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Metallization on FDM Processed Parts Using Electroless Procedure

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Abstract

Metallization has been studied on flat ABS (acrylonitrile-butadiene-styrene) parts. These parts were fabricated on fused deposition modelling machine using layer by layer deposition principle using ABS as part material. Electroless copper deposition has been performed on these parts using three different surface preparation processes namely aluminium paste (Al paste) coated ABS parts, surface prepared using chromic acid for etching and ABS parts prepared using H_2SO_4/H_2O_2 for etching. Surface preparation is followed by Cu (copper) deposition by electroless procedure using four different acidic baths. The acidic baths used are 5 wt% $CuSO_4$ (copper sulphate) with 15 wt% of individual HF (hydrofluoric acid), H_2SO_4 (sulphuric acid), H_3PO_4 (phosphoric acid) and CH_3COOH (acetic acid) acids. Cu deposition is presented and compared based on their electrical performance, scanning electron microscopy (SEM) and energy dispersive X-ray spectrometry (EDS). The results shows that Al pasted samples demonstrated better electrical performance and more uniform Cu deposition.

1. Introduction

Properties such as easy formability, light weight and corrosion resistance provides natural advantage to plastic over metal. However, there are many areas in which due to decorative or technological considerations, metallic properties are required or demanded (Kuzmik et al.(1990)).

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It is in these applications metalizing plastics have opened the door to new use for these materials. Metallization is a process by which a non-conductive material is made conductive. With metallization, physical and mechanical

properties of plastics, such as reflectivity, heat resistance etc. can be improved as per Mittal (2001). Due to this, possibility of utilizing the advantages of both metal and plastic in combination has been increased. Skelly (2008) stated that metallized plastic got widespread applications in fields like oil & gas, automotive industry, electronic industry and others. Domenech et al. (2003) suggested that plastics such as Polysulfone, Polypropylene, Teflon and Acrylonitrile-butadiene-styrene (ABS) etc. can be metalized with different metals. Radulescu et al. (2002) proposed that metals like copper (Cu), zinc (Zn), nickel (Ni), chromium (Cr) etc. using variety of processes like brushing a metal paint, spray metal technique, sputtering, electroless plating etc. Among these processes, electroless plating because of its simplicity and economy finds the widest application. In this method, metal ions in aqueous solutions are deposited on the activated plastic surface by oxi-reduction reactions without the aid of an electric potential, forming a thin metallic layer as given by Hanna et al. (2003). As mentioned by Equbal et al. (2013), different steps involved in electroless plating are cleaning, etching, neutralization, activation, acceleration and deposition. But it is more difficult to control the process with regards to film thickness and uniformity. In addition, it is multi step procedure requiring long deposition time and complex chemical solutions. Some of these chemicals are costly and environmentally hazardous. To overcome these limitations a number of researchers proposes elimination of multiple routes or use of less costly and environment friendly chemicals but, the comparisons among them in terms of coating uniformity and conductivity has not been investigated. To fill this gap the present study proposes a comparative study among the various electroless metallization procedures. The first method as proposed by Li et al. (2008, 2009) uses Al paste for surface conditioning, in second method chemical route for surface preparation has been selected using chromic acid as an etching agent as proposed bas proposed by Jiang et al. (2009) and third method uses environment friendly H_2SO_4/H_2O_2 solution for etching as said by Teixeira et al. (2005).

2. Methodology

Three different routes implemented for preparing the ABS surface for electroless copper deposition were shown in Fig. 1. All reagents used were analytical pure reagent grade. In Route 1, Al paste was applied over the surface of sample whereas in route 2 chromic acid (CrO_3) was used for etching the sample surface. In route 3 all the procedure of surface conditioning as used in route 2 was used except for etching where sulphuric acid (H_2SO_4) and hydrogen peroxide (H_2O_2) was used. After surface conditioning these samples were dipped in four different acidic baths. The different acidic bath used for electroless deposition of copper consist of 5 wt% of copper sulphate ($CuSO_4$) and 15wt% of individual acids namely hydrofluoric acid (HF), sulphuric acid (H_2SO_4), phosphoric acid (H_3PO_4), and acetic acid (CH_3COOH). For part fabrication fused deposition modelling (FDM) machine by Stratasys Inc., USA is used. FDM is one of the rapid prototyping (RP) processes which fabricate the part on the layer by layer deposition principle directly from the CAD model of the part. The layers are stacked one upon other giving the required height to the part as by Equbal et al. (2013). Unlike other RP systems which involve an array of lasers, powders, resins, this process uses heated thermoplastic filaments which are extruded from the tip of nozzle in a prescribed manner. The material used for part fabrication is ABS (ABS P400). It contains 90-100% acrylonitrile/butadiene/styrene resin and may also contain mineral oil (0-2%), tallow (0-2%) and wax (0-2%). The dimension of the fabricated cuboidal samples employed in this study is 20mm×15mm×15 mm. Having excellent electrical conductivity and being relatively inexpensive, copper (Cu) is used for metallization. To generalize the comparison and develop more alternative acidic electroless Cu deposition formulations, four different acidic baths are also employed. A digital multimeter was used to measure the resistance of the metallized ABS parts. The average resistance (R) value together with standard deviation (σ) was calculated. The deposition process which yields the lower average resistance value along with lower standard deviation among all the listed method was considered as better. A ZEISS EVO- MA10 SEM scanning electron microscope (SEM) coupled with an energy dispersive X-ray spectrometer (EDS) was used to examine the appearance and elemental composition of the Cu deposited ABS surfaces. Adhesion assessment of the Al seeded coated ABS samples was performed following the standard ASTM test method ASTM D 3359-02 (Standard Test Methods for Measuring Adhesion by Tape Test).
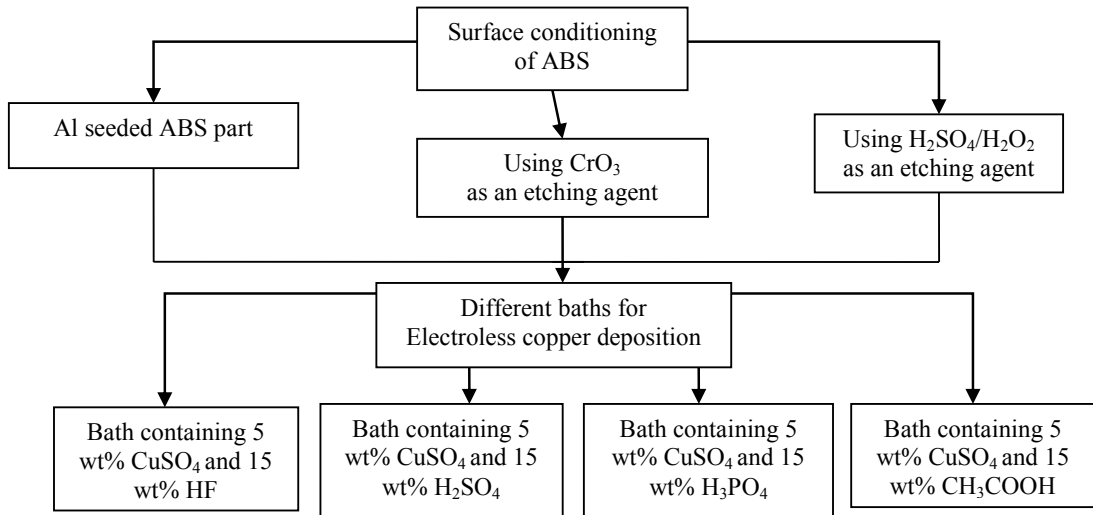
Fig. 1 Different routes for metallization of ABS plastic

3. Result

Table 1 presents the average resistance ($\bar{R}$) values together with standard deviation (σ) for each specimen after electroless copper deposition of samples prepared by route 1, in four different baths at room temperature for 1 hr, 24 hr and 48 hr deposition time. It is observed that as the deposition time increases conductivity of part improves. Best conductivity is observed in HF whereas specimen dipped in CH_3COOH has shown poor conductivity in comparison with other acidic baths. This is further established by the standard deviation value. A low standard deviation indicates that the resistance value measured at various points tend to be very close to the average resistance.

Table 1: Electrical performance of samples prepared from route 1 after electroless Cu deposition from different acidic baths.

Deposition time (Hour(hr))	Acidic bath							
	HF		H_2SO4		H_3PO_4		CH_3COOH	
	$\bar{R}$ (MΩ)	σ	$\bar{R}$ (MΩ)	σ	$\bar{R}$ (MΩ)	σ	$\bar{R}$ (MΩ)	σ
1	2.64	0.42	>	>	>	>	-	-
24	1.39	0.43	1.36	0.14	1.67	1.68	10.74	20.18
48	0.86	0.03	0.92	0.15	1.07	0.14	1.52	0.55
"\>" denotes readings that are beyond the maximum measuring range (100 MΩ) of the multimeter; "-"denotes there is no conductivity.								

Table 2 and Table 3 show the electrical performance of samples whose surfaces were prepared using route 2 and route 3 respectively. These readings are taken at room temperature after 1 hr, 24 hr and 48 hr of deposition time. Conductivity is not obtained at all the measured points, hence average resistance (R) and standard deviation (σ) has been calculated only for those points where resistance value is obtained. For samples prepared through route 3 except CH_3COOH bath all the acidic bath make the sample conductive. Best conductivity (minimum resistance) is obtained for the case of H_2SO_4 bath after 48hr of deposition time in both the routes (route 2 and route 3) but this value is higher for route 3 in comparison to route 2. When compared with Al-seeded samples the resistance value through these routes is very high (in MΩ compared to Ω in Al-seeded samples).

Table 2: Electrical performance of samples prepared from route 2 after electroless Cu deposition from different acidic baths.

Deposition time (Hour (hr))	Acidic bath							
	HF		H$_2$SO4		H$_3$PO$_4$		CH$_3$COOH	
	$\bar{R}$ (MΩ)	σ	$\bar{R}$ (MΩ)	σ	$\bar{R}$ (MΩ)	σ	$\bar{R}$ (MΩ)	σ
1	-	-	-	-	-	-	-	-
24	0.12	0.02	0.11	0.03	-	-	-	-
48	0.11	0.01	0.09	0.01	-	-	-	-
"-"denotes there is no conductivity.								

Table 3: Electrical performance of samples prepared from route 3 after electroless Cu deposition from different acidic baths.

Deposition time (Hour (hr))	Acidic bath							
	HF		H$_2$SO4		H$_3$PO$_4$		CH$_3$COOH	
	$\bar{R}$ (MΩ)	σ	$\bar{R}$ (MΩ)	σ	$\bar{R}$ (MΩ)	σ	$\bar{R}$ (MΩ)	σ
1	-	-	-	-	-	-	-	-
24	4.87	1.01	2.15	0.61	3.07	0.52	-	-
48	4.15	0.56	2.10	0.39	2.95	0.55	-	-
"-" denotes there is no conductivity.								

 To understand the difference in conductivity in each route and different acidic bath growth and distribution of Cu on different samples were studied using SEM (scanning electron microscope) image of all the treated parts. The EDS (energy dispersive spectrometer) of Cu deposited ABS samples were also performed. As good conductivity was obtained after 48 hr deposition time only, SEM and EDS data at this time is presented for route 1. Fig. 2 (a) and (b) shows the SEM image and EDS mapping of copper crystals observed on samples of route 1 after electroless copper deposition from HF bath at room temperature after 48 hr. Deposition of copper is evident from the microphotographs (Fig. 2). It is evident from the figure that small copper crystals are deposited over each other forming a cluster which is linked to each other. EDS mapping shows that there is more uniform distribution of copper after 48 hr of deposition time.
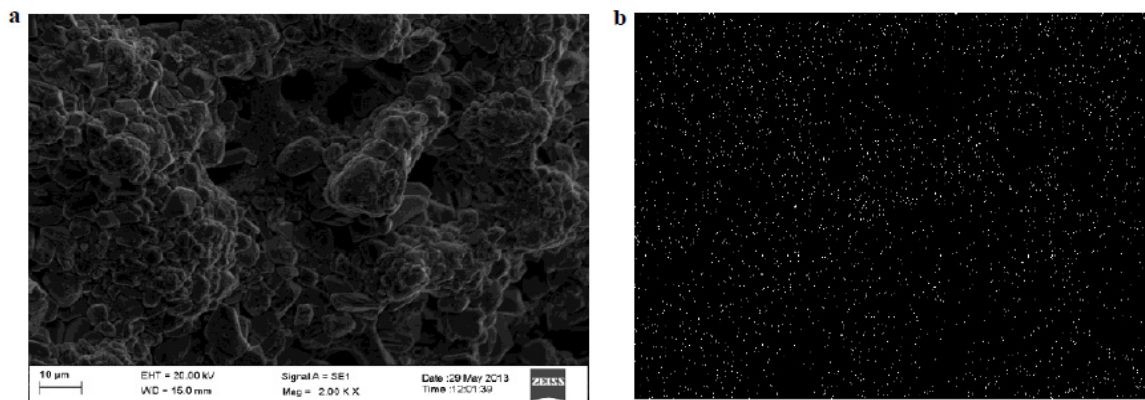

Fig.2. (a) SEM image (b) EDS mapping of copper on ABS sample whose surface were prepared through route 1 in HF bath after 48 hr.

Fig. 3 (a) and (b) presents the SEM image and EDS mapping of Cu deposition on samples of route 1 after electroless Cu deposition in H$_2$SO$_4$ bath at room temperature after 48 hr. Cu crystals are closely connected and provide smooth appearance. This is further justified by their EDS mapping indicating more Cu after 48hr of

deposition time. Fig. 4(a) and (b) shows the SEM image and EDS mapping of Cu crystals observed on samples of route 1 after electroless Cu deposition for H_3PO_4 bath at room temperature after 48 hr of deposition time. It is evident from figure that copper crystals are well allied and gives smooth appearance to the surface after 48 hr of deposition time. The Cu distribution can be further verified by EDS mapping showing more uniform distribution of Cu in sample deposited for 48hr. Fig. 5 (a) and (b) presents the SEM image along with EDS mapping of Cu crystals observed on samples of route 1 after electroless Cu deposition from CH_3COOH bath at room temperature for 48 hr of deposition time. The sample deposited for 48 hr shows smaller Cu crystals cluster together throughout the region. The EDS mapping also shows that the Cu is more uniformly dispersed in sample deposited for 48 hr.

For the route 2 and route 3 it was observed that conductivity is poorer when compared with route 1 which can be clearly verified by comparing Table 1 with Table 2 and Table 3. Further the resistance values have not been achieved at all points. Since the conductivity improves with the deposition time good conductivity is obtained only after 48 hr of deposition time. Therefore the results are presented for maximum deposition time carried out in present study for these undertaken routes.
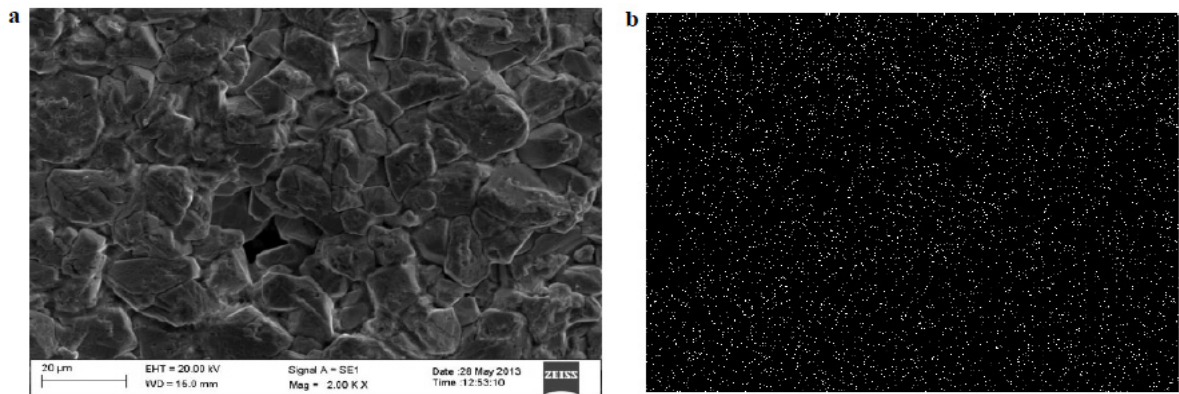

Fig.3 (a) SEM image (b) EDS mapping of Cu on the sample whose surface is prepared through route 1 for H_2SO_4 bath after 48 hr.
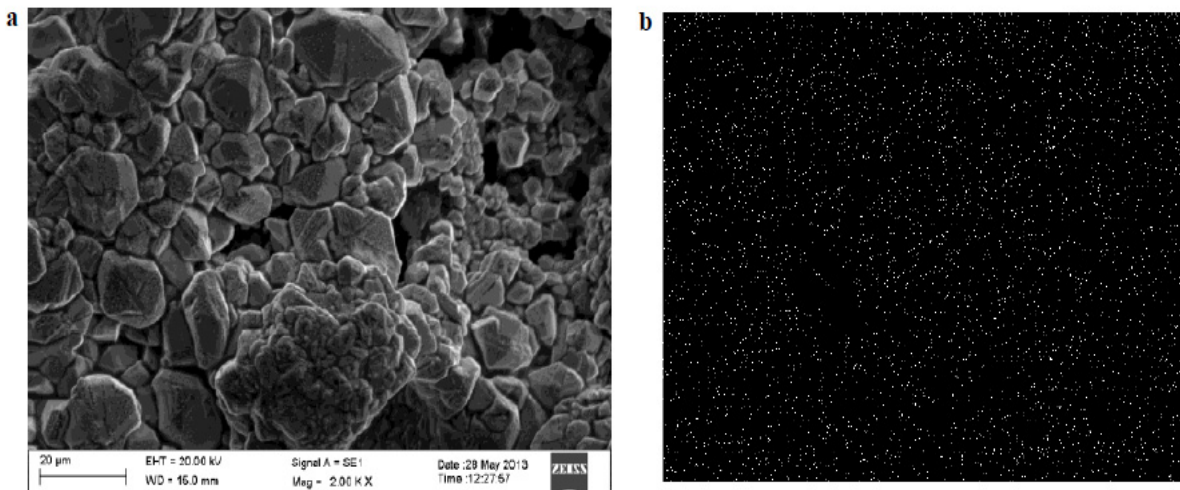

Fig.4 (a) SEM image (b) EDS mapping of Cu deposition for the sample whose surface is prepared from route for H_2SO_4 bath after 48 hr.
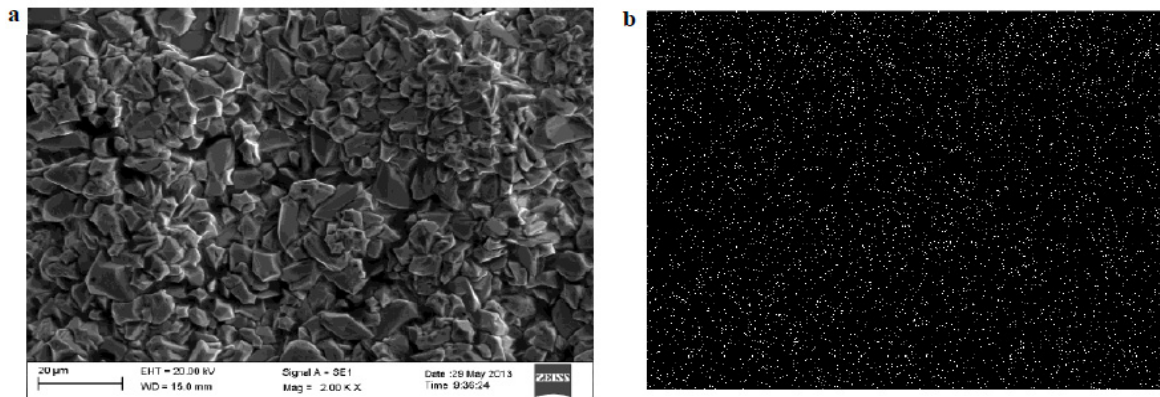
Fig.5 **(a)** SEM image (b) EDS mapping of Cu deposition on the sample whose surface is prepared from route 1 for CH₃COOH bath after 48 hr.

SEM and EDS image for the sample of route 2 after Cu deposition is presented. In HF (Fig.6) after 48 hr of deposition, Cu deposition is not clearly justified in SEM, however few crystals appears in EDS mapping with random distribution. Fig.7 (a) and (b) shows large Cu crystals having localised distribution in the sample.
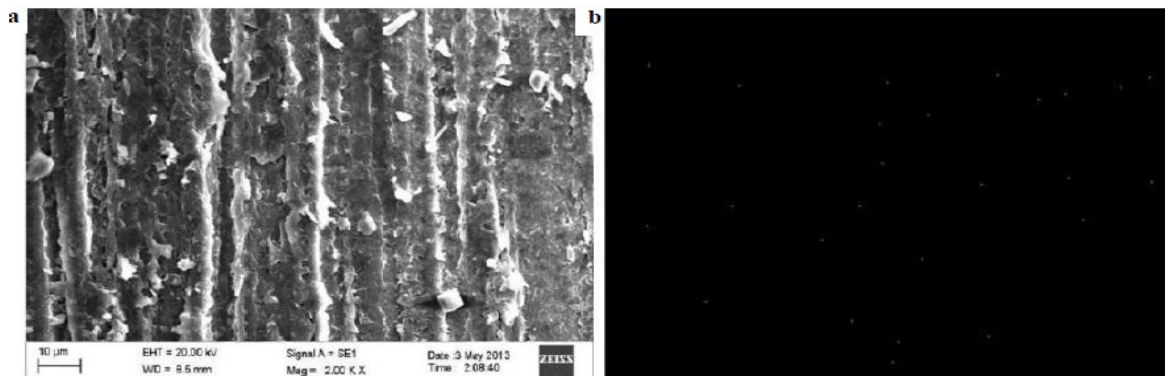

Fig. 6 (a) SEM image (b) EDS mapping of Cu deposition on sample whose surface is prepared through route 2 in HF bath after 48 hr.
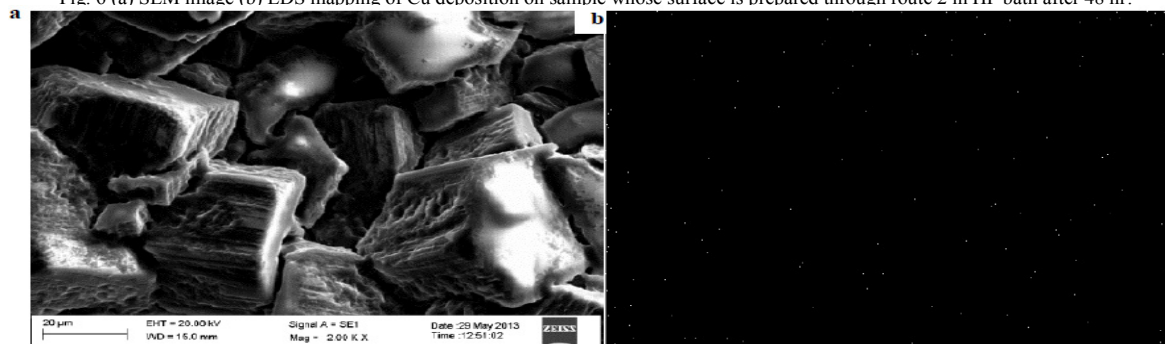

Fig.7 **(a)** SEM image (b) EDS image of Cu deposition on sample whose surface is prepared through route 2 in H₂SO₄ bath after 48 hr.

Fig. 8 show images of the sample deposited in H_3PO_4 bath for 48 hr of deposition time. The image has very poor appearance. The EDS mapping justify the same. Fig. 9 (a) and (b) shows the SEM and EDS image of Cu deposition on samples of route 2 after electroless Cu deposition. The SEM image is very poor with no Cu crystal at all. The EDS mapping of the sample is also shown.
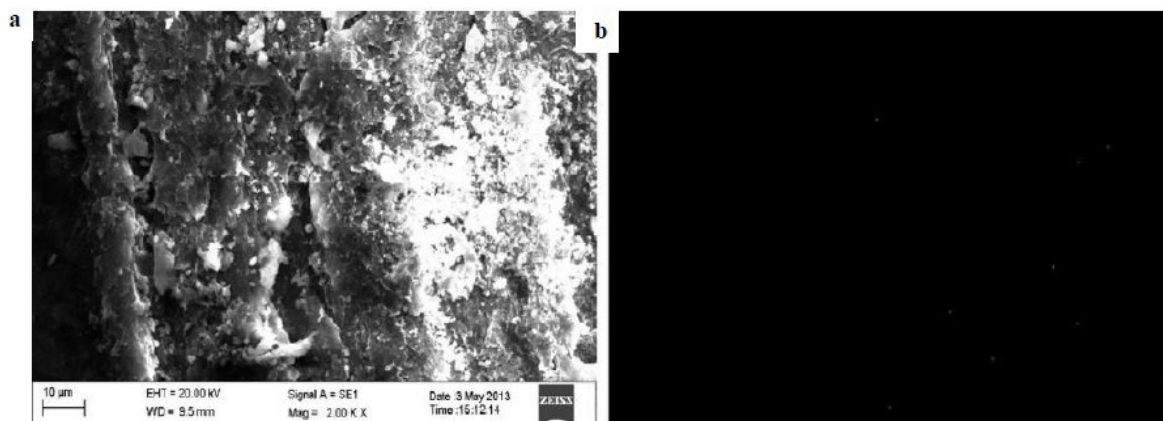

Fig.8 (a) SEM image (b) EDS mapping of Cu deposited on sample whose surface is prepared through route 2 in H_3PO_4 bath after 48 hr.
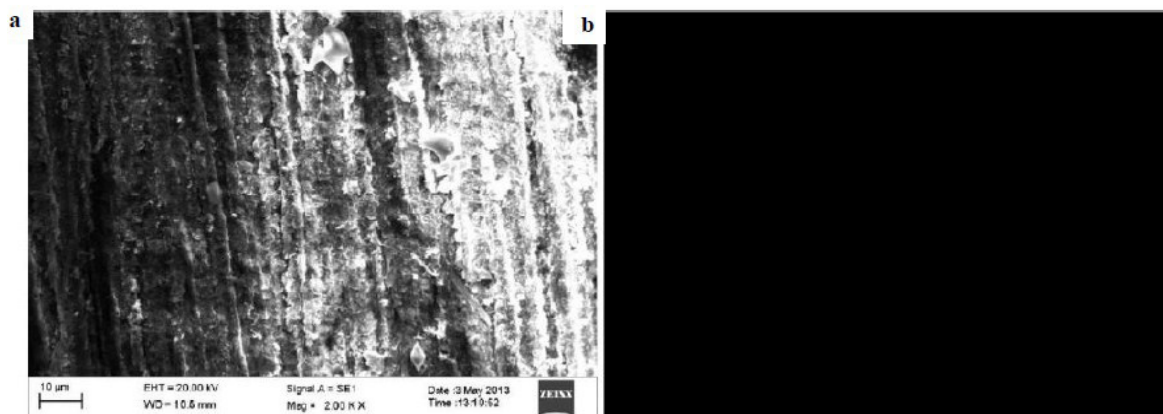

Fig.9 (a) SEM image (b) EDS mapping of Cu deposition on sample whose surface is prepared through route 2 in CH_3COOH bath after 48 hr.

Also as good conductivity was obtained after 48 hr deposition time SEM and EDS data at this time is presented for route 3. Fig.10 a. and 10.b. corresponds to the SEM and EDS images obtained after depositing the samples of route 3 in HF bath. Small copper particles dispersed in the entire part can be seen (Fig.10.a). EDS mapping (Fig.10.b) shows copper deposition only at some areas of the sample which can be verified from Table 3. Fig. 11.a and 11. b presents result for the sample deposited in H_2SO_4 bath after 48 hr of deposition time. SEM image is presented having charged white areas where Cu deposition is expected (Fig.11.a). Figure shows deposition of Cu in whole part which is not dense. Fig. 12.a and b depicts SEM and EDS mapping for the sample of route 3 deposited in H_3PO_4 bath. Fig. 12.a shows SEM image of sample with few Cu particles dispersed in the part. EDS mapping as in Fig.12.b also shows few Cu crystals with localised distribution. Finally the sample deposited in CH_3COOH bath is presented in Fig. 13. a and 13.b. SEM image has very poor appearance with no clear sign of Cu deposition. EDS mapping presented also shows no copper deposition, this also corresponds to no resistance values as indicated in Table 3.
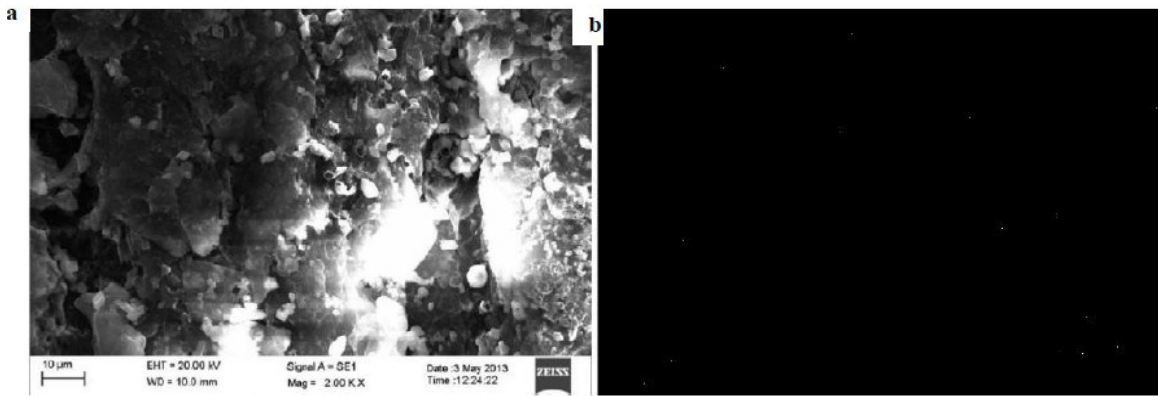
Fig. 10 **(a)** SEM image (b) EDS mapping of Cu deposition on sample whose surface is prepared through route 3 in HF bath after 48 hr.
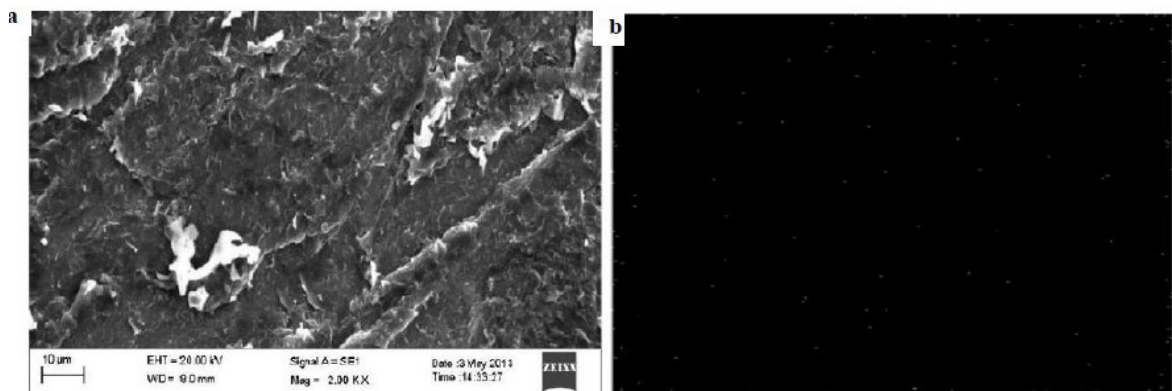

Fig.11 (a) SEM image (b) EDS mapping of Cu deposition on sample whose surface is prepared through route 3 in H_2SO_4 bath after 48 hr.
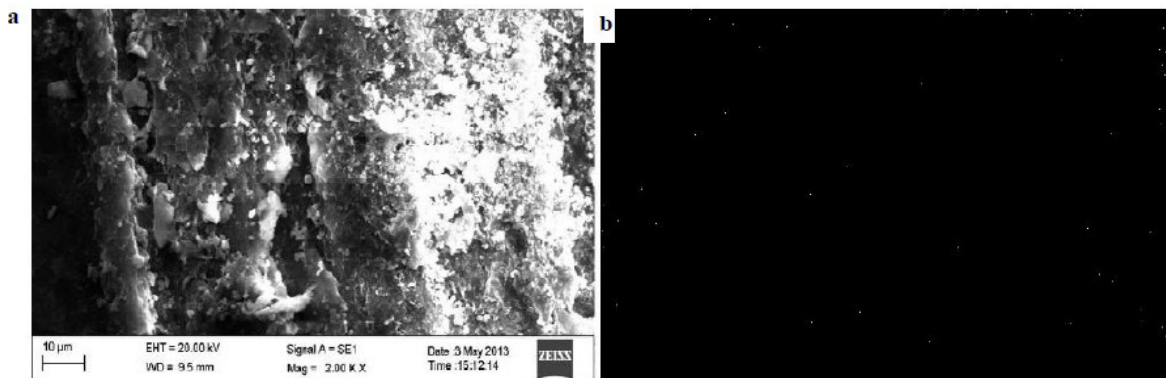

Fig.12 (a) SEM image (b) EDS mapping of Cu deposition on sample whose surface is prepared through route 3 in H_3PO_4 bath after 48 hr.
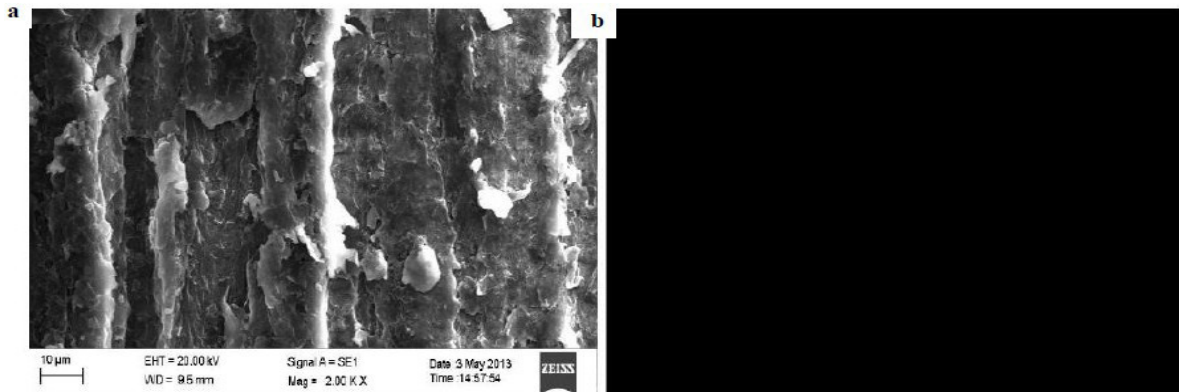
Fig.13 (a) SEM image (b) EDS mapping of Cu deposition on sample whose surface is prepared through route 3 in CH_3COOH bath after 48 hr.

The conductivity value and copper distribution is found superior in Al-seeded parts prepared from route 1. The reason is uniform distribution of aluminium throughout the part by the application of Al- paste. As the Cu gets deposited over the aluminium seeds exposed during etching and its growth increases with the deposition time thus uniform Cu deposition is obtained after 48 hr of deposition time. For the route 2 and route 3 the distribution obtained is poorer when compared with route 1. As the Cu gets deposited only at the site where catalyst palladium (Pd) and/or tin (Sn) colloid has been deposited by removing butadiene from ABS part during etching stage of surface preparation. The etching may not be able to create cavities throughout the part which leads to non-uniform or localized deposition of Cu.

3.4 Adhesion Evaluation for Al coated ABS parts

The adhesion performance was assessed according to the scale defined by ASTM D 3359-02. All the ABS test samples after test shows no flaking and yield results in a scale 4 or 5, meaning excellent adhesion strength as only less than 5% of the deposited materials could be removed by the tape. This is shown in table 4.

Table: 4 Adhesion performance assessments of Cu layers on Al-seeded ABS parts.

Deposition condition	Bath			
	HF	H_2SO4	H_3PO_4	CH_3COOH
Scale	5	5	5	4

4. Conclusion

Metallization of ABS part has been studied on flat surface. The parts are fabricated on a fused deposition modelling machine using layer by layer deposition procedure. Three different routes were employed for preparing the ABS plastics surface for achieving the metallization on them. The different routes applied are Al paste coated ABS parts, ABS parts prepared using chromic acid for etching and ABS parts prepared using H_2SO_4/H_2O_2 for etching. After surface preparation using these routes, Cu is deposited electrolessly using four different acidic baths. The acidic baths used are 5 wt% CuSO4 with 15 wt% of individual HF, H_2SO_4, H_3PO_4 and CH_3COOH acids. Cu deposition in different acidic baths for different routes was presented with their electrical performance measurement, SEM image and EDS analysis in this study. Deposition of copper is achieved through all the three routes. Varying amount of conductivity was obtained for different routes and different acidic bath. In route 1 resistance value was obtained in all the measured points but in route 2 and route 3 resistance values was not obtained in all the measured points. Al-

seeded samples (route 1) gives the best performance when compared with route 2 and 3 both in terms of electrical conductivity and Cu deposition. In route 1 the best conductivity and better Cu deposition is achieved in HF followed by H_2SO_4, H_3PO_4 and then by CH_3COOH bath. The conductivity for the sample dipped in CH_3COOH bath in route 1 shows higher average resistance even after prolonged deposition time when compared with rest of the acidic bath. Among route 2 and route 3 the samples prepared using route 2 shows better performance. For route 2, conductivity was obtained only HF and H_2SO_4 whereas no conductivity is achieved for remaining two baths. In route 3 except for CH_3COOH bath conductivity was obtained for all other baths. Based on the current results development of simpler and more cost-efficient Cu plating bath to further optimize deposition conditions (concentration of acids, deposition temperature and deposition time) is desired. Besides these, the lack of uniformity of Cu layers deposited under current conditions may become another focus of our future efforts.

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