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Electroless metallization of polymers

M. Żenkiewicz*, K. Moraczewski, P. Rytlewski, M. Stepczyńska, B. Jagodziński
Department of Materials Engineering, Kazimierz Wielki University,
ul. Chodkiewicza 30, 85-064 Bydgoszcz, Poland
* Corresponding e-mail address: marzenk@ukw.edu.pl

ABSTRACT

Purpose: The purpose of this article was to review selected issues related to the electroless metallization of polymeric materials.

Design/methodology/approach: The presented issues concerned classic electroless metallization, laser-assisted electroless metallization and electroless metallization of biodegradable polymers.

Findings: The electroless metallization is most commonly used process of polymer metallization. It is possible only when the surface of a polymer product is seeded with metallic catalyst. Due to its good properties of catalysing the oxidation reaction of most reducing agents used in electroless metallization, palladium is the most commonly used catalyst in this process. Lasers can be effective tools for the preparation of polymer surface to be coated with metal layer, especially to clean, roughen, and/or induce chemical reactions on polymer surface prior to or along with metallization process. In recent years, new polymeric materials, produced from renewable resources are intensively studied and polylactide is one of such materials. An increasing interest in application of polylactide to manufacture electronic printed circuit boards and carriers was recently noticed.

Research limitations/implications: A number of various metallization methods are widely reported in literature. In this article a review of only few methods is presented, which are in line with the newest trends in polymer industry and science.

Practical implications: There are a number of methods of electroless metallization of polymer materials, which need to be improved to satisfy specific application conditions. For that reasons researches are leading to find better and universal metallization methods to improve overall properties of deposited metal layer.

Originality/value: This article presents results of some researches related to the electroless metallization of polymeric materials.

Keywords: Electroless metallization; Polymer materials; Laser-assisted metallization; Biodegradable polymers, Scanning electron microscopy

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MATERIALS

1. Introduction

Polymers, complementary to metals and ceramics, constitute one of the most important groups of engineering materials. Rapid utilization of polymers in industrial applications results from their many advantages, such as ease of shaping, low density, relatively good mechanical strength, and low cost of processing. Since the beginning of their usage, covering the surface of polymers with metallic layers has attracted considerable interest both in research and industry.

Initially, metallization of polymers was used only for decorative purpose, however, with the progress in metallization methods metallized polymers became frequently used in automotive, airplane and ship parts, in electronic circuit boards, as a casing for electric field shielding, and in many other appliances. Metallized polymer materials are commonly applied in many different branches of industry. Polymer films, covered with a thin aluminium layer, are commonly used in the foodstuffs industry as packaging. The electronic equipment is screened from electromagnetic irradiation using the material slabs covered with copper [1,2].

A dynamic development of manufacturing technologies and miniaturization of electronic systems, automation and robotics, material requirements as well as the requirements from many other areas of today's technology essentially trigger the development of basic and experimental studies on metallization of polymer materials.

The main advantage of polymer products covered with metallic layer is reduction of mass, energy and production time, as compared with metals or ceramics. Another significant advantage is that even after the failure of metallic coating, high corrosion resistance of polymers prevents formation of electrochemical cells between the substrate and the metallic coating, that normally in the case of metal substrate accelerates corrosion process [2,3].

The paper presents a review of issues related to the electroless metallization of polymeric materials. Classic method of electroless metallization is presented as well as research on laser-assisted metallization and metallization of biodegradable polymer materials. These issues are following in a perspective direction of research on metallization of polymeric materials.

2. Necessary conditions for electroless metallization of polymers

The method of electroless metallization process does not use an external power source. The process involves the flow of electric charges (electrons) from the less electronegative metal or a reducing substance, contained in a plating bath, to metal ions being deposited [4]. The beginnings of this method dates back to the 40 s of the last century. Initially ineffective, mainly because of low yields and insufficient quality of obtained metallic layers. Over time this method was improved by an appropriate choice of plating bath composition and process conditions. This allowed the widespread use in the industry. Electroless metallization scheme showing the overall principles of the process is shown in Fig. 1.

Electroless deposition of a metal layer can be done through a chemical exchange, chemical reduction or auto catalytically [6,7]. The most common method of electroless metallization of polymeric materials is the autocatalytic method [3,8,9].

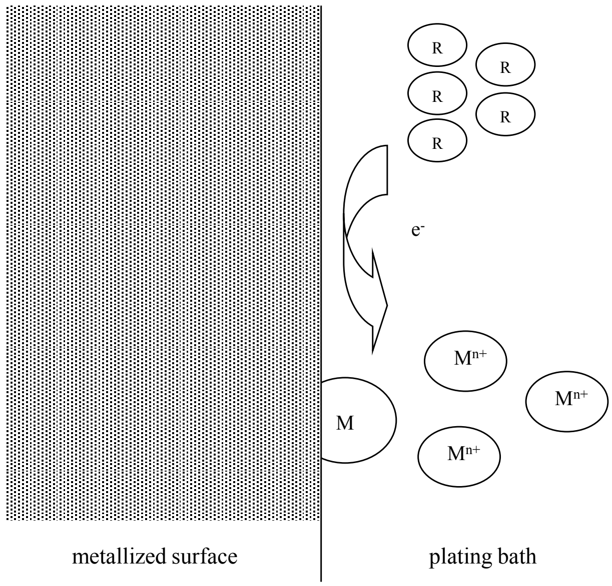

Fig. 1. Electroless metallization scheme using a reducing agent (R) as the source of electrons [5]

The autocatalytic deposition of the metal layer is a particular variant of the process of depositing a metal by chemical reduction. In this method, the metal ions contained in the metal plating bath are reduced in the presence of a catalyst deposited on the surface of a metallized product. The reduction reaction begins when the bath is in direct contact with the catalyst, wherein it occurs only on the surface of the catalyst. The catalyst is a metal deposited on the surface of a metallized product. A necessary condition is that the reduction reaction is catalyzed by deposited metal. Thanks to that after the complete covering of the surface of the catalyst the reaction proceeds further. This process is called autocatalytic metallization [4].

Prior to electroless metallization of polymeric material the proper preparation of its surface is necessary. This is done by appropriate physical and chemical modification of the surface layer of metallic material, and its activation.

In the case of plastics electroless metallization little adhesive strength of formed joints is caused by the large differences in the chemical and physical properties of plastic and metal [10-12]. Thus, the properties of surface layer material on which a metal layer is deposited, significantly affect the adhesive strength of those joints. Thus the modification process of polymers surface layer is one of the most important processes related to the electroless metallization of polymeric materials. An increase in adhesive strength of the metal layer and modified surface layer of polymeric material is due to [13]:

- removal of surface contaminations as well as additives and low molecular weight macromolecules that migrated to the surface layer;
- change in the geometrical structure of the material surface, especially increase in the roughness, which creates additional anchoring areas for a metal being deposited on this surface;
- change in the surface layer chemical composition by implementing new surface functional groups, which may lead to formation of chemical bonds between molecules of the surface and atoms of metal being deposited.

The most commonly used methods of modification are: chemicals, plasma and laser surface treatments.

The chemical methods for modification of the surface layer of polymeric materials consist in the use of strong oxidizing agents, acids, or solvents. The most commonly used chemicals include solutions of sodium dichromate (VI), potassium dichromate (VI), and potassium manganite (VII) in diluted sulfuric (VI) acid [14,15]. Phenol sodium hydroxide, sodium hypochlorite, and metallic sodium are being used as well [16].

The plasma modification methods consist in treatment of the SL with the low-temperature plasma, being a partially ionized gas (or a mixture of gases) composed of electrons, ions, atoms, neutral molecules, and electromagnetic radiation. Such plasma is created upon partial discharges occurring in the air (so called corona discharges) or in a vacuum chamber, generated by a high-frequency electromagnetic field in a gaseous medium, usually oxygen, nitrogen, helium, or air [17,18].

The laser techniques of the surface layer modification of polymeric materials are also used. The methods consist in treatment of a material with a monochromatic beam of high-power laser radiation [19,20]. This radiation is able to change both the geometrical structure of the surface layer of plastic and the chemical composition of that layer. The laser treatment has many advantages compared to the chemical and plasma methods. It enables to modify the surface layer precisely, with no changes in the properties of the material situated underneath. Auto-catalytic metallization of polymer materials is possible only if the catalyst atoms are embedded on metallized surface. This process, called activation, has a considerable effect on the quality of the deposited metal layer. Metallization catalysts are usually metals from groups 8 and 11 of periodic table. The choice of a suitable catalyst depends on the type of reducing agent since the catalytic activity of metals is different to the various reducing agents [21] (Fig. 2).

The most commonly used catalyst in metallization process is palladium, due to its good properties of catalyzing the oxidation reaction of most reducing agents used in electroless metallization [4]. Less frequently used are copper, gold, silver and aluminum (Fig. 2) [9,22].

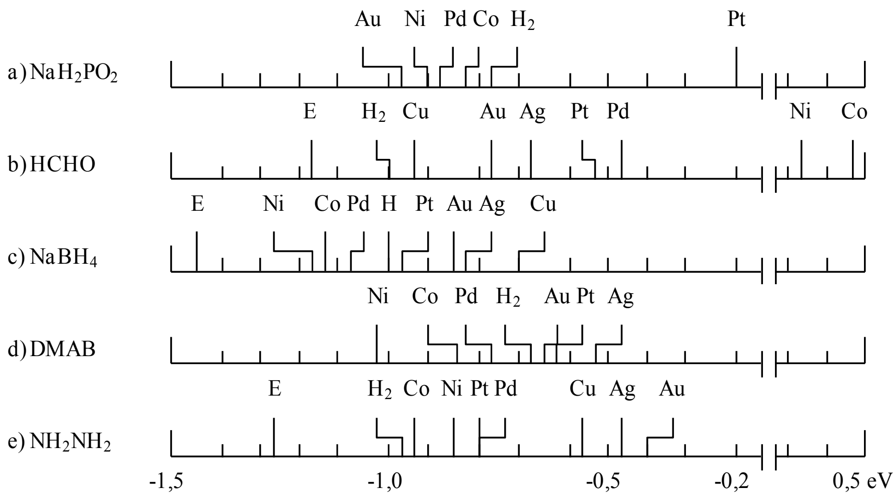

Fig. 2. The catalytic activity of metals with respect to the oxidation of various reducing agents

Various methods of application of this element on the surface of metallized materials have been developed. The most common method of activation is a one step process using a mixed solution of palladium chloride (II) ($PdCl_2$) and tin chloride (II) ($SnCl_2$) [4,13]. The technology of simplified activation process, in which only a dilute solution of $PdCl_2$ is used has been also developed [23,24]. Adsorption of palladium atoms without the use of tin, which has a high chemical affinity for oxygen, is only possible on the surface of the polymeric material comprising nitrogen functional groups. When the material does not contain nitrogen groups, an adequate surface layer modification is required. For this purpose plasma modification in nitrogen (N_2) or ammonia (NH_3) atmosphere can be performed [25] (Fig. 3).

The activation method involving deposition on the surface a layer of the palladium organometallic compounds of are also used. The deposition is followed by decomposition of that compound with formation of palladium metal seeds. It is also possible to form the metal seeds by using the laser beam or plasma through solution of organometallic compounds of palladium located on the surface of a metallized product. The used organometallic compounds of palladium are palladium-acetylacetonate ($Pd(acac)_2$) or palladium dimethyl sulfoxide Pd-DMSO. These methods have been proposed in recent years for the direct metallization of polymeric materials [15,24,26,27]. They allow the deposition of metals such as gold, platinum, nickel or copper without the use of expensive palladium catalyst (Fig. 4).

The activation process is followed by the final stage of electroless metallization. It involves deposition of a metallic layer by immersion in the metallization bath. The coatings obtained in the process of electroless metallization have a good quality and purity. In optimal conditions of metallization, the thickness of deposited layer depends only on the duration of the process. The metallic layers obtained in electroless metallization process, can be further successfully applied in other galvanic processes.

3. Laser-assisted electroless metallization of polymers

Lasers can be effective tools for the preparation of polymer surface to be coated with metal layer. In the electroless metallization techniques lasers can be used to clean, roughen, and/or induce chemical reactions on polymer surface prior to or along with metallization process. In this section, laser-assisted electroless metallization of polymers is reviewed according to the four following approaches: laser modification of (a) neat polymers in gaseous medium, (b) neat polymers in liquid medium, (c) neat polymers coated with films, and (d) polymer composites containing active species (Fig. 5).

Laser surface ablation of polymers can be used for neat polymers as a pre-treatment step for metallization in gaseous medium. The studies of KrF irradiation effects of polymers and its influence on adhesion to evaporated metal layers are presented in [29]. The investigations were concerned with various thermoplastics such as polyamide, acrylonitrile-butadiene-styrene, polypropylene, polystyrene, styrene-acrylonitrile, polycarbonate, poly(butylenes terephthalate), polyoxymethylene and polyimide. It was concluded that polymers with similar molecular structure (linear or cyclic) show very similar absorption, and thus similar ablation characteristics. Irradiation with laser was a suitable pretreatment for metallization of polymer surfaces in these cases, where the original surface roughness was significantly increased. The adhesion of the metallic layers to polymers was comparable to or even better than for the plasma etching and wet chemical etching pretreatments.

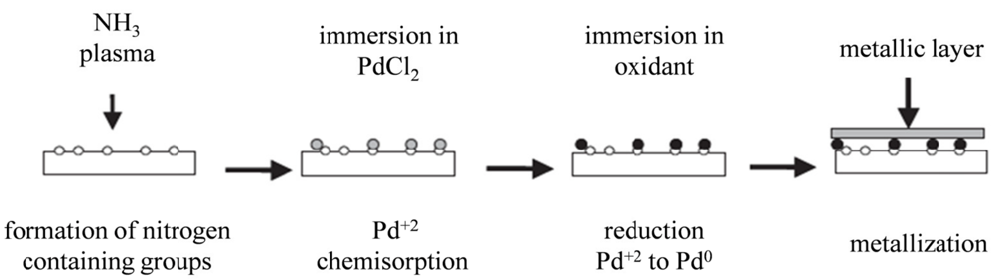

Fig. 3. Scheme of simplified activation process

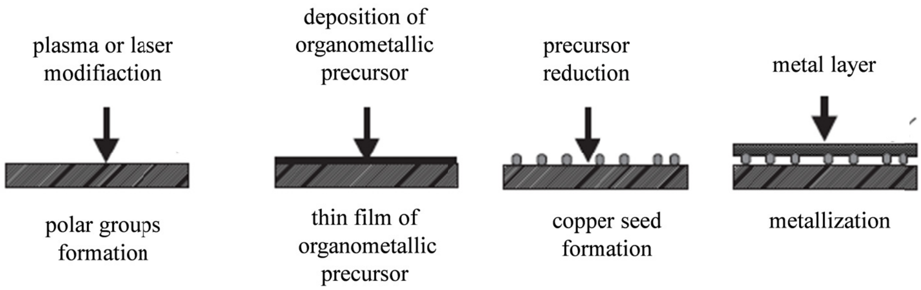

Fig. 4. Scheme of direct activation process

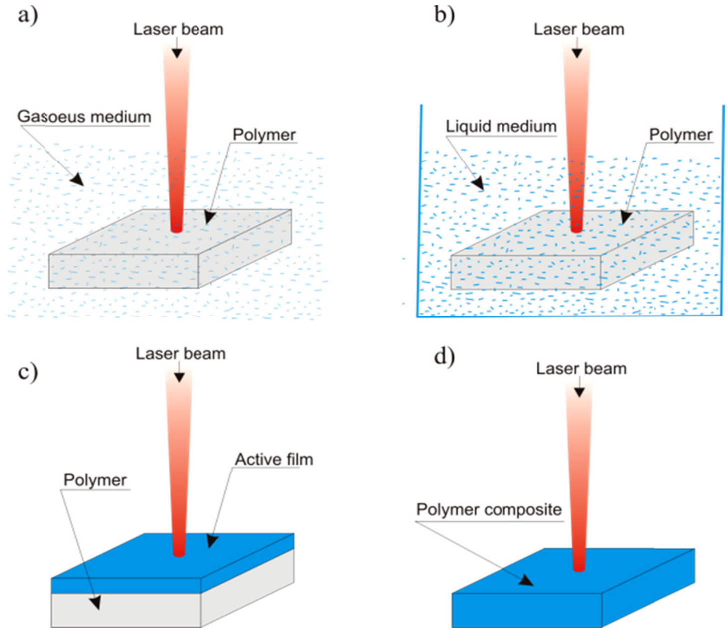

Fig. 5. Approaches for laser modification of (a) neat polymers in gaseous medium, (b) neat polymers in liquid medium, (c) neat polymers coated with films, and (d) polymer composites containing active species [28]

In another approach [30,31], pulsed laser ablation of polyimide, poly (ethylene terephthalate) and polyethersulfone films was performed with XeCl or KrF excimer lasers in air. As a result of this irradiation ablated cationic fragments were deposited onto the surface and transforming it to a positive potential. The electroless plating (chemical plating) of copper or nickel was carried out selectively on the ablated surface of these films, through a surface activation process using a negatively charged colloid. This selective metallization process consisted of two steps. First, the ablated polymer was dipped in the aqueous solution containing a negatively charged colloid composed of palladium and a surfactant as an activation process. Second, the dipped film was rinsed with deionized water and immersed in a plating bath of copper or nickel.

Laser surface modification below the ablation threshold of polymers can also be an effective pretreatment method for metallization of polymers. In [32] authors studied chemical changes induced by KrF laser below the ablation threshold of poly(butylene terephthalate) and polyimide and their influence on adhesion to evaporated aluminium layer. It was found that aluminium layers on polyimide exhibited significantly better adhesion property, indicating an enhancement of the metal/polymer binding, in spite of the reduced oxygen content in such surfaces. In contrast, irradiated poly(butylene terephthalate) surfaces show only a little change in this aspect as compared to unirradiated surfaces. Other example of lasers application was to irradiate poly(ethylene terephthalane) surface with ArF and KrF excimer lasers in oxygen or oxygen/helium atmosphere [32]. This led to an increase in surface energy, and thus, to increase in adhesion strength between evaporated aluminium layer and irradiated poly(ethylene terephthalane).

It was found that Nd:YAG laser (fourth harmonic) can effectively graft nitrogenized species onto polymer surface [34]. Additionally, a one-step procedure of electroless metallization was also proposed by these authors. It consisted only in immersing the laser treated substrates in a simple solution of $PdCl_2$ and HCl, followed by rinsing. Moreover, these studies concerned various gaseous atmospheres and surface functionalization was also performed both by UV lamps and plasma treatment. The strong chemical affinity of tin and the non-affinity of palladium towards oxygenated and nitrogenized species were confirmed. The strong affinity of palladium and nitrogen species was explained by chemical covalent bonding.

The excimer KrF and XeCl lasers were applied in laser-assisted electroless metallization of neat polymers in liquid medium for seeding palladium. The metal atoms deposited only on the areas of the polymer that were illuminated through the liquid containing $PdSO_4$ or $Pd(CH_3CO_2)_2$ [35]. This method did not require prior treatment of the polymer surface. The seeding solution was transparent to the laser light and the metal deposition occurred as a consequence of the photo absorption in the polymer film. The metallization process resulted from electron transfer from the polymer film to the palladium ions, which then became reduced. It was found that palladium content on the polyimide surface increased with the number of pulses, but was independent of repetition rate. The same concept but with different type of laser and different composition of seeding bath was presented in [36]. This process was mainly attributed to heat-induced decomposition of the palladium-amine reactant. The seeding plating bath contained palladium-amine ($[Pd(NH_3)_4]^{2+}$) solution. The chemical reaction was carried out by formaldehyde-assisted reduction of palladium-amine complex molecules to metallic palladium, and was localized on the polymer substrate by a focused laser beam.

In laser-assisted electroless metallization neat polymers coated with films dielectric material is coated with a specially designed thin film, which after laser irradiation becomes catalytic, and thus the material can be directly electroless metallized. Micro-scale palladium lines have been produced by a photothermal laser direct-write process in thin palladium acetate ($[Pd(\mu\text{-}O_2CH3)_2]_3$) films [37]. Palladium acetate (PdAc) is a nonpolymeric metallo-organic compound that forms homogeneous, noncrystalline film after spin coating from chloroform solution. Irradiation with excimer or argon-ion lasers causes photolytic or photo-thermal decomposition of PdAc film and leads to covering the surface with palladium metal. Various structures related to the complex thermal profiles generated by coupling of the incident laser radiation with the exothermic heat resulted from PdAc decomposition reactions were formed. Non-irradiated PdAc film was removed with chloroform rinse and then the samples were immersed in electroless Cu plating solution for selective metallization.

In other work [38], film of palladium-acetylacetonate ($Pd(acac)_2$) was spin-coated from its saturated solution in chloroform. To decompose the film, argon ion laser in either the 488 nm or 458 nm output was used. After laser-induced decomposition, pure palladium appeared on the surface and catalysed the copper electroless deposition. In laser-assisted electroless metallization of polymer composites containing active species, polymer composition has to be modified prior to laser irradiation in order to obtain active catalytic surface for direct electroless metallization process.

There were also studied polyamide composites containing CuO and $Cu(acac)_2$ which after laser irradiation became fully prepared for direct electroless metallization process [39-41]. The composites were produced using typical processing methods such as extrusion and injection moulding. They were then irradiated with various numbers of ArF excimer laser pulses ($\lambda = 193$ nm) at different fluencies. The metallization procedure on the laser-irradiated samples was performed using a commercial metallization bath and formaldehyde as a reducing agent.

a) b)

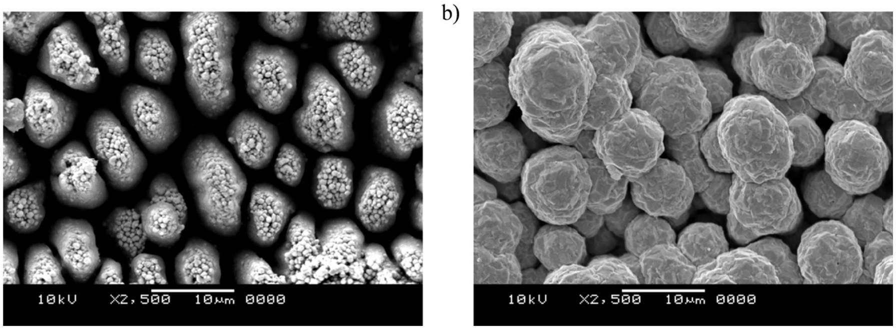

Fig. 6. Scanning electron microscopy images of laser modified surface of polyamide composites surface (a) before metallization, (b) after metallization

Highly synergetic effect between CuO and $Cu(acac)_2$ was found and believed to be due to the heat induced during the material processing as well as energy delivered by laser irradiation and exothermic decomposition of $Cu(acac)_2$. It was found that CuO was reduced to Cu(0). The proposed model of the CuO reduction consists in thermal dissociation of $Cu(acac)_2$ into a copper hydrate complex and pentane-2,4-dione and, in the next step, in reactions between pentane-2,4-dione and CuO, leading to formation of Cu(0) and water as well as carbon dioxide as by-products [40].

4. Electroless metallization of biodegradable polymers

In recent years, new polymeric materials, produced from renewable resources are intensively studied. Polylactide is one of such materials and it is now a subject of many research works and applications [42]. This polymer is regarded as one of the most promising materials that could be an alternative to traditional polymers. Two main branches of polylactide application can be mentioned. One of them includes specialized materials used in medicine, such as surgical threads, implants, and drug carriers. The other one includes common-use products, like packaging materials and various disposable items [43]. An increasing interest in application of polylactide to manufacture electronic printed circuit boards and carriers was recently noticed [44].

Development of new autocatalytic metallization technologies for polylactide 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 polylactide would also lower the price of this polymer, thus making it competitive with regard to the polymers derived from petroleum.

Some results of our researches on polylactide metallization are presented in [45-47]. The modification of polylactide prior to electroless metallization was carried out with three methods. In the chemical method, a 0.25 M solution of sodium hydroxide in water and ethanol was utilized. In the plasma method, a 50 W generator was used, which produced plasma in the air atmosphere under reduced pressure. In the laser method, a pulsed excimer laser (ArF) with fluence of 60 mJ/cm^2 was applied [46]. The atomic force microscope images of modified surface are presented in Fig. 7.

The most profound changes in the examined properties of the polylactide surface layer appear when the chemical modification is applied. For example, the chemical treatment causes a significant increase in the surface roughness of the polymer, which occurs probably due to hydrolytic degradation. As a result, numerous cracks and cavities are formed on the polylactide surface. The chemical modification leads also to an increase in the degree of oxidation of the polymer SL, which occurs because of growth of the number of oxygen atoms contained in the polar functional groups. However, that growth is not accompanied by a significant increase in both the surface wettability and the surface free energy. It resulted probably from the growth of the surface roughness, which may compensate a positive effect resulting from the increase in the extent of oxidation of the surface layer [45,46].

The plasma modification gives the most beneficial results when the duration of the treatment exceeds 10 min. The obtained surface roughness of the samples modified this way is relatively large. The extent of oxidation of the surface layer increases considerably as well. Contrary to the effects of the chemical modification, the increase in degree of oxidation in the case of the plasma treatment is accompanied by both the improvement in the surface wettability and the enhancement in the surface energy [45,46].

The laser modification results in the effects different in relation to those due to chemical and plasma methods. It was found that the more intense treatment (higher number of laser pulses), the less surface roughness. The increase in the extent of oxidation of the surface layer is distinctly smaller than that in the case of the chemical and plasma methods [46].

Performed electroless metallization process has shown that from the methods used to modify the surface only for chemical modification the deposited coating was characterized by good quality (Fig. 8). The deposited copper layer had high adhesion strength and good electrical properties, enabling wide industrial applications of metallized polylactide. Coatings deposited on plasma modified samples had very poor adhesive strength. This excludes their further use. For samples modified with laser coating was not deposited at all [47].

5. Conclusions

Development of methods for metallization materials has enabled a large extension of the possibility of industrial applications. The main advantages of plastic materials and metallized products are significant time savings for their production and lower density than metal products. The hardness and abrasion resistance of metallized polymers is greater than the same products made from materials without a coating. The electroless metallization is most commonly used process of polymer metallization. It is possible only when the surface of a polymer product is seeded with metallic catalyst.

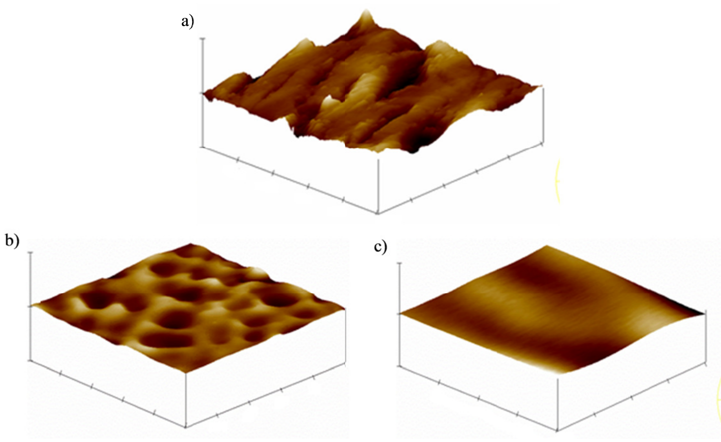

Fig. 7. Atomic force microscope images of (a) chemical, (b) plasma and (c) laser modified surface of polylactide

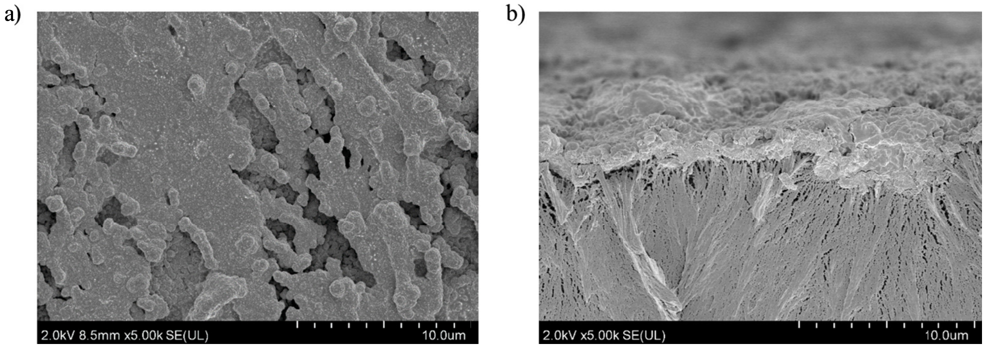

Fig. 8. Scanning electron microscopy images of (a) surface and (b) side of metallized polylactide

Due to its good properties of catalyzing the oxidation reaction of most reducing agents used in electroless metallization, palladium is the most commonly used catalyst in metallization process. The most commonly used process of surface activation of metalized material is a one step process involving the solution of $PdCl_2/SnCl_2$.

Lasers can be effective tools for the preparation of polymer surface to be coated with metal layer. Lasers can be used to clean, roughen, and/or induce chemical reactions on polymer surface prior to or along with metallization process. They can be used in laser-assisted metallization of neat polymers in gaseous medium, neat polymers in liquid medium, neat polymers coated with films, and polymer composites containing active species.

In recent years, new polymeric materials, produced from renewable resources are intensively studied and polylactide is one of such materials. An increasing interest in application of polylactide to manufacture electronic printed circuit boards and carriers was recently noticed. Performed electroless metallization process has shown that from the methods used to modify the surface the deposited coating was characterized by good quality only for chemical modification. The deposited copper layer had high adhesion strength and good electrical properties, enabling wide industrial applications of metallized polylactide.

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Additional information

Selected issues related to this paper are planned to be presented at the 22nd Winter International Scientific Conference on Achievements in Mechanical and Materials Engineering Winter-AMME'2015 in the framework of the Bidisciplinary Occasional Scientific Session BOSS'2015 celebrating the 10th anniversary of the foundation of the Association of Computational Materials Science and Surface Engineering and the World Academy of Materials and Manufacturing Engineering and of the foundation of the Worldwide Journal of Achievements in Materials and Manufacturing Engineering.