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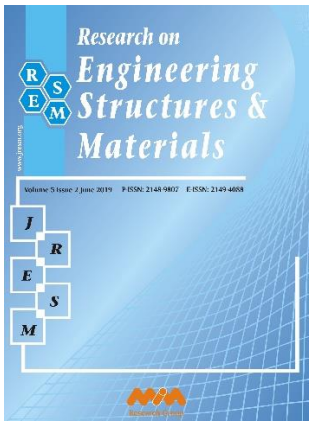

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Research Article

The electroless metal plating process over ABS plastic by using ionic liquids

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Abstract

Electroless metal plating is a coating technique which relies on reduction of metal ions with an autocatalytic chemical reduction process. Ionic liquids are defined as compounds that are sensitive to the environment due to their low pressure that can be negligible, their high heat resistance, and a higher ionic conductivity, to be electrochemically rich, to have wide open liquid range, to have a range of high polar solubility. In this study, the effects of ionic liquids were investigated in the electroless metal plating process over ABS plastic. For this purpose electroless baths were prepared by using two different types of ionic liquids (EMIC & DCA) for copper and nickel plating. Experiments were carried out with 120-500 grit sandpaper and at 80°C plating bath temperature for 30-120 minutes of deposition time and at different pH values as 8-9. X-Ray XDL-B System, X-ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) were used for the characterization and the amount of deposits. According to the experimental and analytical results, the metal plating on ABS plastic was succeeded with two different ionic liquid additions. On the contrary of the traditional processes with chromic and sulphuric acids, the etching and the plating processes were performed with environmentally friendly chemicals. In this way, both it will be provided a significant benefit to public health, and it will be brought innovation to the metal plating industry with the environmentally friendly ionic liquid catalyst.

1. Introduction

Acrylonitrile butadiene styrene (ABS) is a thermoplastic polymer made by polymerizing styrene and acrylonitrile in the presence of polybutadiene. 15 to 35% acrylonitrile, 5 to 30% butadiene and 40 to 60% styrene are the composition of ABS. Plating of plastic materials is providing a long term use to the materials. Especially ABS plastic is very suitable to this work. ABS plastic is an important chemical reagent an engineering material with high thermal stability, high mechanical strength and high resistance [1]. Ionic liquids (ILs) are electrically conductive liquids composed merely of ions. Ionic liquids at room temperature (RTIL) are the salts having very low gas pressure or close to zero. So missing amount of ionic liquids are little both evaporation or using as catalyst or solvent at high temperature. They have a wide liquid range and are very stable at high temperature. Two types of room temperature ionic liquids are EMIC, 1-ethyl-3-methyl imidazolium chloride ($C_6H_{11}N_2Cl$) and DCA, 1-ethyl 3-methylimidazolium dicyanamide ($C_8H_{11}N_5$). For instance 1-ethyl 3-methyl imidazolium trifloromethylsufonit has a liquid range of 471^{0}C with melting point -15^{0}C and deformation temperature 455^{0}C [2]. The characteristic make RTILs applicative for reactions [3]. At the research conducted with RTIL has positive effect on the

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plating performance. In the study, while aluminum did not coat in the electrolitic aqueous solution, at the room temperature the plating is performed with ionic liquid [4]. At the other study, 1-ethyl 3- methyl imidazolium dicyanamide is used for nickel plating and this ionic liquid is approved for metal plating electrode [5]. Electroless plating is the main part of the electroplating process. In this part plastic material has a conductive behavior. It provides homogeneous distribution, durability and preferred thickness. It is nonmagnetic and because of the higher stretching ratio there is no break into pieces under distortion or elongation. The difference of the electroless plating from the electroplating is about energy. Electroless plating does not need electrical energy. So the plating film appears with uniform structure. This method is widely used because of superior features such as providing uniform surface film and resistance of abrasion and corrosion [6, 7]. At related studies, catalysts and activation solutions for the electroless bath are mainly consisting of colloidal suspension of palladium metal and tin ions. The function of the bath is precipitating colloidal palladium (palladium-tin) on the porous ABS surface. Palladium is used as catalyst and the nickel and copper electroless precipitation reaction is begun. Two metals (nickel and copper) are most widely used metals at the decorative plating of the plastics [8-10]. Electroless metal plating technique begins to apply by using catalyst. Many researchers have attempted to deposit metals by using electroless plating technique. For example, electroless nickel and copper plating was obtained over carbon nanotubes and graphite [8, 11]. Fukuhara and coworkers implemented electroless plating process by preparing copper surface catalysts [12]. At another study, Song and friends coated silver by using nickel phosphite catalyst [13]. The surface characterization of the activated ABS plastic was obtained by using Scanning Electron Microscopy (SEM) and Ni coating was also characterized by X-Ray diffraction (XRD) [1].

The main goal of this study is to search the effects of ionic liquids in the electroless metal plating process over ABS plastic. For this purpose electroless baths were prepared by using environmentally friendly chemicals (EMIC & DCA) for copper and nickel plating processes on ABS plastic. On the contrary of the traditional processes with chromic and sulphuric acids, the etching and the plating processes were performed with environmentally friendly chemicals.

2. Material and Method

The electroless copper and nickel plating on ABS plastic material experiments were performed in fume hood at atmospheric pressure and at different plating temperatures. The experiments consist of four steps: preparing the chemicals and materials, etching, plating and the analysis of samples. The investigated parameters were sandpaper size, plating time, plating temperature and effects of ionic liquid types (RTIL).

2.1 Electroless metal plating procedure

1. Initially, 20 mm x 35 mm x 1.5 mm ABS plastic samples are grounded with the 120-320-500 grit sandpaper size.
2. Then the samples are dried in a 65^0C oven for 4 to 5 h.
3. And then the samples are taken from oven and layered in a 10g/L NaOH alcoholic solution.
4. After then, this NaOH alcoholic solution is placed in a water bath at 35-40 ^{0}C for 30 min.
5. Then, the samples are put in a mixture. The composition and the amounts of the chemicals are given in Table 1.

Table 1. Chemicals and amounts of aqueous solution [14]

Chemical	Density (g/ cm3)	Mass (g)	Volume (mL/L)
HNO_3	1.51	378.2 - 453.9	250 - 300
H_2O_2	1.45	13.6 – 20.41	9.38 – 14.08
NH_4F	1.009	2 - 4	1.98 – 3.96

6. Prepared mixture is replaced in an ultrasonic bath for 30 min [14].
7. The resultant samples are washed with deionized water.
8. For the material pretreatment solution of $CuCl_2$ and ionic liquid are weighed with the molar ratio 2:1 and the specimen is immersed in the ionic solution and is left for a week.
9. The specimen is placed at 80^0C plating bath containing the plating solution prepared with the chemicals at Table 2 and Table 3 for Copper and Nickel plating, respectively.

Table 2. Contents of the plating bath for Copper [14]

Chemical	Formula	Concentration (g/L)
Copper Sulfate	$CuSO_4 \cdot 5H_2O$	12-15
EDTA-2Na	$C_{10}H_{14}N_2Na_2O_8 \cdot 2H_2O$	40-45
2,2-Dipyridyl	$C_{10}H_8N_2$	0.04-0.05
Formalin	CH_2O	20-25

Table 3. Contents of the plating bath for Nickel [15]

Chemical	Formula	Concentration (g/L)
Nickel Chloride	$NiCl_2 \cdot 6H_2O$	20
Sodium Hypophosphate	$NaH_2N_2PO_3 \cdot H_2O$	20
Sodium Citrate	$Na_3C_6H_5O_7 \cdot H_2O$	45
Ammonium Chloride	NaH_4Cl	30

10. NaOH is added slowly to the plating bath to adjust the pH. For Copper plating, pH is adjusted at 11-12 and for Nickel plating, this pH value is adjusted at 8-9.
11. At the beginning of the process (10 min to 20 min), no bubbles are seen. But after 50 min to 60 min, a lot of bubbles are obtained according to the reaction.
12. Then samples are purified with deionized water and then the metal plated sample is dried at 45 ^{0}C in an oven.
13. At the end of the experiments, some characterization techniques (XRD, SEM-EDX) and the plating amount of the final samples (X-Ray XDL-B System) are obtained.

3. Results and Discussions

The results of the analyses were evaluated and the effects of plating time and sand paper size on the amount of deposits were investigated. According to the obtained results amount of deposits versus plating time and sand paper size graphs were plotted (Figures 1-4).

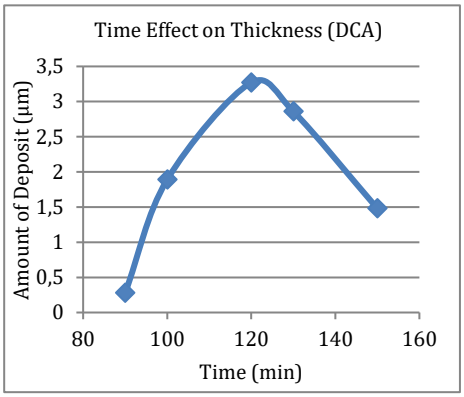

Fig. 1 Time Effect on Amount of Deposit for DCA and 120 grit size Sandpaper.

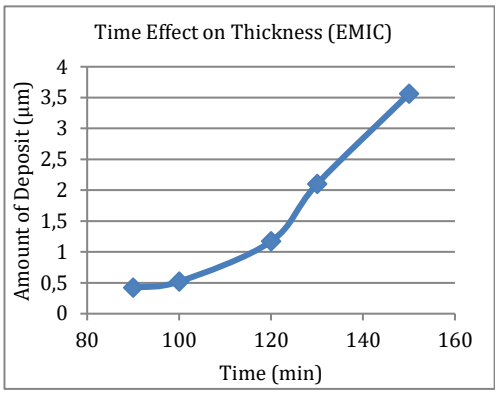

Fig. 2 Time Effect on Amount of Deposit for EMIC and 120 grit size Sandpaper.

According to the results from X-Ray analysis of DCA, stable increase could not be obtained. When plating time increases, firstly the amount of deposit increases from 0.28 to 3.27; however, after 120 min, it decreases from 3.27 to 1.48. But the amount of deposit decreased with increasing plating time of the substrate at constant temperature (80^0C) for DCA. The maximum amount of the deposit is found as 3.27 µm for 120 min by using DCA (Figure 1). The amount of deposit increased with increasing plating time of the substrate at constant temperature (80^0C) by using EMIC (Figure 2). The maximum amount of the deposit was about 3.67 µm for 150 min for EMIC. As a result, it is concluded that EMIC is more suitable ionic liquid then DCA type ionic liquid as catalyst for metal plating on ABS plastic.

Results obtained from X-Ray analysis are evaluated and thickness versus sandpaper size graphs are plotted (Figures 3, 4). It is shown from Figure 4 that, the thickness of the copper film increases when sandpaper size increases by using EMIC. The maximum amount of the deposit was about 3.92 µm for 500 grit of sand paper. Although sandpaper size increases, increase in the thickness of the copper film could not be obtained by using DCA (Figure 3). The reason can be stated that stable increase could not be obtained according to the ingredients of plating bath solution that includes nitric acid, hydrogen peroxide and ammonium fluoride.

After X-ray measurements, the XRD and SEM analyses were performed for the best plated specimens. Figures 5 and 6 were obtained for Cu and Ni plating process, respectively. It can be said from these figures that, there are only Cu (Fig. 5) and Ni (Fig.6) peaks and no additional elements beside them. According to the literature, the results of XRD analysis were obtained as expected [14, 1]. Diffraction peaks were obtained at approximately 45, 50, and 75 degree for Copper and at 20, 35 and 45 degree for Nickel.

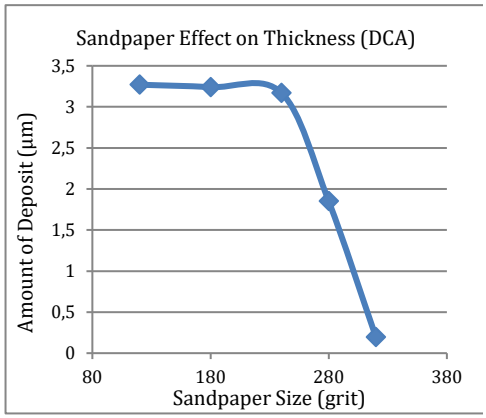

Fig. 3 Amount of Deposit versus Sandpaper Size for DCA and 120 minutes.

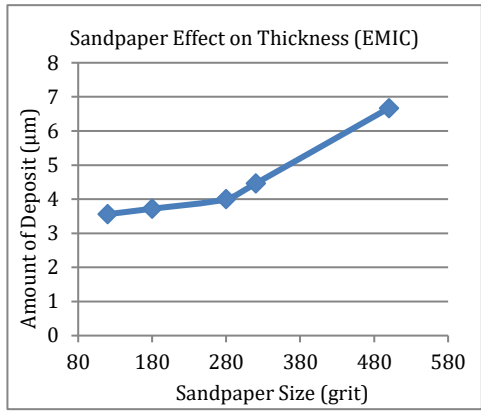

Fig. 4 Amount of Deposit versus Sandpaper Size for EMIC and 120 minutes.

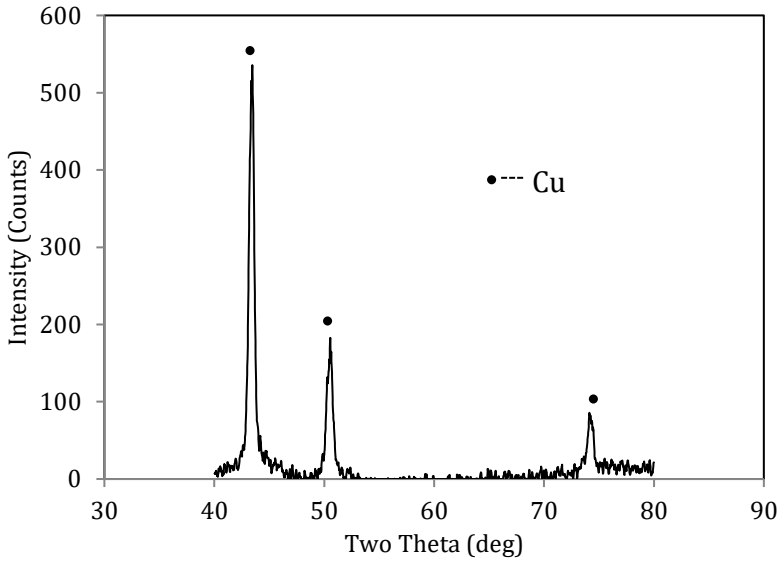

Fig. 5 XRD Analysis for Copper plating with EMIC.

A SEM analysis was obtained for the surface of the Cu and Ni-plated specimens using RTIL. Morphology of deposits are shown in Figures 7 and 8, so materials were deposited on the surface of the substrate and these proves that electroless plating took place. The elemental mapping result using SEM-EDS also indicated that the plating film consisted of Copper and Nickel only, and the metal was homogeneously distributed on the surface of the film.

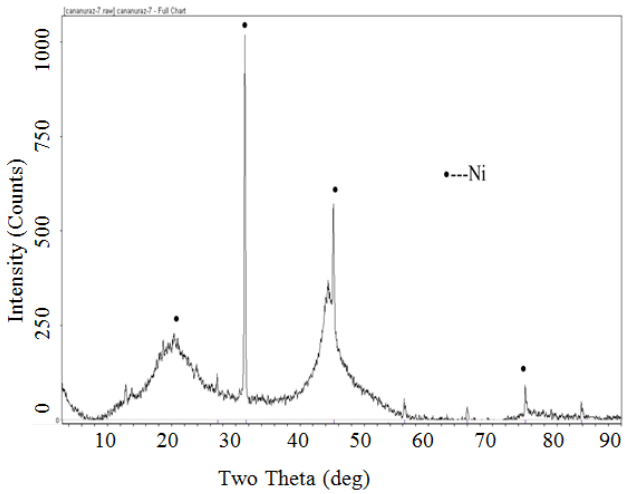

Fig. 6 XRD Analysis for Nickel plating with EMIC.

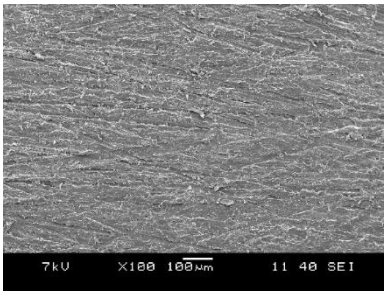

Fig. 7 SEM Analysis of copper plated sample which obtained by using EMIC with 120 grit size sandpaper at 60 minutes.

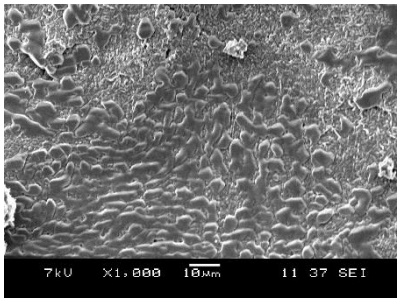

Fig. 8 SEM Analysis of nickel plated sample which obtained by using EMIC with 120 grit size sandpaper at 60 minutes.

4. Conclusion

The effects of ionic liquids were investigated in the electroless metal plating process over ABS plastic in this experimental study. For this purpose two different electroless baths were prepared by using environmentally friendly chemicals (EMIC & DCA) for copper and nickel plating processes on ABS plastic. On the contrary of the traditional processes with chromic and sulphuric acids, the etching and the plating processes were performed with environmentally friendly chemicals. The investigated parameters were the thickness of plate, plating time, sandpaper size effect on the plating amount in the electroless metal plating process over ABS plastic. From the results of this experimental study, the following conclusions can be drawn:

- It is succeeded in demonstrating the electroless plating of dense, smooth, and pure copper and nickel from a RTIL, EMIC.

- The maximum amount of the deposit was achieved about 3.67 μm for 150 min for EMIC.
- XRD results indicated that the deposited films were copper and nickel. The plating film consisted of Copper and Nickel only, and the metals were plated over the surface of the ABS plastic homogeneously.
- The elemental mapping results of SEM-EDS indicated that the plating film consisted of Copper and Nickel only, and the metals were homogeneously distributed on the surface of the film.
- It was concluded that, EMIC that was one of the room temperature ionic liquid used in this experimental study was more suitable ionic liquid then DCA type ionic liquid as catalyst for electroless metal plating on ABS plastic.
- On the contrary of the traditional processes with chromic and sulphuric acids, the etching and the plating processes were performed with environmentally friendly chemicals. In this way, both it will be provided a significant benefit to public health, and it will be brought innovation to the metal plating industry with the environmentally friendly ionic liquid catalyst.

Acknowledgements

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