Electroless Plating of PLA and PETG for 3D printed Flexible Substrates

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Introduction

Since its introduction in the early 1980s [1], 3D printing has acquired a great relevance for research and industry. In the beginning this technique found application in rapid prototyping and custom made machine parts [2]. In the last few years however a new revolution began, as home 3D printers can nowadays be easily acquired on the market. This fact is starting to change the common concept of mass production, since 3D printing has the potential to start a new form of handicraft: the customer can obtain the tridimensional model of the desired object and subsequently print it. The production of some goods can thus move from factories to homes, with potential advantages [3].

Many 3D printing techniques exist, like stereolitography (SLA) [4], selective laser sintering (SLS) [5] or fused deposition modelling (FDM) [6]. Only the latter is however finding the cited commercial success due to the low cost of the materials and the ease of operation. Objects that are complicate or even impossible to manufacture with conventional techniques can be produced in reduced time ranges with this technique. It is on the other hand expensive to manufacture metallic objects. Some 3D printing techniques are suitable for direct metal processing, like SLS [5], while for all the methods is always possible to print the objects and subsequently cast them in a foundry. These two ways are however difficult to apply if the goal is to keep the process inexpensive and homemade.

Another possibility to achieve a metal finishing for 3D printed object is to metallize only the surface of the polymer used in the process. This makes possible to achieve the desired properties of the metals without performing a real bulk metal 3D printing [7]. To perform the metallization processes like PVD can always be applied, but metallization based on wet chemistry is generally preferred for the low cost. Among the polymers used in FDM (PET, ABS, PLA, PETG, PE, …), some can be easily metallized using electroless plating, a method able to give uniform and thick layers of many metals [8]. It is however important to notice that the polymers that are easy to electroless metallize are also difficult to 3D print with good results. These include PET [9] and ABS [10], while the possible metals for the coatings include Cu, NiP and others [11]. PLA and PETG are on the contrary easy to print due to the high dimensional stability of the polymer during solidification.

The main aim of the present work is thus to provide a method to electroless metallize 3D printed PLA and PETG. The optimized method is described and the influence of some parameters on the final quality of the metallic layer is discussed. Adherent and uniform layers of Cu and low phosphorus NiP are obtained and subsequent electrodeposition of other metals is investigated. The electroless coatings or the multilayers obtained can be used for esthetic or functional applications.

Experimental Methods

The samples used for the fundamental characterization of the process were printed using TreeD Filaments PLA wire and Colorfabb PETG wire by mean of a Delta 2040 FDM 3D printer by Wasp. The samples measure 1 cm for 1 cm and were characterized by an outer structural part extending for 2 mm from the border. The inner part was printed with a 50% filling, characterized by a higher distance between the printing tracks. All the chemicals used were purchased from Sigma Aldrich and used as received. The first part of the metallization process was a neutral degreasing, performed in a 50 g/l sodium carbonate, 35 g/l disodium metasilicate, 3 g/l sodium lauryl sulfate solution at room temperature for 2 minute and under sonication. The samples were then rinsed with deionized water. After the degreasing an alkaline etching was done in a 200 g/l KOH solution for PLA and in a 400 g/l KOH solution for PETG (both at 45°C). After washing the substrates, the activation for electroless plating was achieved immersing the samples in the industrial activator Neoganth 834 (Atotech Gmbh.) for 5 minutes at room temperature first and subsequently in a 20 g/l sodium boron hydride solution for 1 minute at room temperature. The process was performed 2 times for PLA samples and the samples were not washed between the palladium solution and the reducing one. At the end of the activation step the samples were immersed in a NiP or Cu electroless solutions. In particular NiP having a P content between 2 and 3 % was deposited from an alkaline solution containing 32 g/l nickel sulfate hexahydrated, 20 g/l trisodium citrate 25 g/l ammonium chloride and 28 g/l sodium hypophosphite [12]. The pH was corrected to 9 using ammonium hydroxide and the plating was performed under stirring. In the case of copper a solution containing 10 g/l copper sulfate pentahydrated, 22.4 g/l TEA, 14.6 g/l EDTA and 3.6 g/l formaldehyde was employed. The pH was brought to 12.8 with sodium hydroxide and the solution was used at 45°C [13]. The electrodeposition of copper on the NiP metallized sample was accomplished using a pyrophosphate alkaline solution at pH 8.5 and 45°C of temperature. For SEM characterization a Zeiss EVO 50 EP was used. Optical microscopy was performed using a Laica DMLM direct illumination microscope. The instrument used for AFM was a NT-MDT SOLVER PRO (in contact mode). Contact angles were measured by mean of a microcamera connected to a PC equipped with a software (Drop Shape Analysis) able to fit the shape of water droplets dispensed by a needle. The adhesion between the polymer and the metal was estimated via a peel test performed using a transparent adhesive tape. After the test the area of the coating still adherent to the surface was measured.

Results and Discussion

The first part of the experimentation was focused on the development of an optimized method to electroless metallize PLA and PETG. To achieve this, suitable samples were employed. These were characterized by the presence of two zones that reproduced the different morphologies employed in 3D printing of real objects (figure 1).

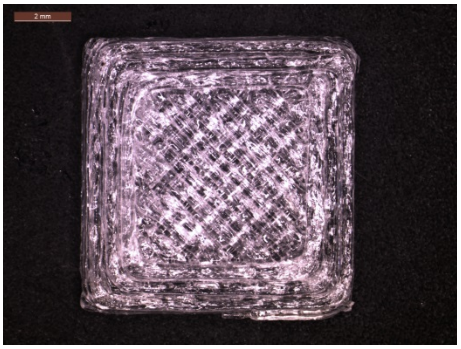

Figure 1. PETG sample employed for the characterization of the plating process.

The outer part of the samples was constituted of a structural zone having a high density of material and a low porosity. This printing style is used to confer mechanical strength and is typical only of the external parts of the object. For the inner part, like in the samples employed, a filling is added to lower the weight and the cost of the final piece. This part was characterized on the samples by a high porosity and the only difference with respect to the structural part was the distance between the solidified polymeric wires that form the object. The filling is of particular interest when using wet metallization due to its intrinsic porosity, which increase the risk of solution entrapment during the various steps of the process.

Influence of etching time

After the initial degreasing step, an alkaline etching was applied to the PLA and PETG samples. This method is extensively used to modify the surface of the two polymers [14-16] and was used in the present work to increase their surface roughness and to modify the surface energy. A proper etching is necessary to provide adhesion between the polymer and the metallic layer on top. This happens thank to the formation of cavities on the surface (which can mechanically interlock with the metal) or to the chemical modification of the surface itself (in particular an increase in wettability is beneficial for electroless plating). It is thus vital to find the optimal etching time to achieve the best adhesion.

Figure 2 represents the degradation reaction occurring in the case of PLA [15] when immersed in a solution containing OH^-.

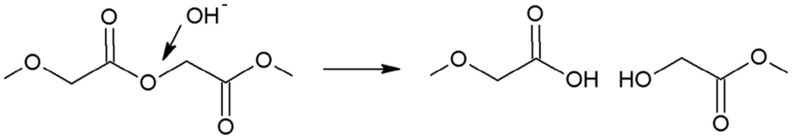

Figure 2. Degradation reaction of PLA in alkaline conditions.

When the polymeric chains break new -OH and -COOH chemical groups are introduced on the surface, modifying thus contact angle and quality of the final coating. A similar mechanism, involving the breaking of an ester bond [17], can be observed in the case of PETG (figure 3).

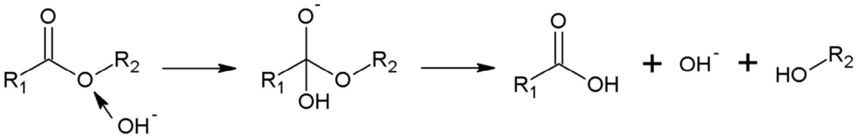

Figure 3. Degradation reaction of PETG in alkaline conditions.

Also for PETG new -OH and -COOH chemical groups are introduced by the degradation process. This reaction is in general slower than the one occurring for PLA, and for this reason a 400 g/l KOH solution was used instead of a 200 g/l KOH. The formed groups are the same for the two polymers and for this reason only their surface density, coupled with the properties of the polymers, determines the surface energy after the treatment.

The effect of different etching times on surface roughness, contact angle and metal adhesion was investigated for PLA and PETG. Figure 4 and 5 depict the variation of these three parameters for PLA.

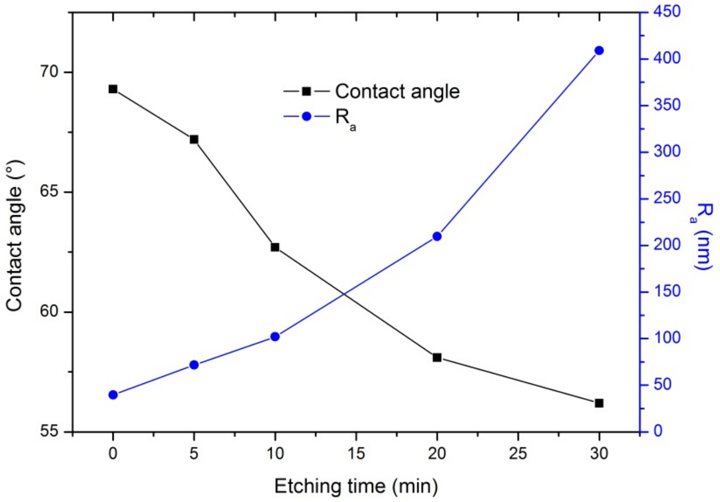

Figure 4. Influence of etching time on contact angle and roughness for PLA

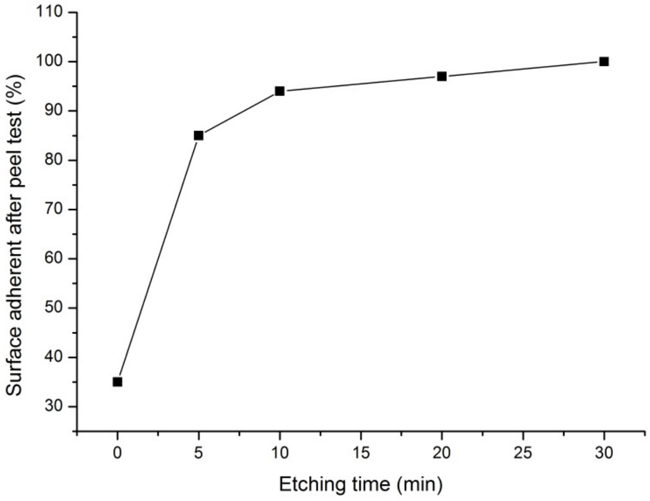

Figure 5. Influence of etching time on adhesion for PLA (percentage of coating not removed by the peel test).

From figure 3 is evident that increasing etching times had a considerable effect on the surface. Contact angle decreased up to 57°, as observed in the literature [15], while roughness R_a increased one order of magnitude. The combined effect of the variation of these two parameters is evident in figure 4 on the adhesion of the NiP coating. Optimal adhesion was reached for the longest etching time, while in the other cases partial detachment of the layer was always observed.

The roughness increase can be visualized using AFM. Figure 6 represent the surface profile recorded for three samples at different etching times.

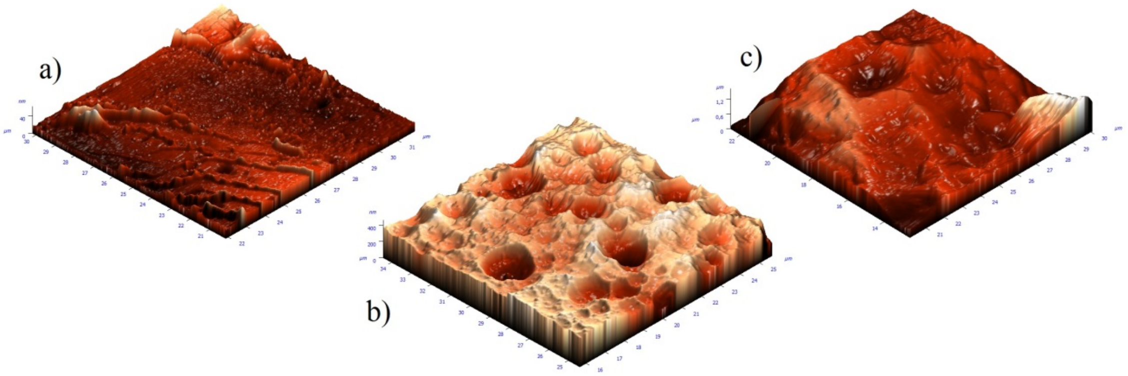

Figure 6. AFM surface profiles for PLA untreated (a), 10 minutes etched (b) and 30 minutes etched (c).

The modification of the surface is evident also from the SEM images acquired using the secondary electrons signal (figure 7).

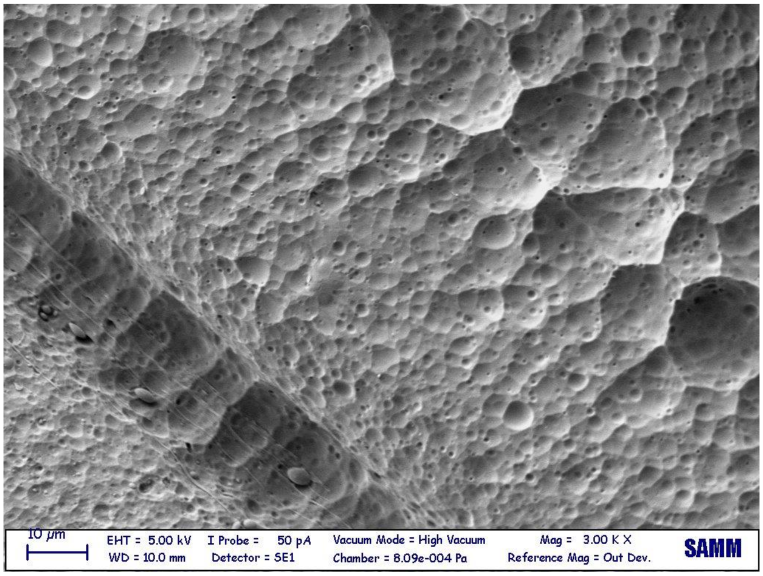

Figure 7. PLA surface after 20 minutes of etching observed at 3000X.

The same parametres can be employed to analyze the effect of pretreatment in the case of PETG (figure 8 and 9).

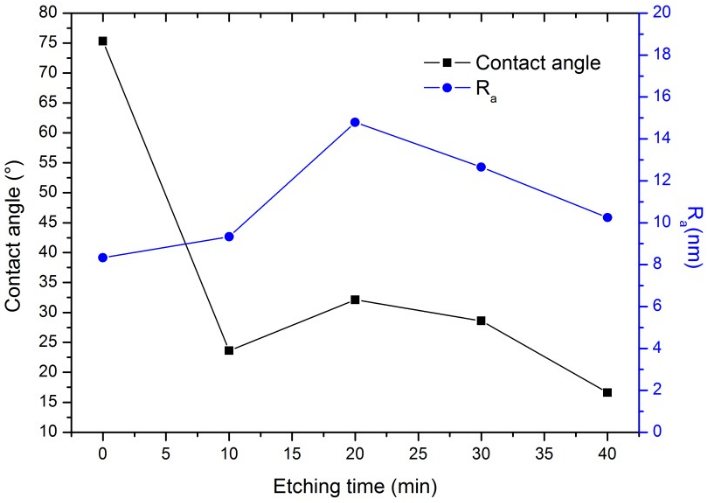

Figure 8. Influence of etching time on contact angle and roughness for PETG

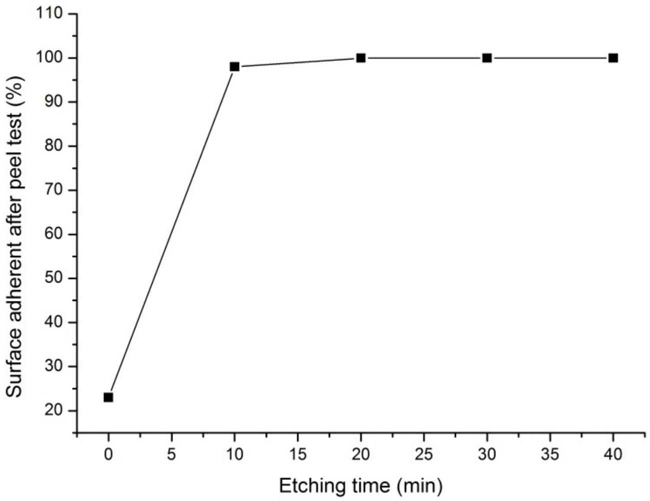

Figure 9. Influence of etching time on adhesion for PETG (percentage of coating not removed by the peel test).

For PETG the surface roughness was not significantly affected by the immersion in KOH, while the contact angle reached very low values. Adhesion was satisfactory also at low etching times. When comparing the PETG case with PLA is possible to appreciate the greater influence of surface energy over roughness on the final adhesion of the substrate. PETG became almost superhydrophilic after immersion in KOH, and the NiP adhesion was good even if roughness R_a is in the order of 10 nm. On the contrary PLA could not reach low enough contact angles with alkaline etching and the only way to achieve suitable adhesion of NiP was to increase roughness. In the case of PLA this was possible because the degradation reaction tends to remove considerable amounts of material from the surface, while in the case of PETG the degradation mainly forms new chemical groups on the surface. This difference in behavior is connected to the chemistry of the two materials: PLA is less resistant to alkaline etching, and thus a real removal of material from the surface coupled with a limited -COOH/-OH groups formation is present. PETG on the contrary is more resistant and the polymeric chains are not completely disaggregated and solubilized, but new chemical groups are formed on the surface due to the ester bond breaking.

The limited surface damaging of PETG is evidenced also by the SEM image of the surface (figure 10), where the creation of superficial nanoporosity can be observed.

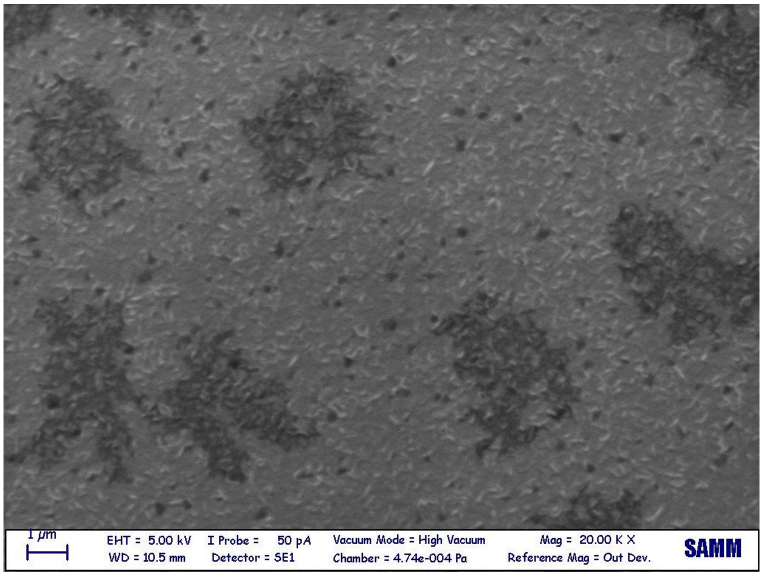

Figure 10. PETG surface after 40 minutes of etching observed at 20000X.

The AFM analysis, where the actual dimension of the surface roughness can be better observed, confirmed the SEM observation (figure 11).

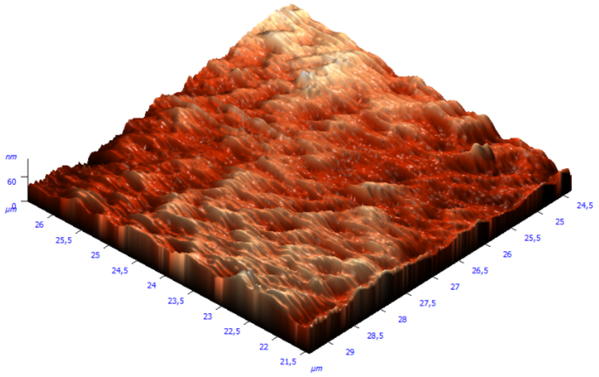

Figure 11. AFM of PETG surface after 40 minutes etching in KOH.

Activation

As a consequence of the different surface energies, PLA and PETG react differently when activated for electroless plating. The Pd absorption on the polymer surface was nearly immediate, but PLA required the absorption/reducing process to be performed two times to achieve uniform activation. This fact can be correlated with the relatively high contact angle after etching observed in the case of PLA, which probably reduced the quantity of Pd absorbed by the surface. PETG on the other hand guaranteed a good uniformity with one activation cycle as a consequence of the low contact angle after etching. The activation process itself lowered the contact angle of the surface, as visible in figure 12. Both PLA and PETG present values decreased by nearly 5°.

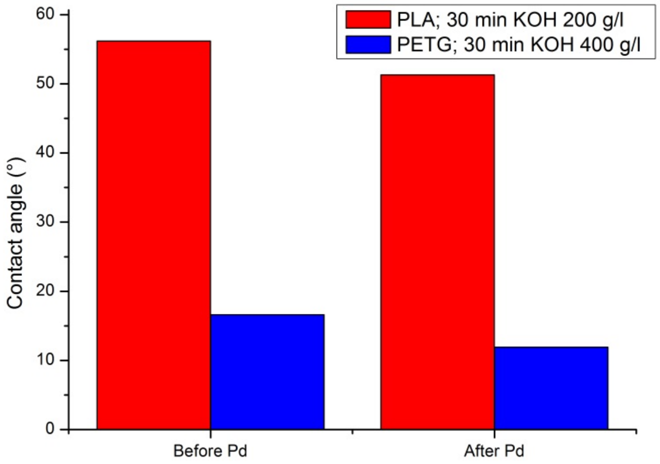

Figure 12. Contact angle after Pd nuclei formation on PLA and PETG.

The Pd nuclei formed were evidenced on the surface of PETG using SEM (figure 13). The same analysis was not performed in the case of PLA because the low heat resistance of the polymer made difficult the observation of the surface at the high magnifications needed to observe the nuclei. In the case of PETG treated for 30 minutes in KOH, a particle density of 1.25×10^4 particles/mm^2 was estimated.

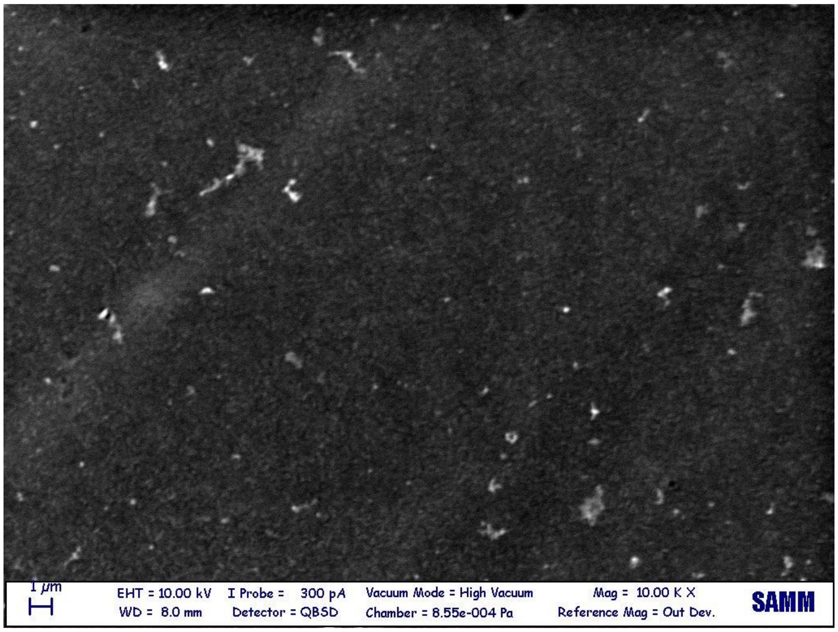

Figure 13. SEM image of Pd nuclei formed on PETG etched for 30 minutes.

NiP and Cu plating

After the activation steps the samples were electroless plated in NiP or Cu. Figure 14 depicts the SEM analysis of the layers formed on PETG and PLA. The zone of the sample considered for SEM is the filling, and complete coverage of the surface can be observed up to the second polymer layer below the outer one (figure 14 a). Both the samples were immersed in the NiP solution for 14 minutes, obtaining thus around 1 µm of thickness.

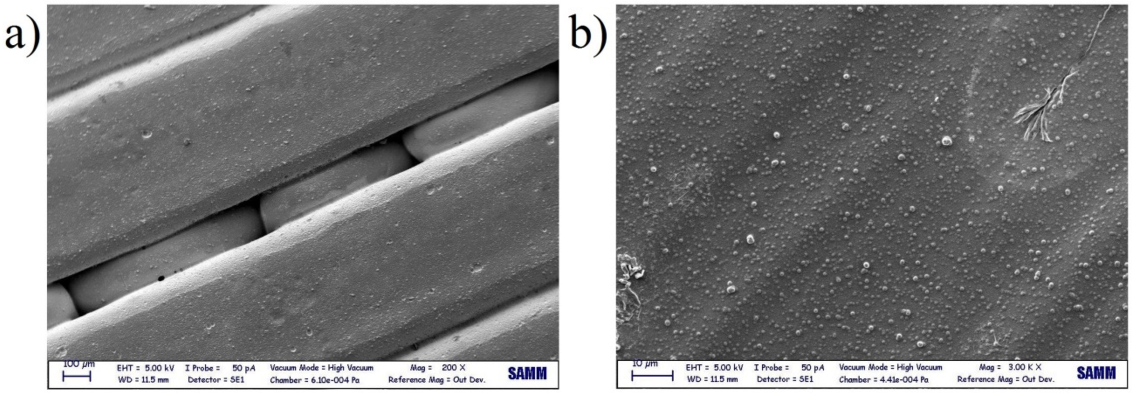

Figure 14. NiP metallized PLA (a) and PETG (b) after 30 minutes etching. (b) reports a particular of the metallic layer.

Similar results were obtained in the case of Cu, as evidenced in figure 15 (20 minutes of deposition; 1.9 µm thickness). For both metals the cross sections of the samples evidenced penetration of the electroless plating up to the second, in some zones third, layer of polymeric material. This data is strongly dependent on the distance between the printing lines, and thus on the porosity of the filling.

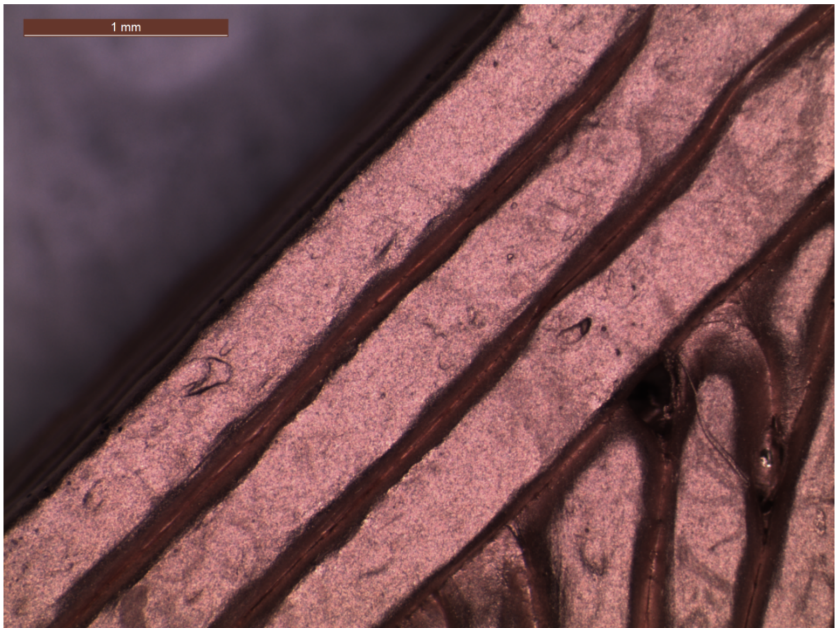

Figure 15. Cu metallized PETG after 30 minutes of KOH etching.

The evolution of surface roughness was evaluated by mean of AFM and the results are reported in table I.

TABLE I. R_a for PLA and PETG with respect to the coating applied. Data in nm.

Polymer	**R_a (untreated)**	**R_a (etched)**	**R_a (etched + NiP)**	**R_a (etched + Cu)**
PLA	39.68	261.09	185.71	216.31
PETG	8.33	10.25	43.53	51.22

A roughness reduction was observed in the case of PLA when NiP and Cu plated, probably to some limited levelling by the plating solution. In the case of PETG on the contrary a roughness increase was observed and this is due to the metal nuclei forming on the surface, which present a dimension considerably larger than the minimum feature size on the surface of PETG both treated and untreated.

As stated the metallic layers obtained are characterized by a good adhesion to both the polymers, with good resistance to delamination when subjected to peel test. Only PETG however was able to achieve adhesion values high enough for the plating of flexible substrates (figure 16). The sample in figure 15 was etched for 30 minutes in KOH, activated and plated for 14 minutes in NiP solution to obtain 1 µm of coating thickness. A severe repeated bending of the sample at a radius of around 5 cm didn't cause any delamination of the NiP layer. Moreover, the resistance of the layer between the two shortest edges was found to change from 7 Ω when not curved to 5.5 Ω.

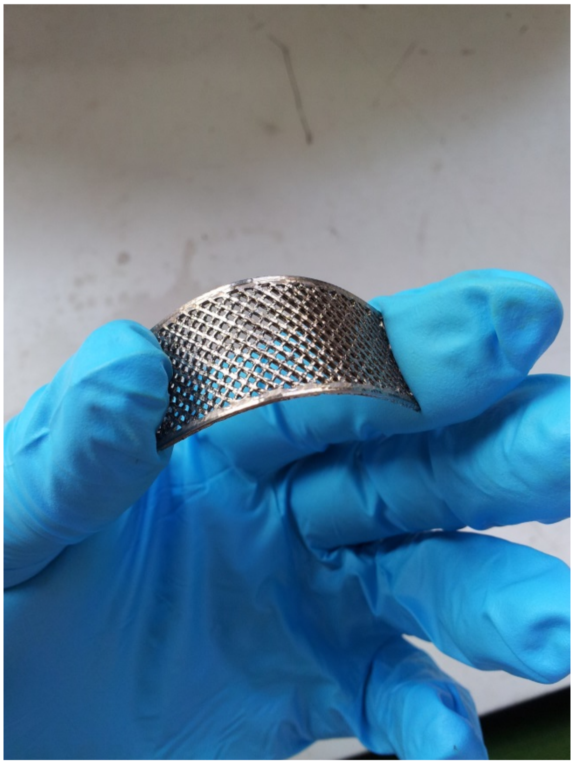

Figure 16. NiP plated PETG flexible demonstrator.

In the case of PLA minor delamination of the layer was noticed in correspondence of the zones characterized by a higher stress.

Multilayers electrodeposition

The electrodeposition of multilayers was investigated once the polymeric samples were made conductive by the first electroless deposited NiP or Cu layer. As an example, Cu was deposited on a 1µm NiP layer deposited on a PETG demonstrator. An alkaline pyrophosphate solution was employed to deposit around 10 µm of pure copper at 20 mA/cm^2. The result obtained is shown in figure 17.

Figure 17. A Cu/NiP plated PETG demonstrator.

Similar results were obtained in the case of PLA. On the copper layer obtained in the way described in the text is possible to electrodeposit a wide range of metals, making possible a multiplicity of possible decorative and functional application for the 3D printed and metallized objects.

Conclusions

Electroless NiP and Cu metallization of both PLA and PETG was achieved applying to the two polymers an optimized all-wet pretreatment and a plating step in two alkaline solutions. The layers obtained were characterized by a good adhesion to the substrate, but only in the case of PETG adherence was enough to avoid partial delamination on flexible substrates. Multilayer production was demonstrated testing the possibility of electrodeposition of Cu on a base NiP layer. The results obtained evidence possible applications of the 3D printed and electroless metallized objects in decorative and functional applications. The first may include homeware production or architectonic parts manufacturing as examples, while the latter may include conductive parts for instruments or functional microstructures.

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