Laser modification of polylactide surface layer prior autocatalytic metallization

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ARTICLE INFO

ABSTRACT

The paper presents the results of laser modification as a method of surface layer preparation to autocatalytic metallization of polylactide. Laser modification was performed using an ArF excimer laser with a fluence of 15, 30 or 60 mJ/cm². The number of 10, 50, 100, 500 and 1000 laser pulses were used. The effects of laser modification on the geometrical structure, surface wettability, surface energy and chemical composition of polylactide surface layer have been studied. Copper plating was conducted to determine the effectiveness of laser modification as a surface preparation method prior autocatalytic metallization. Studies have shown that the best quality of copper layer was obtained for a sample modified with 10 laser pulses with fluence of 15 mJ/cm². For the remaining samples modified with higher laser fluence or more pulses deposited layers were inferior quality or did not deposit at all.

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1. Introduction

In the process of metallization of polymeric materials, the metal layer is usually deposited by chemical reaction between metal ions and a reducing agent contained in the solution. The process takes place in the presence of a catalyst. If the deposited metal is at the same time a catalyst of metallization process, the process is carried on autocatalytically and the deposited layer may have theoretically unlimited thickness. This effect is the core of the electroless metallization of polymeric materials. Therefore, the process of metallization of polymeric materials is known as autocatalytic metallization [1].

The properties of surface layer of polymeric materials (chemical composition, geometric structure, wettability, surface energy) have a significant impact on the metallization process, as well as on the adhesion, structure and electrical conductivity of deposited metal layer [2]. The surface layer of most polymeric materials is non-reactive, hydrophobic and has a low surface energy [3]. These features greatly hinder metallization processes. Thus, in the processes of metallization of polymeric materials, surface modification is a necessary step to modify the surface layer properties. The modification causes physical changes of surface layer, improving the adhesion of the deposited metal layer. This modification causes also chemical changes of surface layer, allowing chemisorption of the catalyst [4–8].

One of the latest physical methods to modify the surface of polymeric materials is the laser method. Lasers allow precise modification of properties of a small surface area without affecting the properties of the inner layer. Laser modification process is simple, easily controlled and environmentally safe. Depending on purpose of surface modification (physical or chemical), type of laser, modification conditions and type of the modified material, the process of laser modification can take place in different ways [9–11]. Laser treated materials including polymers can be used in many applications including electronics, sensors or for biocompatibility enhancement [12–14].

In recent years the number of available lasers operating in different light wavelength ranges and modes has rapidly increased. In laser modification of different materials surface layer, mainly gas lasers (CO_2 and excimer) or solid lasers (Nd:YAG) are used [9]. Very recently other lasers based on Nd:glass system having fs- or ns-pulse duration are applied for successful surface processing of polymers [15–17].

Excimer lasers are pulsed lasers utilizing radiation with a wavelength of 193 to 351 nm, with photon energy in the range of 3.5 to 7.9 eV. A result of which a single photon can break most of the interatomic bonds, enabling ablation of inorganic and organic materials [18,19].

The increasing problem of environmental pollution with plastics waste caused the sought for new biodegradable polymeric materials obtained from renewable materials, which can be an alternative to polymers derived from petroleum. One of such material is a polylactide (PLA), which is currently the subject of intensive scientific and application studies [20]. This polymer is recognized as one of the most

promising materials that can be an alternative to polymers derived from petroleum. There are two main areas of its application.

The first includes special materials used in medicine, such as sutures, implants and drug carriers. The second relates to the products of everyday use in the form of packaging materials and a variety of disposable products. In last year's an increased interest in application of PLA as a material for the manufacture of electronic printed circuit boards can be observed [21], however it is still necessary to develop an efficient method of PLA metallization. The use of chemical and plasma modification in the process of PLA surface preparation prior metallization have been so far investigated [22,23]. There is however no information in the literature concerning the use of lasers in the preparation of the PLA surface to metallization.

The PLA laser modifications is not yet fully studied, one can find different effects of PLA surface changes as a result of the laser modification. In the case of pulsed lasers, these changes depend not only on the laser fluence, but also on the number of applied pulses [24–26]. The aim of this study is to investigate the possibility of applying the laser modification in the preparation of PLA surface layer to autocatalytic metallization.

2. Materials and methods

2.1. Materials

The study involved the use of the following materials:

- Polylactide (PLA) type 2002 D (Cargill Down LLC, USA), average molecular weight of about 155.5 kDa, containing 3.5% structural units D and 96.5% structural units L.
- Distilled Water 'Aqua purificata' (Maggie Co., Poland).
- Diiodomethane CH_2I_2, 99% pure p.a. (Sigma – Aldrich, Germany), with the molar mass of 267.84 g/mol.
- Palladium (II) chloride $PdCl_2$ pure p.a. (POCH, Poland), molecular weight 177.31 g/mol.
- Tin (II) chloride $SnCl_2$ pure (Chempur, Poland), molecular weight 189.60 g/mol.
- Hydrochloric acid HCl 35–38% pure p.a. (Chempur, Poland), molecular weight 36.46 g/mol, density 1.19 g/dm³.
- Autocatalytic copper plating bath M - Copper 85 (MacDermid, USA).
- Formaldehyde HCHO 36% pure (POCH, Poland), molecular weight 30.03 g/mol,

2.2. Methods

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

In the process of laser modification, the ArF LPX 300 excimer laser (Lambda Physik, Germany) with wavelength of 193 nm (which corresponds to the photon energy equal 6.4 eV) was applied. The samples were modified with laser pulses at fluence (Ej) of 15, 30 or 60 mJ/cm². An accurate value of the laser pulse energy was determined with the FieldMax II TOP (Coherent Inc., US) measuring device. The samples were modified with 10, 50, 100, 500 or 1000 laser pulses. The duration of one pulse was 20 ns with pulse repetition rate of 5 Hz. The specimens were marked with symbols PX_Y where X stands for fluence and Y – the number of pulses.

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

The goniometer DSA 100 (Krüss GmbH, Germany) was used to measure the contact angle. The angle measurements were taken the day after the sample modification was completed, applying water (polar liquid) and diiodomethane (dispersion liquid). The drops of the liquids were placed onto the surface of the samples, their volume was continuously increased and at the same time, the dynamic contact angle was measured. 12 measurements of the contact angle were taken for each sample and the lowest and the highest values were rejected. From the other 10 values of the contact angle the arithmetic mean was calculated, assuming it as a result of the measurements and applying it for the calculations of surface energy (SE).

The SE was calculated with the Owens and Wendt method, according to the algorithm given in [27]. It is assumed that the SE (γ_S) has two components: dispersive (γ_S^d) and polar (γ_S^p). In such case:

$$\gamma_S = \gamma_S^d + \gamma_S^p \tag{1}$$

Considering the two components of SE Owens and Wendt proposed the equation:

$$\gamma_{SL} = \gamma_S + \gamma_L - 2\left(\gamma_S^d + \gamma_L^d\right)^{0.5} - 2\left(\gamma_S^p + \gamma_L^p\right)^{0.5} \tag{2}$$

From the Eqs. (1) and (2):

$$\gamma_L \frac{1 + cos\Theta}{2} = \left(\gamma_S^d \gamma_L^d\right)^{0.5} + \left(\gamma_S^p \gamma_L^p\right)^{0.5} \tag{3}$$

To determine the γ_S from the equation, contact angles (Θ) measurements must be made for two different liquids with known values of γ_L^d and γ_L^p. The first liquid should have high value of γ_L^d and low value γ_L^p. The second liquid should have low value of γ_L^d and high value γ_L^p. For this reason water ($\gamma_L^d = 21.8$ mJ/m², $\gamma_L^p = 51.0$ mJ/m²). and diiodomethane ($\gamma_L^d = 48.5$ mJ/m², $\gamma_L^p = 2.3$ mJ/m²) are the most common test liquids used in investigation of SE. Using these two liquids SE is calculated from the set of equations:

$$\begin{cases} \left(\gamma_S^d\right)^{0.5} + 1,53\left(\gamma_S^p\right)^{0.5} = 7,80(1 + cos\Theta_W) \\ \left(\gamma_S^d\right)^{0.5} + 0,22\left(\gamma_S^p\right)^{0.5} = 3,65(1 + cos\Theta_{W.}) \end{cases}$$

The content of oxygen and carbon atoms in surface layers of tested samples was determined using energy-dispersive X-ray spectroscopy with EDS detector mounted in the SEM microscope. The EDS studies were performed with an accelerating voltage of 10 kV, current 10 uA, and the working distance of about 15 mm. The spectra were obtained from areas with ×500 magnification. For all sample three spectra were taken, each from a different area of the sample surface. The measurement result was the arithmetic average of the atoms content expressed in at. %.

Autocatalytic copper plating was carried out through multistep process including activation, rinsing, acceleration, autocatalytic metallization, rinsing and drying. Surface activation was conducted by a one-step process.

The one-step process was conducted by immersing the samples into an aqueous solution containing 0.25 g/L $PdCl_2$, 12 g/L $SnCl_2$ and 60 mL/L 38% HCl acid at 25°°C for 5 min. The specimens were subsequently immersed into acceleration solution containing 32 mL/L 38% HCl acid at 25°C for 5 min. It was necessary to treat the activated surface with an accelerator in order to selectively remove the stabilizing stannous ions, thus exposing the catalytically active Pd^0.

After acceleration processes the samples were rinsed in deionized water to prevent contamination of the plating bath.

The activated samples were consequently immersed in autocatalytic copper plating bath at 46 °C for 5 min. The pH value of the bath at a temperature of 46 °C was 12.8. Following the recommendations of the