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Investigation on electroless copper metallization on FDM built ABS parts

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In this work, metallization of copper on acrylonitrile-butadiene-styrene (ABS) substrate has been fabricated by fused deposition modelling (FDM) using electroless process avoiding chemicals detrimental to environment. Four acidic baths containing five weight percentages of HF, H_2SO_4, HNO_3 and H_3PO_4 varying copper sulphate ($CuSO_4$) at 10, 15 and 20 weight percentage in each bath has been used for metallization. The metallization process in each bath has continued for seventy two hours. Copper coating obtained on the substrate by the use of different baths has been evaluated for electrical resistance, thickness of copper coated layer, percentage of copper present on the coated surface and adhesion performance. Scanning electron microscopy (SEM) and energy dispersion X-ray spectroscopy (EDX) results have indicated that all the baths are quite capable of deposition of copper on ABS substrates. However, HF bath has exhibited superior coating performance as compared to other baths. The thickness of copper coated layer and percentage of copper present in the coated layer has been found to be highest by the use of HF bath with fifteen weight percentage of $CuSO_4$.

Keywords: Acrylonitrile-butadiene-styrene (ABS), Fused deposition modelling (FDM), Copper metallization

1 Introduction

Plastics have recently found extensive application in automobile, electronics and aerospace industries due to their inherent favourable properties like high strength to weight ratio, light weight, corrosion resistance and durability. However, metallization on plastics have become essential when property like conductivity (both electrical and thermal) have been desired from application point of view in order to replace metals by metallizedplastics[1,2]. Among various plastics, metallization on a crylonitrile-butadiene-styrene (ABS) parts have been extensively used due to its superior impact resistance and toughness. The acrylonitrile in ABS plastic has provided chemical and thermal stability while the butadiene has added toughness and strength. Styrene has given the finished polymer a nice glossy finish. Copper, gold, silver and aluminium have been successfully metallized on an ABS substrate. However, copper coating on ABS parts has posed difficulty due to unavailability of appropriate activation agents. Although various methods have existed for plating, electroless copper plating has been preferred due to cost consideration and ease of metallization. Electroless metallization process has been considered as a process of metallizing the nonconductive surface without requiring electrical power. However, surface preparation has essentially needed in electroless metallization by enlarging the surface pores by a strong oxidizing agent. After etching, the surface has been subjected to activators like palladium and tin chloride. After activation, surface has been immersed in solution for copper or tin coating. The general steps being adopted for electroless deposition have been listed as etching followed by neutralization, activation and acceleration. For etching, normally chromic acid (Cr_2O_3) or sulphuric acid (H_2SO_4) has been used[3]. But these acids have been found to betoxic in nature and hazardous to the environment. Again, palladium (Pd) catalyst used during activation step has been found to be not only costly but also detrimental to environment. Thus, it has been insisted to find suitable activation agents to be employed avoiding palladium. Hence, environment friendly electroless metallization on ABS parts has been desired because it can eliminate etching process as well as the use of palladium (Pd).

Among various steps involved in electroless metallization process, the important ones have found to be etching and activation. The former has involved in the enlargement of the surface area for metal plastic contact while the latter has formed activator particles in the porous region which is important for metallization process. Equbal and Sood[1] have used a solution of sulphuric acid (H_2SO_4) and hydrogen

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*Corresponding author (E-mail: anshuman.sahu123@gmail.com) peroxide (H_2O_2) for etching purpose. In another route of surface preparation, the authors[1] have used chromic and sulphuric acid for the purpose of etching process. In both the methods, Pd/Sn colloidal solution has been used for activation. Acceleration has been done by the solution of sodium hydroxide (NaOH), copper sulphate ($CuSO_4$) and ethylene diaminetetra acetic acid disodium ($EDTANa_2$) before copper electroless coating. Since Pd/Sn has small particle size, it has been easily dispersed into the substrate. As a result, activation has taken place easily. Then, the samples have been immersed inside the acidic baths for electroless coating. The authors[1] have used four chemical baths like H_2SO_4, HF, H_3PO_4 and CH_3COOH for electroless deposition of copper on ABS surface. Uniform deposition of metal on the substrate and uniform conductivity on the surface has been obtained in all cases except for CH_3COOH bath. Electroless deposition by the H_2SO_4 bath has exhibited superior performance among all the acidic baths. It has been observed that the proposed process of metal plating has not considered being environment friendly. Moreover, the process has used expensive palladium catalyst. Sahoo *et al.*[2] have used environmental friendly process for electroless coating of copper on ABS parts. They have used aluminium enamel paste to coat the plastic surface and thereby creating the activation sites for deposition of copper using different concentration of copper sulphate solution for acidic baths of H_2SO_4, HF, H_3PO_4, HNO_3 and CH_3COOH. Among all baths, HF bath has shown superior result in terms of uniform electrical conductivity on the deposited surface, percentage of copper crystal formation and adhesion strength as compared to other baths if the deposition time is small. Zhang *et al.*[3] have performed electroless plating of copper and nickel on poly tetrafluoroethylene films and tested the adhesion strength. Similarly, different researchers have performed copper, nickel, gold metallization on ABS parts[4-8].

Teixeira and Santini[9] have conducted direct metallization of nickel on ABS parts using etchant of H_2SO_4, HNO_3 and H_2O_2 solution followed by electroless coating of nickel in nickel chloride and hypophosphite solution. Bazzaoui *et al.*[10,11] have suggested the method of nickel electroplating on ABS plastic substrate by painting with polypyrrole followed by copper electroplating and nickel electroplating subsequently. Nigam *et al.*[12,13] have performed the metallization of copper on ABS surface by thermal spray coating.

Critical analysis of literature has suggested that conventional etching reagent used for copper coating on ABS parts are sulphuric acid and chromic acid. For surface activation, generally palladium and tin chloride have been used. Both the etchants and palladium have been treated as hazardous to environment. In order to create a safe, cost effective and environment-friendly way for metallization process on ABS plastic surface, a suitable experimental procedure has been adopted. In this work, metallization of copper on acrylonitrile-butadiene-styrene (ABS) substrates fabricated by fused deposition modelling (FDM) using electroless process has been studied avoiding chemicals detrimental to environment. Four acidic baths such as HF, H_2SO_4, HNO_3 and H_3PO_4 have been used containing varying weight percentage of copper sulphate ($CuSO_4$) for metallization on ABS substrate.

2 Material and Method

Considering the cost of tooling, complexity of the fabrication process and flexibility, rapid prototyping (RP) possesses exhibit significant advantages over subtractive manufacturing processes. Therefore, fused deposition meddling (FDM) process was used for fabrication of acrylonitrile-butadiene-styrene (ABS) parts. The 3D models of specimens were generated by solid modelling software (SOLIDWORKS 2018). Then, it was converted into machine compatibility format such as STL file. The STL file was undergone a slicing process where the layer thickness was maintained at 0.254 mm. The build-up time was noted by pre-processing software, which ultimately depended on orientation of the part with respect to machine axis. As the physical model was prepared layer by layer manufacturing process, the overhangs of the model needed to be supported. Hence, two types of materials were used in FDM process. The support material was used for supporting overhangs while the main material was used for the object. The FDM machine (model: FORTUS 400mc) was used to prepare ABS parts.

2.1 Experimental procedure for metallization

The electroless depositions of copper on ABS parts were performed by the use of different acidic baths. In this electroless copper deposition method, etching and activation were not required. The replacement was aluminium-carbon enamel (Al-C-enamel) paste and it was directly applied on the surface of ABS parts. The paste served as their placement of both etching and activation reagents. It was completely environment friendly and less costly. With the help of redox reactions, a thin layer of metal was formed on the surface without the help of electric potential.

For electroless copper coating, an Al-C-enamel paste was directly applied on the surface of ABS parts eliminating etching, neutralization, activation and acceleration. Then, the final stage was electroless coating process. Here, the ABS parts were kept inside different acidic baths containing copper sulphate for some hours. A thin layer of copper was produced on ABS parts surface by electroless deposition after some hours. The procedure was depicted in Fig. 1.

2.2 Al-C-enamel paste preparation

The constituents such as aluminium powder, enamel, carbon powder and distilled water were taken separately with a weight ratio of 40:36:3:21. The constituents were mixed together thoroughly with the help of a magnetic stirrer. Then, the paste was applied to the samples by a fine paint brush. After the paste was applied to all samples, they were heated in an oven for one hour at 60°C for drying. After drying the samples, they were scoured in a 330-grid size sand paper to generate micro-irregularities for easy deposition of copper particles. Then, ABS parts were cleaned with soap and then rinsed thoroughly with distilled water to remove dirt and unwanted impurities. The samples were cleaned by distilled water and again heated in an oven for about one hour. Now, the samples were ready for copper deposition.

2.3 Electroless copper deposition

The electroless baths were prepared for all twelve samples. Twelve solutions were prepared consisting of HF, H_2SO_4, HNO_3, H_3PO_4 of five weight percentage with 10,15 and 20 weight percentage of $CuSO_4$ solution. The ABS parts were put in the solution for seventy two hours. Then, the samples were taken out from acid bath solutions and heated in an oven for 30 min at 65°C temperatures. The process of metallization was shown in Fig. 1. The ABS parts after applying Al-C-enamel paste was shown in Fig. 2(a). Similarly, the parts during the electroless deposition inside the acidic baths were shown in Fig. 2(c). After successful copper deposition on ABS parts, the samples were shown in Fig. 2(b). The metallization of copper on ABS parts was

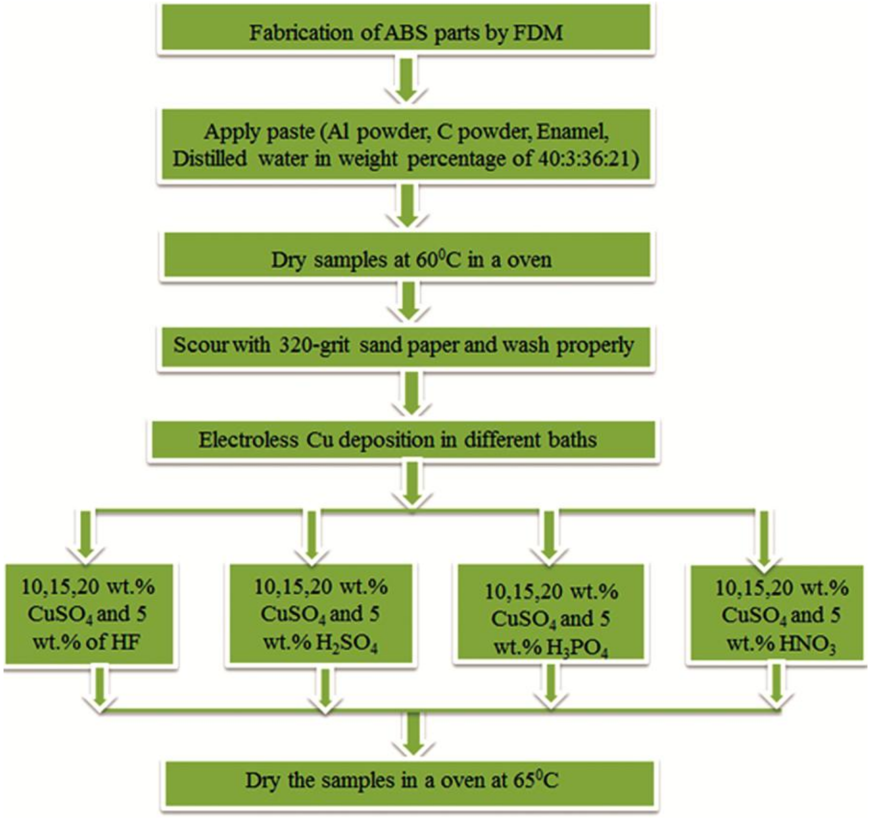


Fig. 1 — Experimental procedure.

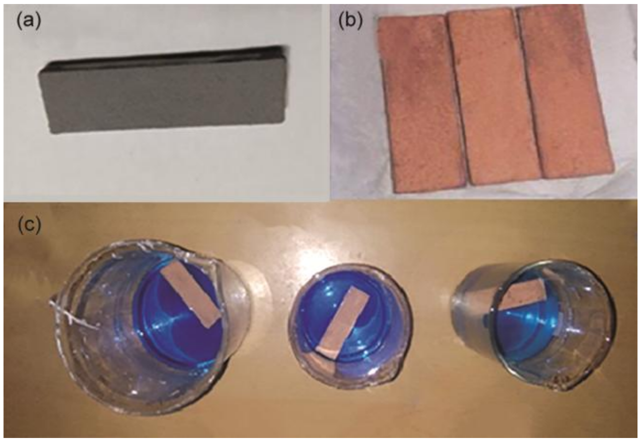


Fig. 2 — Metallization process (a) ABS samples for experiment after Al-C-enamel paste, (b) successfully deposited Cu on ABS parts, and (c) parts immerged into various baths.

performed with the help of an intermediate layer of Al-C-enamel. Copper deposition on the Al particle present on the ABS surface was occurred by oxidation and reduction reaction. The oxidation was described as an anodic process which was characterized by the loss of electrons while reduction was indicated as a cathodic action by gain of electrons. $CuSO_4$ was dissociated into Cu^{2+} and SO_4^{2-} in the presence of strong acid which helps for faster dissociation as shown in Eq. (1). Then, displacement reaction was occurred where the surface of the Al substrate becomes anodic (Al) and cathodic (Cu) as shown in Eqs (2 and 3). The displacement process was continued until nearly the whole substrate was covered with copper[2]. Then, oxidation (dissolution) of the Al anode virtually was stopped and copper deposition ceased. The reaction kinetics of the electroless copper metallization was presented in Eqs (1 to 3).

$$CuSO_4 \xleftrightarrow{H^+} Cu^{2+} + SO_4^{2-} \qquad \ldots (1)$$

$$\text{Anodic: } 2Al \longleftrightarrow 2Al^{3+} + 6e^- \qquad \ldots (2)$$

$$\text{Cathodic: } 3Cu^{2+} + 6e^- \longrightarrow 3Cu \qquad \ldots (3)$$

2.4 Analysis of copper deposited ABS surface

After electroless copper deposition on FDM built ABS parts, various tests were carried out. The conductivity test was done to perform the electrical performance of the samples. Adhesion test was carried out to measure the metal plastic bonding as per ASTM standard. Then, SEM and EDS were performed to analyse the thickness and weight percentage of copper deposition as well as the microstructure.

2.4.1 Electrical performance measurement

A digital multi-meter was used to measure the resistance (R) of the copper coated surfaces and the average resistance ($\overline{R}$) and standard deviation (σ) of the resistance across the surface were calculated as represented in Eqs (4 and 5).

$$\overline{R} = \frac{\sum_{i=1}^{n} R_i}{n} \qquad \ldots (4)$$

$$\sigma = \frac{\sqrt{\sum_{i=1}^{n} (R_i - \overline{R})^2}}{n-1} \qquad \ldots (5)$$

where, R_i was the measured resistance at ith point on the surface in Ω/cm^2 and n was total number of points taken for measurement. Here, the resistance (R) of the copper coated surfaces was measured at four different positions and corresponding average resistance ($\overline{R}$) and standard deviation (σ) of the resistance across the surface were calculated.

2.4.2 Adhesion test

For adhesion test, the samples were studied on the basis of ASTM test method (ASTM 3359-2) at room temperature[14]. The surface was cleaned. With the help of a knife, grid lines were cut 2 mm apart on the surface of the copper coated layer. It was ensured that the depth of cut should reach to the ABS surface. Then, a tape was placed across the cut surface and a 25 kg weight was placed on the surface for 5 min. The tape was removed in such a way that it should be jerked.

2.4.3 SEM/EDX characterization

The surfaces of the specimens were observed by scanning electron microscope (SEM) JEOL JSM-6480LV. The elemental analysis was done by EDX test. Then, the percentage of copper was noted for all surfaces produced by different baths containing of HF, H_2SO_4, HNO_3, H_3PO_4 of five weight percentage and 10,15,20 weight percentage of $CuSO_4$ solution.

2.4.4 Thickness measurement

SEM images of the transverse section of the coated samples were taken to measure the copper layer thickness of the samples. The thickness was measured using image viewer application available in MATLAB 14a.

3 Results and Discussion

By following the procedure as discussed in material and method section, the ABS parts were fabricated by the FDM process and the electroless copper metallization on the surface of ABS parts were done. On the copper coated ABS parts, certain characteristic features were determined namely electrical performance, adhesion test, copper coated layer thickness and percentage of copper on the surfaces with SEM and EDX characteristics.

3.1 Electrical resistance of copper coated surface

The electrical resistance of copper coated ABS parts were presented in Table 1. The duration of immersion in different baths was taken as seventy two hours. After the dipping duration was finished, it was observed that the resistance of the coated layer using HF solution with 15 weight percentage of $CuSO_4$ solution was found to be 0.45 Ω/cm^2. It happened to be the least among all coated layers. Using H_2SO_4 solution, it was found out that the minimum resistance was obtained for 10 weight percentage of $CuSO_4$ solution. For H_3PO_4 solution, minimum resistance was found for both 15 and 20 weight percentage $CuSO_4$ solution. It was observed that a lot of difference in resistance at different positions on the copper coated surface produced was found by the use of HNO_3 bath for different weight percentages of $CuSO_4$ solution. It was attributed to non-uniform deposition of copper due to over etching of aluminium by HNO_3 solution. Therefore, conductivity and copper deposition was better in HF, H_2SO_4, H_3PO_4 baths as compared to HNO_3 bath.

3.2 Cu crystal formation and EDX characterization

It was found that the microstructure of copper was uniform throughout the surface after it was undergone 72 hours in $CuSO_4$ solution. Fifteen weight percentage solution of $CuSO_4$ under HF has the best microstructure as shown in Fig. 3. Figure 4 showed that the SEM image of twenty weight percentage copper sulphate of HNO_3 solution and it was seen that there was non-uniform deposition of copper crystal. The formation of copper crystal in H_2SO_4 and H_3PO_4 baths are shown in Figs 5 and 6 at different magnifications. It was noticed that there was non-uniform deposition of copper crystal on ABS surface by the use of H_2SO_4 and H_3PO_4 baths.

The EDX analysis of the surface of copper coated surface by different acidic bath was shown

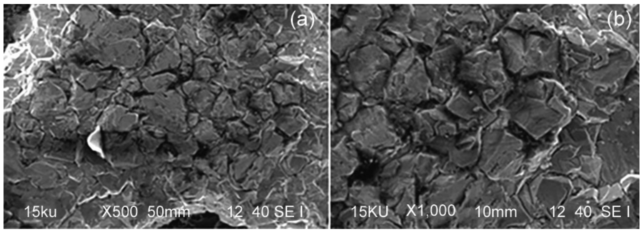


Fig. 3 — Copper crystals on ABS substrate using HF bath at 15 weight percentage of $CuSO_4$ solution (a) 500 magnification, and (b) 1000 magnification.

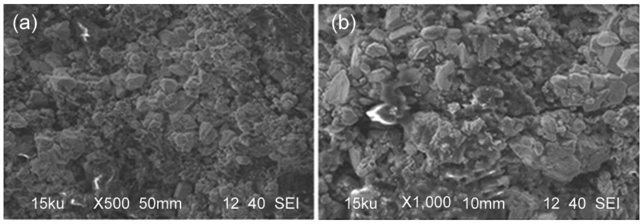


Fig. 4 — Copper crystals on ABS substrate using HNO_3 bath at 20 weight percentage $CuSO_4$ solution (a) 500 magnification, and (b) 1000 magnification.

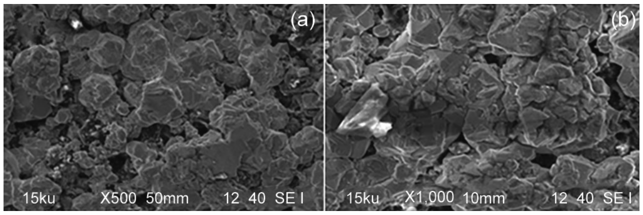


Fig. 5 — Copper crystals on ABS substrate using H_2SO_4 bath at 10 weight percentage $CuSO_4$ solution (a) 500 magnification, and (b) 1000 magnification.

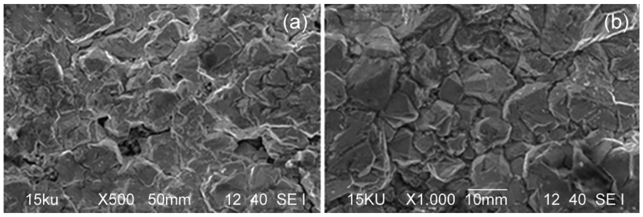
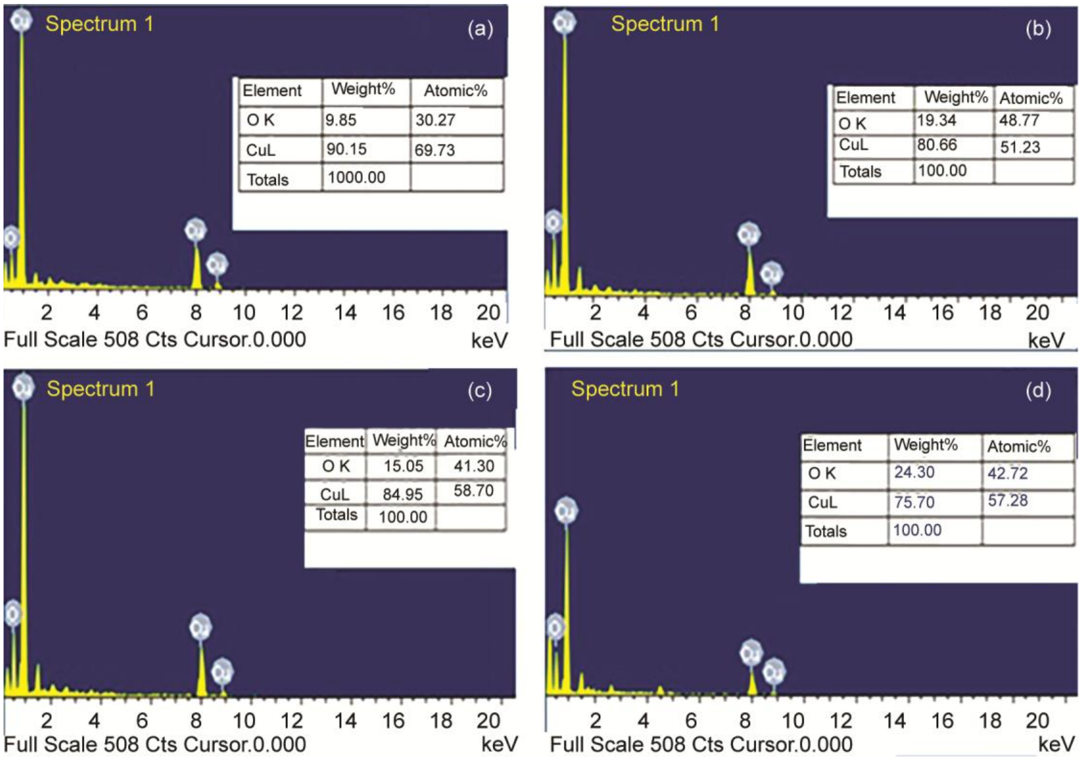


Fig. 6 — Copper crystals on ABS substrate for H_3PO_4 bath at 15 weight percentage $CuSO_4$ solution (a) 500 magnification, and (b) 1000 magnification .

Table 1 — Electrical properties of Cu coated ABS parts.

Deposition time 72 hours	Electrical resistance							
	HF		H_2SO_4		H_3PO_4		HNO_3	
$CuSO_4.5H_2O$ (in wt.%)	$\overline{R}$ (Ω/cm^2)	σ	$\overline{R}$ (Ω/cm^2)	σ	$\overline{R}$ (Ω/cm^2)	σ	$\overline{R}$ (Ω/cm^2)	Σ
10	0.5	0.064	0.55	0.028	0.67	0.135	0.75	0.237
15	0.45	0.037	0.56	0.028	0.65	0.019	0.8	0.10
20	0.6	0.01	0.6	0.09	0.65	0.02	0.85	0.13



(a)

Element	Weight%	Atomic%
O K	9.85	30.27
CuL	90.15	69.73
Totals	1000.00	

(b)

Element	Weight%	Atomic%
O K	19.34	48.77
CuL	80.66	51.23
Totals	100.00	

(c)

Element	Weight%	Atomic%
O K	15.05	41.30
CuL	84.95	58.70
Totals	100.00	

(d)

Element	Weight%	Atomic%
O K	24.30	42.72
CuL	75.70	57.28
Totals	100.00	

Fig. 7 — EDX analysis of copper deposited ABS samples prepared in different baths (a) HF bath, (b) H_2SO_4 bath, (c) H_3PO_4 bath, and (d) HNO_3 bath.

in Fig. 7. The percentage of copper present on the surface of the ABS parts after electroless coating was shown in Fig. 8. It was found that copper weight percentage was maximum for HF bath and it was above 90% while lowest was for HNO_3 bath. It was due to over itching of Al in presence of HNO_3. For HF bath, maximum percentage of copper was found by the use of 15% of $CuSO_4.5H_2O$. It was noted that maximum percentage of copper was found with the use of 10% of $CuSO_4.5H_2O$ for other acidic bath.

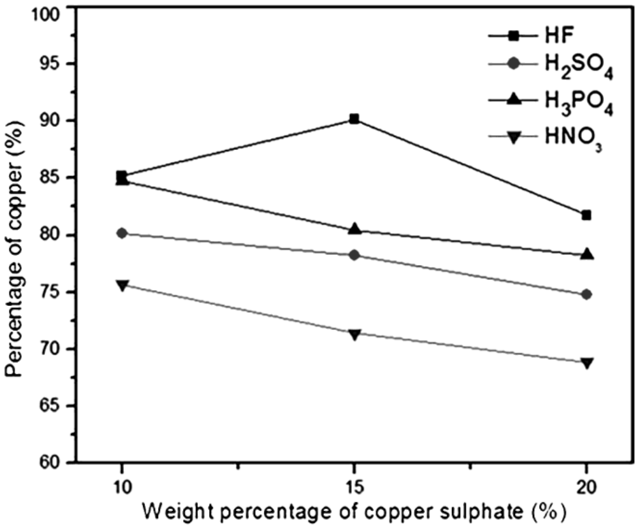


Fig. 8 — Weight percentage of copper for different acidic baths.

3.3 Thickness of Cu coated layer on ABS parts

SEM images of the copper coated layer were taken to measure the thickness of the samples. Out of which, the best sample was selected from each four acids which were shown in Fig. 9. Here, it was found that HF, H_2SO_4, H_3PO_4 solutions can produce copper deposited layer of thickness 79.49, 70.83 and 66.71 µm respectively. However, the thickness value was reduced to 47.98 µm with the use of HNO_3 due to over etching. In HF, H_2SO_4, H_3PO_4 baths, the copper coated layer were uniform while it was non-uniform in case of HNO_3 bath. The thickness of copper layer on ABS surface for different baths was shown in Fig. 10. For HF bath, maximum copper layer thickness was found at 15% of $CuSO_4.5H_2O$. For H_2SO_4 and H_3PO_4 baths, maximum copper layer thickness was found at 10% of $CuSO_4.5H_2O$. While for HNO_3 bath, maximum copper layer thickness was found at 20% of $CuSO_4.5H_2O$.

3.4 Adhesion test on copper coated ABS parts

Adhesion test was performed for different baths such as HF, H_2SO_4, H_3PO_4 and HNO_3. It was carried

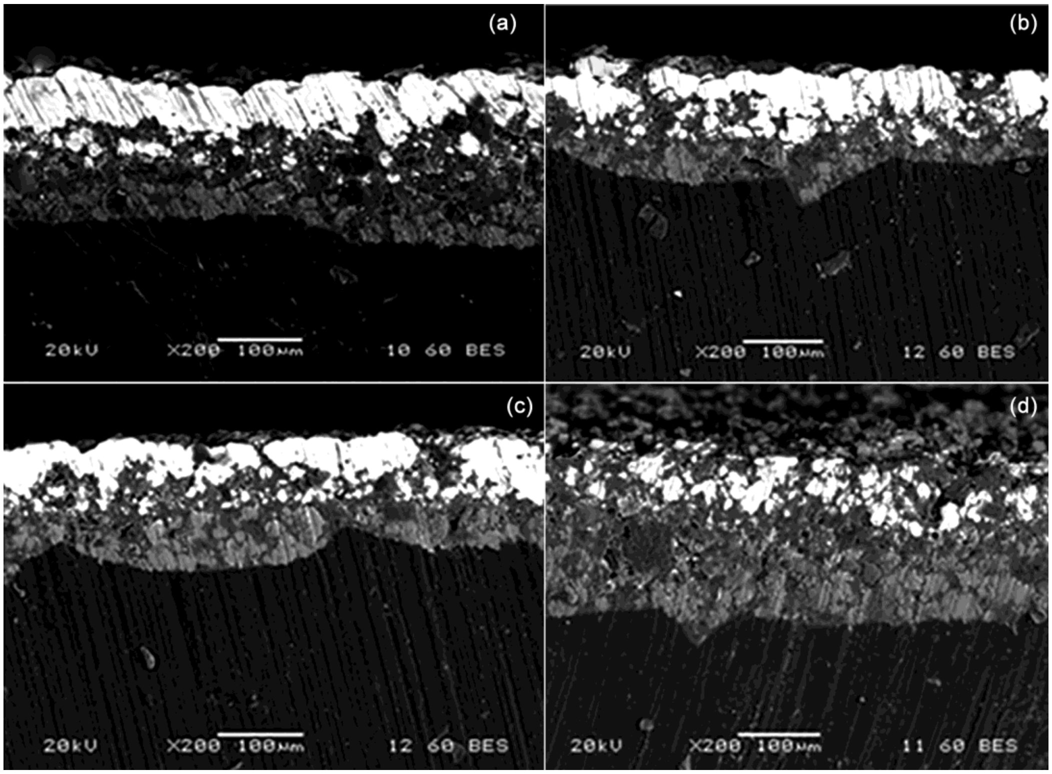


Fig. 9 — SEM images of thickness of Cu layer on ABS surface (a) 15% HF, (b) 10% H_2SO_4, (c) 10% H_3PO_4, and (d) 20% HNO_3.

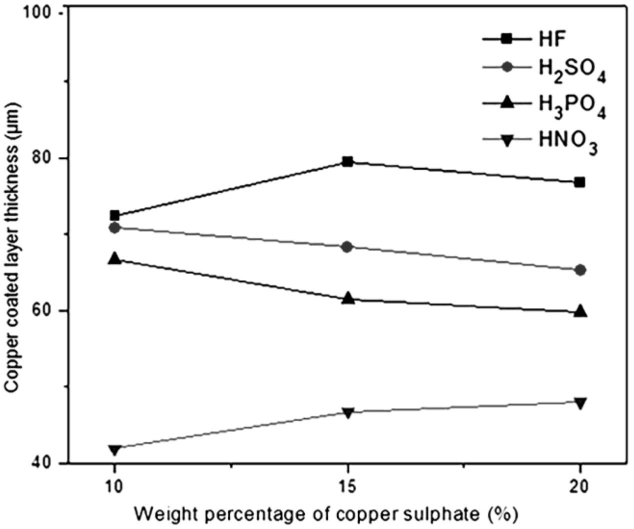


Fig. 10 — Thickness of copper layer on ABS surface for different baths.

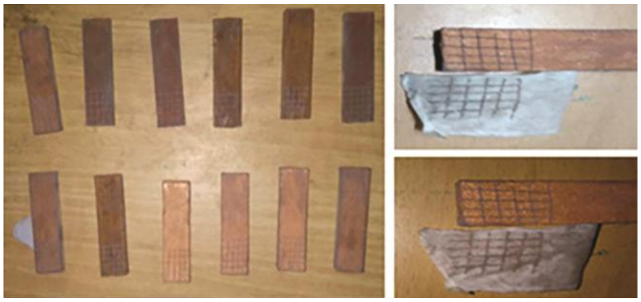


Fig. 11 — Standard tape test results of electroless copper deposited ABS parts for different baths.

Table 2 — Adhesion performance analysis of electroless copper deposited layers on ABS parts.

Concentration of $CuSO_4$ (in wt.%)	HF	H_2SO_4	H_3PO_4	HNO_3
10	3B	4B	5B	3B
15	4B	4B	4B	4B
20	4B	4B	3B	3B

out based on ASTMD 3359- 02 standard tape test as shown in Fig. 11. The adhesion performance was rated according to the scale defined by ASTM D 3359-02 as given in Table 2. All samples exhibited excellent adhesive strength as the samples yielded value between 3 to 5. It indicated that only 5 to 15% of copper removal had taken place after removal of the tape.

4 Conclusions

In this work, copper metallization has been done on ABS substrate prepared by fused deposition modelling (FDM) process using electroless coating process by using different acidic baths. After carrying out a systematic study, the following conclusions have been drawn.

1. Electroless metallization of copper on FDM built ABS parts has been performed with acidic HF, H_2SO_4, H_3PO_4 and HNO_3 baths. It has been found that adhesion strength of coating prepared by all the baths has been excellent.
2. It has been found that the coatings prepared by all baths has exhibited good electrical conductivity with uniform copper deposition except for HNO_3bath due to over etching of aluminium particles in presence of HNO_3.
3. The percentage of copper present on the surface of copper coated layer produced on ABS parts by use of HF bath has been highest among all the baths. Similarly, the thickness of copper coated layer produced by the use of HF bath has been found to be highest followed by H_2SO_4, H_3PO_4 and HNO_3 baths.

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