.org/10.1016/j.surfcoat.2006.09.052>
- [5] Beil S., Horn H., Windisch A., Hilgers C., Pochner K.: *Surface and Coating Technology* **1999**, 116–119, 1195.  
[http://dx.doi.org/10.1016/S0257-8972\(99\)00155-3](http://dx.doi.org/10.1016/S0257-8972(99)00155-3)
- [6] Charbonnier M., Alami M., Romand M.: *Journal of Electrochemical Society* **1996**, 143, 472.  
<http://dx.doi.org/10.1149/1.1836467>
- [7] Alami M., Charbonnier M., Romand M.: *The Journal of Adhesion* **1996**, 57, 77.  
<http://dx.doi.org/10.1080/00218469608013645>
- [8] Mallory G.O.: "Electroless plating: Fundamentals and applications", Noyes Publications/William Andrew Publications, New York 2002.
- [9] Teixeira L.A.C., Santini M.C.: *Journal of Materials Processing Technology* **2005**, 170, 37.  
<http://dx.doi.org/10.1016/j.jmatprotec.2005.04.075>
- [10] Luan B., Yeung M., Wells W., Liu X.: *Applied Surface Science* **2000**, 156, 26.  
[http://dx.doi.org/10.1016/S0169-4332\(99\)00339-6](http://dx.doi.org/10.1016/S0169-4332(99)00339-6)
- [11] Aronson C.L., Beholz L.G., Beloskur D. *et al.*: *Polymer Bulletin* **2005**, 53, 401.  
<http://dx.doi.org/10.1007/s00289-005-0344-y>
- [12] Bertrand P., Lambert P., Travaly Y.: *Nuclear Instruments Methods in Physics Research Section B* **1997**, 131, 71.  
[http://dx.doi.org/10.1016/S0168-583X\(97\)00149-3](http://dx.doi.org/10.1016/S0168-583X(97)00149-3)
- [13] Charbonnier M., Romand M., Harry E., Alami M.: *Journal of Applied Electrochemistry* **2001**, 31, 57.  
<http://dx.doi.org/10.1023/A:1004161707536>
- [14] Yang G.H., Kang E.T., Neoh K.G. *et al.*: *Colloid and Polymer Science* **2001**, 279, 745.  
<http://dx.doi.org/10.1007/s003960100485>
- [15] Auras R., Lim L.-T., Selke S.E.M., Tsuji H.: "Poly(lactid acid). Synthesis, Structures, Properties, Processing, and Applications", John Wiley & Sons, Inc., Hoboken, New Jersey 2010.
- [16] Schramm R., Reinhardt A., Franke J.: "Capability of biopolymers in electronics manufacturing", 35th International Spring Seminar on Electronics Technology (ISSE), Bad Aussee, Austria, 9–13 May 2012, p. 345.
- [17] Domenech S.C., Lima E. Jr., Drago V. *et al.*: *Appl. Surf. Sci.* **2003**, 220, 238.  
[http://dx.doi.org/10.1016/S0169-4332\(03\)00815-8](http://dx.doi.org/10.1016/S0169-4332(03)00815-8)
- [18] Yang J., Wan Y.Q., Wang S.G. *et al.*: *Polymer International* **2003**, 52, 1892. <http://dx.doi.org/10.1002/pi.1272>
- [19] Owens D.K., Wendt R.C.: *Journal of Applied Polymer Science* **1969**, 13, 1741.  
<http://dx.doi.org/10.1002/app.1969.070130815>
- [20] <http://srdata.nist.gov/xps/>
- [21] De Jong S.J., Arias E.R., Rijkers D.T.S. *et al.*: *Polymer* **2001**, 42, 2795. [http://dx.doi.org/10.1016/S0032-3861\(00\)00646-7](http://dx.doi.org/10.1016/S0032-3861(00)00646-7)
- [22] Yuan X., Mak A.F.T., Yao K.: *Polymer Degradation and Stability* **2003**, 79, 45.  
[http://dx.doi.org/10.1016/S0141-3910\(02\)00237-9](http://dx.doi.org/10.1016/S0141-3910(02)00237-9)
- [23] Taddei P., Monti P., Simoni R.: *Journal of Materials Science: Materials in Medicine* **2002**, 13, 469.  
<http://dx.doi.org/10.1023/A:1014742003146>
- [24] Yudina T.F., Pyatachkova T.V., Ershova T.V., Strogaya G.M.: *Russian Journal of Electrochemistry* **2001**, 37, 741.  
<http://dx.doi.org/10.1023/A:1016729020537>
- [25] Chen D., Li Y., Lu Q. *et al.*: *Applied Surface Science* **2005**, 246, 167. <http://dx.doi.org/10.1016/j.apsusc.2004.11.005>
- [26] Charbonnier M., Romand M., Goepfert Y.: *Surface and Coating Technology* **2006**, 200, 5028.  
<http://dx.doi.org/10.1016/j.surfcoat.2005.05.006>
- [27] Żenkiewicz M., Moraczewski K., Richert J., Stepczyńska M.: *Przemysł Chemiczny* **2012**, 91, 1000.
- [28] Shahidi M., Ghoranneviss M.: *Fibers and Polymers* **2012**, 13, 971. <http://dx.doi.org/10.1007/s12221-012-0971-5>
- [29] Hitchcock S.J., Carroll N.T., Nicholas M.G.: *Journal of Materials Science* **1981**, 16, 714.  
<http://dx.doi.org/10.1007/BF00552210>
- [30] Norkus E., Vaskelis A., Jaciauskiene J. *et al.*: *Electrochimica Acta* **2006**, 51, 3495.  
<http://dx.doi.org/10.1016/j.electacta.2005.09.043>
- [31] Kupfer H., Hecht G., Ostwald R.: *Surface and Coating Technology* **1999**, 112, 379.  
[http://dx.doi.org/10.1016/S0257-8972\(98\)00782-8](http://dx.doi.org/10.1016/S0257-8972(98)00782-8)
- [32] Zaporojtchenko V., Zekonyte J., Faupel F.: *Nuclear Instruments and Methods in Physics Research B* **2007**, 265, 139.  
<http://dx.doi.org/10.1016/j.nimb.2007.08.040>
- [33] Lu Y., Xue L., Li F.: *Surface and Coating Technology* **2010**, 205, 519. <http://dx.doi.org/10.1016/j.surfcoat.2010.07.020>
- [34] Katada A., Buys Y.F., Tominaga Y. *et al.*: *Colloid and Polymer Science* **2005**, 284, 134.  
<http://dx.doi.org/10.1007/s00396-005-1348-8>

Received 22 VIII 2014.