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SURFACE ANALYSIS OF ABS 3D PRINTS SUBJECTED TO COPPER PLATING

3D printing in FDM (Fused Deposition Modelling) technology is commonly used, mainly in the preparation of prototypes, but also for the production of ready-made elements. Objects printed using the FDM method have characteristic, adverse surface features related to the limitations of this technology. That is why surface treatment of 3D prints becomes crucial. One of the method is metal plating of elements. The most frequently used material in FDM technology is PLA (polylactic acid) and ABS (acrylonitrile butadiene styrene). Study of surface parameters determination for ABS prints after galvanic copper plating is presented in this paper. For this purpose, samples printed with ABS were smoothed in acetone vapour. Most favorable parameters of the surface were obtained for samples that had contact with acetone vapour for 60 minutes. Ultimately, surface analysis of samples after graphite coating and subjected to copper plating was performed. It was found that surface parameters are close to results obtained with traditional methods of metal processing.

Keywords: FDM, ABS smoothing, cooper plating, surface analysis

1. Introduction

3D printing technology, which is about creation of physical objects based on digital models is no longer considered as curiosity. Despite of the fact that three-dimensional printing started only in 1984, thanks to computer technology development, it has arrived under the roof of common users. 3D printing is considered as additive method, that means that in this technology an object is created by deposition of material layers [1-3]. At first, 3D printing was used as one of rapid prototyping method. Currently it is used also for ready objects. Many 3D printing technologies are used. The most popular are: SLS (Selective Laser Sintering), in which layers of powder material are melted with laser, DMLS (Direct Metal Laser Sintering), that extends previous method with metal powders, MJP (Multi Jet Printing), which is about UV hardening of photopolymer layers or CJP (Color Jet Printing), here ink-colored anhydrite powder is consolidated using proper adhesive [1,2].

All of the above methods, despite of good results, require expensive devices and materials. Therefore, the most commonly used method nowadays is FDM technology (Fused Deposition Modelling). This technology relies on depositing layer of thermoplastic material through special system consisting of extruder, that supplies material and a heated head in which plasticization takes place [1-3]. Big advantage of FDM technology is wide spectrum of materials used for prints, very often of diverse properties. From flexible materials up to wood imitations. Undoubtedly, for common usage, the most popular polymers in FDM print are PLA (polylactic acid) and ABS (acrylonitrile butadiene styrene). From practical point of view, thermal requirements during printing and surface treatment of printed material differentiate those materials. In case of PLA, surface treatment is only grinding. On contrary, ABS allows for surface smoothing by using acetone. It allows for minimizing problem of surface roughness deriving from FDM technology. On top of that, ABS is one of few plastic, which can be coated with metal layers during galvanic treatment [4-6].

The metal plating of 3D prints, as one of surface treatment methods is the subject of this paper. From the moment when plastic became a part of everyday life, attempts were made to plate it with metal coating. It started with decorative purposes, afterwards also for specific technical applications [7,8]. The biggest advantage of metal plated products from plastic is reduction of labour consumption in relation to materials produced entirely from metal. The key is proper technology of injection mould. Additionally metal plated materials are lighter (1.04-1.07 g/cm^3 in case of ABS), and also have corrosion resistance. Needless to say, there is also big saving on non-ferrous metals during decorative products manufacturing. Amongst industrial methods of plastics metal plating one can find: chemical application of metals, galvanic application of metals, metal plating spraying, vacuum evaporation technique or cathode sputtering [9].

The main purpose of this paper is to describe metal plating conditions for galvanic method of ABS prints obtained with FDM

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technology as well as surface analysis. Opposite to object that were manufactured by injection, elements printed from ABS do not meet strict requirements needed for metal plating. Industrial course of galvanizing metal plating on ABS is complex (Fig. 1). It requires a number of steps involving various chemical reagents and is available only for large industrial plants [8-10]. In this paper, simplified galvanizing process is presented, that can be used by any amateur of 3D printing. It bases on smoothing of printed surface, plating it with conducting material and copper plating in electrolytic tank (Fig. 2). Similar to traditional galvanizing metal plating technologies of plastics, copper plating is primary operation before coating with other metals [8,10]. Therefore, quality of surface plated with copper can be considered as key parameter before further plating.

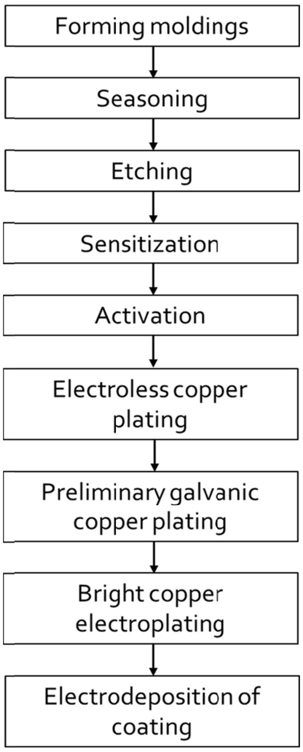

Fig. 1. Diagram of industrial galvanic process of metal plating on ABS polymer

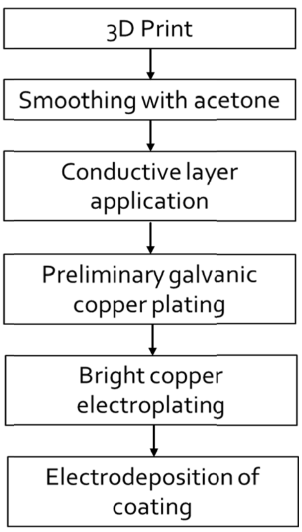

Fig. 2. Diagram of simplified galvanic process of metal plating of 3D prints from ABS polymer

2. Experiment

In this section, detailed description of preparation process of samples for plating is presented. For this experiment were prepared samples of rectangular shape with eyelet attached, that was aimed to use as plating rack for another tests (Fig. 3). Samples were designed in CAD program and were printed using FDM technology from ABS material. Prints were prepared in 3D printer Up mini 2 from Tiertime company. Standard printing parameters were applied i.e. head temperature of 270°C, layer thickness 0.2 mm and model filling of 20%.

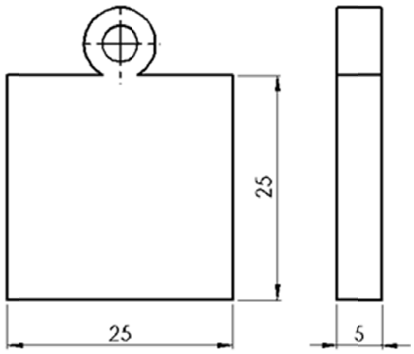

Fig. 3. Dimensions of studied samples

At first an attempt was made to smooth surface of printed samples, this was related to the fact that for chosen thickness of the layer, surface roughness occurred. Therefore it was agreed to dissolve ABS prints in acetone, that is commonly used method by amateurs. Four randomly selected samples were placed in glass vessel for 30, 60, 90 and 120 minutes. They were hanged next to the container filled with acetone. Due to the weight of acetone vapour and intensity of evaporation process, cooling fan was placed inside of the vessel. It was aimed to evenly distribute acetone vapour in order to enable contact with the sample surface. Table 1 presents the change of sample external dimensions resulting from reaction of ABS with acetone vapour. Measurement was performed using slide caliper of reading accuracy 0.01 mm. In Fig. 4 the view of sample edges after smoothing is presented. Side length of white squares presented in the picture was 1 mm. It is clearly visible that on sample subjected to smoothing with acetone vapour for 60 minutes, layers derived from 3D printing were no longer visible. Longer time of smoothing resulted with more intense sheen of the sample surface.

Next stage of the experiment was surface analysis of samples subjected to smoothing. Surface parameters determination was performed on optical profilometer FRT MicroProf with aberration head CWL. 3D picture of sample surface of dimensions: 7 by 7 mm (Fig. 5) were taken. Subsequently, for selected intersection, roughness profile and waviness (using Gauss filter

TABLE 1

Change of external dimensions of ABS samples subjected to smoothing in acetone vapour

Sample no.	Dimensions before smoothing, mm			Smoothing time, min	Dimensions after smoothing, mm			Percentage difference before and after smoothing, %		
	Length	Width	Depth		Length	Width	Depth	Length	Width	Depth
1	25.08	24.95	5.00	**30**	24.96	24.96	5.02	–0.48	0.04	0.40
2	25.00	24.9	5.05	**60**	25.06	25.01	5.04	0.24	0.44	–0.20
3	25.11	25.06	5.04	**90**	25.27	25.23	5.22	0.64	0.68	3.57
4	25.15	25.01	5.00	**120**	25.38	25.32	5.41	0.91	1.24	8.20

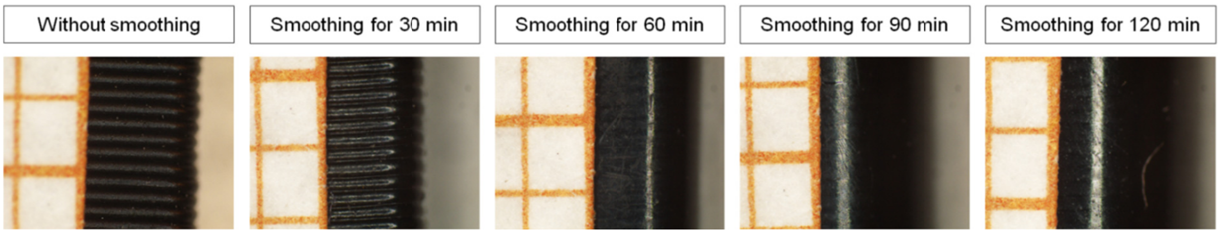

Fig. 4. Microscopic pictures of sample edges subjected to smoothing in acetone vapour

0.8 mm) was determined (Fig. 6). Table 2 presents uppermost parameters of sample surface. Surface analysis confirmed results of macroscopic observations. In sample subjected to smoothing in acetone vapour for 60 minutes, characteristic layers vanished for models printed in FDM technology. Smoothing for 90 minutes resulted with further decrease of parameters Ra and Rz, however Sa parameter doubled (parameters are explained in Table 2). Smoothing for 120 minutes caused an increase of all parameters of the surface. Distinct increase of waviness results in this case from applied printing parameters. Long contact with acetone caused substantial dissolving of sample surface and as a result weakening of its structure. This is indicated by change of outer dimensions, where sample after smoothing for 120 minutes increased its thickness by 8.2% (Table 1). Comparing outer geometry and surface of samples subjected to smoothing in acetone vapour it can be stated that most convenient smoothing time is 60 minutes. It allows for obtaining most favorable parameters of surface with keeping the same dimensions and structure of the sample.

In traditional process of metal plating of ABS with copper, a wide range of steps aimed at surface development of material and giving electrolytic conductance is performed. Surface development allows for mechanical adhesion of metal plate on the material. It is done through etching with strong oxidizing agent of free polybutadiene, which is a component of copolymer ABS. Apart from oxidizing agents in dips there are also used other components such as wetting agents and moderators. After etching, samples are submersed in reduction bath and next in sensitizing bath. Finally sample is placed in activating bath for deposition on the surface small quantities of noble metals in order to initiate of electroless metal deposition to form continuous layer. In this way plastic material is given electrical conductivity. Next step is metal plating. Initially in less concentrated electrolyte, next up to desired thickness in more concentrated electrolyte [8,10].

Complexity of industrial metal plating of ABS is not profitable for amateur 3D printing. Short series and single 3D prints are most common among that. Therefore, in this study it was decided to enable electrical conductivity on sample surface of ABS through mechanical application of conducting film. For this purpose, surface of the sample was covered with few commonly available powder materials. Those were high-purity (99.0-99.9%) metal powders with dendritic shape particles of diameter smaller than 0.5 mm: Cu, Mg, Al, Fe and graphite. Powders were mixed with acetone and applied with small brush until whole sample surface was covered. Acetone was expected to cause powders to stick to the ABS surface. Two variants of samples were prepared. First were samples without smoothing of the surface, second samples were smoothed with acetone vapour for 60 minutes.

TABLE 2

Surface parameters of samples subjected to smoothing in acetone vapour

Surface parameter	Smoothing time, min				
	0	**30**	**60**	**90**	**120**
Roughness parameter (ISO 4287)					
Ra (average roughness)	556 μm	173 μm	0.638 μm	0.538μm	0.660 μm
Rz (average maximum height of the profile)	1640 μm	1080 μm	4.15 μm	3.29 μm	4.37 μm
Areal roughness (ISO 25178)					
Sa (arithmetical mean height of the surface)	607 μm	214 μm	5.57 μm	12.6 μm	22.5 μm
Sp (maximum height of peaks)	778 μm	347 μm	18.2 μm	24.9 μm	54.7 μm

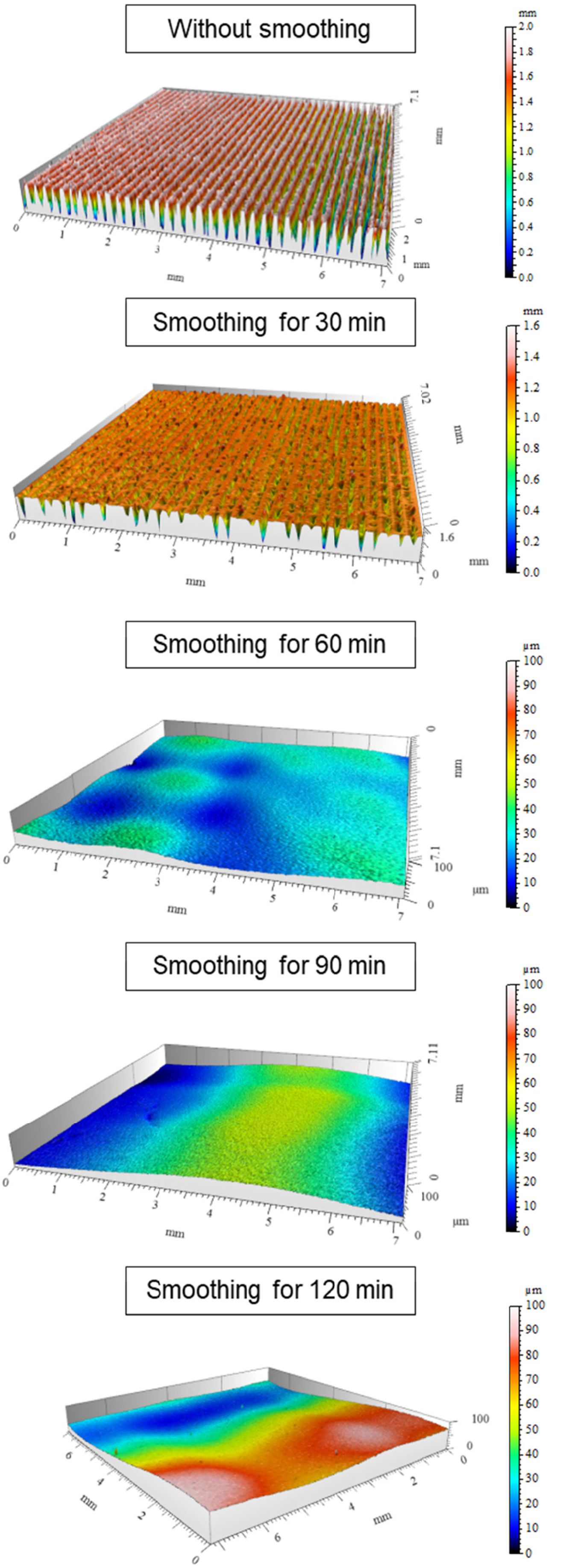

Fig. 5. 3D picture of surface sample subjected to smoothing in acetone vapour. Area: 7×7 mm

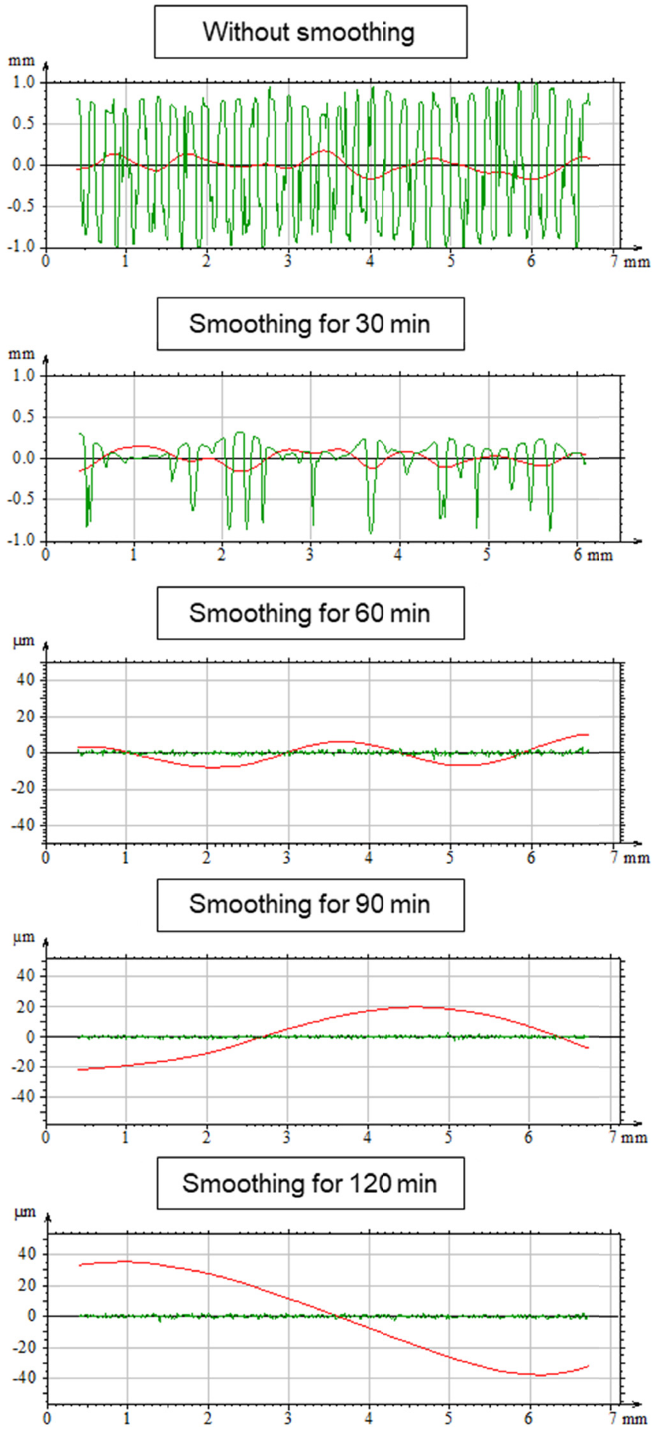

Fig. 6. Roughness profile (green curve) and waviness profile (red curve) of selected intersection of samples subjected to smoothing in acetone vapour

Subsequently electrical resistance of sample surface was measured using standard electric meter Metex 3800 and Wheatstone MW-4 bridge. Results are presented in Table 3.

In case of layer prepared from metal powders, lowest value of electrical resistance was shown by Fe. For the other powders, resistance was either out of the measuring range for electric meter or close to value of 1 MΩ for Wheatstone MW-4 bridge. It could be a result of too high granularity of powders and its insufficient purity.

TABLE 3

Average electrical resistance of layer on sample's surface printed from ABS

Layer	Average value of electrical resistance, Ω	
	Metex 3800 meter	Wheatstone MW-4 bridge
Cu powder	∞	$\sim 1\cdot 10^6$
Cu powder (sample after smoothing for 60 min)	∞	$\sim 1\cdot 10^6$
Mg powder	∞	$\sim 1\cdot 10^6$
Mg powder (sample after smoothing for 60 min)	∞	$\sim 1\cdot 10^6$
Al powder	∞	$\sim 1\cdot 10^6$
Al powder (sample after smoothing for 60 min)	∞	$\sim 1\cdot 10^6$
Fe powder	2500 ± 200	1200 ± 60
Fe powder (sample after smoothing for 60 min)	1250 ± 80	900 ± 50
graphite	300 ± 40	260 ± 30
graphite (sample after smoothing for 60 min)	160 ± 20	120 ± 15

Significantly lower value of electrical resistance was indicated by graphite layer. During preparation, graphite was grinded in mortar into dust. Average value of electrical resistance was even five times lower comparing to commercially available graphite spray. Producers of conductive sprays based on graphite declare resistance of 1000 Ω. It is worth to mention that for both Fe and graphite, prior smoothing of samples enabled lowering of measured value of electrical resistance.

Based on presented results, for next stage of experiment, which was metal plating with copper, samples subjected to smoothing in acetone vapour for 60 minutes were selected and then covered with graphite. Those samples were hanged on copper wires in specially designed electrolytic tank, which scheme is presented in Fig. 7. Samples were cathode, copper plate (Cu 99.9%) were anodes. Surface ratio of immersed anodes to cathodes was 1:1. Current density was calculated, which for given geometry was 0.3 A/dm^2.

Copper plating was performed in two steps. Standard sulfate bath was used with composition stated below:

1. Electrolyte for initial copper plating: copper sulfate ($CuSO_4\cdot 5H_2O$) 150 g/l, sulfuric acid (VI) (H_2SO_4) 30 g/l, distilled water.
2. Electrolyte for copper plating for thickness: copper sulfate ($CuSO_4\cdot 5H_2O$) 220 g/l, sulfuric acid (VI) (H_2SO_4) 75 g/l, distilled water.

Both stages of copper plating lasted 4 hours. Every 30 minutes change of samples location, stirring and temperature measurement of electrolyte was done. Through all time of the experiment, temperature of electrolyte was close to room temperature, which is 19-22°C.

Due to the fact that during first experiments samples not always were covered with copper evenly, it was decided to thicken graphite plate in place of contact copper wire – sample. Additionally fastening was modified by sticking on to one of sample side copper plate and thorough covering it with graphite

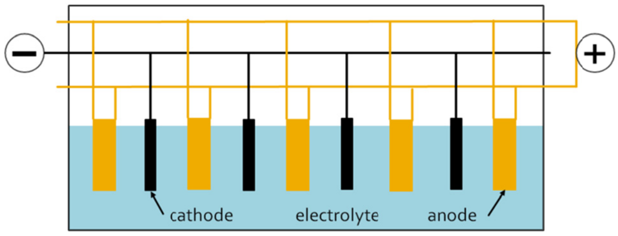

Fig. 7. Scheme of electrolytic tank for copper plating used in this work

(Fig. 8). It was designed to increase conductive surface having contact with the sample. Results of copper plating on both types of fixing with analysis of obtained surfaces are presented in next chapter.

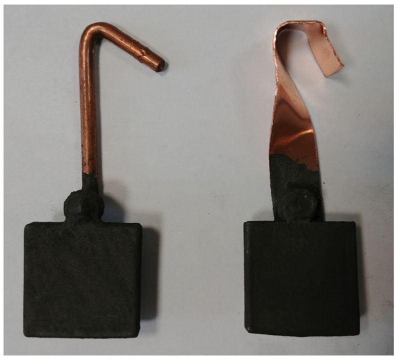

Fig. 8. Two methods of sample hanging

3. Results and discussion

As a result of two-step metal plating, obtained samples covered with copper layer (Fig. 9).

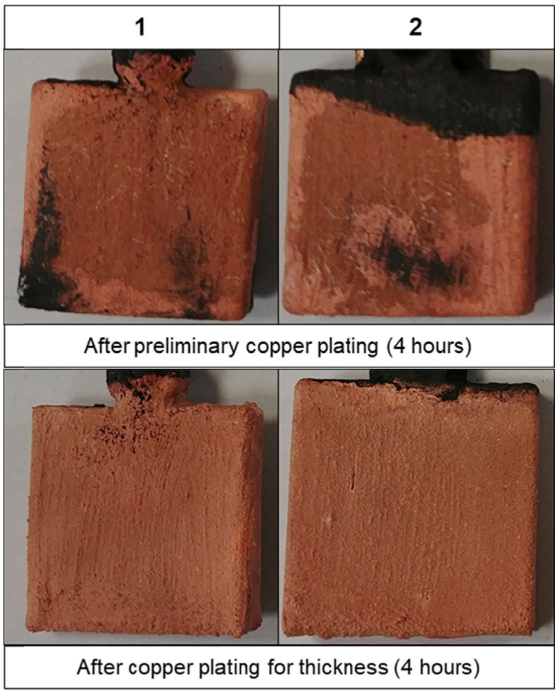

Fig. 9. View of samples after copper plating. 1. Sample hanged on copper wire. 2. Sample hanged on copper plate

Two samples were selected, that were weighted together with fastening before and after every stage of the process. Results are presented in Table 4. Incidentally it was also checked, how fastening of the sample influenced on layer application. For both cases, during preliminary copper plating for 4 hours, not all submersed in electrolyte surface was covered. It indicates, that time of preliminary metal plating should be elongated. Increase of current density resulted with accumulation of copper crystal on the cathode in shape of dendrites. Decision was made to continue the experiment by copper plating in more concentrated electrolyte. It was aimed to verify, if during copper plating for thickness copper will cover free surface from previous step. It was confirmed, which is visible in Fig. 9. Based on Table 4 it is also visible that copper plating for thickness enabled covering samples with copper of twice bigger mass than during preliminary copper plating for the same time. No distinct influence of the fastening of the sample in electrolyte tank was stated. The only difference was related to the fact that samples with plate, at the beginning of experiment were covering with copper faster and on a greater surface, so after 4 hours it looked similarly to samples hanged on copper wire.

TABLE 4

Mass change of samples with hanger during copper plating

Stage	Sample mass (mass gain), g	
	Hanged on copper wire	**Hanged on copper plate**
Before copper plating	8.12	7.16
After preliminary copper plating (4 hours)	8.31 (0.19)	7.41 (0.25)
After copper plating for thickness (4 hours)	8.85 (0.54)	7.82 (0.41)

Surface analysis of samples subjected to copper plating was performed once more using optical profilometer FRT MicroProf with aberration head CWL. Fig. 10 presents graphic results of surface analysis of samples of dimension 7×7 mm before copper plating. Fig. 11 presents results for samples subjected to two-stage copper plating. Comparison of the most important measured surface parameters is presented in Table 5.

Quality of samples covered with copper is undoubtedly higher than samples printed with ABS not subjected to smoothing. However, relative to samples smoothed for 60 minutes, surface parameters deteriorated by few classes. It was a result of presented in this paper approach to enable electrical conductivity of the sample's surface. Covering with grinded graphite mixed with acetone causes damages of previously smoothed surface. Next stages of copper plating resulted with increasing value of all surface parameters, that is in line with expectation and is an outcome of the process itself.

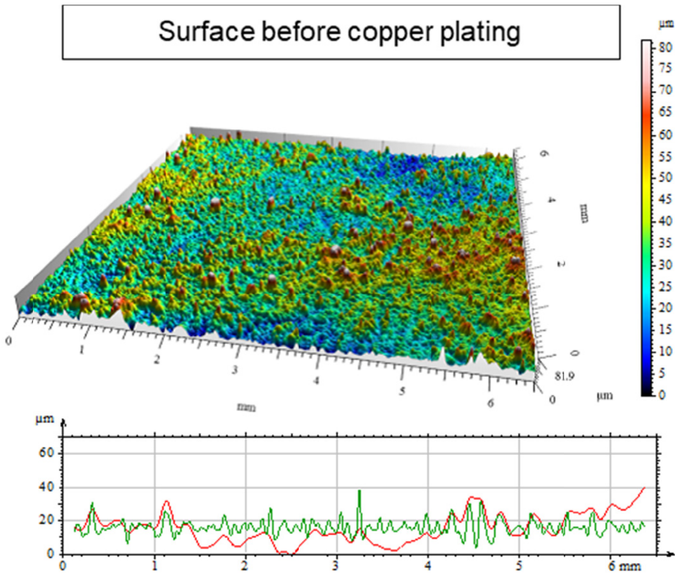

Fig. 10. 3D picture of surface sample before copper plating. Area: 7×7 mm. Roughness profile (green curve) and waviness profile (red curve) of selected intersection

The method of copper plating of 3D prints from ABS presented in this paper can be an alternative for industrial processes as well as it can be used also by amateurs of 3D printing. The surface analysis of samples subjected to copper plating indicated that surface parameters are close to the ones obtained with traditional methods of metal processing such as casting, rolling, milling or turning. Ways to minimize surface roughness can be in this case finding alternative for conductive layer in form of graphite or usage of electro-polishing [11]. Copper plating of prints from ABS can be used also for decorative purposes, specifically for patination. On top of that, those copper layers present good solidity, so average electrical resistance measured on its surface with standard electric meter was approx. 1 Ω. This enables application of metal plated 3D prints from ABS also in electronics.

TABLE 5

Surface parameters of samples subjected to cooper plating

Surface parameter	Hanged on copper wire			Hanged on copper plate	
	Copper plating				
Roughness parameter (ISO 4287)	No	Preliminary	For thickness	Preliminary	For thickness
Ra (average roughness)	5.04 μm	4.87 μm	5.78 μm	6.08 μm	8.88 μm
Rz (average maximum height of the profile)	29.5 μm	21.0 μm	24.9 μm	26.8 μm	36.9 μm
Areal roughness (ISO 25178)					
Sa (arithmetical mean height of the surface)	8.8 μm	21.5 μm	16.7 μm	15.3 μm	20.4 μm
Sp (maximum height of peaks)	49.8 μm	99.8 μm	102.0 μm	85.0 μm	120.0 μm

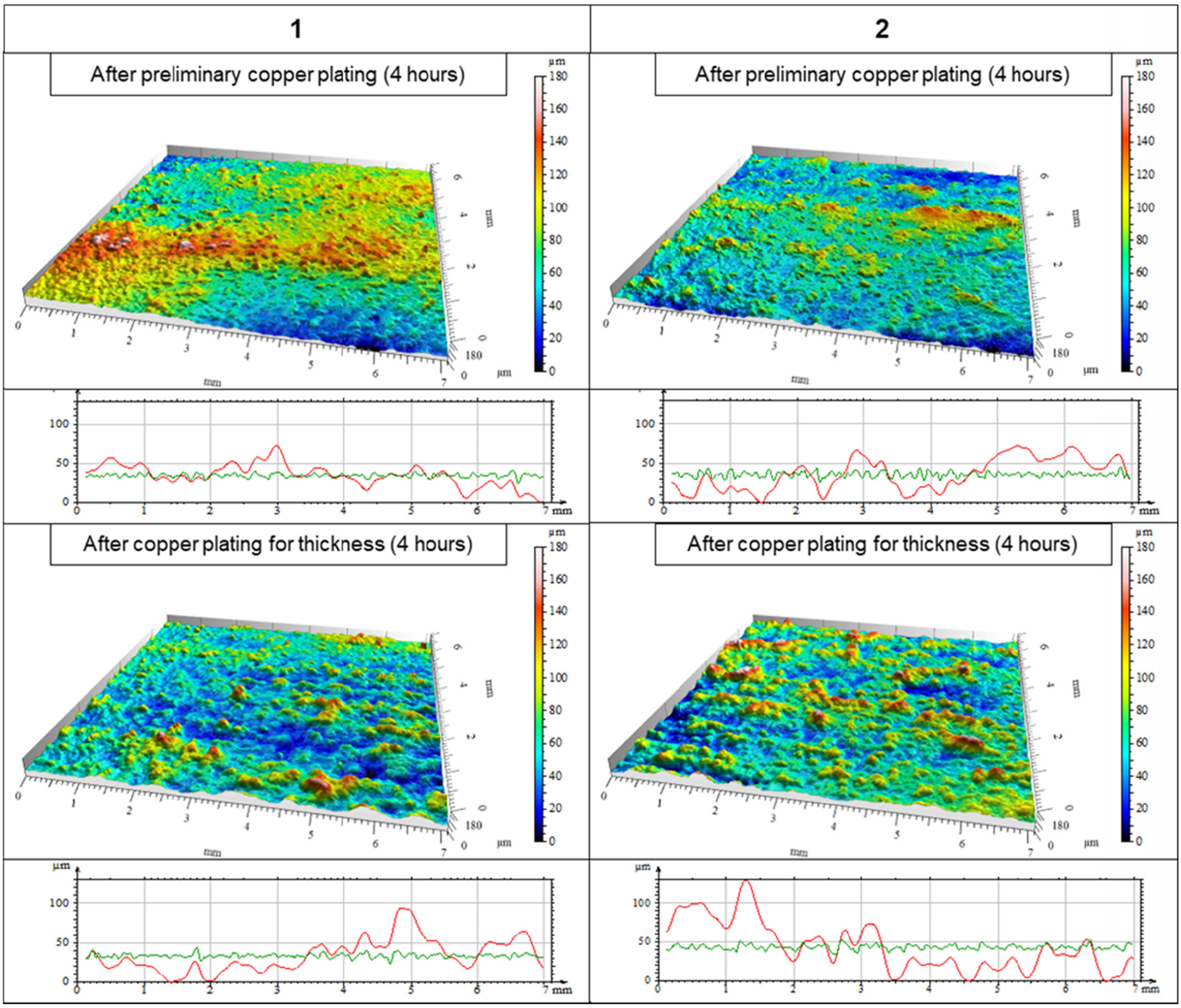

Fig. 11. 3D picture of surface sample subjected to copper plating. Area: 7×7 mm. Roughness profile (green curve) and waviness profile (red curve) of selected intersection. 1. Sample hanged on copper wire. 2. Sample hanged on copper plate

4. Conclusions

1. 3D prints from ABS in FDM technology can be subjected to smoothing in acetone vapour. In this paper surface of samples after 30, 60, 90 and 120 minutes of smoothing was examined. Most favorable parameters of the surface were obtained for samples that had contact with acetone vapour for 60 minutes.
2. By applying of grinded graphite mixed with acetone on the ABS samples surface, conductive layer can be obtained. Prior smoothening of the sample additionally decreases electrical resistance of the layer.
3. Copper plating of ABS prints requires application of specific parameters. Low concentration electrolyte will elongate plating time and too big current density will result with dendrites creation. On top, fastening of the sample must ensure electrical conductivity in place of contact of fastening and sample.
4. Surface parameters for 3D prints from ABS subjected to copper plating are close to results obtained with traditional methods of metal processing.
5. Simplified process of copper plating of 3D prints from ABS described in this paper is an alternative for complicated industrial processes, especially for decorative purposes. Covering with copper layer allows for further metal plating attempts or, with proper thickness of the layer, also electropolishing.

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