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Fabrication of Electrically Conductive Patterns on Acrylonitrile-Butadiene-Styrene Polymer Using Low-Pressure Cold Spray and Electroless Plating

Previous studies have shown that metallic coatings can be successfully cold sprayed (CS) onto several polymer substrates. However, the electrical performance of the cold-sprayed polymers is not generally enough to utilize them as an electronic device. In this study, an environment-friendly metallization technique has been proposed to achieve highly electrically conductive metal patterns onto polymer substrates using cold spray deposition and subsequent electroless copper plating (ECP). Copper feedstock powder was CS onto the surface of the acrylonitrile-butadiene-styrene (ABS) parts. The as-CS powders then served as the activating agent for the selective ECP to modify the surface of the polymers to be electrically conductive. A series of characterizations were conducted to investigate the morphology, analyze the surface chemistry, evaluate the electrical performance, mechanical adhesion, and mechanical strength performance of the fabricated coatings. Moreover, simple electrical circuits were presented for the ABS parts through the described method. Findings demonstrated that low-pressure cold spray copper deposition followed by the ECP processes could be used as an environmental-friendly manufacturing method of electrically conductive patterns on ABS polymer.
[DOI: 10.1115/1.4049578]

Keywords: ABS, cold spray, electroless plating, metallization, polymer

1 Introduction

Polymers have been widely used in industrial applications due to their excellent properties, including lightweight, high strength-to-weight ratio, good durability, high corrosion resistance, low cost, and ease of manufacturing. However, polymers cannot be used directly when electrical conductivity, thermal conductivity, and surface hardness are demanded. Obtaining a conductive layer on a nonconductive material is known as metallization. Through the metallization process, the physical and mechanical properties of polymers could be improved as demanded [1]. Therefore, there is a significant demand for the fabrication of metallic coatings on polymer surfaces to utilize them for further applications [2]. Metalized acrylonitrile-butadiene-styrene (ABS) is broadly used in many industries such as the electronics industry, auto-industry, petroleum industry, defense industry, etc., owing to its excellent impact resistance, good dimensional stability, and cost-effectiveness [3,4]. It has been reported that ABS parts can be metalized with aluminum (Al), gold (Au), copper (Cu), silver (Ag), and chromium (Cr) by using different methods such as chemical vapor deposition, thermal spray deposition, cladding, magnetron sputtering, electroless metallization, etc. [5–7]. Among these methods, electroless metallization has wide applications due to its ease of implementation, flexibility, and cost-effectiveness [5]. A typical electroless metallization process of ABS is illustrated in Fig. 1. As can be seen from Fig. 1(*a*), the electroless plating process begins with surface conditioning. The surface is first cleaned to remove unwanted materials such as dust, grease,

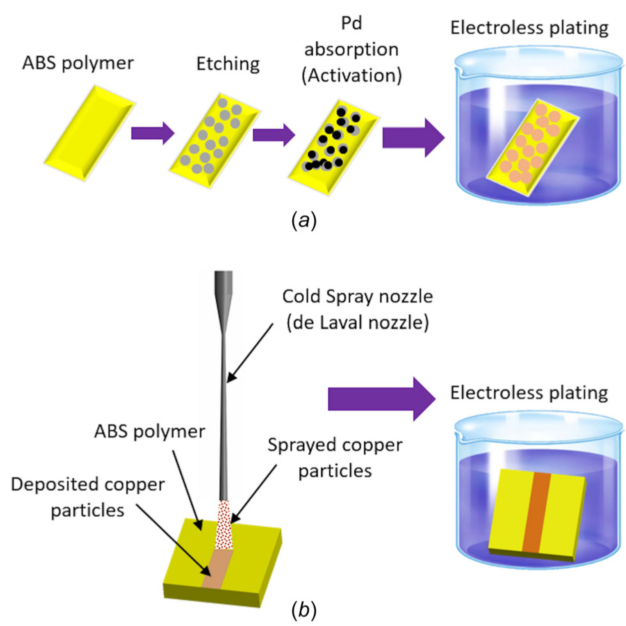

Fig. 1 (*a*) Schematic illustration of a typical metallization process of ABS parts and (*b*) proposed manufacturing approach

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Contributed by the Manufacturing Engineering Division of ASME for publication in the Journal of Micro- and Nano-Manufacturing. Manuscript received June 23, 2020; final manuscript received December 30, 2020; published online February 12, 2021. Assoc. Editor: Ping Guo.

etc. Then, the surface is generally etched in acid baths such as sulfuric acid (H_2SO_4) bath of chromic acid (CrO_3) bath [8,9]. The objective of the etching is to obtain microporosity on the surface area, providing more intimate contact between metallic layers and the polymer surface, increasing the surface energy and wettability of ABS plastics [1,10]. Following the etching process, colloidal palladium is deposited into the etched regions to initiate the electroless plating, which is called activation [9,11]. In the final step, electroless plating, a metal layer is formed on the activated surface through redox reduction. However, the acid baths used for etching the surface are significantly toxic and hazardous to the environment. In addition to environmental hazards, the process becomes very expensive due to the high cost of the palladium. As a result, it is very crucial to develop a cost-effective and environment-friendly process that eliminates the toxic and hazardous etching process, as well as the use of expensive activation material.

Although several methods were reported [11–16] to address these issues associated with obtaining metal layers on an ABS surface through palladium-free electroless plating, a chemical surface etching process was continued to be used in the related studies. In some studies, an ABS surface was metalized through a UV grafting method as a palladium-free metallization technique without chemical etching [17,18]. However, this method needs to be a polymer assembly process as well as several additional curing processes to obtain silver (Ag) film on the ABS surface. Laser direct structuring (LDS) technique has become popular in recent years to fabricate metal patterns on ABS parts [19,20]. In the LDS technology, metal seeds such as palladium (Pd), gold (Au), copper (Cu), etc., are added inside the polymer matrix by plastic injection molding, and the seeds are then activated by laser irradiation before the electroless plating process. Although metal patterns with high precision could be selectively fabricated onto polymer surfaces by the LDS technology, the process has a high demand for laser equipment and a complex plastic injection molding process, which makes it cost-intensive.

In this work, as shown in Fig. 1(*b*), we propose an environment-friendly manufacturing method for the metallization of ABS parts combining low-pressure cold spray deposition (LPCS) and electroless plating, which replaces both conventional toxic sensitizing-activation and chemical surface etching. ABS parts built by fused deposition modeling as an additive manufacturing (AM) method were used in this study since ABS is widely used as a raw material in the material extrusion (ME) based AM. An LPCS system has achieved the deposition of the copper layer on the ABS polymers without any delamination of the ABS parts owing to the use of relatively low-pressure driving gas.

Even though the ABS surface was successfully metalized using the LPCS, the continuous electrical conductivity was not obtained on the ABS surface due to the existence of the high porosity on the polymer surface. Therefore, we utilized the as-CS coating as the activating agent for the subsequent electroless copper plating (ECP) to decrease the porosities on the as-sprayed surface and to gain electrical conductivity to the ABS surface. Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) analyses were conducted to study the microstructure and elemental composition of the fabricated metal coatings. Besides, interfacial adhesion between copper layers and substrates, mechanical strength, and electrical performance of the coated samples were studied.

2 Materials and Methods

2.1 Materials. The substrate materials used in this work are ABS parts made by the Sindoh (3DWOX1) AM machine using ME technology. The part material used in the extrusion process is ABS M30, having a diameter of 1.75 mm. The dimensions of the fabricated rectangular samples built by the ME method in this study are in 50.48 mm width, 50.48 mm length, and 6.35 mm height. Commercially available irregular shaped copper powders ($-45+5\ \mu m$) supplied by the Centerline (U.S.) were used as the feedstock material of the cold praying process. SEM image of the copper powder used in the experiments is presented in Fig. 2. For the ECP process, copper sulfate pentahydrate ($CuSO_4{\cdot}5H_2O$), ethylene diamine tetra-acetic acid (EDTA), potassium ferrocyanide($K_3Fe(CN)_6$), hydrochloric acid (HCl), formaldehyde (H_2CO), and sodium hydroxide (NaOH) were purchased from the Sigma-Aldrich Corp. (U.S.) (St. Louis, MO) and all the chemicals were used without any further purification.

2.2 Cold Spray Deposition. Cold spray is an emerging solid-state coating deposition technology developed in the 1980s [21]. In the cold spray process, the solid powder feedstock material is accelerated to higher velocity (300–1200 m/s) through a convergent-divergent nozzle (de-Laval nozzle) using compressed gases (typically nitrogen, air, or helium) [21,22]. When powders impact the surface of the substrate exceeding a critical impact velocity, they are plastically deformed, resulting in a metallic or composite coating in the solid-state. During this process, the high kinetic energy of the particles is transformed into strain energy inducing severe plastic deformation at high strain and strain-rate. As a result, it allows for impinging the particles to bond, breaking up the oxide layers [23].

Recently, the studies regarding the metallization of various polymers using cold spray technology have been reported [22,24–29]. Regarding ABS polymer, although cold spray copper embedding on the ABS substrate has been successfully realized, no continuous copper layer build-up has been achieved. The main reason for this phenomenon is the weak mechanical erosion resistance of ABS polymer [28]. Also, the deposition window of metal particles onto the ABS polymer is very narrow. Even though the first layer of copper embedding can be successfully achieved on the ABS surface, upcoming particles erode/remove the previously embedded layer on the surface, resulting in significant erosion on the surface [28]. To achieve a thick metal coating on the ABS surface by cold spray deposition, the particles must have low enough velocity for anchoring to the polymer, but the upcoming particles must have high enough impact velocity to bond the previously deposited particles [29]. Therefore, this phenomenon leads to a significant challenge for deposition and erosion of the copper particles on the ABS surface.

In addition to the difficulty of achieving continuous copper layer build-up on the ABS surface, obtaining high and continuous electrical conductivity on the polymer surface using the cold spray deposition is another challenge due to resulting high porosity on the surface and discontinuities among the copper particles. A large amount of localized plastic deformation of the substrate envelopes the copper particles forming an intermittent copper layer, and it

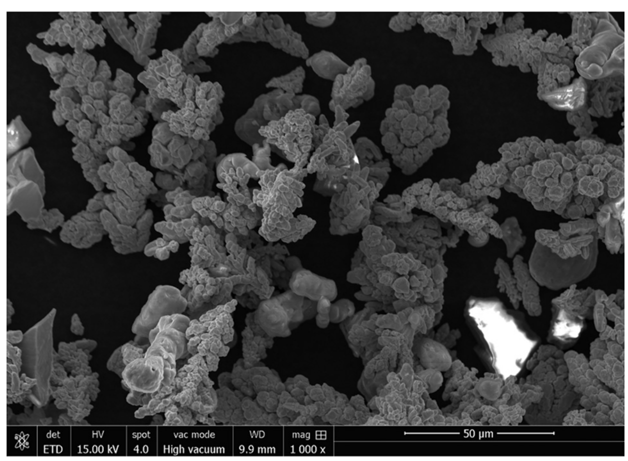


Fig. 2 Morphology of copper powders used in the experiments

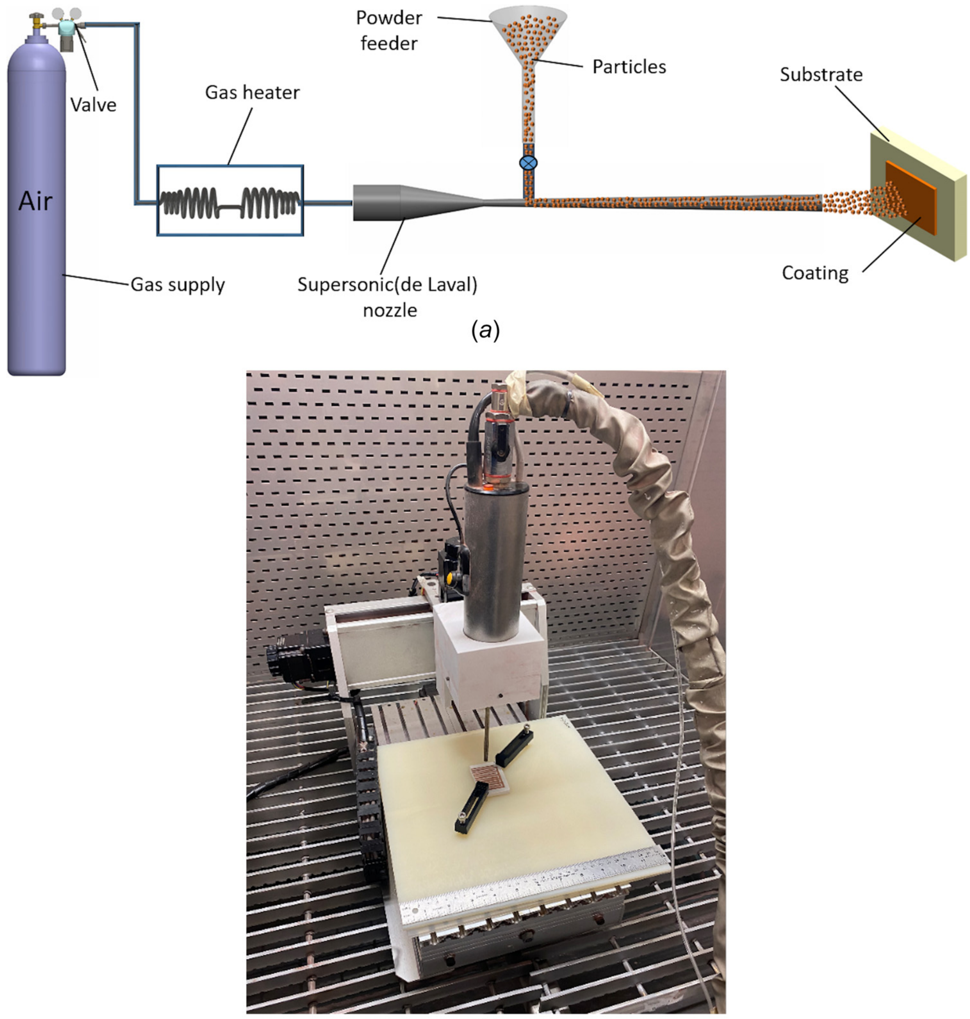


Fig. 3 (*a*) Schematic illustration of the cold spray system and (*b*) image of the experimental setup

prevents the continuous electrical conductivity along with the coating layer.

In this study, we address this problem by utilizing the successfully cold sprayed (CS) first layer (as-sprayed layer) of copper for further ECP process to gain electrical conductivity on the polymer surface. The as-sprayed layer served as the activating agent owing to its excellent adhesion strength. Therefore, the proposed approach does not need expensive Pd absorption and even the chemical etching process. The installation of the cold spray deposition system used in the experiment is schematically shown in Fig. 3(*a*). A commercially available low-pressure cold spray machine (RS Technology, Ltd., Model K205/407R) was used in the coating experiments as shown in Fig. 3(*b*). Compressed air was used as the driving gas. The stagnation pressure (gauge) and the stagnation temperature of the driving gas were set as 0.8 MPa and 298 K, respectively. Air was then heated during expansion. The temperature of the air at the nozzle exit was measured as 40 °C. The substrate was located 4.5 mm away from the nozzle exit, and the gun transverse speed of 20 mm/s was used for the coating experiments. All the experiments were carried out at room temperature. The operating parameters of the cold spray deposition process are listed in Table 1.

2.3 Electroless Copper Plating. For the ECP process, a laboratory-made ECP bath was used, which contains 18 g/L of copper sulfate pentahydrate ($CuSO_4{\cdot}5H_2O$) as the copper ion source, 48 g/L of EDTA as the complexing agent, 57.3 mg/L of potassium ferrocyanide($K_3Fe(CN)_6$) as the stabilizing agent, 18 mL/L of hydrochloric acid (HCl), and 10 mL/L of formaldehyde (H_2CO) as the reducing agent in the de-ionized water. The ECP process was conducted at room temperature, and the *p*H value of the solution was adjusted to 12 via sodium hydroxide (NaOH). The anodic and cathodic reactions of the ECP process are given in Eqs. (1) and (2) below:

Table 1 Cold spray operating parameters used in the experiments

Gas inlet pressure	0.8 MPa
Gas inlet temperature	298 K
Nozzle transverse speed	20 mm/s
Nozzle stand-off distance	4.5 mm

$$\text{Anodic: } 2H_2CO + 4OH^- \leftrightarrow 2HCOO^- + H_{2(gas)} + 2H_2O + 2e^- \quad (1)$$

$$\text{Cathodic: } CuEDTA^{-2} + 2e^- \leftrightarrow Cu + EDTA^{-4} \quad (2)$$

2.4 Characterization. The Quanta FEG 650 SEM equipped with X-ray (EDX) detector was used to examine the morphology

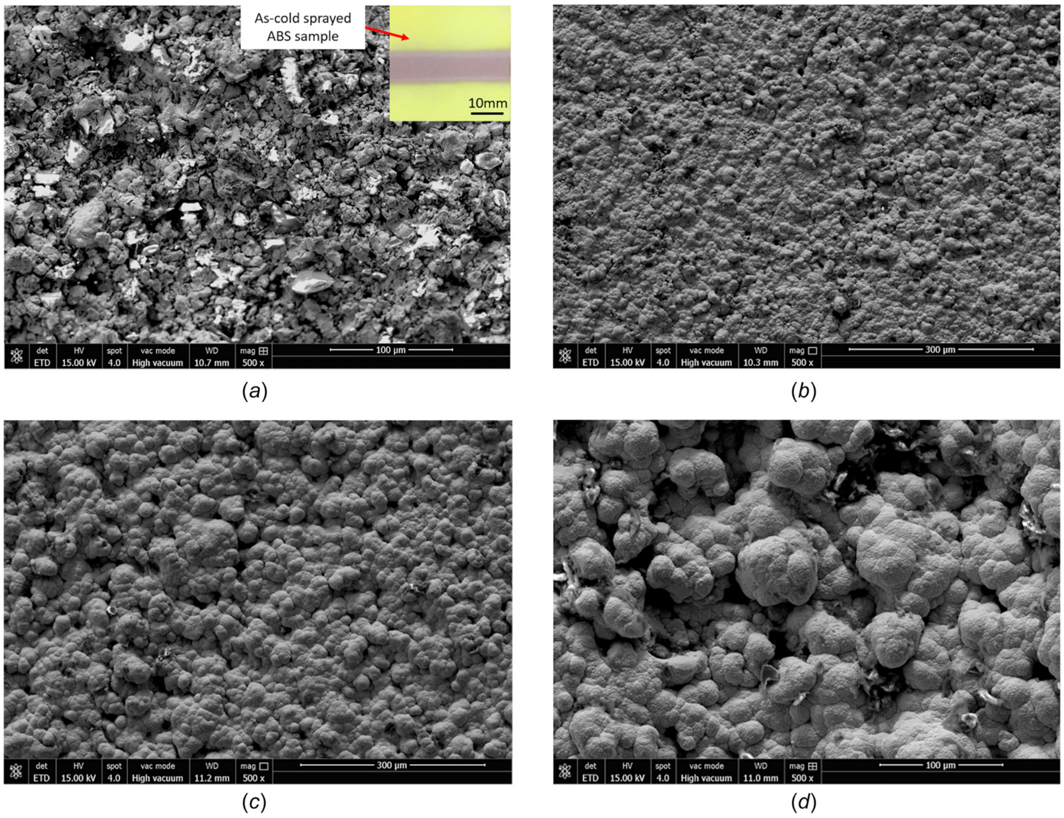


Fig. 4 SEM images of the studied ABS samples for different conditions: (*a*) as-sprayed ABS surface, (*b*) 2 h of ECP, (*c*) 4 h of ECP, and (*d*) 6 h of ECP

and elemental analysis of both as-cold sprayed and electroless plated ABS surfaces. The electrical performance of fabricated patterns was measured by a 4-point probe system (Jandel, RM3-AR) with a constant current of 100 mA at room temperature to remove any contact resistance error from the measurements. The average sheet resistance was determined from five consecutive regions along with the fabricated patterns. The tensile test was conducted by a tensile test machine ADMET Expert 7603 at room temperature based on the ASTM D-638 standard. Moreover, the adhesion assessment of the copper-deposited ABS parts was also studied at room temperature considering the ASTM D3359-02 standard test method.

3 Results and Discussion

3.1 Scanning Electron Microscopy/Energy-Dispersive X-Ray Spectroscopy Characterization. Scanning electron microscopy images of the samples for different plating times are given in Fig. 4. Regarding the SEM analysis, when the ECP time increases, the density of the coppers formed on the ABS surface increases as well. However, it can be seen from Fig. 4(*a*) that there are a considerable number of porosities on the as-cold sprayed ABS surface. The main reason for this high porosity is the local plastic deformation on the substrate due to the high impact velocity of the upcoming particles. As shown in Figs. 4(*b*) and 5, the porosities decreased as increasing the plating time, and nearly bulk copper formation was obtained on the surface after 6 h of plating as given in Fig. 4(*d*). The reason for this tendency is the chemical copper deposition on the as-sprayed surface during the subsequent ECP process. The ECP led to decrease porosities, providing copper deposits on the previously cold sprayed layer. When the ECP time was further increased, some contaminants on the sample surface were observed due to the autocatalytic nature of the ECP.

Point EDX results of the ABS samples are given in percent by both weight (wt %) and atomic percent (at %) in Fig. 5. It is clear from the EDX results that all the ABS surfaces were coated with copper. It can also be seen from Fig. 5(*a*) that the as-sprayed ABS surface has the maximum oxide and carbon ratio. The reason for this could be the oxide layer thickness of the copper powders used in the cold spraying process. Additionally, it was monitored that there is not a significant change in the copper weight after the 2 h of ECP even though copper size increases with increasing ECP time as illustrated in Fig. 4. The reason for this might be a simultaneous increase in the amount of carbon and oxide following an increase in the copper weight after the 2 h of ECP.

Another EDX analysis of the as-cold sprayed sample is shown in Fig. 6. As can be seen from Fig. 6, a bromine peak was also observed for a different surface point of the as-cold sprayed ABS sample. Bromine is widely used in ABS and plays a vital role as a flame-retardant element [30]. This result shows that some local regions on the cold sprayed surface include very poor conductor and/or insulator elements, resulting in an intermittent copper layer on the surface. The reason for this could be a large amount of localized plastic deformation of the substrate. When the particles are impacted on the ABS surface, some local regions could experience lip formations, leading to excessive enveloping of the copper particles by the substrate due to the mechanical interlock between the particles and the substrate. For this reason, it could not obtain the electrically conductive layer on the ABS surface by means of only cold spray deposition.

3.2 Electrical Performance Measurement. A four-point probe technique was used to measure the sheet resistance of the copper coated ABS parts. The average sheet resistance ($\overline{R_s}$) and the standard deviation of resistance (σ) were calculated according to Eqs. (3) and (4) due to the variation of the resistance from point to point on the surface. In these equations, R_{si} is the measured sheet resistance at the ith place on the surface, and n is the total number of measurements

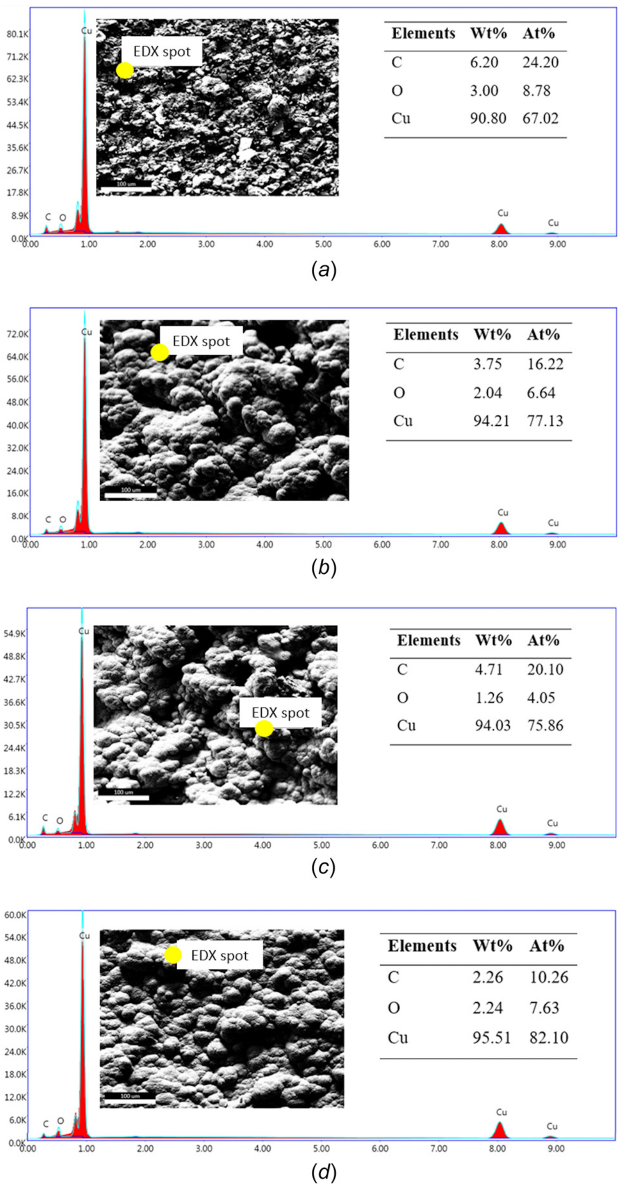


Fig. 5 EDX analysis of the ABS samples: (*a*) as-sprayed ABS surface, (*b*) 2 h of ECP, (*c*) 4 h of ECP, and (*d*) 6 h of ECP

$$\overline{R}_s = \frac{\sum_{i=1}^{n} R_{si}}{n} \tag{3}$$

$$\sigma = \sqrt{\frac{\sum_{i=1}^{n} \left(R_{si} - \overline{R}_s\right)^2}{n-1}} \tag{4}$$

As can be seen from Table 2, when ECP time increases, the sheet resistance of the film decreases. The resistance deviation was also reduced with increasing ECP time. The reason could be the increase of the copper coating density through the ECP process. After a certain time, however, there is no such significant difference for the resistance since the surface behaves like bulk copper as shown in the SEM images in Fig. 4(*d*). It was also observed that after 6 h of plating some residuals and contaminants form on the ABS surface, resulting in a decrease of conductivity. The reason for this problem might be over-plating because ECP is an autocatalytic reaction and even if the surface is completely plated, the reaction inside the bath continues due to the existence of enough copper source and reducing agent. Therefore, ABS parts with 6 h of ECP were selected as the candidate for further characterization studies owing to its better conductivity performance.

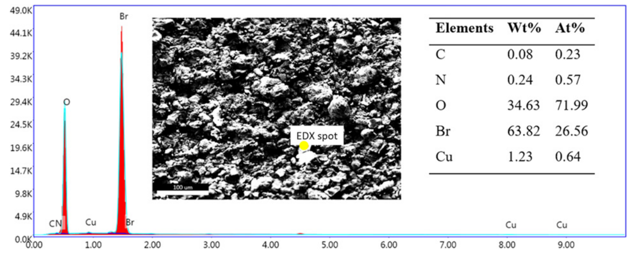


Fig. 6 EDX analysis of the as-sprayed ABS sample

Table 2 Electrical performance of the copper-deposited ABS parts

	Sheet resistance obtained after electroless plating	
Plating time (h)	$\overline{R}_s$ (mΩ/sq)	σ
2	4.734	0.699
4	3.330	0.256
6	2.854	0.136

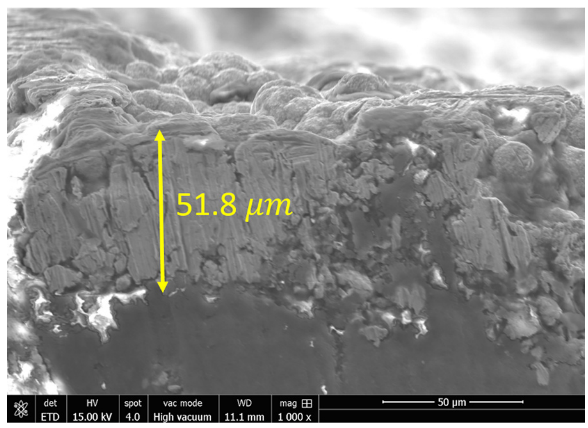


Fig. 7 Cross section SEM image of the ABS sample after 6 h of ECP

The resistivity (ρ) of the fabricated copper layers was calculated through the relationship given in Eq. (5) where 4.532 is a correction factor regarding the shape of the cell, t is the thickness of the coating, and $\overline{R_s}$ is the average measured sheet resistance [31]

$$\rho = 4.532 \times \overline{R}_s \times t \tag{5}$$

The sheet thickness was obtained from the cross section SEM image of the part as shown in Fig. 7. Therefore, the electrical resistivity of the copper pattern for the 6 h plated sample was calculated as 6.699×10^{-7} Ωm. In Table 3, the electrical resistance of the fabricated patterns by the proposed method was compared with some other methods reported in the literature. As can be seen from Table 3, the proposed method offers higher conductivity comparing to already available metallization methods of ABS polymer.

3.3 Tensile Test Measurement. The tensile test was conducted to investigate the effect of the aqueous medium treatment (ECP process) on the mechanical strength of the ABS samples.

Table 3 Comparison of the proposed method with other metallization techniques for electrical conductivity assessment

Method	Film thickness (μm)	Sheet resistance (Ω/cm^2)	Reference
Etching + plating	64.04	0.102	[9]
Etching + plating	—	0.03	[13]
Laser assisted selective metallization	—	0.025	[32]
This study	51.8	0.002854	

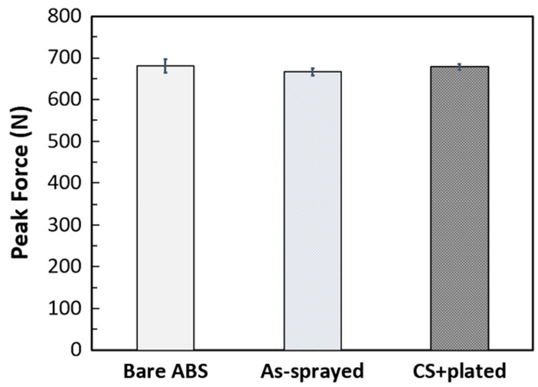


Fig. 8 Tensile test results of the samples

The tests were carried out based on the widely used ASTM D638 tensile test standard [33]. Each specimen having a thickness of 2 mm was tested with a crosshead speed of 1 mm/min at room temperature until fracture, and each experiment was repeated three times for the sake of repeatability. According to the tensile test results shown in Fig. 8, there is not a significant difference among the bare ABS, as-cold sprayed ABS, and plated samples (cold sprayed (CS) + plated) in terms of the peak force. As-sprayed samples have shown slightly smaller peak force than the bare ABS samples. The reason could be that impact of the cold sprayed copper particles on the ABS surface might cause local deformations to develop and grow on the material surface, which can lead to a decrease in mechanical strength. On the other hand, the peak force of the plated samples has increased comparing to as-sprayed samples, reaching up to nearly 99.6% of the bare ABS sample. This could be because of the decrease in the porosity as the plating process bonds the particles together through the chemical reaction, which increases the material's mechanical strength. Moreover, the results indicate that 6 h of ECP in an aqueous medium is not detrimental to the mechanical properties of the polymer.

3.4 Adhesion Assessment. Mechanical adhesion performance of copper-deposited ABS parts through the cold spray and ECP was studied according to the standard ASTM test method (ASTM D3359-02) [34]. First, the surface of the parts was cleaned before the implementation of the test. Then, six cross-cuts were

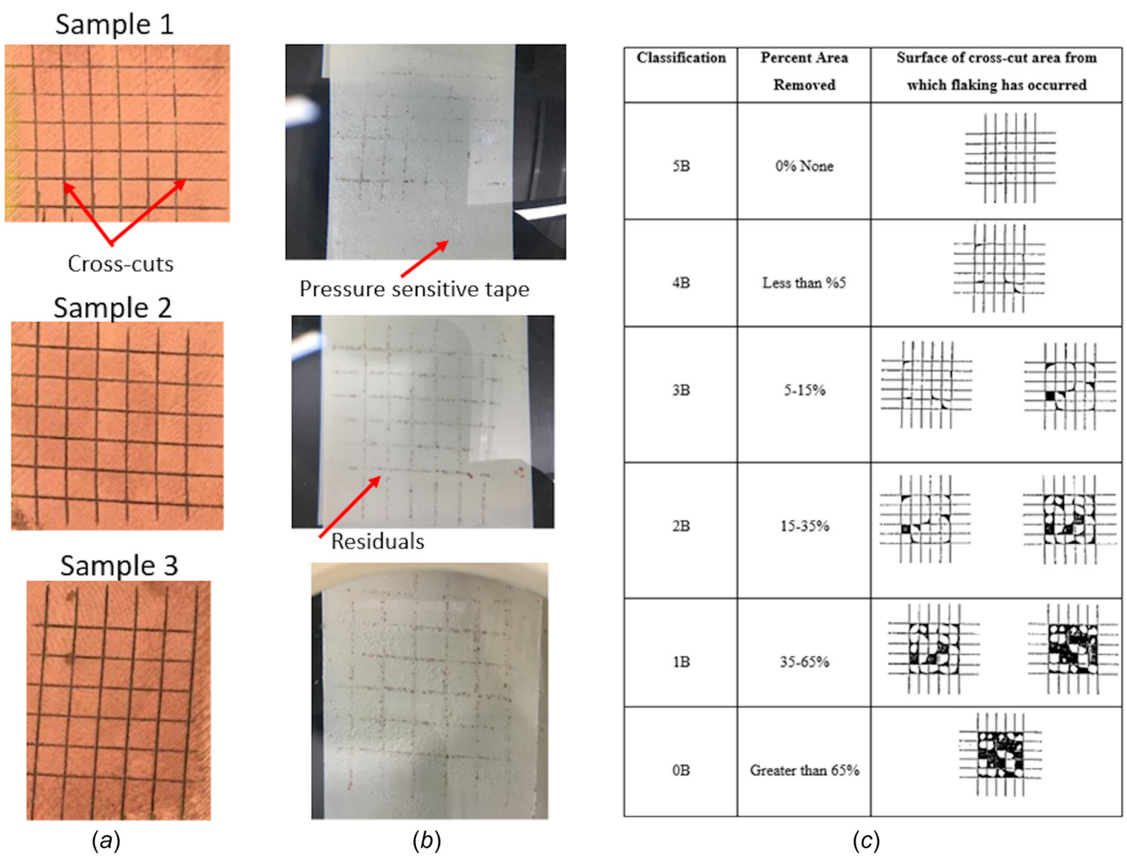
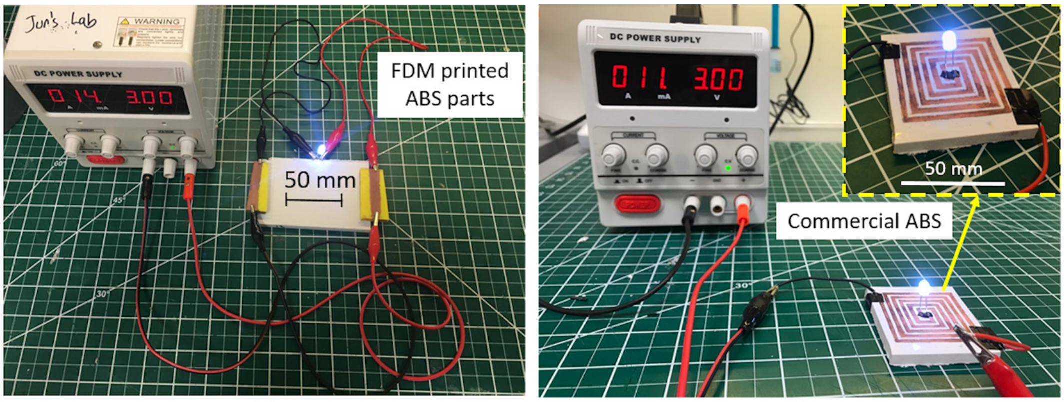


Fig. 9 (*a*) The cross-cut samples, (*b*) cross-cut residuals on the pressure-sensitive tape, and (*c*) classification of adhesion test results based on the ASTM D3359-02



(*a*) (*b*)

Fig. 10 Images of the obtained copper circuits on the ABS parts: (*a*) fused deposition modeling build ABS parts and (*b*) commercial ABS part

carried out on the three samples since the dry film thickness of the coating was measured as about 52 μm as illustrated in Fig. 7. Next, the cuts are implemented in a way that they can reach to the ABS surface as shown in Fig. 9(*a*). After implementing the cuts, the surface was cleaned, and then a pressure-sensitive tape was applied over the surface and then removed. The residuals on the tape were then analyzed using a magnifying glass as given in Fig. 9(*b*). Finally, adhesion performance was evaluated by comparison of the coating residuals on the tape with the descriptions and illustrations shown in Fig. 9(*c*). As a result, the samples have a classification of 5B or 4B that indicates an excellent adhesion strength of copper on the ABS parts, meeting the requirement for industrial applications.

3.5 Applications and Prospect. We fabricated a copper circuit on the ME printed ABS parts as illustrated in Fig. 10(*a*) to show the validity of practical applications. First, the additively manufactured ABS parts were cold sprayed. Then, the surface of the parts was modified to be electrically conductive through the ECP process. Moreover, the commercial ABS parts supplied by the ePlastics (U.S.) were also used to show the versatility of the described technique. As shown in Fig. 10(*b*), the conductive copper circuit was achieved by masking on the commercial ABS part. Any form of conductive copper patterns can be easily structured via masking on the ABS polymer using the described method. It is also notable to point out that even smooth/flat ABS surfaces could be easily copper deposited by cold spray without any need for the initial surface etching process. Therefore, we successfully demonstrated that the surface of the ABS parts could be modified through the outlined technique. The given manufacturing approach could be easily used to fabricate electrical circuits or conductive paths where the wiring is problematic or not feasible. The described method could also be employed in a wide range of applications such as polymer-based sensors, automotive electronics, multifunctional electronics, smart structure applications, decorative purposes, and even educational purposes such as conductive LEGO bricks.

4 Conclusion

In this paper, a Pd-free environment-friendly technique was introduced for the metallization of ABS surfaces combining the LPCS and ECP. The following results can be drawn from this study:

- The copper feedstock was successfully deposited onto the ABS surface with a high adhesion using a low-pressure cold spray machine.
- The typical environmentally hazardous sensitizing-activation pretreatment of the ABS surface was replaced with the cold spray deposition.
- The as-cold spray-coated ABS surfaces were not electrically conductive due to excessive local plastic deformation of the substrate, resulting in high porosity on the surface. This problem was accomplished by introducing the ECP process for the as-sprayed ABS samples to obtain continuously conductive patterns on the polymer surface.
- The ABS surface was successfully modified to be electrically conductive, having a resistivity of 6.699×10^{-7} Ωm.
- The tensile test results indicated that there is not a significant difference between the different samples (Bare ABS, as-sprayed ABS, both as-sprayed and plated ABS) for mechanical strength.
- Achieved copper layer on the ABS polymer exhibited an excellent adhesion property, reaching the 5B or 4B level according to the ASTM D3359-02 adhesive tape test.

Overall, the described manufacturing approach could be used as an environment-friendly method for electrically conductive surface metallization of ABS polymer, which can be applied to large-scale manufacturing. Continuous conductive copper patterns with excellent adhesion can be conveniently fabricated by the proposed method. Moreover, the proposed approach has the potential for various polymer materials where high adhesion performance and continuous electrical conductivity are needed.

Acknowledgment

The first author gratefully acknowledges the scholarship support provided by the Republic of Turkey Ministry of National Education, the Office of Overseas Scholarship Programs.

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