

## Autocatalytic Metallization of Polymer Materials Produced by the Additive Technology

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### ABSTRACT

The article describes each stage of the autocatalytic electroless metallization process of thermoplastic polymers produced with 3D printing technology. In particular, the influence of the preparation of the sample's surface layer on the quality of the finished metallic coating was assessed. Samples made of polylactide filament and polylactide with the addition of copper were subjected to metallization. In the metallization process, six different etching solutions were prepared to etch the polymer's surface layer. The concentration of sulfuric acid VI was 200 g/dm<sup>3</sup> or 100 g/dm<sup>3</sup>, sodium hydroxide 100 g/dm<sup>3</sup>, and potassium permanganate 50 g/dm<sup>3</sup> or 20 g/dm<sup>3</sup>. The microscopic analysis and measurement of the arithmetic mean of the ordinates of the surface roughness profile of the samples for the selected process steps are presented.

**Keywords:** electroless metallization, polymer materials, 3D printing.

### INTRODUCTION

The first metallic coatings with good adhesion to the surface of polymeric materials were developed in the 1950s. At that time, the metallization process was primarily applied to decorative elements. The first coatings used on the polymer elements were made of copper and nickel [1]. These two materials have good mechanical strength and high thermal and electrical conductivity. Over the years, the electronics industry has challenged scientists to create stable, highly conductive metallic coatings on polymers. Jean-Jacques Pireaux and Steven Kowalczyk organized a symposium on the metallization of polymers in Montreal, supported by the American Chemical Society, to meet the challenge, in 1989 [2]. At this symposium, scientists worldwide discussed and exchanged insights on the metallization of plastics. Currently, the metallization of plastics is used in producing automotive parts like headlight housing [3] and aircraft components metallization of construction and display elements [4] and in the electronics

industry to produce printed circuits, PCBs (Printed Circuit Board), and antenna components [5].

In the metallization process, mainly thermoplastics are used [6]. However, it happens that scientists investigate the metallization process of thermosets such as polyurethanes. Professor Piotr Rytlewski from the Faculty of Materials Science and Engineering of the Kazimierz Wielki University in Bydgoszcz developed a method of electroless metallization with laser activation of a polyurethane coating containing glass microspheres and a copper (II) compound with L-tyrosine [7]. In the research, different sizes of glass microspheres were introduced into the sample matrix, the outer layer of the material was activated with a laser, and then electroless metallization was performed using the M-Copper 85 solution. As a result of these studies, the team from the University of Bydgoszcz proved that the use of glass microspheres enables the reduction of the content of the organic complex of copper and L-Tyrosine in the metalized material without affecting the quality of the final coating.

In the latest research, scientists use additive technology to manufacture plastic parts that are later metalized. The 3D printing technology allows for producing geometrically advanced elements at a low cost. The combination of additive technology and the metallization process provides for the development of functional elements with unique properties. A team of scientists from the University of Mercer in the United States used the metallization process to increase the durability of polymer structures produced by the FDM method [8]. High Vacuum Magnetron Sputtering was used to apply a thin layer of copper to the polymer material. This technology is widely used in many industries, mainly for coating glass surfaces; however, a team of scientists proved that it works just as well in polymer materials [9].

Deposition of metallic coatings on polymers can be carried out using several processes. The first is the electroless metallization process, which should be distinguished by two methods: metallization by reduction of metal ions and autocatalytic metallization [10]. Other processes that can be used to deposit a metal layer on a polymer surface include the physical deposition of a metal layer (PVD) and the chemical deposition of a metal layer from the gas or liquid phase (CVD) [11]. The essence of the metallization process by reducing metal ions is the transport of electrons from the reducer to the metal ions. The attachment of electrons reduces the metal ions to a metallic form and allows them to be deposited on the previously prepared surface layer of the polymer [1]. The discussed method is uneconomical because the reduction reaction occurs in the entire bath volume, and only a tiny part of the metal covers the polymer surface. The second method of electroless metallization solves the problem of the course of the metal ions reduction reaction in the whole bath volume. The metal ions in the galvanizing bath react with the reducer present directly on the surface layer of the polymeric material. The reducer, the most used palladium chloride, reduces metal ions to a metallic form and improves the adhesion of metallic particles to the surface. The palladium compounds on the surface layer create active regions that allow the metal layer to be deposited. This method is often used in the electronics industry to produce integrated circuits [12]. The second process of depositing a metal layer on a polymeric substrate is the PVD process. The essence of this process is the transport of atoms of a given substance to

the surface of the coated object (polymer material or metal) [13]. In a Chemical Vapor Deposition (CVD) process, a gas-phase chemical reaction is carried out near the substrate [14]. As a result of the response of gaseous reactants, a product (in the solid phase) is formed and deposited on a given surface. The process can be applied to polymer and metal surfaces.

The surface roughness should be determined to verify the surface quality in materials engineering tests. The arithmetic mean of the roughness profile ordinates is the fundamental parameter that determines the surface roughness (Ra) [15]. The required criterion for working surfaces is the Ra value less than or equal to  $0.8 \mu\text{m}$ . The Ra value should be equal to or less than  $0.4 \mu\text{m}$  for surfaces where we expect high smoothness. In Poland and many other European countries, the roughness Ra is the most frequently used roughness parameter [16]. According to the latest ISO 21920-3: 2021 standard, roughness class settings have been introduced that have tolerance ranges for individual roughness parameters such as Ra, Rz, Rp, Rv, and others [17]. Moreover, for each class, the correct test parameters were determined, such as the length of the measuring section, etc., which improves the accuracy of the obtained results.

Research on autocatalytic metallization of polymers is aimed at specific applications, such as creating coatings with good adhesion on decorative elements made of polymer materials. Such coatings are important in many industrial applications where durability and aesthetic appearance of the product are required. The autocatalytic polymer metallization method can be scaled to larger production. However, this requires appropriate adjustment of technological processes to ensure uniformity and quality of the coating at each stage of production. The aim of the conducted research was to investigate the metallization process of polymer materials, focusing on several key aspects including the etching baths used, the type of polymer material, the structure of the polymer surface layer, and the mechanisms and reactions occurring during metallization. In the article published in the journal "Applied Surface Science," research on the engineering of surface composites of polyimide was presented Lai et al. [18]. Three types of aminosilanes, differing in the number of amino units, were used for surface silanization of PI. This process allowed the creation of amino functionalities, which in turn

contributed to achieving a high degree of copper surface coverage. However, these studies, based on this metallization technology, also show that palladium forms connections with tin atoms on the top layer of polylactide, which constitutes a significant difference compared to previously described methods.

## MATERIALS AND METHODS

In the research, polylactide (PLA) was implemented as a substrate for the metallization process. PLA is one of the basic materials used in additive manufacturing. The substrate is made of two types of filaments - pure polylactide and polylactide doped with copper powder in 1%. In the FFF (Fused Filament Fabrication) technology, samples with dimensions of 2×1×1 cm were produced using the incremental method (3D printing). The filament used was PLA from Snapmaker, and the PLA was filled with copper (1%) during the production of the filament. SolidWorks, 3D Gence Slicer 4.0 and Cura software were used to prepare the design of samples and files for printing. 3D printers Gence One and Snapmaker A150 created the sample pack. The sample number corresponds to the number of the solution in which the etching of this material was carried out. The numerical designation of etching solutions, which are assigned

to types of samples, is placed on Figure 1. The designation PLA and PLA Cu indicates the type of filament from which these samples were printed - respectively polylactide and polylactide with copper admixture. In the sample preparation process, additional abrasive treatment of the samples' external surface was implemented to prepare it correctly for the metallization process. In the research process, approximately 30 samples were produced by the FFF method, but a smaller number was selected because others, after the grinding process, were characterized by a roughness coefficient greater than 0.8 μm. Materials requiring such low surface roughness are used in aerospace technologies and electronics, and studies on the Polishing of alumina ceramic by picosecond laser were presented in the journal Surface and Coatings Technology Ximin et al. [19]. The following reagents were used in the metallization process: sulfuric acid (VI) (H<sub>2</sub>SO<sub>4</sub>) (98%V. pure, Chempur), potassium permanganate (KMnO<sub>4</sub>) (pure for analysis, Chempur), tin (II) chloride (SnCl<sub>2</sub>) (pure for analysis, Chempur), palladium (II) chloride (PdCl<sub>2</sub>) (analytical pure, Actinium), hydrochloric acid (HCl) (36%V., pure, Chempur), copper sulphate pentahydrate (CuSO<sub>4</sub>×5H<sub>2</sub>O) (analytical pure, Chempur), sodium hydroxide (NaOH) (analytical grade, Chempur), sodium potassium tartrate (Rochelle salt – NaKC<sub>4</sub>H<sub>4</sub>O<sub>6</sub>) (pure, Warchem), formaldehyde (HCHO) (35%V.

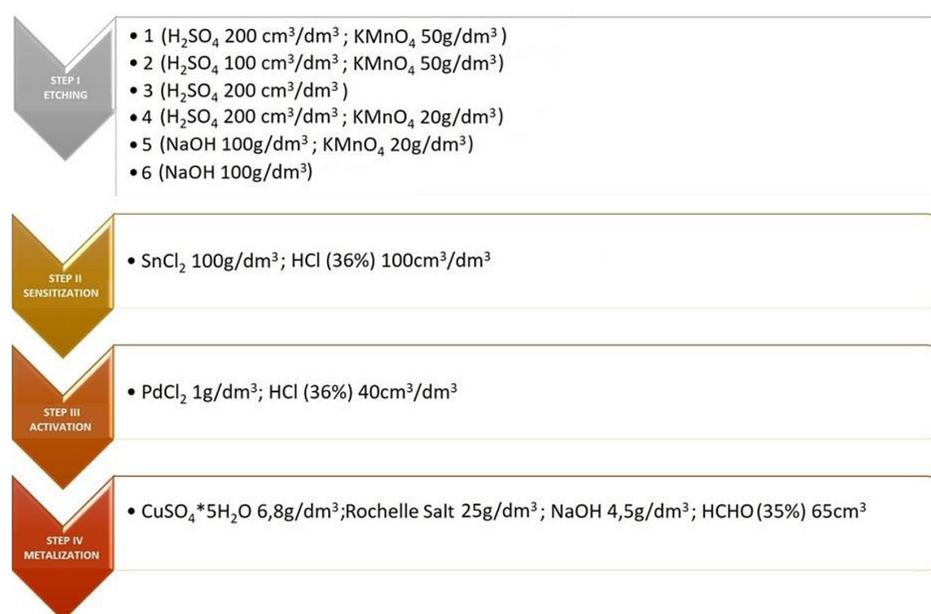


Figure 1. Diagram of the autocatalytic metallization process [20]

pure, Warchem) and water (H<sub>2</sub>O) (demineralized). Glass vessels – beakers with a capacity of 50 ml were used as tanks for metallizing baths.

The copper coatings on the polymer samples were made using autocatalytic electroless metallization. Autocatalytic metallization requires several sample preparation steps. The first stage is the etching process, the second is sensitization, the third is activation, and the last is the direct metallization process. In the first stage of sample preparation, etching solutions were used to increase the geometric surface of the top layer of samples with a smooth surface obtained during the grinding of the sample surface. During this stage, the samples were immersed in aqueous solutions of acids and bases to produce the so-called cavities (pits) on the surface of a polymeric material. The samples subjected to metallization were differentiated by etching the top polymer layer. Six pickling baths were used in the tests. Four discussed aqueous solutions containing various concentrations of sulfuric acid (VI) and potassium permanganate (KMnO<sub>4</sub>). This compound is characterized by excellent oxidizing properties, which helps to etch the polymeric material, but it is a very toxic compound and harmful to the environment. For this reason, in our research, we replaced chromium (VI) oxide with potassium permanganate, which has a meager environmental impact. One aqueous solution contained sodium hydroxide and potassium permanganate. The composition of the solutions is given in the diagram in Figure 1. [20].

During the selection of etching solution components, guidance was taken from the research of Matthias Schneider from the University of Potsdam [21], Amrita Sarkar from the Department of Chemistry and Biochemistry [22], University of South Carolina, and Srinivasa Kartik Nemani in the journal *Advanced Materials* [23]. Sensitization involves applying tin ions to the surface layer by

bathing the products in an aqueous solution of tin chloride acidified with hydrochloric acid. After this step, the samples were placed in a vessel containing demineralized water to form a stable tin hydrate on the surface of the plastic. In the next step, the samples were immersed in a bath containing an acid solution of palladium chloride to activate the surface of the samples. In the redox reaction of tin ions with palladium ions, palladium ions are reduced to metal palladium and deposited on the top polymer layer. After the activation step, the samples were also introduced into the demineralised water bath. Metallic palladium constitutes active areas that are necessary for the process of applying a metallic coating [24].

After the polymer surface layer was prepared, the test samples were placed in the metallization bath. The solution used for metallization contains copper sulfate hydrate, which acts as a metal ion donor, formaldehyde as a reducing agent, and auxiliary substances such as sodium potassium tartrate (NaKC<sub>4</sub>H<sub>4</sub>O<sub>6</sub>) (Rochelle salt) and sodium hydroxide (NaOH). The metallization process is given in the photo in Figure 2. After the metallization stage, the samples should be transferred to a bath in demineralized water and then dried at 45 °C for 30 minutes [25]. The duration of each metallization stage is approximately 10 minutes. This period was chosen based on previous studies on metallization.

In each etching solution, two cubic samples were placed, each with four surfaces designated for examination. This means that eight research surfaces were planned for each solution. Roughness measurements and the results of microscopic analysis conducted with a light microscope showed similarities for all research surfaces in a given solution. Therefore, for the needs of subsequent stages of the metallization process, one sample with four research planes was selected. In each phase of the process,



**Figure 2.** Autocatalytic metallization - the last stage in which the tested samples are placed in a metallizing bath

from the four planes, the one that represented the most consistent results in terms of roughness and pore quality was chosen.

Microscopic photos were analyzed at each stage of the process to determine the quality and surface structure of the polymer samples. The structure of the samples' surface layer was visualized using a Leica digital microscope. A series of photos was taken at 20 times magnification, and a series of photos at 180 times magnification.

The samples' roughness was measured on a Taylor Hobson Surtronic 25 profilometer. The profilometer has been equipped with a standard stylus (examination needle) that is 12.5 mm in length. As for the speed of the needle, it was 0.5 mm/s during the examination. In the research, the arithmetic mean of the roughness profile ordinates ( $R_a$ ) was measured [16]. Dependence of the  $R_a$  coefficient appearing in equation No. 1. The profilometer is given in Figure 3. For each sample, ten roughness measurements were conducted, and the obtained results were averaged.

$$R_a = \frac{1}{l_e} \int_0^{l_e} |z(x)| dx \quad (1)$$

where:  $l_e$  – length of the section on which the measurement was carried out;  $z(x)$  – a function that describes the surface of the object;  $dx$  – elementary width of the elementary surface area;  $z_i$  – deviation of the measurement point from the mean line.

## RESULTS

The photos were taken with a Leica digital microscope to visualize the structure of the polymer surface layer. In Figures 4 and 5, the photos were taken at approximately 20x magnification. To visualize changes in the surface layer of the

samples, images of each sample before etching, before metallization, and the final samples are presented in Figures 6 and 7.

Using this microscope and the function of combining individual images, 3D imaging of the respective layers was performed. The imaging was approximately thirty times magnified and consisted of twenty-seven surface images. Surface mapping can be found in Figure 8. As a result of the analysis of coatings deposited by electroless metallization, pictures were taken using a scanning electron microscope (SEM). The selection criterion for SEM study samples was the quality of the copper coating. Analyzing images from the digital microscope, samples that exhibited the best coating properties, such as uniformity and lack of defects, were selected. The images were taken approximately 10,000 times. The results of the observations are summarized in Figure 9.

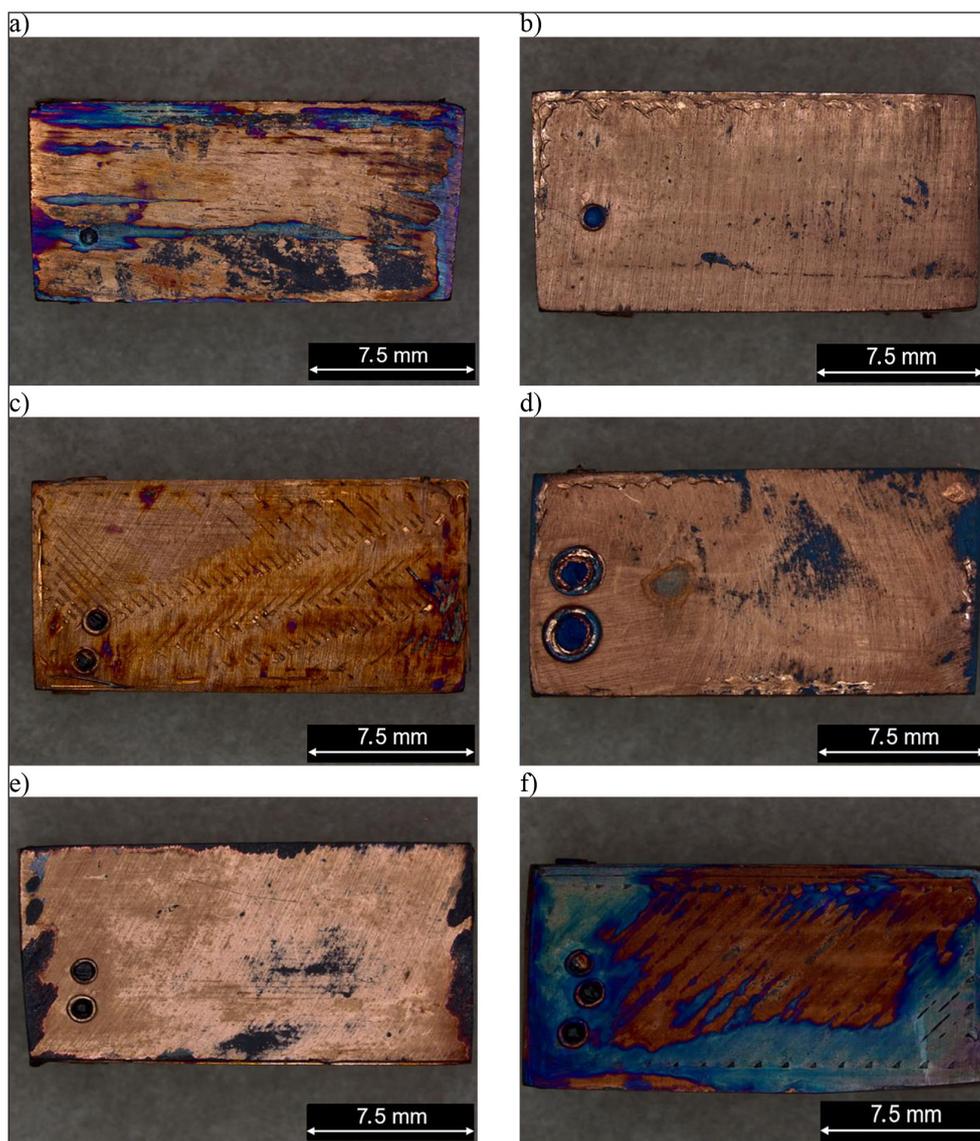
Moreover, the arithmetic mean of the roughness profile ordinates ( $R_a$ ) was measured to determine changes in surface roughness after the selected process steps. During the research, 10 roughness measurements were performed on each sample. Tables 1 and 2 contain parameters concerning the roughness of the samples.

## ANALYSIS OF THE RESULTS

Photographs of each of the twelve samples were taken for microscopic analysis. The first group of photos presents selected planes of polymer samples with a 20-fold approximation. Photos from the first group can be found in Figures 4 and 5. The second group of photos in Figures 6 and 7 contains photos of the samples at a 180-fold approximation. These photos were taken at



Figure 3. The Surtronic 25 profilometer by Taylor Hobson

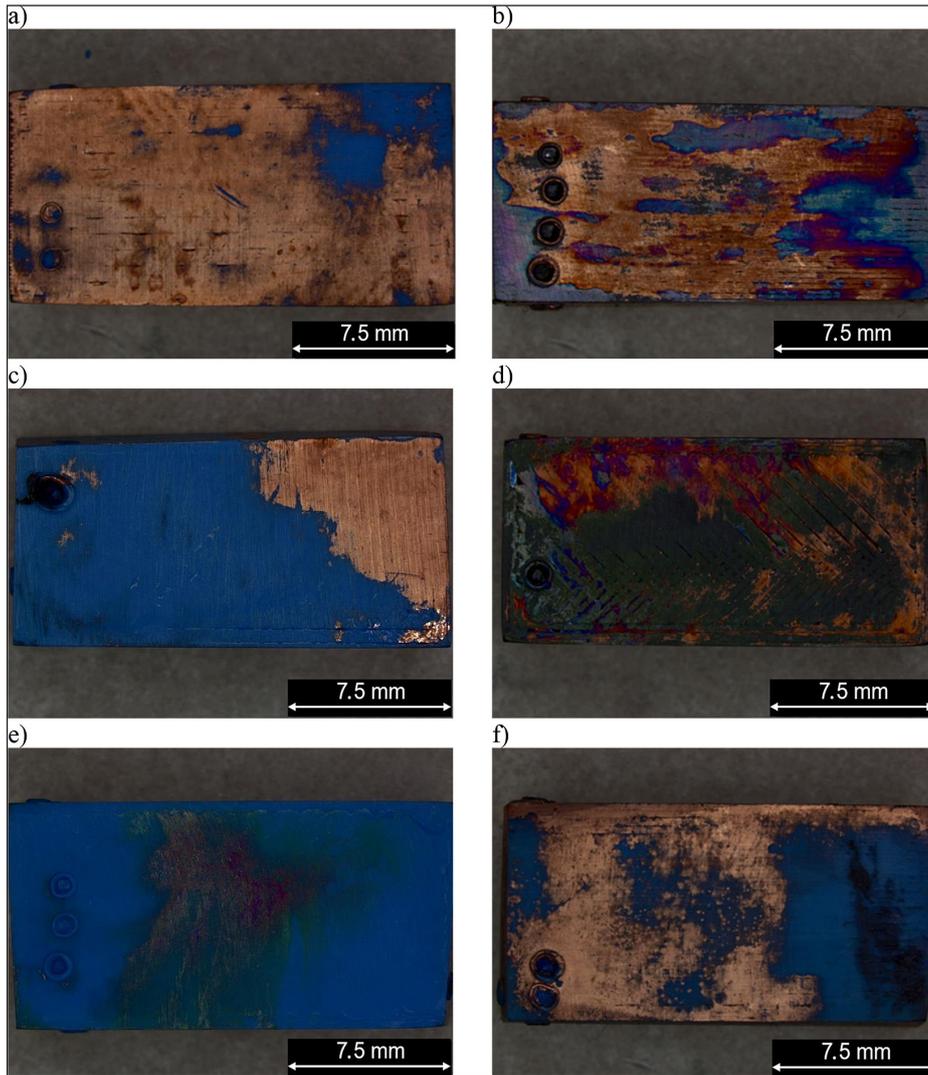


**Figure 4.** Samples after the metallization process, approximation 20x, samples: (a) 1PLA, (b) 1PLA Cu, (c) 2PLA, (d) 2PLA Cu, (e) 3PLA, (f) 3PLA Cu

three different metallization stages - before the etching process, after the etching process, and after applying the metallic copper layer. The same test area was selected for each sample to observe changes in the structure of the surface layer. As a result of the microscopic analysis of the photos from the first group, it should be stated that the best copper coating is used for samples with the designation 1 PLA, 1 PLA Cu, 2 PLA, and 2 PLA Cu. Photos of these samples can be found in Figures 4a–4d. The copper coating on the samples as mentioned earlier completely covered the surface of the polymer top layer. It should also be noted that the samples etched with solution 5 showed a satisfactory metallic coating. Samples 5 PLA and 6 PLA have a blue-violet area. This area is due to

the reaction of copper ions and sodium hydroxide to form blue-violet copper hydroxide particles. Samples 3 PLA Cu, 4 PLA, 4 PLA Cu, and 6 PLA Cu have only a partial metallic coating. Photos of these samples can be found in Figures 4f, 5a, 5b and 5e. The second group of photos requires more detailed analysis because three photos of the same area were selected for each sample.

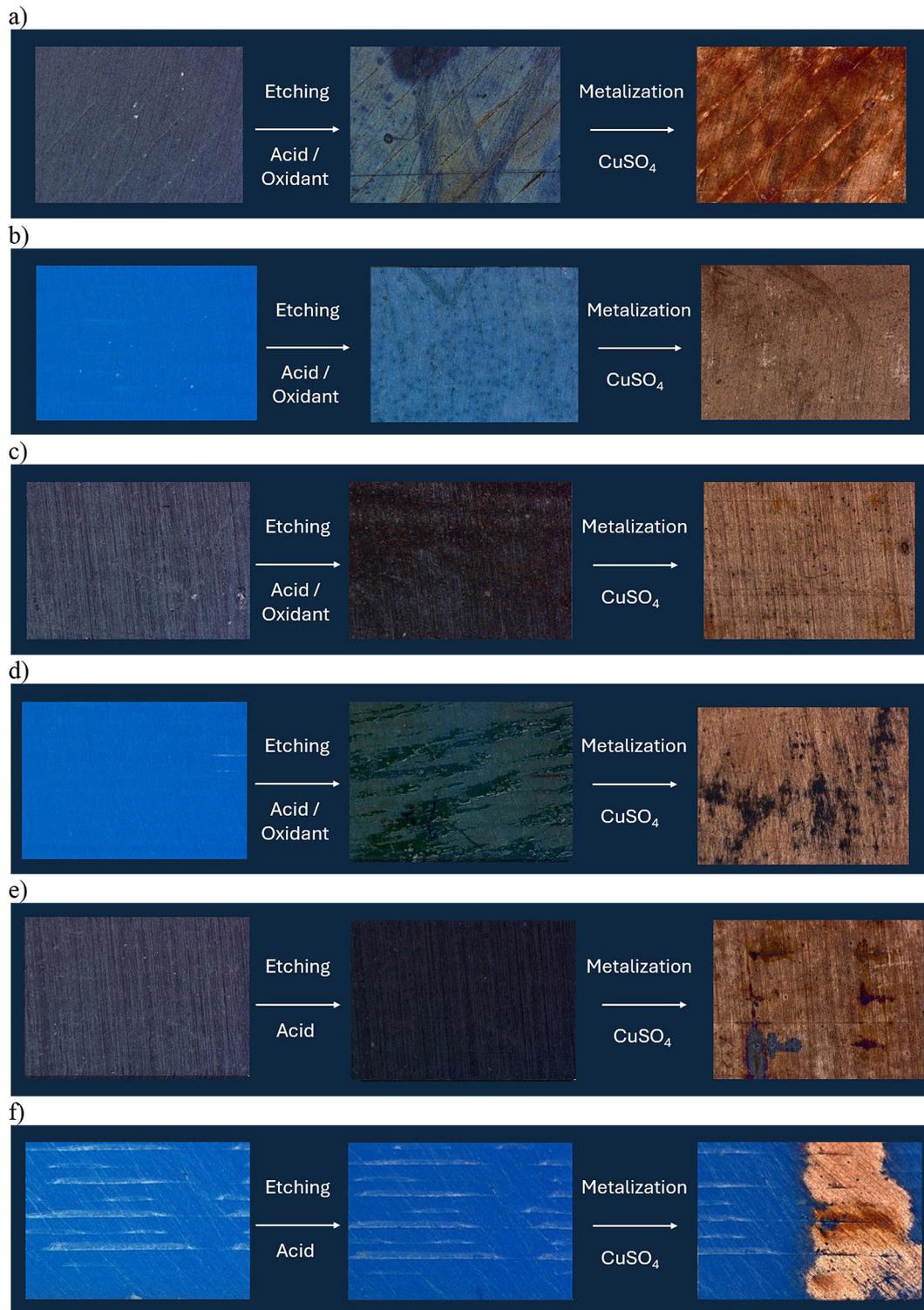
For the first four samples, where the metallic layer is almost wholly homogeneous, we can see a significant difference between the polymer surface layer before and after the etching process. The photos taken after the etching process show the micro pores produced by a chemical reaction of the polymer material and the acidified oxidizing solution. Sample 5 PLA



**Figure 5.** Samples after the metallization process, approximation 20x, samples: (a) 4PLA, (b) 4PLA Cu, (c) 5PLA, (d) 5PLA Cu, (e) 6PLA, (f) 6PLA Cu

**Table 1.** Arithmetic mean of roughness profile ordinates (Ra) at selected stages of metallization

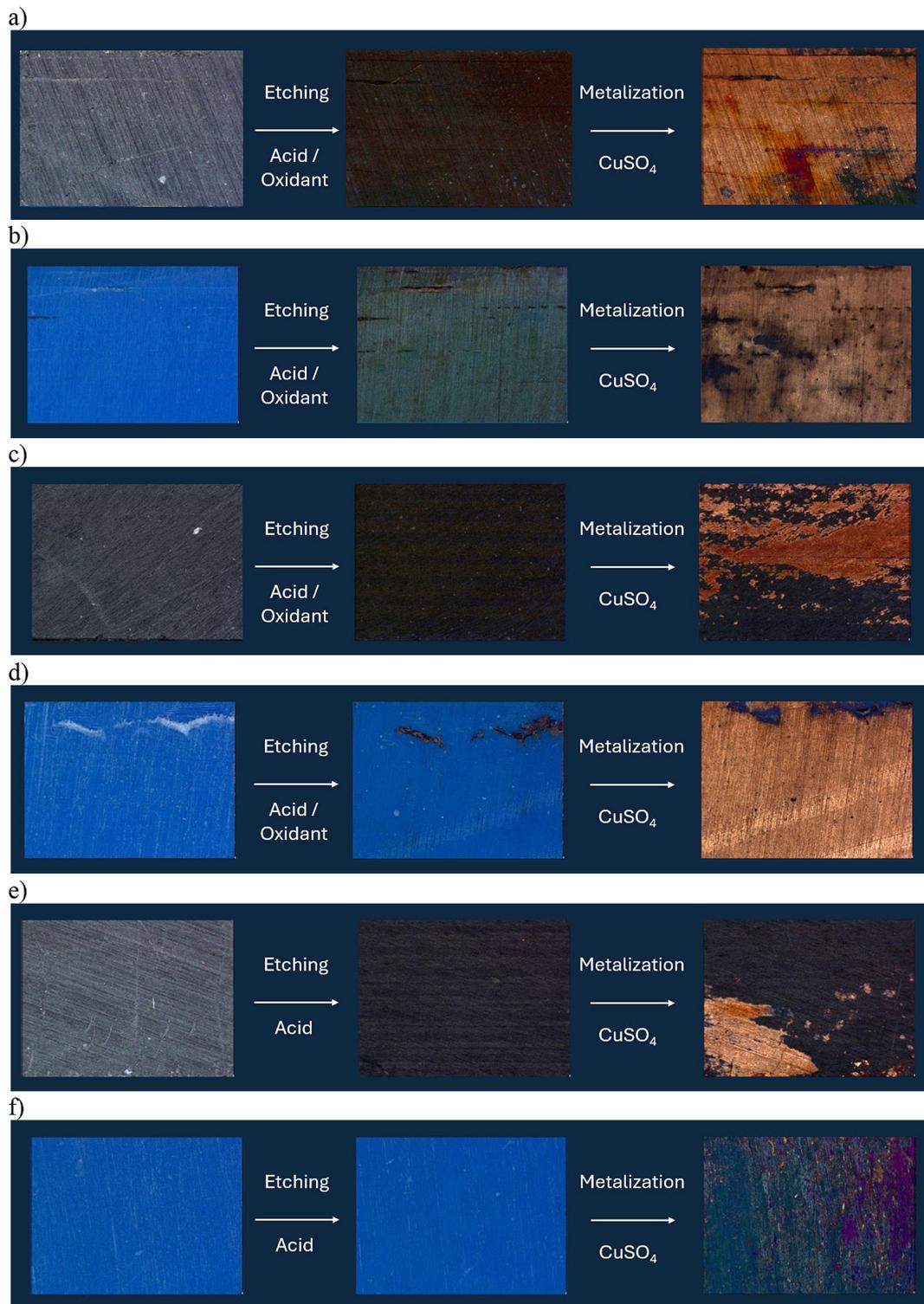
Samples	The arithmetic mean of the roughness profile ordinates (Ra) [µm]					
	Before etching		After etching		After metallization	
	Results	Standard deviation	Results	Standard deviation	Results	Standard deviation
1 PLA	0.64	0.0216	1.05	0.0205	0.29	0.0205
1 PLA Cu	0.58	0.0374	1.12	0.0249	0.75	0.0183
2 PLA	0.60	0.0271	0.95	0.0362	0.65	0.0125
2 PLA Cu	0.31	0.0267	0.72	0.0521	0.29	0.0170
3 PLA	0.63	0.0298	0.70	0.0333	0.69	0.0189
3 PLA Cu	0.46	0.0437	0.50	0.0221	0.46	0.0283
4 PLA	0.62	0.0221	0.70	0.0189	0.40	0.0211
4 PLA Cu	0.60	0.0226	0.83	0.0170	0.69	0.0183
5 PLA	0.52	0.0279	0.93	0.0216	0.88	0.0240
5 PLA Cu	0.36	0.0340	0.57	0.0156	0.52	0.0226
6 PLA	0.56	0.0229	0.94	0.0194	0.88	0.0221
6 PLA Cu	0.60	0.0260	0.75	0.0133	0.91	0.0245



**Figure 6.** Photos selected stages of metallization, 180x zoom.: a) 1PLA, b) 1PLA Cu, c) 2PLA, d) 2PLA Cu, e) 3PLA, f) 3PLA Cu

Cu show a surface tilt deformation of about 320 micrometers, which can be observed in the 3D visualization of the top layer (in Figure 8d) due to the polymer deformation caused by the excessive power of the etching bath resulting from the presence of sodium hydroxide and potassium permanganate. More

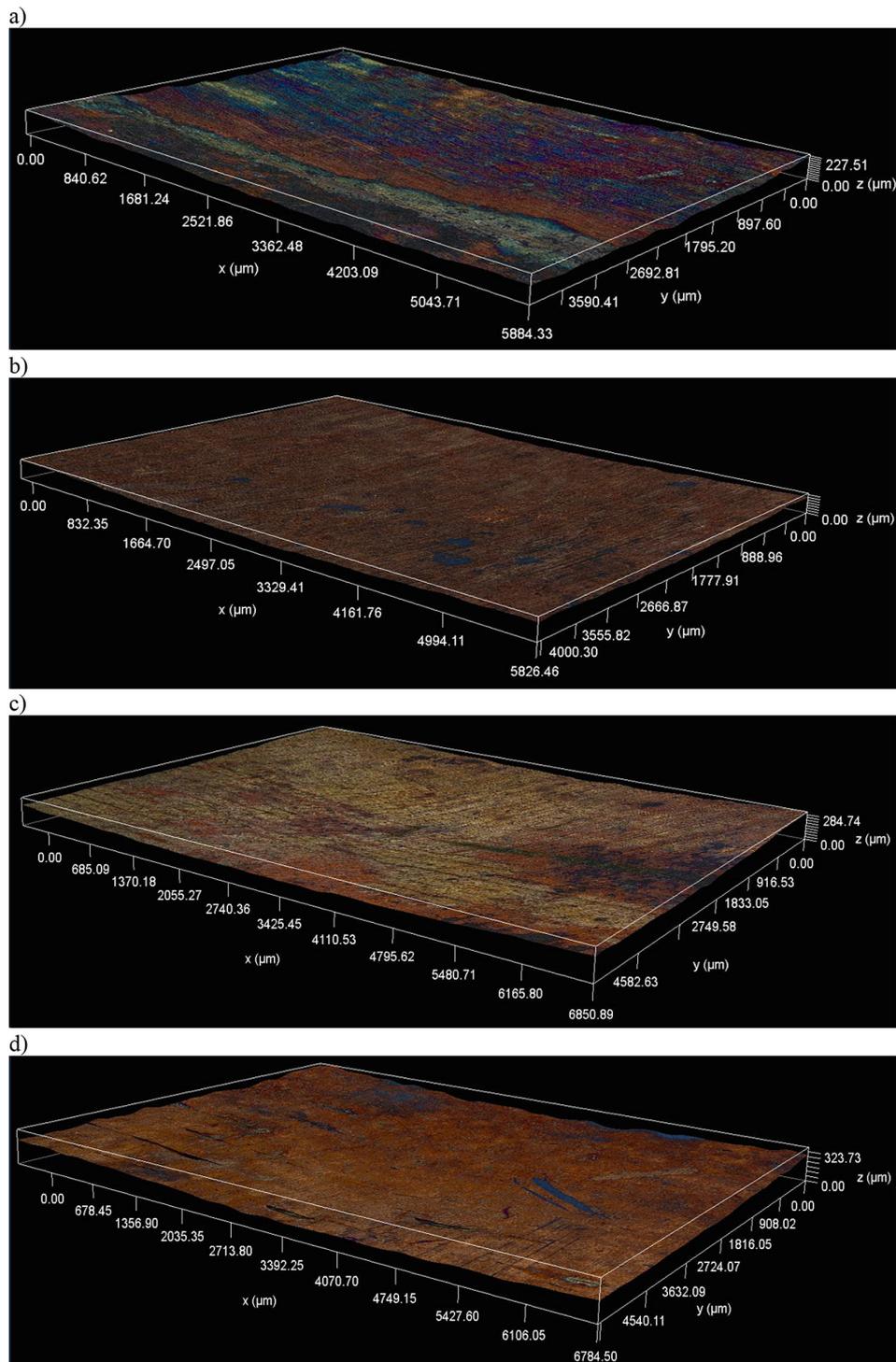
considerable differentiation of the surface layer in the form of large cavities does not improve the adhesive properties of the metallic coating. In areas of differentiation of the surface layer (occurrence of pores with a size of 40  $\mu\text{m}$ ), there is a lack of a copper coating. The photos of the samples etched



**Figure 7.** Photos of samples at selected stages of metallization, 180x zoom. Samples: a) 4PLA, b) 4PLA Cu, c) 5PLA, d) 5PLA Cu, e) 6PLA, f) 6PLA Cu

in solution 5 show a clear correlation between the pore size in the polymer surface layer and the final metallic coating. For areas with pores and surface irregularities exceeding approx. 40  $\mu\text{m}$ , the final copper coating is not of satisfactory quality. On the other hand, the resulting metallic surface is of better

quality in areas where the pores are smaller than 20  $\mu\text{m}$ . Photos from the surface layer analysis after the activation and metallization process can be found in Figures 6 and 7. Our 3D imaging of the metallic layer samples on a polymer substrate has unveiled a significant finding. The sample surface, along with

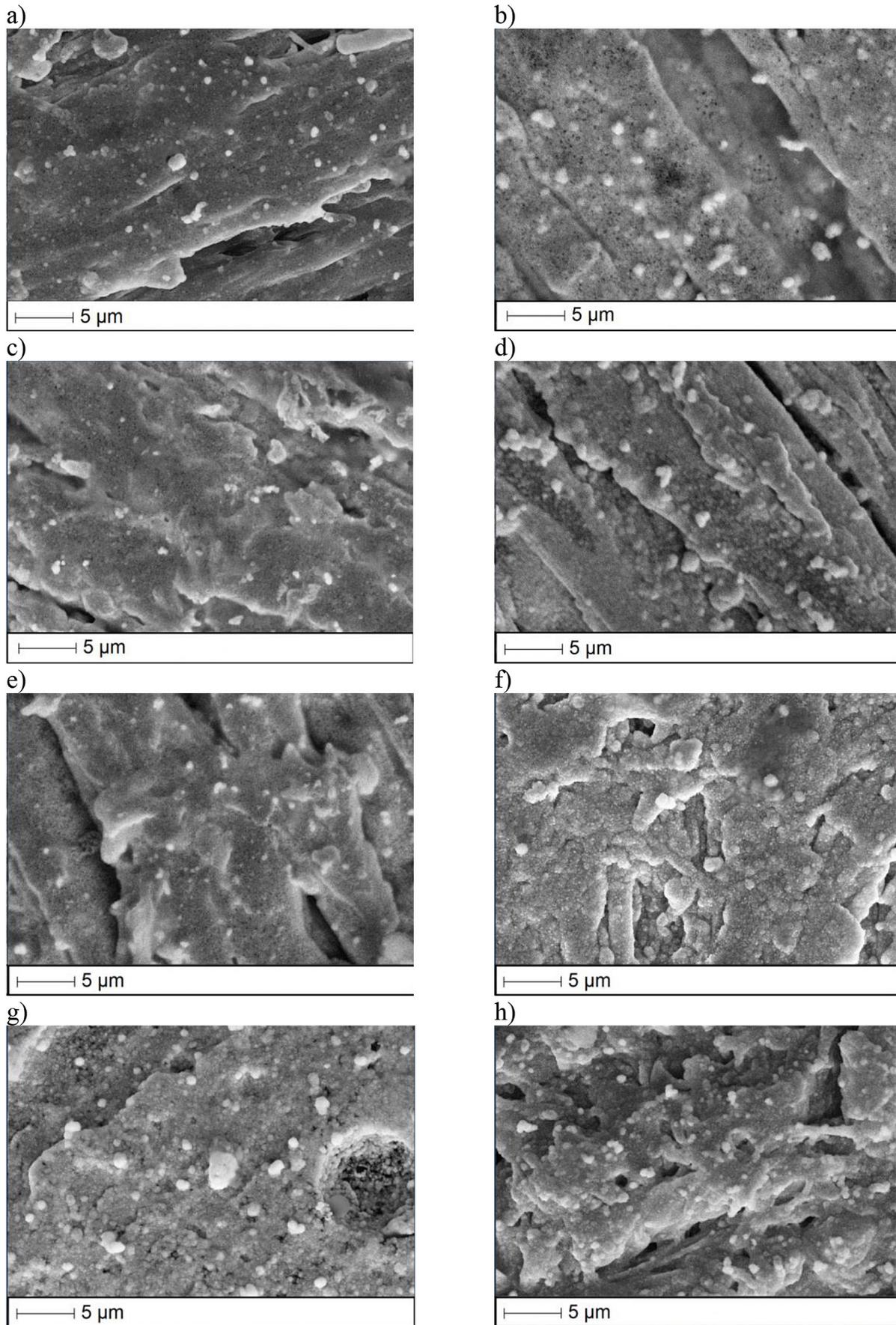


**Figure 8.** 3D surface mapping made with a Leica microscope, samples: a) 1PLA, b) 1PLA Cu, c) 3PLA, d) 5PLA Cu

the copper coating, exhibits height variations ranging from 180  $\mu\text{m}$  to 324  $\mu\text{m}$ . This substantial difference in height variations could be attributed to the deformation of the polymer material, a result of its interaction with acid and base solutions during the metalization of the top layer. This finding underscores the crucial role of the polymer substrate in the overall

structure and performance of the metallic layer samples. The 3D imaging can be found in Figure 8.

Upon meticulous analysis of the SEM images, we can confidently conclude that the copper deposited on each sample is in the form of globules, ranging in size from 0.1  $\mu\text{m}$  to 3  $\mu\text{m}$ . The size of the copper was measured based on SEM (Scanning



**Figure 9.** SEM view of the surface, approximation of 10,000, samples: (a) 1PLA, (b) 1PLA Cu, (c) 2PLA, (d) 2PLA Cu, (e) 3PLA, (f) 5PLA, (g) 5PLA Cu, (h) 6PLA

**Table 2.** Percentage changes in roughness between individual stages of metallization

Samples	Percentage change in roughness after etching [%]	Percentage change in roughness after the metallization step [%]
1 PLA	0.64	1.05
1 PLA Cu	39.05	72.38
2 PLA	48.21	33.04
2 PLA Cu	36.84	31.58
3 PLA	56.94	59.72
3 PLA Cu	10.00	1.43
4 PLA	8.00	8.00
4 PLA Cu	11.43	42.86
5 PLA	27.71	16.87
5 PLA Cu	44.09	5.38
6 PLA	36.84	8.77
6 PLA Cu	40.43	6.38
	20.00	21.33

Electron Microscopy) images. Six measurements were performed on each sample, which allows for obtaining representative data regarding the size of the copper globules. All measurements were conducted within the same surface area range, ensuring the consistency of the results.

The type of etching bath did not affect the size of the copper globules, suggesting that the etching process did not influence the morphology of the deposited copper. This may indicate that the copper deposition conditions were stable and repeatable across different samples. The surface structure of each layer is characterized by numerous surface defects on a microscopic scale, with pores on the surface of copper layers measuring between 0.5  $\mu\text{m}$  and 10  $\mu\text{m}$ . Microscale defects do not affect the final use of the functional element. However, it's important to note that despite these surface defects, the selected macroscopic layers are of excellent quality, providing comprehensive coverage of the entire research surface. This assurance is backed by the SEM microscope photos shown in Figure 9. Moving on to the analysis of the arithmetic mean of the roughness profile ordinates (Ra), it should be noted that after the etching process, the Ra parameter value increased for each tested sample. Another important aspect is the decrease in the Ra parameter value for almost all tested samples (except for the 6 PLA Cu sample) after the metallization process.

After the etching stage, the highest roughness parameter values were obtained for the surfaces of samples 1 PLA, 1 PLA Cu, and 2 PLA, while

the lowest values were shown for samples 3 PLA Cu, 3 PLA, and 5 PLA Cu. However, to determine the effectiveness of the etching step, attention should be paid to the percentage change in the roughness parameter between the pre-etch and post-etch stages of the surface layer. The most considerable percentage change of the roughness parameter (Ra) after the etching step occurred for samples 1 PLA Cu and 2 PLA Cu, while the minor change of this parameter after this stage was observed for samples 3 PLA and 3 PLA Cu.

After metallization, most of the tested samples obtained the Ra parameter lower than the value of 0.8  $\mu\text{m}$ , which means that they meet the acceptance criterion for working surfaces. Furthermore, the measurements indicate that samples 1 PLA, 2 PLA Cu, and 4 PLA exhibit a parameter that is at or below the threshold of 0.4  $\mu\text{m}$ . This finding confirms the exceptional smoothness characterizing the surfaces of these specimens. In addition, the most significant reduction in Ra parameter value after the metallization stage was noted for samples 1 PLA and 2 PLA Cu, while the most minor reduction occurred for samples 3 PLA, 5 PLA, and 3 PLA Cu. Results of roughness tests are reproducible: the lowest standard deviation was 0.0125 and the largest was 0.0521.

## CONCLUSIONS

Based on the research on the metallization of polymer materials, conclusions were drawn about the etching baths used in the research, the type

of polymer material, the structure of the polymer surface layer, and the mechanisms and reactions taking place during the metallization process. Samples etched in solutions No. 1 and No. 2 containing sulfuric acid ( $H_2SO_4$ ) and potassium permanganate ( $KMnO_4$ ) are characterized by the best visual quality of copper coatings. In contrast, samples etched in solution No. 3 containing only sulfuric acid have the lowest quality coating. This is due to the oxidizing properties of potassium permanganate, which cause the polymeric material to digest faster. Small pores and caverns (less than  $20\ \mu m$ ) facilitate the adhesion of palladium particles, which creates active areas that increase the adhesion of the metallic coating. It is related to the mechanism of autocatalytic metallization, in which copper ions react with metallic palladium deposited on the polymer surface layer. Larger pores and surface irregularities larger than  $40\ \mu m$  negatively affect the adhesion of the metallic layer of the polymeric material. This is due to the breaking of the continuity of the polymer coating and the inability to fill the cavities with a thin metal coating. Copper particles contained in polylactide do not affect the metallization process of polymeric materials. The volume of copper particles in the polymer is 1%, which is too small for the copper particles to influence the polymer surface layer. The metallic coating on the samples etched in solutions no. 5 and no. 6 is blue violet in colour. This colour is the result of the reaction of copper ions with sodium hydroxide, which was deposited in the pores of the polymeric material. As a result of this reaction, copper hydroxide is formed with a bluish-purple colour.

Increasing the Ra parameter for sample 6 PLA Cu results from the deposition of an uneven layer of copper structures on the top layer of the polymer. The copper structures deposited unevenly as the sodium hydroxide solution etched small caverns at random locations on the surface during the etching step. During the activation process, active sites were created in these caverns, which caused the accumulation of copper structures on the sample's surface. The final values of the roughness parameter of each test sample are within the lowest tolerance limit for class Sc3 according to ISO 219020-3: 2021. This makes it possible to classify metallized polymer materials in the third roughness class according to the current standards.

The developed conclusions will help to continue research on the production of a composite polymer material containing metal

coatings. The autocatalytic metallization process enables the production of copper coatings on the surface of a polymeric material produced with additive technology. An essential element in the process is using an appropriate bath to etch the polymer material. The suitable solution ensures the formation of a sufficiently large number of cavities and pores that will allow the formation of a sufficiently sizeable active area surface by the adhesion of metal palladium on the polymer surface layer. Active areas will enable an even metallic coating deposition in the last metallization stage. As a PLA etching solution, an aqueous sulfuric acid (VI) with potassium permanganate should be used [25]. Dr Moraczewski from the Kazimierz Wielki University in Bydgoszcz used chromium (VI) oxide as one of the components of the etching solutions in his fundamental research on the metallization process [20]. In addition, the potassium salt of permanganic acid is used as a therapeutic agent that disinfects and soothes skin diseases. Further research on the electroless metallization process will be aimed at pro-ecological activities, removing substrates that are harmful to the environment from the process. The formaldehyde used as the reducing agent will be replaced with sodium hypophosphite, and tin compounds will be removed from the sensitization stage of the polymeric material. Next, the team will focus on optimizing the metallization conditions to obtain coatings of satisfactory quality, adhesion, and durability.

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