Materials Letters 280 (2020) 128574

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/mlblue

# Flame-sprayed Zn-Al coatings on ABS without chemical surface preparation

Dayi Gilberto Agredo Diaz [a,b,*], Raúl Gilberto Valdez Navarro [b], Nicolas Ortiz Godoy [a], Arturo Barba Pingarrón [b], Jesús Rafael González Parra [b], Jhon Jairo Olaya Florez [a], Magdalena Trujillo Barragán [b], Irma Angarita Moncaleano [a], Cesar Armando Ortiz Otalora [c]

[a] Universidad Nacional de Colombia-sede Bogotá, Facultad de Ingeniería, Departamento de Ingeniería Mecánica y Mecatrónica, Bogotá, Colombia
[b] Universidad Nacional Autónoma de México-Facultad de Ingeniería-División de Ingeniería Mecánica e Industrial-Centro de Ingeniería de Superficies y Acabados (CENISA), Ciudad de México, Mexico
[c] Universidad Pedagógica y Tecnológica de Colombia, Facultad de Ciencias, Grupo de Superficies, Electroquímica y Corrosión, Tunja, Colombia

ARTICLE INFO

*Article history:*
Received 30 May 2020
Received in revised form 11 July 2020
Accepted 21 August 2020
Available online 27 August 2020

*Keywords:*
ABS
Electrical conductivity
Metallization
SEM
Wire flame spray
XRD

ABSTRACT

Metallization of polymeric materials is a process that manages to combine the properties of polymers and metals, to expand its range of applications. In this research, the deposition of a Zn-Al alloy on a polymeric substrate (ABS) using wire flame spray was carried out, with a predominant advantage by not using chemical surface preparation processes, thus obtaining materials at low cost, friendly to the environment, without affecting the properties of the substrate, avoiding its degradation by temperature, and gaining a level of electrical conductivity appropriate to nature of the coatings. Substrate roughness is measured by interferometry, coating morphology by SEM, the composition by EDS, structure by XRD, adhesion by Pull-Off, and electrical resistivity is evaluated using the 4-point test. The SEM results show a coating with a thickness of the order of 89 μm, homogeneous in its composition with a Zn and Al crystalline structure, an adhesion strength of 888 N, with a porosity of 0.87% with an average pore size of 10 μm. The electrical conductivity study of the coated material shows a good electrical response, with a value of 2682 S/m.


## 1. Introduction

One of the recent interests of the industries is focused on the metallization of polymeric materials, which can improve their visual aspect, changing the level of electrical or thermal conductivity or increasing their surface hardness [1]. In these cases, one of the most widely used materials as a substrate is ABS (Acrylonitrile-Butadiene-Styrene) because of its high mechanical resistance, good toughness, high chemical stability and low density [2–4], making it an important candidate in petrochemical, electronic, textile, automotive and aerospace applications.

In [5], the deposition of several metals on polymeric substrates is performed, however, the authors suggest taking special care with the process variables to avoid erosion phenomena in the substrates. In [6] were studied the deposition of metallic coatings using Cold Spray technologies, however, for the moment, those techniques represent a high-cost alternative, due to the still-high price of the equipment necessary for their realization. Shrutee et al. [7], explore the use of the electric arc thermal spray technique to deposit copper and zinc base materials on ABS, an advantage of Zn alloys is that they have a good electrochemical response [8].

In [9], the various thermal spray technologies that have been used to generate coatings on polymers, the surface preparation techniques, and the effect of different operating parameters on the quality of the coatings are reviewed. Moreover, the possible phenomena that originate the distribution of temperatures within the polymer during the process, the characterization of the coatings, and the approach of potential applications of the coated materials, particularly in the electric and thermal field are reported. In this research, the metallization of ABS with a Zn-Al alloy is explored using wire flame spray technique, where the preparation of the substrates was carried out by shot blasting, a mechanical method that incorporates the use of ceramic particles, this has an advantage with respect to the preparation of surfaces by chemical agents, in turn, given the low melting temperature of the projected material, possible degradation is avoided.

* Corresponding author.
*E-mail address:* dgagredod@unal.edu.co (D.G. Agredo Diaz).

https://doi.org/10.1016/j.matlet.2020.128574
0167-577X/

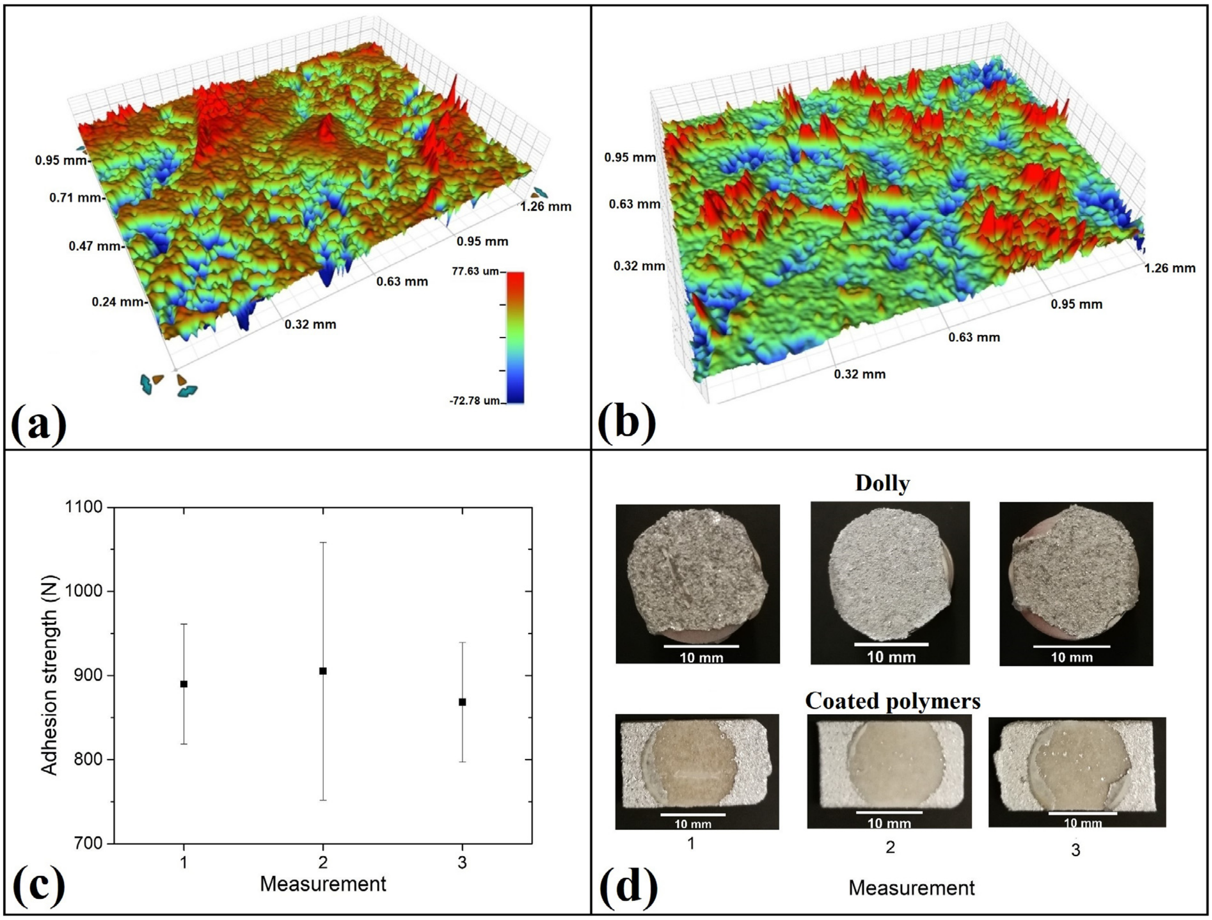


**Fig. 1.** (a) Substrate roughness, (b) Coating roughness, (c) Adhesion strength of coatings, (d) Result of samples subjected to the Pull-Off test.

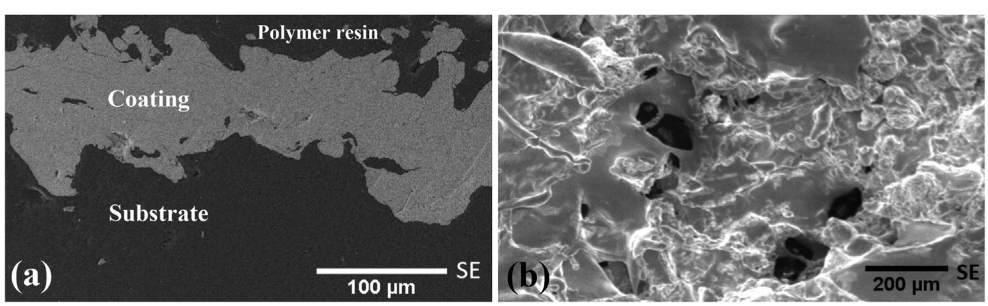


**Fig. 2.** (a) Cross section of the coating, (b) Surface of the coating.

## 2. Materials and methods

The ABS samples were 33 × 19 × 3 mm in size and are obtained by injection on a Demag ErgoTech Pro 50–270 machine from raw pelletized material. The surface of the substrates was prepared by shot blasting with $SiO_2$ particles of irregular morphology with 1 mm particle size at a distance of 20 cm for 5 min, it is important to mention that it has not been possible to metallize these polymers by thermal spraying without the generation of an adequate roughness. Roughness was measured by white light interferometry on a Bruker ContourGT-K kit with a Cutoff of 0.8 mm.

For the application of the coatings, a Sulzer Metco Wire jet-96 gun with cone-shaped nozzle, a projection distance of 20 cm was used, normal to the surface of the substrates with a wire consumption speed of 0.0342 m/s, a wire diameter of 3 mm is used with a composition of Zn (85% wt) and Al (15% wt). The spray parameters used are shown in Table 1 and are reported in [8], it has a gas flow ratio of 1:1.8 (oxygen/acetylene), these parameters are considered adequate to generate a good combination of mechanical properties of the coatings. The adhesion strength was determined using Elcometer 106 Pull-Off Adhesion Tester equipment under ISO 4624 standard, reporting a value for nine measurements.

**Table 1**
Flame spray parameters.

| Fluid | Pressure (Pa) | Flow ($m^3/s$) |
|---|---|---|
| Oxygen | $206.843 \times 10^3$ | $43.26 \times 10^{-5}$ |
| Acetylene | $103.421 \times 10^3$ | $23.59 \times 10^{-5}$ |
| Compressed air | $482.633 \times 10^3$ | |

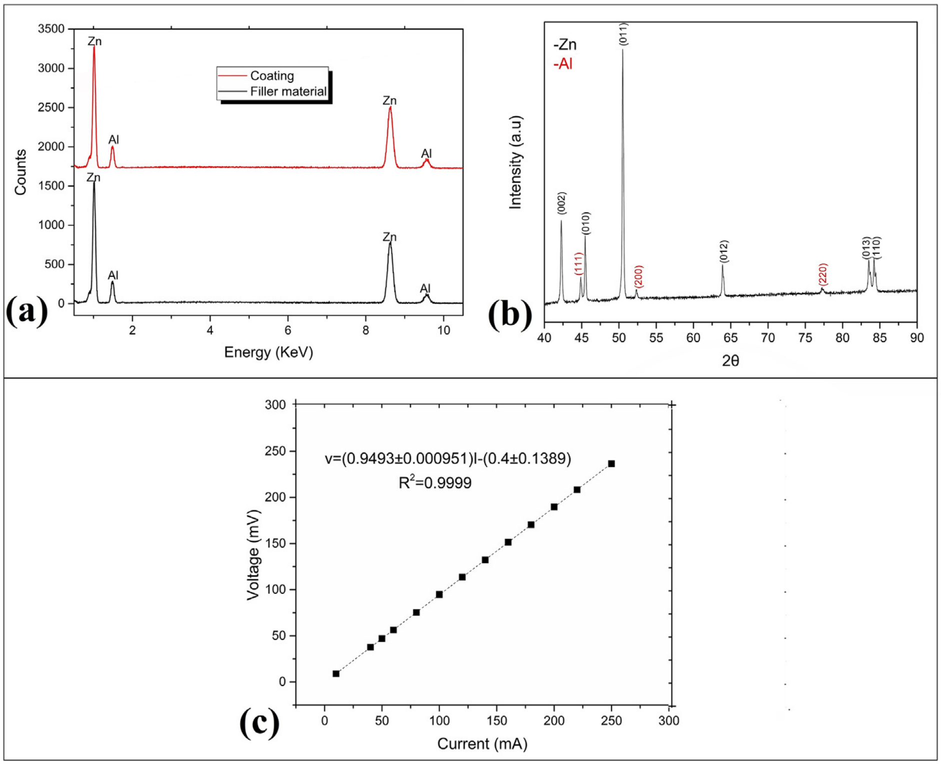


**Fig. 3.** (a) EDS microanalysis, (b) Diffraction pattern, (c) Voltage as a function of current.

The morphology was characterized using a scanning electron microscopy (SEM) in a Vega3 Tescan electron microscope, a cross section cut is made and mounted in polymer resin for cold mounting. The elemental composition of the coatings was determined using a Bruker XFlash 410-M EDS probe. The structural characterization was carried out using X-ray diffraction (XRD) in a PANalytical X́Pert Pro diffractometer with a Co anode (target), a $K\alpha$ = 1. 789 Å, a current of 40 mA and a voltage of 40 kV.

The electrical resistivity of the material was evaluated employing the 4-point method under the guidelines of DC electrical resistivity measurement on rectangular solids of a non-conductive substrate [10].

## 3. Results and discussion

The roughness of the substrate shows a value of Sa = 10 ± 0.0 01 μm, while the roughness of the coating has a value of Sa = 7 ± 0.001 μm, in Fig. 1a and 1b the previously described is detailed. This surface finish was suitable for the correct mechanical anchoring of the coatings, this is according to the nature of the process and reported in [11]. Results of the adhesion test, Fig. 1c, show an average value of adhesion strength of 888 ± 18 N, these results are in agreement with those reported in [8], and are linked to the good anchorage of the coating to the substrate. An adhesive/cohesive failure occurs with a predominance of adhesion failure, Fig. 1d shows these results in detail [12].

In the cross section of the coated material, Fig. 2a, a good anchorage of the coating to the substrate is observed. A coating thickness of 89 ± 30 μm is obtained, this high standard deviation is a consequence of the high irregularity in the substrate, where the coating must adapt to the topography of the polymer, in turn, the porosity of the coating is calculated, obtaining 0.87 ± 0.01%, with an average pore size of 10 μm. The surface micrograph, Fig. 2b, shows open pores and unmelted particles, which nucleated after the solidification process, these results are in agreement with what was reported in [13]. A good fusion between the particles is observed, evidenced by elongated splashes. However, the level of porosity given by the air bubbles can act as a source of cracks, which can cause poor cohesion in the coating when subjected to tensile forces. The formation of elongated splashes on the surface of the substrate causes the formation of a highly compact coating with a low level of defects, which is in agreement with the results presented in [8,12–14].

The EDS microanalysis, Fig. 3a, applied to the filler material and the coating does not show changes in its elemental composition. An average composition of 79.20 ± 2.18% in weight of Zn and 20.80 ± 2.8% in weight of Al is obtained. The X-ray diffraction results show the phase formation of Zn with a hexagonal crystalline structure in 83% proportion according to the ICSD database and reference pattern 96-901-1600 and an Al phase with cubic crystal structure in a proportion of 17% according to the ICSD database and reference pattern 01-089-2837, this is shown in Fig. 3b. These results show that no oxides or compounds foreign to the nature of the filler material are being formed in the coating that could affect its properties.

Fig. 3c shows the behavior of the voltage as a function of the current, an electrical resistivity value of (3.72 ± 0.048) $\times 10^{-4}$ Ω m is obtained for the coated ABS, this represents a conductivity value of 2682 S/m, in the case of uncoated ABS, there are theoretical values of 666–$4\times 10^{-14}$ S/m. These values are within the orders of magnitude reported in [15,16], it is important to mention that resistivity is affected by the structure and/or defects in the material, which causes that the number of electrons per unit volume can vary significantly, this is the reason because as the porosity increases, the free path of the electrons decreases and the electrical conductivity also decreases.

## 4. Conclusions

It has been possible to deposit a layer of metallic material on a polymeric substrate with a low-cost technique and without the use of any chemical reagent, in the surface preparation process, which has allowed obtaining good adhesion coatings.

A layer with a thickness of 89 ± 30 μm, a porosity of 0.87%, and an average pore size of 10 μm was obtained, with no evidence of cracks or the presence of rust in the coating.

The electrical resistivity is of the order of $10^{-4}$ Ω m, this value is related to the few defects found in the coatings, which increases the electron transport capacity, this opens up a range of possibilities for electrical and thermal conduction applications, however, this last property must be studied in future works, just as it will be important to evaluate the magnetic response with possible approaches in electromagnetic shielding.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Acknowledgments

This work was supported by Dirección General de Asuntos de Personal Académico– UNAM –Programa de Apoyo IT 101318 and PE100218.

## References

[1] A. Viscusi, M. Durante, A. Astarita, L. Boccarusso, L. Carrino, A.S. Perna, Experimental Evaluation of Metallic Coating on Polymer by Cold Spray, Procedia Manuf. 47 (2020) 761–765, https://doi.org/10.1016/j.promfg.2020.04.232.

[2] A.M. Donald, E.J. Kramer, Plastic deformation mechanisms in poly (acrylonitrile-butadiene styrene) [ABS], J. Mater. Sci. 17 (1982) 1765–1772, https://doi.org/10.1007/BF00540805.

[3] O. Meincke, D. Kaempfer, H. Weickmann, C. Friedrich, M. Vathauer, H. Warth, Mechanical properties and electrical conductivity of carbon-nanotube filled polyamide-6 and its blends with acrylonitrile/butadiene/styrene, Polymer (Guildf). 45 (2004) 739–748, https://doi.org/10.1016/j.polymer.2003.12.013.

[4] B.E. Tiganis, L.S. Burn, P. Davis, A.J. Hill, Thermal degradation of acrylonitrile-butadiene-styrene (ABS) blends, Polym. Degrad. Stab. 76 (2002) 425–434, https://doi.org/10.1016/S0141-3910(02)00045-9.

[5] R. Lupoi, W. O'Neill, Deposition of metallic coatings on polymer surfaces using cold spray, Surf. Coatings Technol. 205 (2010) 2167–2173, https://doi.org/10.1016/j.surfcoat.2010.08.128.

[6] P.C. King, A.J. Poole, S. Horne, R. de Nys, S. Gulizia, M.Z. Jahedi, Embedment of copper particles into polymers by cold spray, Surf. Coatings Technol. 216 (2013) 60–67, https://doi.org/10.1016/j.surfcoat.2012.11.023.

[7] S. Nigam, S.S. Mahapatra, S.K. Patel, Study of Various Aspects of Copper Coating on ABS Plastic by Electric Arc Spraying, Mater. Today Proc. 5 (2018) 8446–8453, https://doi.org/10.1016/j.matpr.2017.11.540.

[8] D.G. Agredo Diaz, N. Ortiz Godoy, R. Valdez Navarro, A. Barba Pingarrón, J.J. Olaya Flórez, J.R. González Parra, A. Covelo Villar, M.A. Hernández Gallegos, Caracterización electroquímica de recubrimientos Zn-Al sobre fundición nodular grado 2, obtenidos por proyección térmica por flama con alambre, Av. Investig. En Ing. 17 (2020). https://doi.org/10.18041/1794-4953/avances.1.5747.

[9] R. Gonzalez, H. Ashrafizadeh, A. Lopera, P. Mertiny, A. McDonald, A Review of Thermal Spray Metallization of Polymer-Based Structures, J. Therm. Spray Technol. 25 (2016) 897–919, https://doi.org/10.1007/s11666-016-0415-7.

[10] E.M. Girotto, I.A. Santos, Medidas de resistividade elétrica DC em sólidos: Como efetuá-las corretamente, Quim. Nova. 25 (2002) 639–647, https://doi.org/10.1590/s0100-40422002000400019.

[11] S. Singh, H. Singh, S. Chaudhary, R. Kumar, Effect of substrate surface roughness on properties of cold-sprayed copper coatings on SS316L steel, Surf. Coat. Technol. 389 (2020), https://doi.org/10.1016/j.surfcoat.2020.125619 125619.

[12] B.C. White, W.A. Story, L.N. Brewer, J.B. Jordon, Fracture mechanics methods for evaluating the adhesion of cold spray deposits, Eng. Fract. Mech. 205 (2019) 57–69, https://doi.org/10.1016/j.engfracmech.2018.11.009.

[13] P.R.C. Alcover Junior, A.G. Marenda Pukasiewicz, Evaluation of microstructure, mechanical and tribological properties of a Babbitt alloy deposited by arc and flame spray processes, Tribol. Int. 131 (2019) 148–157, https://doi.org/10.1016/j.triboint.2018.10.027.

[14] X.L. Zhou, A.F. Chen, J.C. Liu, X.K. Wu, J.S. Zhang, Preparation of metallic coatings on polymer matrix composites by cold spray, Surf. Coatings Technol. 206 (2011) 132–136, https://doi.org/10.1016/j.surfcoat.2011.07.005.

[15] A. Małachowska, M. Winnicki, Ł. Konat, T. Piwowarczyk, L. Pawłowski, A. Ambroziak, M. Stachowicz, Possibility of spraying of copper coatings on polyamide 6 with low pressure cold spray method, Surf. Coatings Technol. 318 (2017) 82–89, https://doi.org/10.1016/j.surfcoat.2017.02.001.

[16] A. Ganesan, J. Affi, M. Yamada, M. Fukumoto, Bonding behavior studies of cold sprayed copper coating on the PVC polymer substrate, Surf. Coatings Technol. 207 (2012) 262–269, https://doi.org/10.1016/j.surfcoat.2012.06.086.