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Influence of Concentration of Copper Electrolyte, Voltage, and Time of Electroforming on Conductive Acrylonitrile Butadiene Styrene Parts on Deposition Rate and Microstructure

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P A P E R   I N F O

A B S T R A C T

This article presents a study on influence of Copper Concentration Electrolyte (CCE) and voltage on deposition rate of electroformed Conductive Acrylonitrile Butadiene Styrene (CABS) produced through Fused Deposition Modeling. Additive manufacturing is widely recognized as a rapid production technology. In this research, copper electroforming was selected as subsequent treatment following additive manufacturing. The novelty lies in implementation of pre-treatment process involving electroforming. The pre-treatment process employs carbon conductive paint to render the ABS part conductive. The copper electroforming process involves the use of variable parameters such as electrolyte content of (100, 150, and 200 gram $CuSO_4$ and 50 ml H_2SO_4) in 1 liter H_2O, voltage (1, 2, and 3 Volts), and time (2, 4, 6 and 8 hours). The variables under observation include the copper deposition rate and the microstructure. The analysis of research based on Kruskal-Wallis test. The difference in electrolyte copper concentration and the coating time does not provide significant differences, while the duration of electroforming affects the thickness of the copper deposit. Furthermore, the concentration of copper electrolyte influences the solution's conductivity, at high concentrations leading to improve conductivity and consequently facilitating a fast deposition rate. The difference in voltage has a significant effect on the deposition rate and microstructure.

Graphical Abstract
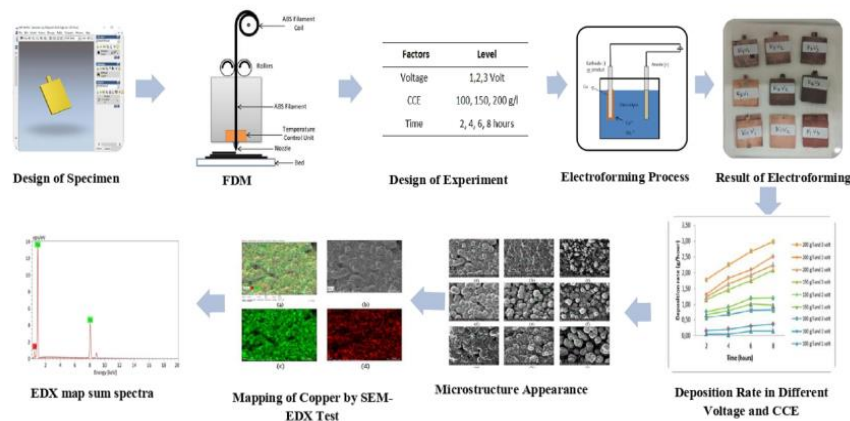
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1. INTRODUCTION

Increasing industrial demand for specialty products with low batch sizes is needed these days. As is the case with batik stamp canting with patterns that often change. Fused Deposition Modeling (FDM) is a technology that can meet the demand for low-cost batch products (1). The traditional FDM process encompasses several key stages. Initially, a virtual or CAD representation of the physical object is crafted. This CAD model is then transformed into the STL (Standard Triangle Language) format, where the object's surface is approximated using triangles. Subsequently, the object in STL format is divided into horizontal layers, determined by the chosen layer thickness. In the third phase, a toolpath is devised for each layer, specifying G and M code instructions for the machine to produce the desired object. Finally, the post-production phase involves the elimination of support materials (2).

Metal coatings are intended service life of functional parts by increasing their resistance to wear, abrasion, heat, corrosion, hardness or crack density (3). Metal coating on FDM product has been carried out to improve properties and wider use. Although electroforming is an old technique, it can be adapted for modern manufacturing purposes. The electroforming technique is specifically used for the manufacture of metal parts. Electroforming's capacity to produce intricate components with precise tolerances and cost-effectiveness has led to its widespread adoption in both traditional/macro manufacturing and emerging micro-manufacturing domains. This versatile technique finds application in various areas such as tooling, mold-making, the fabrication of micro-electromechanical systems (MEMS), and the innovative LIGA process, which involves a combination of lithography, electroforming, and plastic molding. Additionally, electroforming is utilized in the fields of micro-optics and medicine (4).

Good thermal and electrical conductivity makes copper one of most useful metal (5). This study develops materials for stamp canting batik which are usually made of copper metal. For this purpose of increase productivity, in this development the canting stamp batik is made using conductive ABS material which is electroformed by copper. Copper is a widely used metal for the process of plating. Electroplated copper finds significant applications in various areas, such as plating on plastics, printed wiring boards, zinc die castings, automotive bumpers, rotogravure rolls, electro-refining, and electroforming (6). Electroforming of FDM products can increase the tensile strength by 12 to 25 times (7). Research on copper plating on PLA to make gear shapes has been carried out by Matsuzaki et al. (8). Meanwhile, Phull et al. (9) examined the optimum conditions for the electroforming treatment using ABS as the coated

material. The optimum conditions for coating ABS with copper are 2 Volts, 200 g/l $CuSO_4$ and H_2SO_4, and duration of 7 hours. The difference in results was found to be that the optimum voltage was 9 Volts when using electrolyte from $CuSO_4$ and KCl (10).

The process stages in ABS electroforming are soak cleaning, etching, sensitization, activation, acceleration, metallization, and metal plating (11). The process of soak cleaning until metallization is a pre-treatment process. In this study the pretreatment was carried out using carbon conductive paint to coat ABS to make it conductive. The use of this CCP is more practical because the process is brushed on the ABS surface.

This study aims to investigate the influence of voltage and CCE on the deposition rate and surface morphologies of plated materials. To analyze the influence of CCE and voltage on the deposition rate, ANOVA was employed. What distinguishes this research from previous studies is the innovative use of conductive ABS and a pretreatment process involving carbon conductive paint. The data gathered in this study will play a pivotal role in the development of batik stamp canting made from conductive ABS, followed by a copper electroforming process. The deposition rate is crucial for determining the speed of producing a copper layer on conductive ABS, which will be instrumental in future stamp canting production. Additionally, the appearance of the specimens will be assessed to ensure the surface smoothness required for the stamp canting's testing process.

1. 1. Fused Deposition Modeling
Fused Deposition Modeling (FDM) is a popular form of Additive Manufacturing technology that works by heating and extruding thermoplastic material in a controlled manner to build a three-dimensional object. It involves melting a filament of thermoplastic material and laying down successive layers of material to build the final product. FDM is widely used due to its affordability, accessibility and its ability to produce objects with good mechanical properties. The process is relatively slow compared to other 3D printing methods, but it is well-suited for creating low-cost prototypes, complex geometries, and final products made of thermoplastic materials (12).

Figure 1 shows schematic of FDM. In this method, plastic filament is directed into a heating block where it is heated to a semimolten state. The molten material can be printed onto an adjustable stage to form a layer of the desired object. The stage is adjusted (lowered) and another semimolten layer is printed (13).

Acrylonitrile Butadiene Styrene (ABS) is a thermoplastic polymer extensively utilized in the production of a wide range of items, including toys, automotive parts, electronic housings, lego bricks (11), and air craft wing in industrial robot (2). ABS is a
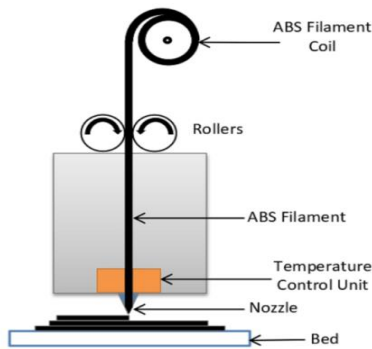
Figure 1. Schematic of Fused Deposition Modeling [13]

commercial material with relatively and moderate glass transition temperature (110°C) (14). It is renowned for its remarkable qualities, such as high impact resistance, toughness, and heat resistance. Moreover, ABS exhibits great versatility in molding, making it a preferred choice for manufacturing products with specific shapes and sizes. This engineering plastic contains a uniformly distributed butadiene part in the acrylonitrile-styrene matrix, resulting in excellent toughness, dimensional stability, ease of processing, chemical resistance, and cost-effectiveness.

Applying metal plating on ABS can enhance its strength and structural integrity, as well as improve its durability and thermal resistance, thereby imparting metallic properties to the ABS material (11).

Conductive polymers have been produced for various purposes, including for the manufacture of electrical components such as microchips and semiconductors. Many of them are conductive polymer composites used as solar panels that convert heat energy into electrical energy to generate electricity (15). Guo et al. (16) employed graphene nano-tubes to enhance the thermal and electrical conductivity of polymer nano-composites. Addition of graphene resulted in a remarkable increase in thermal conductivity, reaching up to 5000 W/m.K, and electrical conductivity, reaching up to 108 S/m. In another study aiming to enhance electrical conductivity (17), a polypropylene based polymer served as the matrix, while carbon black was used as the conductive filler. Despite the benefits of using graphene and carbon nanotubes as nanofillers in conductive composites for 3D-printing, their high cost remains a significant challenge.

1. 2. Electroforming   Basically, electroforming is a special technique developed from electroplating. The difference is the purpose of the coating. Electroplating is usually intended to protect and improve the decorative appearance of the surface and protect against corrosion. Meanwhile, for electroforming, the form of metal

deposited results is used as its function. Therefore it needs a thick layer [4]. Electroforming is a metal forming process that involves depositing metal onto a conductive substrate to form a solid, uniform, and reproducible object. The process typically involves coating a non-conductive substrate (e.g., a plastic or wax mold) with a thin layer of metal and then using electrical current to deposit additional metal onto the substrate, building up a thick layer of metal. The result is a metal object that is an exact replica of the original substrate. Elecrodeposition of Ni at various temperatures of electrolytes was performed by Syamsuir et al. (18).

Electroforming is commonly used in industries such as aerospace, medical devices, and electronics to create complex and precise metal parts. In this study, the copper electroforming process aims to improve heat resistance properties which will be applied to objects related to heat such as canting stamp batik, as a tool to transfer wax from the pan to the cloth with a wax temperature of 115-135°C.

The electroforming circuit is the same as the electroplating circuit consisting of a DC power supply, bath, copper electrolyte, cable, anode and cathode (or product) as shown in Figure 2.

Pre-threatment   ABS plastic is a non-conducting material. In order to be electroformed, the condition of the material must be able to conduct electricity. Therefore, before copper coating is performed, the ABS surface is made conductive using carbon conductive paint (19). Carbon conductive paint, also known as conductive carbon paint, is a type of coating that is made up of conductive carbon particles mixed with a binding agent. This paint is used to create electrical circuits on a variety of surfaces, including paper, plastic, glass, and metal. The conductive carbon particles in the paint allow it to conduct electricity, making it ideal for creating circuits and other electrical connections. The paint can be applied using a brush, roller, or spray gun, and it dries quickly to create a smooth, conductive surface. This strategy of conductive paint is a simple technique as only a single step is required before electroplating/ electroforming (20).
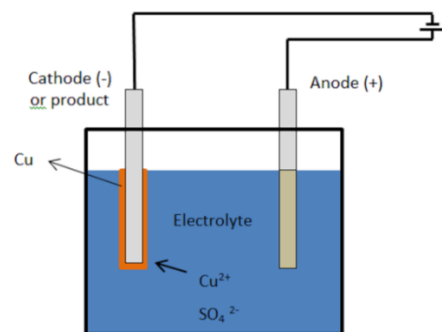

Figure 2. Copper Electroplating Scheme

Carbon conductive paint is commonly used in electronics manufacturing, where it is used to create printed circuit boards, flexible circuits, and other electronic components. It is also used in other industries, such as automotive manufacturing and aerospace, where it can be used to create conductive coatings for antennas, sensors, and other components. One of the benefits of carbon conductive paint is its versatility. It can be used on a variety of surfaces, and it can be easily applied using standard painting techniques. Additionally, it is relatively inexpensive compared to other conductive materials, making it a popular choice for many applications.

However, it is important to note that carbon conductive paint may not be suitable for high-performance applications or those that require high levels of conductivity. In these cases, more specialized materials such as copper or silver may be necessary.

1. 3. Data Analysis   ANOVA (Analysis of Variance) is probably the most widely used statistical method for comparing quantitive differences in the value of the dependent variable between groups (21). ANOVA test is generally used to analyze the average difference between variables in a group or the average of variables between groups. ANOVA analysis can be divided into several models based on the number of independent variables that affect the dependent variable, namely one-way ANOVA which is an ANOVA test if there is only one independent variable, and two-way ANOVA which is an ANOVA test method when there are two or more independent variables that affect the dependent variable. Some of these studies use the ANOVA method in their analysis (21-24).

In carrying out the ANOVA test, several conditions must be met in order for the ANOVA test method to be used. The first was the data normality test. The data normality test is one of the prerequisite tests before carrying out the ANOVA test. The normality test is a test to analyze whether the sample or population used in a research for an independent variable and dependent variable has been normally distributed. If a variable is not normally distributed, the results of the statistical test will have a decreasing effect. The second one was the homogeneity test. Homogeneity test is a test used to analyze whether two or more populations have a homogeneous relationship in a particular distribution. The homogeneity test aims to see that the groups being analyzed already have the same conditions from the start. If both prerequisites have been met, then the ANOVA hypothesis test can be carried out.

Kruskal-Wallis test is a flexible nonparametric technique used to compare multiple independent samples, making it suitable for determining whether these samples come from the same distribution. It offers a robust alternative to the parametric one-way analysis of variance (ANOVA) by not assuming normality of

random error, although it does require the independence of random error. When the Kruskal-Wallis statistic shows a significant outcome, nonparametric multiple comparison tests can be beneficial for conducting further analysis (25).

The Kruskal-Wallis test, introduced by Kruskal and Wallis in 1950s, is a nonparametric counterpart to the one-way ANOVA. Its purpose is to determine whether multiple samples are derived from the same distribution. Essentially, the test extends the Wilcoxon-Mann-Whitney two-sample test (originated by Wilcoxon in 1945, and Mann and Whitney in 1947) to accommodate situations involving more than two independent samples (25).

The Kruskal-Wallis test avoids assumptions about normality but does rely on the assumption that each group's observations stem from populations with the same distribution shape, and that the samples are both random and independent. The test statistic used in one-way analysis of variance is the ratio of treatment sum of squares to residual sum of squares. The Kruskal-Wallis test applies the same principle, although, like many nonparametric tests, it employs ranks of the data instead of the original raw data (25).

1. 4. Characterizaton   For visual appearance, the picture was captured using a digital microscup. Afterwards, the captured figures we analyzed by visual appearance. To examine the structural characteristics of the copper deposition on conductive ABS, a SEM-EDX image of the deposited copper's microstructure was acquired. SEM-EDX, a valuable tool in forensic science, allows for the simultaneous analysis of object morphology and elemental composition, enabling effective classification and discrimination of evidence materials. Furthermore, employing chemo-metric analysis methods could improve the obtained results. Several instances illustrating challenges related to classifying and distinguishing specific types of micro-traces are also showcased (26). The combination of scanning electron microscopy with microanalysis (SEM-EDX) holds significant importance as an analytical technique for studying the morphology and chemical properties of diverse materials. In various scenarios, SEM-EDX elemental maps are commonly employed and treated as images, which can lead to the simplification and compression of the comprehensive spectroscopic information found within EDX hyper-spectral data cubes (27). The usefulness of SEM–EDX methods in solving problems of analysis of microtraces for forensic purposes was confirmed in the course of international tests (26).

2. EXPERIMENTAL WORK

2. 1. Material and Method   In this study, the specimens were fabricated using conductive ABS

material, with each specimen measuring 20x20x2mm. Copper electrolyte is made from a mixture of $CuSO_4$ and H_2SO_4 (28), which is dissolved in distilled water. For the copper deposition process, variations of $CuSO_4$ concentration at 100 g/l, 150 g/l, and 200 g/l, along with H_2SO_4 at 50 ml/l of H_2O, were employed. The deposition rate was meticulously monitored over different time intervals of 2, 4, 6, and 8 hours.

2. 2. Design of Experiment   The experimental design employed in this study was measured to assess the quality of electroforming. Specifically, the present work utilized a design of experiments (DOE) approach with three factors, each examined at three and four different levels, as detail stated in Table 1.

2. 3. Preparing Specimen   The specimens were meticulously crafted using both two-dimensional as shown in Figure 3(a) and three-dimensional solid design as shown in Figure 3(b). Both of them were drawn using ArtCam Pro 9.1 software. The 3D solid images were saved in STL format and subsequently utilized in the 3D printing process. To accomplish this, the .STL format underwent processing with slicer software, specifically Ultimaker Cura 4.12.1, which facilitated the transformation into G-code format. The final step

TABLE 1. Design of Experiment

Factors	Level
Voltage	1,2,3 Volt
CCE	100, 150, 200 g/l
Time	2, 4, 6, 8 hours

involved fabricating the specimens using the Anet ET4 3D printing machine.

2. 4. Electroforming Process   The electroforming setup consists of two main components: a bath containing the electrolyte used for the electroforming process and a rectifier responsible for providing the DC power supply necessary for the operation. The baths are made from a plastic material, requiring the use of conductive ABS to achieve conductivity. The electroforming equipment is shown in Figure 4. In addition, carbon conductive paint was applied to further enhance the conductivity of the setup. The specimen was connected with a cable to the negative pole (cathode). Meanwhile, the inert anode was connected to the positive pole (anode).

In accordance with the design of experiment, electroforming specimens were produced. Figure 5 shows the result of electroforming proess. The specimen will be subjected to SEM-EDX testing.
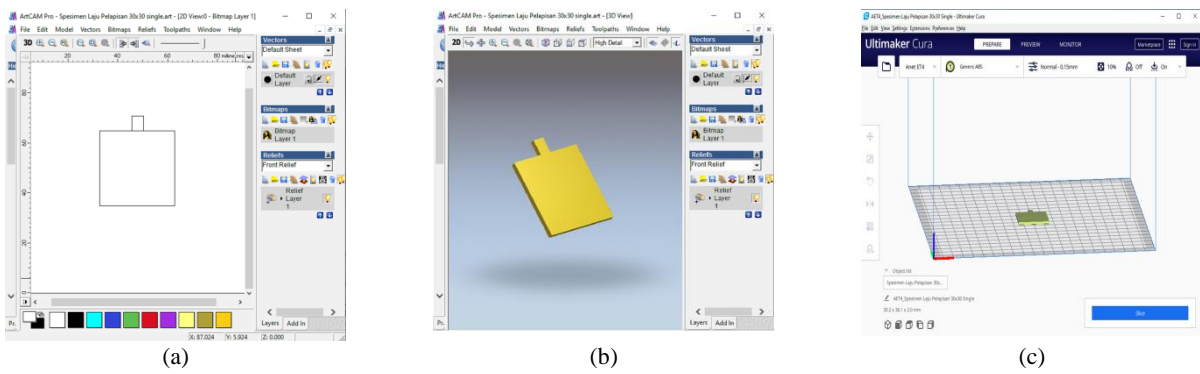

Figure 3. Design of specimen (a) 2D design (b) 3D design (c) slicing process
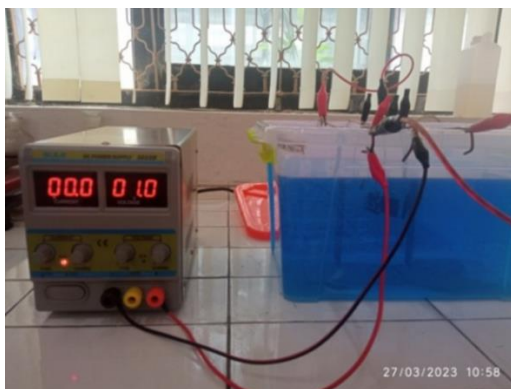

Figure 4. Electroforming equipment

Figure 5. Specimen of microstructure

3. RESULT AND DISCUSSION

3. 1. Deposition Rate   In this section, we discuss the influence of process parameters, which is voltage and CCE on the deposition rate of copper. The experimental results are summarized in Table 2, with the deposition rate presented in weight per hour units. $CCE_1 = 100$ g/l, $CCE_2 = 150$ g/l, $CCE_3 = 200$ g/l, $V_1 = 1$ Volt, $V_2 = 2$ Volt, $V_3 = 3$ Volt.

To comprehensively analyze the data, we evaluate both the main effects and interaction effects, which are graphically represented in Figure 6. This figure shows the coating rate of the experimental results is visually presented. The blue line represents the coating rate achieved at a CCE of 100 g/l $CuSO_4$, while the green line corresponds to the coating rate at 150 g/l concentration. The orange line depicts the coating rate when using a CCE of 200 g/l $CuSO_4$. Additionally, different symbols are used to indicate the voltage applied during the electroforming process. The triangular symbol represents a voltage of 1 Volt, the rhombus symbol represents 2 Volts, and the square symbol represents 3 Volts.

At a CCE of 100 g/l and a voltage of 1 Volt, the deposition rate varies intermittently. However, with an increase in voltage to 2 volts, the graph shows a clear upward trend in the deposition rate. Further raising the voltage to 3 volts leads to a substantial increase in the deposition rate. Comparing different CCE, at 150 g/l and a voltage of 1 volt, the deposition rate surpasses that of 100 g/l at 3 Volts. Additionally, at 2 and 3 Volts, both CCEs exhibit higher deposition rates. Similarly, when the CCE is 200 g/l, the pattern of increasing deposition rate remains consistent. A notable surge is observed between 2 and 3 Volts.

The deposition rate of copper electroforming is also influenced by the concentration of copper ions in the electrolyte solution. When the concentration of copper ions increases, the rate of copper deposition also

TABLE 2. Deposition rate of experiment

| CCE (g/l)	Time (h)	1 Volt		2 Volt		3 Volt	
		Weight (g)	Mean Deposition Rate (g/h)	Weight (g)	Mean Deposition Rate (g/h)	Weight (g)	Mean Deposition Rate (g/hrs)
100	2	0.09	0.04	0.22	0.11	0.83	0.41
100	4	0.17	0.04	0.62	0.16	1.96	0.49
100	6	0.84	0.14	0.99	0.17	3.10	0.52
100	8	1.17	0.15	1.73	0.22	3.70	0.46
150	2	0.22	0.11	0.18	0.09	0.78	0.39
150	4	0.45	0.12	0.45	0.11	2.17	0.54
150	6	1.16	0.19	1.07	0.18	3.39	0.56
150	8	1.24	0.15	1.79	0.22	7.04	0.88
200	2	0.17	0.08	0.16	0.08	0.94	0.47
200	4	0.72	0.18	0.72	0.18	1.69	0.42
200	6	1.02	0.17	0.97	0.16	3.51	0.58
200	8	1.23	0.15	2.20	0.28	3.77	0.47
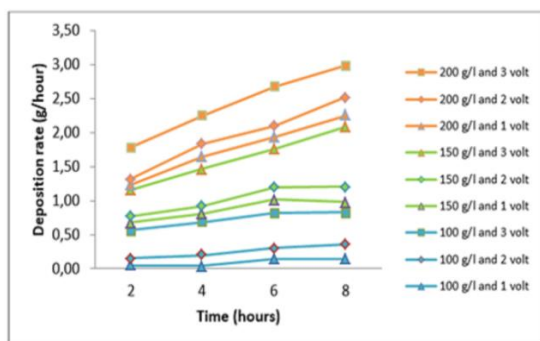
Figure 6. Deposition on different voltage and concentration of copper sulfate

increases. This is because the resistance of the solution drops and more current flows, resulting in more copper deposits.

3. 2. Data Analysis   In order to investigate statistically significant differences, normality test must be performed. After getting the results of the normality test, if the data is normally distributed, an ANOVA test will be carried out. However, if the data is not normally distributed, a nonparametric test will be performed with Kruskal-Wallis test. All statistical data were analyzed using SPSS 16.0. All statistical analyses were performed using SPSS 16.0 for Windows.

The analysis was applied to the study of influence of CCE, voltage and time on deposit rate. The first is to know the effect of CCE on the deposition rate. Then the CCE data normality test was carried out. Result of normality test for CCE showed in Table 3.

In the normality test, if the significance value (P-value) is <0.05, it is concluded that the data is not normally distributed. Significance value (P-value) > 0.05 concludes that the data is normally distributed. The significance value of CCE 100g/l is 0.047 or less than 0.05. The significance value for CCE 150 g/l is 0.009 or less than 0.05. And the significance value for CCE 200 g/l has a value of 0.062 greater than 0.05. In general, there are two data less than 0.05 so it can be concluded that the data is not normally distributed. With these data, parametric one way ANOVA cannot be continued. However, the test can be continued with Kruskal-Wallis nonparametric test as an alternative to the one way ANOVA parametric test.

For a significance value (2-tailed) < 0.05, there is an average difference (hypothesis accepted) and if the significance value (2-tailed) > 0.05, there is no difference (hypothesis rejected). Based on the results of Kruskal-Wallis test on CCE (Table 4), it shows a significant value of 0.806 or the hypothesis is rejected, meaning that the difference in CCE concentration is not significantly different.

The second analysis is the influence of voltage on the deposit rate. In the normality test, if the significance value (P-value) < 0.05, it is concluded that the data is not normally distributed. Significance value (P-value) > 0.05 concludes that the data is normally distributed.

The results of the normality test for the voltage data are presented in Table 5. The significance value (P-value) for a voltage of 1 Volt is 0.174, which is greater than 0.05, indicating that this dataset follows a normal distribution. Similarly, for a voltage of 2 Volts, the significance value is 0.656, also greater than 0.05, confirming the normal distribution of this data. However, for a voltage of 3 Volts, the significance value is 0.004, which is less than 0.05, indicating that this dataset is not normally distributed. As a result, there are data points that do not conform to a normal distribution.

TABLE 3. Normally test of CCE

	CCE	Kolmogorov-Smirnov[a]			Shapiro-Wilk		
		Statistic	df	Sig.	Statistic	df	Sig.
Deposite_rate	CCE 100 g/l	0.242	12	0.050	0.859	12	0.047
	CCE 150 g/l	0.286	12	0.008	0.797	12	0.009
	CCE 200 g/l	0.280	12	0.010	0.868	12	0.062

a. Lilliefors Significance Correction

TABLE 4. Kruskal – Wallis result for CCE

Test Statistics[a,b]

	Deposite_rate
Chi-Square	0.432
df	2
Asymp. Sig.	0.806

a. Kruskal Wallis Test

b. Grouping Variable: CCE

Given the presence of non-normally distributed data, Kruskal-Wallis nonparametric test is employed for further analysis. The interpretation of Kruskal-Wallis test results follows a significance value (2-tailed) less than 0.05, indicating acceptance of the hypothesis and an average difference. Conversely, if the significance value (2-tailed) is greater than 0.05, the hypothesis is rejected, signifying no significant difference.

Applying Kruskal-Wallis test to the voltage data as shown in Table 6, the significance value obtained is

TABLE 5. Normality test for voltage

	Voltage	Kolmogorov-Smirnov[a]			Shapiro-Wilk		
		Statistic	df	Sig.	Statistic	df	Sig.
Deposite_rate	Voltage 1 Volt	0.187	12	0.200[*]	0.903	12	0.174
	Voltage 2 Volt	0.149	12	0.200[*]	0.951	12	0.656
	Voltage 3 Volt	0.226	12	0.090	0.769	12	0.004

a. Lilliefors Significance Correction

*. This is a lower bound of the true significance.

TABLE 6. Kruskal-Wallis test result for voltage

Test Statistics[a,b]

	Deposite_rate
Chi-Square	24.346
df	2
Asymp. Sig.	0.000

a. Kruskal Wallis Test

b. Grouping Variable: Voltage

0.000, which is less than 0.05. Therefore, the hypothesis is accepted, demonstrating a significant difference among the voltage levels. This finding implies that the voltage variation has a notable effect on the rate of copper deposition.

In conclusion, Kruskal-Wallis test provides evidence of a significant impact of voltage on the copper deposition rate. The non-normal distribution of some data points highlights the importance of employing nonparametric tests for accurate analysis.

The third data analysis is the influence of time. Table 7 showed that the significance value (P-value) for 2 hours is 0.011 or less than 0.05, not normally distributed. The

significance value (P-value) for 4 hours is 0.013 or less than 0.05, not normally distributed. The significance value (P-value) for 6 hours is 0.000 or less than 0.05, not normally distributed. And the significance value (P-value) for 2 hours is 0.012 or less than 0.05, not normally distributed. It means that it can be concluded that the time data is not normally distributed. Then Kruskal-Wallis test was carried out. Based on the results of Kruskal-Wallis test for voltage (Table 8), a significance value of 0.260 or more than 0.05 or the hypothesis is rejected. It's means that there is no significant difference.

Based on data analysis, the three treatments do not meet the normality test. This is due to the outlayer data, causing data not to be normally distributed. The result of Kruskal-Wallis test of the three treatments, namely CCE, voltage and time, only voltage gave a significant difference. Differences in concentration do not provide significant different results. And the length of the bedding also does not provide significant different data. The length of the coating will increase the thickness over time.

3. 3.   Visual Appearance   Based on Figure 7(a), conductive ABS surface appears striped as a result of the printing process. Figure 7(b) shows the mottled surface

TABLE 7. Normally test of time

Time		Kolmogorov-Smirnova			Shapiro-Wilk		
		Statistic	df	Sig.	Statistic	df	Sig.
Deposite_rate	Time 2 hours	0.267	9	0.063	0.778	9	0.011
	Time 4 hours	0.377	9	0.001	0.783	9	0.013
	Time 6 hours	0.414	9	0.000	0.617	9	0.000
	Time 8 hours	0.300	9	0.019	0.779	9	0.012

a. Lilliefors Significance Correction

TABLE 8. Kruskal-Wallis test result for time

Test Statistics[a,b]

	Deposite_rate
Chi-Square	4.012
df	3
Asymp. Sig.	0.260

a. Kruskal Wallis Test

b. Grouping Variable: Time

of the carbon conductive paint. Carbon granules appear as spots. Figure 7(c) shows the appearance of the copper surface. This surface follows the mottled surface of the carbon conductive paint.
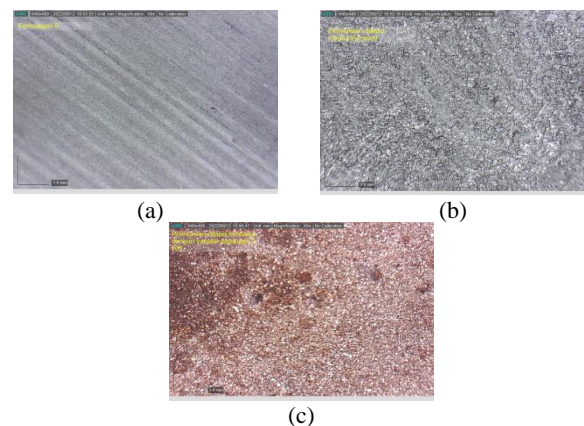

(a)   (b)

(c)

Figure 7. The visual appearance (a) conductive ABS surface (b) carbon conductive paint surface (c) copper electroforming surface

3. 4. Microstructure   In order to analysis the structural nature of the deposition of copper on the substrate, a SEM image of the microstructure of the deposited copper was obtained. At the firtst row of Figure 8, namely Figures 8(a), 8(b), and 8(c) were image for CCE_3 200 g/l. In the second row of Figures 8(d), 8(e), and 8(f) were image for CCE_2 150 g/l. In the last (bottom) row of Figures 8(g), 8(h), and 8(i) were image for CCE_1 100 g/l. At the same CCE concentration, the stress difference affects the size and appearance of the copper grains. The greater the concentration, the more copper grains appear separated or not united.

In the first (left) column, Figures 8(a), 8(d), and 8(g) were image for 1 Volt. In the second (center) column, Figures 8(b), 8(e), and 8(h) were image for 2 Volt. And the last (right) column of Figures 8(c), 8(f), and 8(i) were image for 3 Volt. The greater the voltage, the larger the copper grain size appears. The higher of voltage was larger the particle size. The particle density varies between treatments. At the highest concentration and highest voltage it appears that the particles were not so dense. It can see that the smallest copper particle sizes exist at the lowest concentrations and various voltages. Therefore the voltage value determines the deposition rate and grain size.

In the different research, surface roughness was investigated. Voltage, CCE and time can affect surface roughness. High voltage causes high roughness. This experiment was carried out by Phull et al. (9) who coated ABS plastic with voltages of 2, 3 and 4 volts. The results show that a voltage of 2 volts with a time of 6 hours provides the most optimal roughness value.

Figure 9 shows visual appereance mapping form SEM-EDX 1000x magnification. Figure 9(a) showing the Ch1, Cu and O. Figure 9(c) showing Cu mapping and it can be seen that Cu is evenly distributed on the spot captured with 93.61%. Figure 9(d) is mapping of O which is red colour.

The SEM-EDX image (Figure 10) represents the outermost surface area (18). In this study, not all images are presented in the manuscript, but their values are taken and arranged in Table 9. We will focus on looking at the spread of copper. The difference in concentration will provide a distribution of copper.

Based on the results of mapping with SEM-EDX (Table 9) it can be seen that the maximum average value was achieved at a CCE concentration of 100 g/l with a voltage of 2 volts reaching 99.65%. The average mapping value for CCE 100 g/l for 3 stress levels is 97.09%. While the average value for CCE 150 g/l was 96.49%, and the average value for CCE 200 g/l was 96.27%. In this case the concentration of 100 g/l is optimal enough to provide an even copper coating.
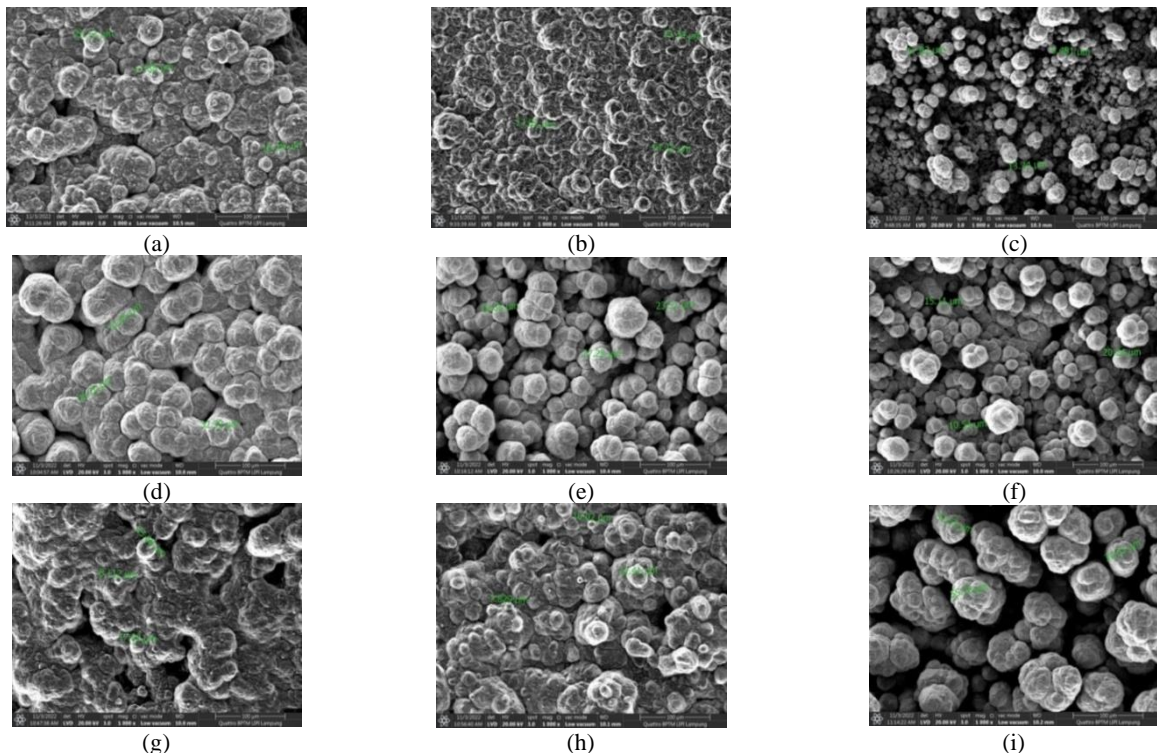
Figure 8. Comparison of SEM image (a) CCE_3V_1, (b) CCE_3V_2, (c) CCE_3V_3, (d) CCE_2V_1, (e) CCE_2V_2, (f) CCE_2V_3, (g) CCE_1V_1, (h) CCE_1V_2, (i) CCE_1V_3
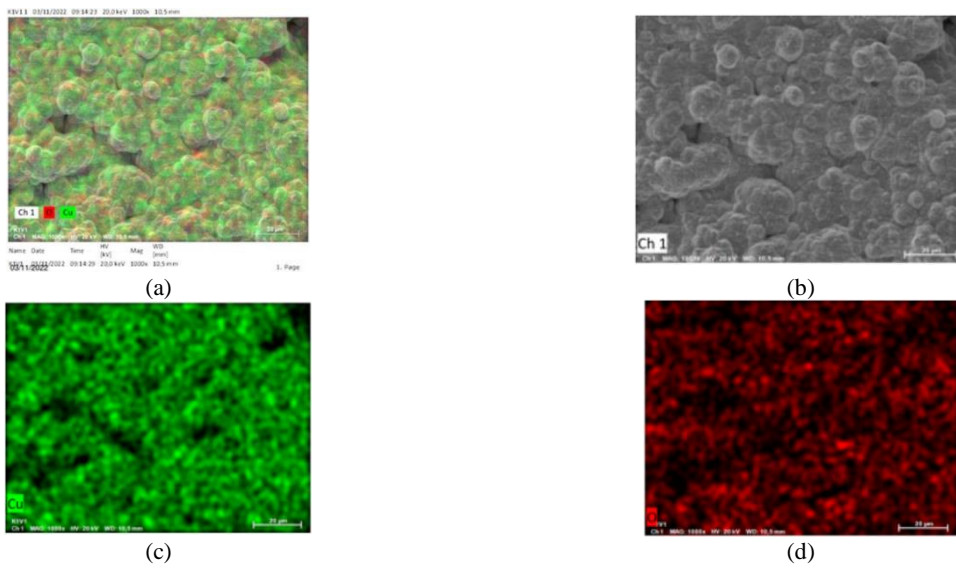
(a)

(b)

(c)

(d)

Figure 9. Mapping of Copper from SEM-EDX

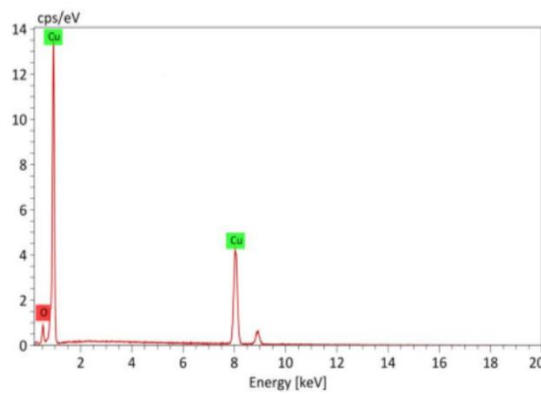**Figure 10.** EDX map sum spectra

TABLE 9. Composition of deposited copper from SEM-EDX

| Element | Mass Norm. (%) | | | | | | | | |
| | CCE 100 g/l | | | CCE 150 g/l | | | CCE 200 g/l | | |
	1 Volt	2 Volts	3 Volts	1 Volt	2 Volts	3 Volts	1 Volt	2 Volts	3 Volts
Copper	93.61	99.65	98.03	97.61	97.34	94.53	96.57	95.30	96.94
Oxygen	6.39	0.35	1.92	2.39	2.66	5.47	3.43	4.70	3.06

4. CONCLUSION

The rate of copper deposition in an electroplating bath is directly influenced by the concentration of copper sulfate. As the concentration of copper sulfate increases, so does the deposition rate. This is attributed to the availability of more copper ions at the cathode, where the plating occurs. However, the relationship between concentration and deposition rate is not linear. With increasing copper sulfate concentration, the deposition rate increases at a decreasing rate. This is because the concentration of copper ions near the cathode eventually reaches a saturation point, limiting the rate at which copper ions can diffuse to the cathode. Despite these variations, according to Kruskal-Wallis Test, the differences in concentration do not significantly impact the deposition rate. The voltage applied during electroplating also affects the copper deposition rate. Higher voltage leads to a faster deposition rate, but it may result in a rougher surface finish. The differences in

voltage provide significant effects, especially at 3 Volts, where large and weakly attached or brittle copper deposits impact the grain structure. Deposition time plays a role in determining the thickness of the copper deposit. Longer deposition times result in thicker deposits, but they extend the overall plating process duration. The ideal combination of voltage, time, and copper electrolyte concentration depends on the specific application. In general, it is crucial to use the lowest voltage and concentration that still produce the desired results. This approach ensures a high-quality deposit and maximizes process efficiency. A concentration of 100 g/l and a voltage of 2 Volts seem sufficient to achieve the desired copper coating complexity on the surface of conductive ABS.

However, it is important to acknowledge that this research still has some limitations. Several additional factors can influence the electroforming process of conductive ABS, and they deserve consideration. The temperature of the electrolyte, for instance, plays a significant role in both the deposition rate and the deposit's quality. Higher temperatures lead to faster deposition rates, but they may also result in a more brittle deposit. Moreover, the purity of the electrolyte is another crucial factor that impacts the conductivity of the solution and the overall quality of the deposit. A purer electrolyte tends to offer better conductivity and, consequently, a higher quality deposit. Furthermore, the surface finish of the mold employed during the process can affect the adhesion of the copper deposit. A rough surface on the mold generally promotes better adhesion, but it could also lead to a rougher surface finish on the final product. Taking these additional factors into account will enhance the comprehensiveness and accuracy of the research findings. By addressing these limitations, future studies can achieve a more thorough understanding of the electroforming process of conductive ABS.

5. ACKNOWLEDGEMENT

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Persian Abstract

چکیده

این مقاله مطالعه‌ای را در مورد تأثیر الکترولیت غلیظ مس (CCE)و ولتاژ بر نرخ رسوب آکریلونیتریل بوتادین استایرن رسانا (CABS)تولید شده از طریق مدل‌سازی رسوب ذوب شده ارائه می‌کند. تولید افزودنی به طور گسترده ای به عنوان یک فناوری تولید سریع شناخته شده است. در این تحقیق، الکتروفرمینگ مس به عنوان تیمار بعدی پس از ساخت افزودنی انتخاب شد. تازگی در اجرای فرآیند پیش تصفیه شامل الکتروفرمینگ نهفته است. فرآیند پیش تصفیه از رنگ رسانای کربنی برای رسانایی بخش ABS استفاده می کند. فرآیند الکتروفرمینگ مس شامل استفاده از پارامترهای متغیری مانند محتوای الکترولیت (۱۰۰، ۱۵۰ و ۲۰۰ گرم $CuSO_4$ و ۵۰ میلی لیتر H_2SO_4) در ۱ لیتر H_2O، ولتاژ (۱، ۲ و ۳ ولت) و زمان (۲، ٤، ٦ و ۸ ساعت). متغیرهای تحت مشاهده شامل نرخ رسوب مس و ریزساختار است. تحلیل پژوهش بر اساس آزمون کروسکال والیس. تفاوت در غلظت مس الکترولیت و زمان پوشش تفاوت قابل توجهی ایجاد نمی کند، در حالی که مدت زمان الکتروفرمینگ بر ضخامت رسوب مس تأثیر می گذارد. علاوه بر این، غلظت الکترولیت مس بر رسانایی محلول تأثیر می گذارد و در غلظت های بالا منجر به بهبود رسانایی و در نتیجه تسهیل سرعت رسوب سریع می شود. تفاوت ولتاژ تأثیر قابل توجهی بر میزان رسوب و ریزساختار دارد.