

## Applications of lasers in metallization of thermoplastic and thermosetting polymers

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### Materials

#### ABSTRACT

**Purpose:** This work focuses on the studies of chemical and physical changes induced by ArF-laser irradiation leading to formation of surfaces catalytically highly active and fully prepared for the direct electroless metallization for the case of thermoplastic and thermosetting polymer composites. The only pretreatment method for surface to be activated was laser irradiation. There are compared two polymer composites: thermoplastic and thermosetting with the same qualitative and quantitative contents of the selected copper compounds. Additionally, there is presented wide context of laser applications in electroless metallization of polymeric materials.

**Design/methodology/approach:** The composites contained the same amount of copper(II) oxide (CuO) and copper(II) acetoacetate  $\text{Cu}(\text{acac})_2$ , while varied with the type of polymer matrix. There were chosen polyamide 6 as thermoplastic and polyurethane resin as thermosetting polymer matrixes. The composites were irradiated with various numbers of ArF excimer laser pulses ( $\lambda = 193 \text{ nm}$ ) at constant fluence of  $100 \text{ mJ/cm}^2$ . The metallization procedure of the laser-irradiated samples was performed by use of a commercial metallization bath and formaldehyde as a reducing agent. The samples were examined using FTIR, contact angle measurement and SEM techniques.

**Findings:** It was found that laser irradiation induce catalytic properties in the studied composites. However, better catalytic properties were achieved for the thermoplastic than thermosetting polymer composites.

**Research limitations/implications:** In order to better understand the differences in laser interactions between thermoplastic and thermosetting composites more examples of various polymer matrixes should be investigated.

**Practical implications:** Suitable condition for laser irradiation of the composites associated with the best catalytic properties were proposed. Better catalytic properties were achieved for thermoplastic than thermosetting composite.

**Originality/value:** Comparison of new thermoplastic and thermosetting polymer composites intended for laser direct electroless metallization is firstly reported in this article.

**Keywords:** Thermoplastic composites; Thermosetting composites; Electroless metallization; Laser surface treatment

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## 1. Introduction

### 1.1. Fundamentals of laser-polymer interaction

Laser is a relatively new emerging tool applying to induce new properties of engineering materials [1-5]. The first operating laser was constructed by Theodore H. Maiman in 1960 in California. In the same year, he reported physical and engineering fundamentals of operation of the constructed laser in the Nature journal [6]. The term "laser" originated as an acronym for Light Amplification by Stimulated Emission of Radiation. Physical explanation of this phenomenon was presented by Albert Einstein 43 years before constructing the first laser [7]. In the last 50 years in industry and science there were rapidly developed new technologies for constructing lasers generating radiation at different wavelengths (Fig. 1).

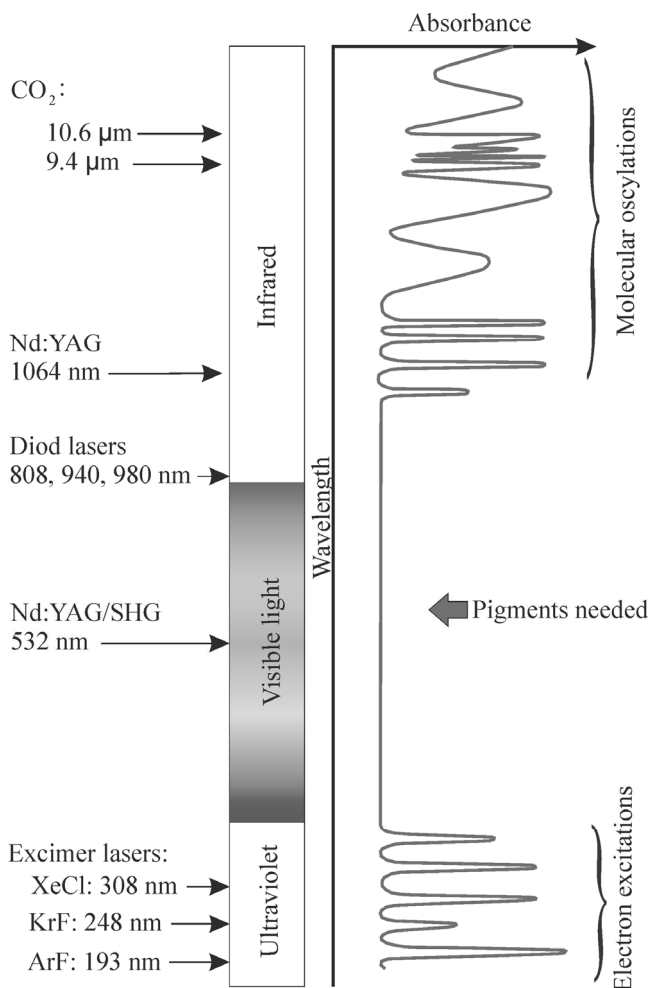


Fig. 1. Electromagnetic spectrum and lasers operating at specific wavelengths

Wavelengths of the radiation, generated power and operation mode (pulsed or continuous) have major influence on the properties of laser irradiated polymer materials. Generally, polymer materials effectively absorb ultraviolet (UV) and infrared (IR) radiation, whereas being transparent for visible light. In order to modify polymers by visible light they have to be doped with absorbing pigments.

Interactions of laser radiation and polymer matter differ greatly depending on the applied wavelength of radiation. Generally, UV radiation causes photolytic breaking of molecular bonds in polymer materials, while thermal effects are reduced. As a result of the molecular bonds breaking free radicals are formed. These radicals can initiate chemical reaction, mainly oxidation if irradiation was performed in an oxygen-containing atmosphere, and crosslinking of the polymer chains. The quantum yield  $\Phi$  for molecular bond dissociation is given by [8]:

$$\Phi = \exp \left[ - \left( \frac{h\omega_d}{h\omega_{ph}} \right) \right] \quad (1)$$

where,  $h\omega_d$  is the bond dissociation energy and  $h\omega_{ph}$  is the energy of single laser photon. The extreme rapidity of the UV bond-breaking process eliminates heat conduction.

Different mechanism occurs in the case of infrared radiation absorbed by polymer materials. Energy of this radiation is transformed into form of molecular bond vibrations, thus resulting in a large increase in temperature and in a variety of associated effects such as melting and thermal degradation of the polymer material. In the literature UV-laser modification of polymer materials is assumed to be photochemical process, whereas IR-laser modification is reported as photothermal process [9-11].

The fluence (energy per unit area) is very important parameter of laser surface treatment. The irradiated material starts to be ablated when the value of laser fluence (so-called ablation threshold) is high enough to initiate ejection of polymer fragments. With increasing laser fluence above the ablation threshold ablation depth depends on laser fluence and on absorption coefficient of the treated polymer according to the empirical Lambert's law [12]:

$$F(L) = F_0 e^{-\alpha L} \quad (2)$$

$$L = \frac{1}{\alpha} \ln \left( \frac{F}{F_{th}} \right) \quad (3)$$

where  $F(L)$  is the laser fluence within an examined material at a depth  $L$ , measured from the material surface, and  $F_0$ , fluence of the incident laser radiation, and  $\alpha$ , an absorption coefficient. Fig. 2 illustrates the ablation depth as a function of laser fluence.

Laser fluence lower than the ablation threshold induces mainly chemical reactions in the surface layer of polymeric material with minor changes in surface morphology. Applying higher fluences than ablation threshold lead mainly to significant changes in surface morphology resulted from laser induced polymer ablation. The ablation rate depends on the kind of a modified material,  $F$  value, laser radiation wavelength, laser

pulse duration, and surrounding atmospheric conditions [13]. Because of so many variables, including the two-step absorption and attenuation of the radiation beam by the material being ejected, there is a number of models for the course of the ablation process [14,15]. Laser fluences above and below ablation threshold both can be used for the preparation of polymer surface to be metallized depending on the applied methods.

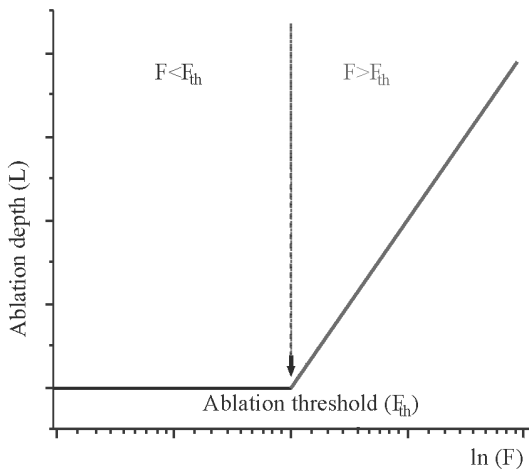


Fig. 2. Dependence of ablation depth on laser pulse fluence

## 1.2. Polymer metallization

Most of the polymer materials are inert, hydrophobic and have low surface energy. These features significantly reduce effectiveness of metallization procedures. In order to improve adhesion properties polymer materials have to be modified prior to metallization process. Laser modification of surface layer causes its chemical and physical changes that can improve adhesion strength of polymer material and deposited metal. There are three main methods commonly used to metalize materials. These are physical vapour deposition (PVD), chemical vapour deposition (CVD) and electroless metallization [16-21].

The most common and most frequently applied method of industrial polymer metallization is electroless metallization. Electric field is not needed in this method, but metal deposition results from the flow of electrons from the metal more electronegative or from reducing substance to the metal ions present in metallization bath (Fig. 3).

Electroless deposition was firstly developed by Brenner'a and Riddella'a and patented in 1950 [22]. Initially, it was very slow process and deposited metal layers were of poor quality. Over time, this process has been improved through the proper selection of bath composition and metallization conditions, which lead to its wide application in industry.

Electroless metallization methods involve a variety of multi-step sequences for the preparation of surface to be coated. Conventionally, substrates are successively cleaned with solvents to remove surface contaminants, chemically etched to obtain a micro-roughened oxidized surface, and seeded with a catalyst

such as palladium. Two- or one-step chemical procedures are commonly used. In the two-step procedure, substrate is treated successively in dilute  $\text{SnCl}_2$  (sensitization step) and  $\text{PdCl}_2$  (activation step) acidic solutions, whereas in the one-step procedure a colloidal suspension containing both Sn and Pd species (a  $\text{SnCl}_2/\text{PdCl}_2$  acidic solution) is used. In order to reduce the number of wet-chemical steps and to minimize or avoid environmental and occupational risk, developing new alternative physical methods is highly desirable [23,24].

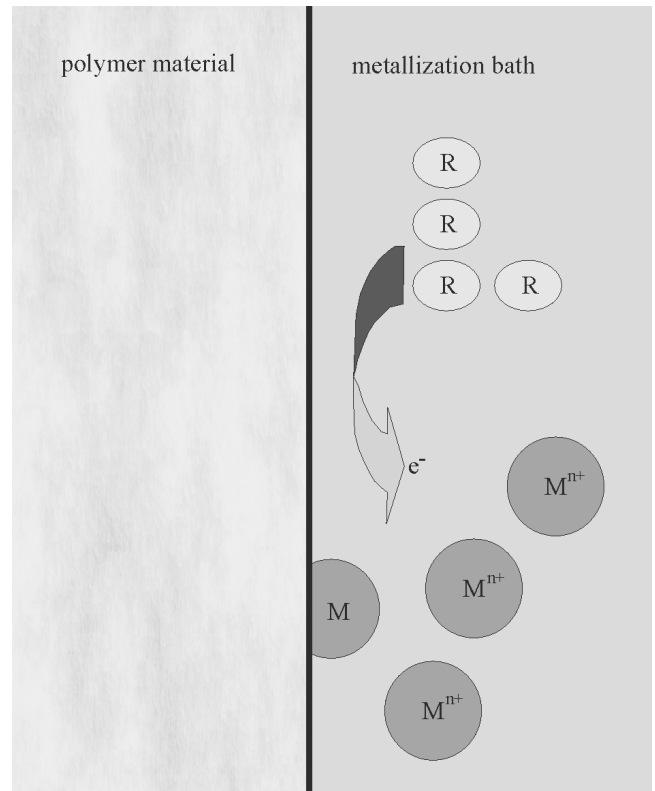


Fig. 3. Schematic presentation of electroless metallization with a reducer (R) as a source of electrons ( $e^{-}$ ) for metal ions ( $M^{n+}$ ) intended to be deposited

New laser modification methods can be applied for metallization of polymers. Laser pretreatment methods can be classified into the ablative or non-ablative groups. Methods from the former group consist mostly in surface roughening as a result of ablative ejection of material fragments, while those from the latter group in changing surface energy by implementation of polar functional groups mostly as a result of surface photooxidation. These methods aim to improve adhesion of an evaporated metal layer to polymer substrate but are not appropriate as pretreatment methods in electroless chemical metallization procedure.

Laser irradiation of specially designed polymer composites containing nonconductive metal compounds can result in surface totally prepared for chemical metallization and, thus, in elimination of conventional chemical pretreatment steps [25,26].

In the case of these methods, organometallic or metal oxide compounds embedded in polymer matrix are photolytically reduced to metallic species that form crystallization centres for growth of an electroless deposited metallic layer. Designing new composites specially intended for the laser-assisted selective electroless metallization is very important due to the growing demand for miniaturization of mechatronic elements.

### 1.3. Research objectives

This work focuses on the studies of chemical and physical changes induced by laser irradiation, which cause formation of surfaces catalytically highly active and fully prepared for the direct electroless metallization. There were compared to polymer composites: thermoplastic and thermosetting with the same qualitative and quantitative contents of specially selected copper compounds. The content of the composites is new and was not reported elsewhere.

## 2. Experiments

### 2.1. Materials

The following materials were applied for the preparation and metallization of thermoplastic and thermosetting composites:

- Polyamide (PA6), designated as Tarnamid (Azoty Tarnów, Poland),
- Polyurethane resin (PU) based on poly(styrene-methyl methacrylate-acrylonitrile) (Haering GmbH, Germany),
- Copper(II) acetylacetonate of the chemical formula:  $[\text{CH}_3\text{COCH}=\text{C}(\text{O}-)\text{CH}_3]_2\text{Cu}$ , further referred to in this article as  $\text{Cu}(\text{acac})_2$  (Sigma-Aldrich, Germany). Its molar mass was 261.76 g/mol, melting point  $T_m = 245^\circ\text{C}$ , purity 97%,
- Copper(II) oxide  $\text{CuO}$  (Sigma-Aldrich, USA). Its molar mass was 79.55 g/mol,  $T_m = 1326^\circ\text{C}$ , purity 98%,
- Bath for autocatalytic metallization process, type M - Copper 85 (MacDermid, USA),
- Formaldehyde 36%  $\text{HCHO}$  (POCH, Poland), with molar mass 30.03 g/mol.

### 2.2. Sample preparation

Thermosetting composite coatings were prepared by mechanical mixing of polyurethane resin with  $\text{CuO}$  and  $\text{Cu}(\text{acac})_2$  powders in amount of 79.2, 15.0, 5.0 and 0.8 wt%, respectively (further referred to as composite A). Mixed components were initially degassed in vacuum chamber under pressure of 0.2 mbar during 15 minutes. Polycarbonate samples were coated with the prepared composite resin using dip-coating method and then dried for 48 hours.

A co-current twin-screw extruder, type TSK 20 (Bühler, Germany), equipped with segmented screws of diameters of 20 mm and length/diameter ratio of 40, was used to prepare granulated thermoplastic composite containing: 80.0 wt% of PA6,

15.0 wt% of  $\text{CuO}$ , and 5.0 wt% of  $\text{Cu}(\text{acac})_2$  (further referred to as composite B). Prior to the extrusion, the mechanically mixed components were dried at  $120^\circ\text{C}$  for 16 h. The temperatures of barrel heating zones I, II, III, IV, and of the die of the extruder were set to 260, 260, 265, 265, and  $260^\circ\text{C}$ , respectively. Square plates ( $60 \times 60 \times 1$  mm) were produced from the granulated composite, using a laboratory injection moulding press type Battenfeld Plus 35/75 (Battenfeld GmbH, Germany). The temperatures of barrel heating zones I, II, and III of the die of the injection moulding press were set to 290, 295, and  $290^\circ\text{C}$ , respectively. Individual samples ( $20 \times 10 \times 1$  mm) were cut out from the moulded plates.

### 2.3. Laser irradiation and electroless metallization

The samples were irradiated with 20-ns ArF excimer laser pulses ( $\lambda = 193$  nm) at the frequency of 5 Hz (LPX300, Lambda Physik, Fort Lauderdale, USA). In the experiments, no beam homogenizing devices were used. Laser pulses of the fluences of  $100 \text{ mJ}/\text{cm}^2$  and irradiating the surface area of  $1 \times 3 \text{ cm}^2$  were applied. These fluence values were set to be higher than the PA6 and PU and lower than the Cu ablation thresholds. The exact value of a laser fluence was set using a laser build-in excitation control system (LPX Laser Control System, Lambda Physik, Fort Lauderdale, USA) and pulse energy detector, type FieldMax II (Coherent Inc., USA). The samples were irradiated with 50, 100 and 500 laser pulses at each of the applied fluences. Considering the type of a composite (A or B) and irradiation conditions, the samples discussed in this work are designated as presented in Table 1.

Table 1. Designations of samples due to polymer matrix and irradiation conditions (N, number of laser pulses)

| Sample | Polymer matrix | N   |
|--------|----------------|-----|
| A0     | PU             | 0   |
| A1     | PU             | 50  |
| A2     | PU             | 100 |
| A3     | PU             | 500 |
| B0     | PA6            | 0   |
| B1     | PA6            | 50  |
| B2     | PA6            | 0   |
| B3     | PA6            | 500 |

The metallization procedure of the laser-irradiated samples was performed by use of a commercial metallization bath M - Copper 85 (MacDermid, USA) and formaldehyde as a reducing agent. The samples were immersed in the metallization bath for 60 minutes at  $46^\circ\text{C}$  to deposit copper layers.

### 2.4. Measurements

FTIR spectra of the composites were recorded with a spectrometer Nicolet iS10 (Thermo Scientific, USA) in the attenuated total reflection mode over the range of  $400\text{--}4000 \text{ cm}^{-1}$ , using a resolution of  $2 \text{ cm}^{-1}$  and 32 scans.

The contact angle measurements were carried out using a DSA 100 goniometer (Krüss GmbH, Hamburg, Germany), water as the polar test liquid, and diiodomethane as the non-polar test liquid. During a measurement, the volume of a droplet resting on a sample surface was constantly increased and, at the same time, the dynamic contact advancing angle was measured. The liquid feed rate was set to 5  $\mu\text{L}/\text{min}$  and the droplet volume growth was monitored in the range of 3-9  $\mu\text{L}$ . The profile of the droplet was analysed while taking into account the point of the contact of three phases: the studied sample, test liquid, and air. Such a method enabled to obtain precise and repeatable results. One hundred measurements of the contact angle were carried out for each sample, from which a mean arithmetic value, standard deviation, and confidence interval were calculated. The standard deviations from the mean values of the contact angles of water and diiodomethane were 0.7-1.2° and 0.9-1.6°, respectively.

The surface energy of the studied samples was determined by the Owens-Wendt method, being commonly used in the studies of polymeric materials. According to the method, the surface energy ( $\gamma_s$ ) of a solid is equal to a sum of the dispersive ( $\gamma_s^d$ ) and polar ( $\gamma_s^p$ ) components:

$$\gamma_s = \gamma_s^d + \gamma_s^p \quad (2)$$

and the energy ( $\gamma_{SL}$ ) relating to the interface between the solid and the test liquid is expressed as:

$$\gamma_{SL} = \gamma_s + \gamma_L - 2 \left[ (\gamma_s^d \gamma_L^d)^{0.5} + (\gamma_s^p \gamma_L^p)^{0.5} \right] \quad (3)$$

Possible errors of the obtained surface energy values might result from inaccuracies of both the contact angle measurements and the assumed surface energy values for the test liquids. Considering the conditions of the measurements and the results of the statistical analysis of these errors, it was estimated that the latter did not exceed 0.5  $\text{mJ}/\text{m}^2$ .

Scanning electron microscopy measurements were performed by use of a scanning electron microscope 5500LV (JEOL, Japan). Prior to the measurements, samples were coated with thin gold layers. The SEM images were taken at the accelerating voltage ranging from 5 to 15 kV and electron beam current, from 57 to 65  $\mu\text{A}$ .

### 3. Results and discussion

#### 3.1. General analysis of catalytic properties

Catalytic properties of laser irradiated composites were initially assessed based on the degree of surface coverage with copper. Photographic images of the composites irradiated with ArF laser and electroless metalized are presented in Fig. 4. As can be seen in the figure, the method of sample manufacturing affected their overall quality. As mentioned previously, composite B was firstly extruded using twin-screw extruder. This process is

used to produce composites with high dispersion of powders and nano-powders. Then the extruded granulate was used to produce the samples by means of injection moulding, thus the sample surfaces were very smooth. On the other hand, manufacturing of samples A were accompanied by powder agglomeration despite intensive mechanical mixing of the composite components.

Composite B irradiated with 50 laser pulses at fluence of 100  $\text{mJ}/\text{cm}^2$  could be partially metalized, while composite A irradiated at the same dose left uncovered. After reaching 100 laser pulses copper layer is also apparent on the surface of composite A. The overall visual quality of copper layers is in favour of composites B. In summary, it can be concluded that composites B has better catalytic properties as compared to composite A.

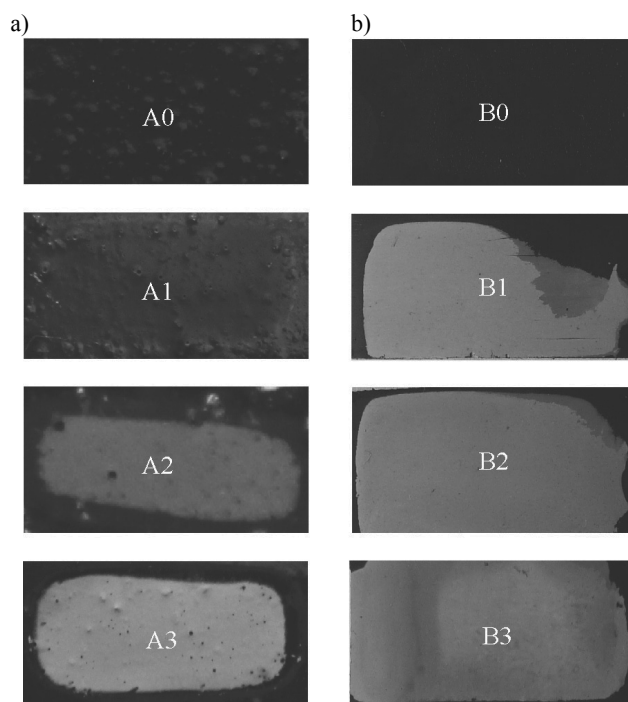


Fig. 4. Photographic images of the samples: (a) A0, A1, A2, A3, and (b) B0, B1, B2, B3

#### 3.2. FTIR analysis

FTIR spectra analysis was performed in order to assess the influence of laser irradiation on changes in chemical structure of composite surface layers. While the composition of the copper compounds in composites A and B is the same, the differences in FTIR spectra will reflect mainly the effects of polymer matrixes PA6 or PU on chemical alterations of the surface layers. Figs. 5a and 5b present FTIR spectra of studied composites.

The apparent general tendency of the spectra transformation is an increase in absorbance for the wavenumber range from about 4000-2000  $\text{cm}^{-1}$  with increasing number of laser pulses regardless of polymer matrix used. Absorbance in this range is characteristic for metallic copper ( $\text{Cu}^0$ ). The significantly higher absorbance

increase for B than A samples point out on higher  $\text{Cu}^0$  concentration in B than A samples. There can be distinguish various mechanisms for an increase of copper concentration. On the one hand, these are photolytic dissociation of copper compounds and side reactions leading to reduction reactions of copper compounds, and on the other, ablative removal of polymer matrix, all resulted from laser irradiation. Because the composition of copper compound is the same for A and B composites, one can assume that the most influential factor for the difference in  $\text{Cu}^0$  agglomeration is effectiveness of laser ablation of polymer matrix. Based on this assumption and recording an increase in absorbance attributed to  $\text{Cu}^0$ , it can be concluded that more effectively ablated is PA6 than PU polymer matrix. Laser ablation of polymers is considered to be mainly the thermal process. Generally, it is well known that thermosetting polymers are more resistant to heat degradation processes as compared with thermoplastics.

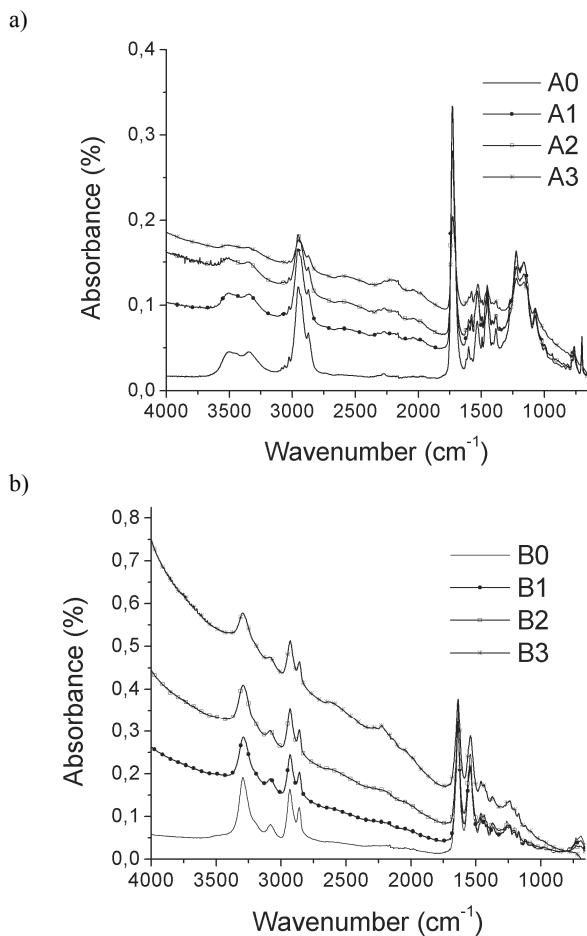


Fig. 5. FTIR spectra of the samples: (a) A0, A1, A2, A3, and (b) B0, B1, B2, B3

In addition to these changes, there was a marked decline of the absorption band at about 1720  $\text{cm}^{-1}$  attributed to carbonyl groups (C=O) for A and B composites, as well. This decline

results from laser induced ablative removal of polymer fragments, in which these functional groups were present.

### 3.3. Contact angle and surface energy

In order to determine changes in thermodynamics of laser irradiated composite surfaces contact angle measurements were performed. Surface energy was also calculated based on the contact angle results. Surface energy is commonly considered as an indirect measure of material adhesion properties. Results of contact angle measurements for samples A and B are presented in Figs. 6 and 7, respectively.

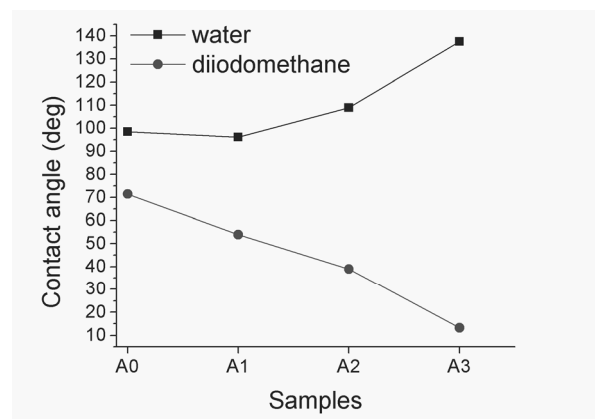


Fig. 6. Contact angles of water and diiodomethane for samples A0, A1, A2 and A3

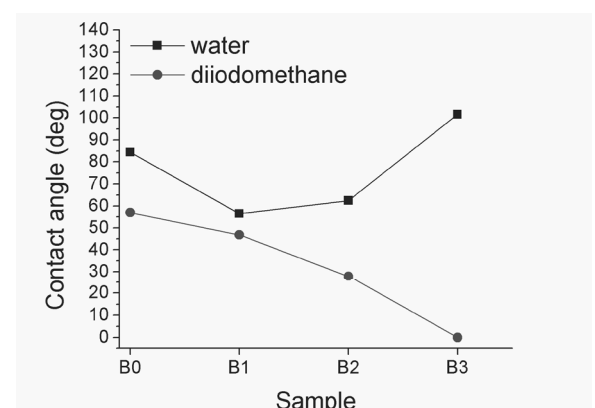


Fig. 7. Contact angles of water and diiodomethane for samples B0, B1, B2 and B3

The general tendency is an increase in water contact angle, while decrease in diiodomethane contact angle followed by increasing number of laser pulses. The values of water contact angle initially decreased (samples A1 and B1), and next increased with exposition to successive laser pulses, however, that increase is higher for samples A than B. The values of diiodomethane

contact angle decreased steadily with increasing number of laser pulses. However, this decrease was higher for samples B than for samples A.

The results of surface energy calculations are presented in Fig. 8. The values of surface energy are increasing with increasing number of laser pulses but for the case of samples B that increase was saturated after exposition to 50 laser pulses. These results are generally in line with those obtained from visual assessment of metalized composites (Fig. 4). Surface of composite B was rapidly transformed reaching catalytic properties, whereas surface of composite A became catalytic under exposition to higher number of laser pulses.

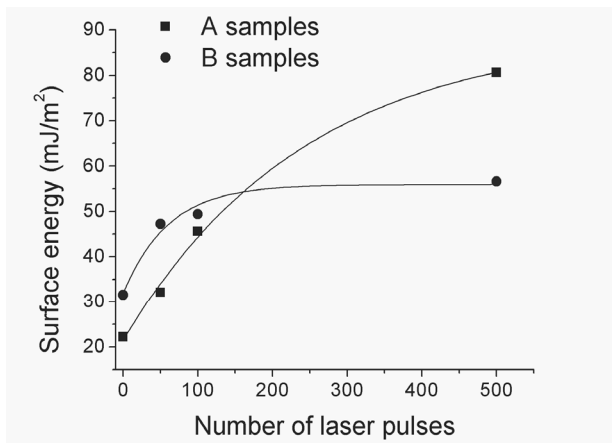


Fig. 8. Surface energy for samples A and B versus the number of laser pulses

### 3.4. Scanning electron microscopy

Laser irradiated samples A and B are presented in Fig. 9 and Fig. 10, respectively. On the surface of the samples A1 and B1 bright surface areas of copper agglomerations are apparent. The number of these areas was increasing with increasing number of laser pulses (to compare samples A3 and B3).

The value of applied laser fluence ( $100 \text{ mJ/cm}^2$ ) is lower than the ablation threshold of metallic copper, while higher than the ablation threshold of PA6 and PU. In these irradiation conditions, deep grooves are formed by laser ablation of polymer fragments in between the copper agglomerates (A1, B1, and A3, B3). The emission of electrons is hindered from the grooves, thus these sites are represented by dark black areas on the surface. By comparing surface morphologies of the samples A1 and B1, it is well seen that the deeper grooves were formed in surface layer of sample B1 than A1. This finding also confirms higher ablation rate of PA6 than PU polymer matrix.

Fig. 11 presents granular structure of electroless deposited copper layers on the surfaces of laser modified composites A3 and B3. The morphology of the copper layers is similar for metalized sample A3 and B3. The copper layer started to grow on the copper structures formed and agglomerated by laser irradiation. In effect, granular surface structure was formed for both A3 and B3 samples.

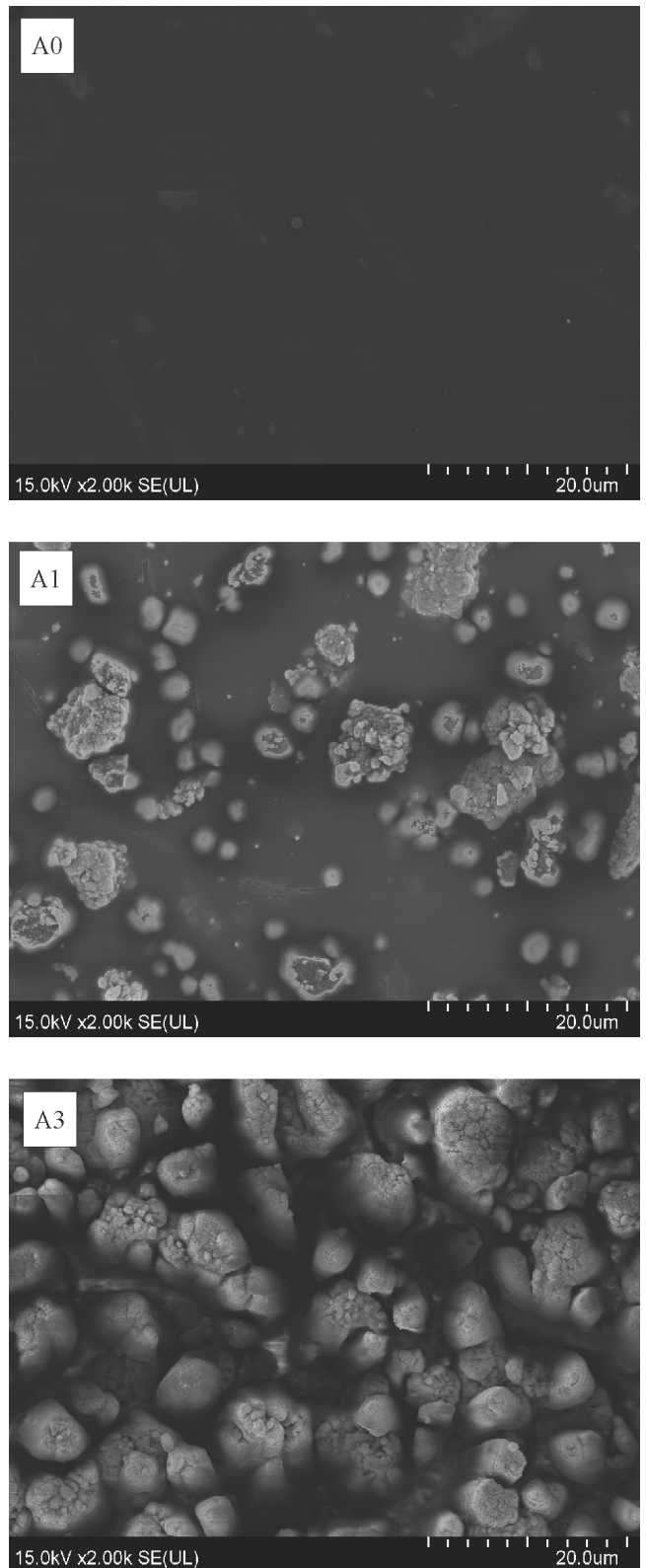


Fig. 9. SEM images of the samples A0, A1 and A3

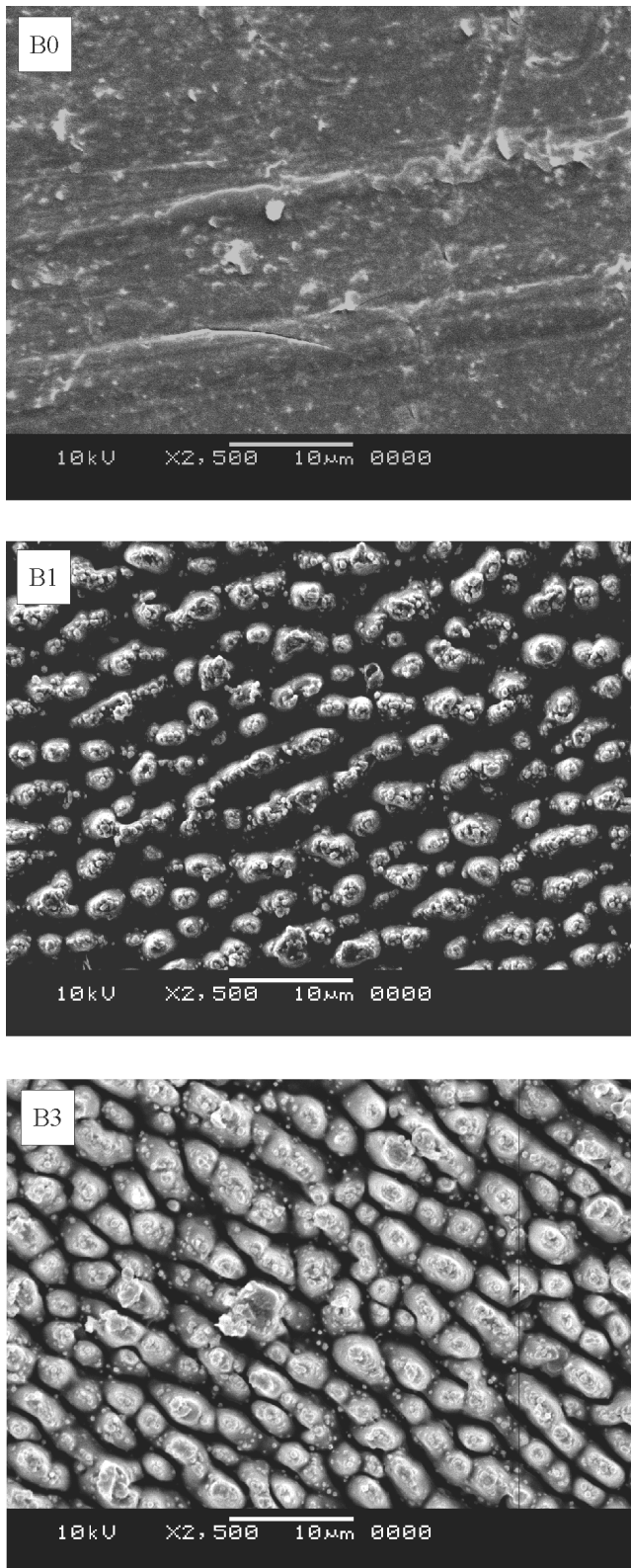


Fig. 10. SEM images of the samples B0, B1 and B3

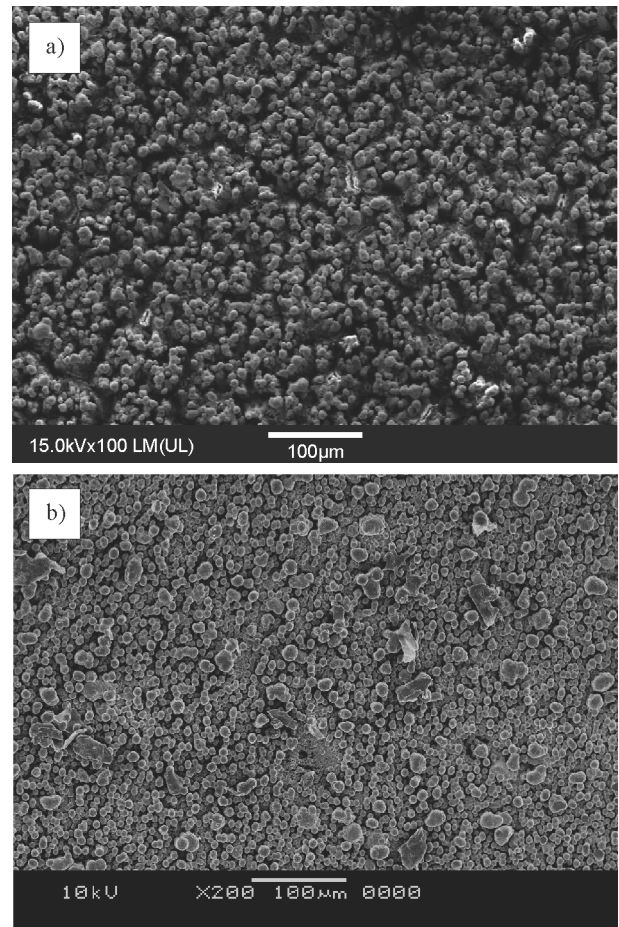


Fig. 11. SEM images of laser irradiated and electroless metalized (a) sample A3 and (b) sample B3

#### 4. Conclusions

This work focused on the chemical and physical changes induced by ArF-laser irradiation, which caused formation of surfaces catalytically highly active and fully prepared for the direct electroless metallization. There were compared two polymer composites: thermoplastic and thermosetting with the same qualitative and quantitative contents of the selected copper compounds. The copper compounds were  $\text{Cu}(\text{acac})_2$  and  $\text{CuO}$ . It was found that:

- greater surface area was coated with copper on the thermoplastic than thermosetting composites irradiated at the same energy dose,
- laser irradiation lead to increase in the content of metallic copper in the surface layer of both, thermoplastic and thermosetting composites, however that increase was higher for thermoplastic composite;
- the surface energy of thermoplastic composite increased after exposition to 50 laser pulses and next was unchanged, whereas for composite B surface energy was contentiously increasing with increasing number of laser pulses;



- more agglomerated copper structures were on the thermoplastic than thermosetting composite surfaces irradiated at the same energy dose; also deeper grooves were formed in surface layer of thermoplastic than thermosetting composites.

Generally, better catalytic properties were achieved for thermoplastic than thermosetting composite. Suitable conditions for laser irradiation of the composites associated with the best catalytic properties were also proposed.

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