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Formation of Polyacetylene Films on Copper Substrate by Abnormal Glow Discharge

Formación de películas de poliacetileno sobre sustrato de cobre mediante descarga luminiscente anormal

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Abstract

The formation of polymeric films by plasma has become an alternative for the coating of metallic materials that require varying their surface characteristics and improving their resistance to corrosion; because by this method it is possible, in principle, to polymerize any gaseous hydrocarbon. In this work, the study of the formation of acetylene polymer films on a copper substrate, previously treated in an abnormal luminescent discharge regime in argon-hydrogen atmosphere, is presented. The polymeric formation was carried out in a continuum current abnormal glow discharge in an atmosphere of 60% Ar, 35% H_2 and 5% C_2H_2 at a pressure of 2 Torr, at a temperature of 600 °C and with deposition times between 5 and 120 s. The structural and morphological analysis of the polymeric film deposited at different temperatures was performed by Infrared Spectroscopy and Scanning Electron Microscopy. Additionally, a characterization of the materials was carried out using corrosion resistance analysis.

Keywords: Abnormal Glow Discharge; Corrosion Resistance; Polymers; Acetylene; Copper Substrate.

Resumen

La formación de películas poliméricas por plasma se ha convertido en una alternativa para el recubrimiento de materiales metálicos que requieren variar sus características superficiales y mejorar su resistencia a la corrosión. El método de descarga luminiscente anormal en corriente continua se ha propuesto como una estrategia favorable para la producción de películas poliméricas, debido a que por este método es posible, en principio, polimerizar cualquier hidrocarburo gaseoso. En este trabajo se presenta el estudio de la formación de películas poliméricas de acetileno sobre un sustrato de cobre, previamente tratado en régimen de descarga luminiscente anormal en atmósfera de argón-hidrógeno. La formación del polímero se llevó a cabo en una descarga luminiscente anormal en corriente continua en una atmósfera de 60% Ar, 35% H_2 y 5% C_2H_2 a una presión de 2 Torr, a una temperatura de 600 °C y con tiempos de

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deposición entre 5 y 120 s. El análisis estructural y morfológico de la película polimérica depositada a diferentes temperaturas se realizó mediante Espectroscopia Infrarroja y Microscopía Electrónica de Barrido. Además, se llevó a cabo una caracterización de los materiales mediante un análisis de resistencia a la corrosión.

Palabras clave: descarga luminiscente anormal; resistencia a la corrosión; polímeros; acetileno; sustrato de cobre.

1. Introduction

The formation of polymers in gaseous environments mainly occurs in amorphous or ceramic coatings, limiting potential applications for these coatings in corrosion resistance. This research focused on studying the formation of polymeric films on a metallic material, specifically copper, using abnormal glow discharge in direct current [1] . Copper is one of the key materials utilized in the industry due to its various properties and low production costs on an industrial scale. However, investigating different coatings that can protect it against corrosion could extend its lifespan. Therefore, the purpose of this research was to analyze the formation of polymer films as a potential coating option to safeguard copper against corrosion.

Corrosion is one of the biggest issues that affects the useful life of metallic materials used in industry, in this way, the coating of these materials with corrosion-resistant polymeric films has become an attractive alternative since it does not affect the mechanical properties of the material. However, the high cost associated with the production of anticorrosive polymeric films has generated a negative economic impact on industries [1]. Consequently, the search for polymeric coatings with more efficient and prolonged effects against corrosion, as well as the study of new techniques for the formation of anticorrosive polymeric films that require less energy, time and temperature of formation, has become a topic of current interest for the industrial and scientific sectors.

One of the most widely used techniques for the formation of thin coating films with shorter production times is the plasma method in the regime of the luminescent discharge. In particular, the use of plasma in the abnormal glow discharge (AGD) regime for the production of polymers from a hydrocarbon allows at the same time the formation of thin polymeric films that are deposited on the metal surface (substrate) [2]. This technique allows polymer layers to be deposited on the surface of a material, thus generating a fine film of micrometric units that can improve the physicochemical properties of the metal surface it covers [3]. The type and characteristics of the polymeric materials produced using this method will depend on the atmosphere, temperature, and pressure conditions used during the process.

The formation of organic polymers under electrical discharge in gaseous media has been known for many years. In 1929, Schoepfle and Connel reviewed the effects of cathode rays, silent electric discharges, and alpha particles on hydrocarbons, showing that some polymerization almost always occurs [4,5]. In 1931, Linder and Davis studied the gaseous and solid polymers formed by the action of a glow discharge on hydrocarbon vapors [6]. This method of abnormal glow discharge offers the production of polymer films from gaseous hydrocarbons. The formation of thin polymer films is generally carried out on ceramic materials, which makes it difficult to form polymers. However, the abnormal glow discharge method allows for the generation of polymer films on metal surfaces. The abnormal glow discharge method generates electron-rich species within the plasma, enabling the formation of polymer chains on the metal material. This method performs the polymerization of gaseous hydrocarbons, thus overcoming the limitations of conventional polymerization methods [4], [5], [6].

“A new SP-promoted polymerization method was developed for synthesizing polymeric films directly from liquid monomers with a negatively biased bipolar square pulse [7].”

The search for new applications of polymer films has become a source of inspiration to treat materials such as copper, which is a relevant material in technological and industrial development due to its excellent thermal and electrical conductivity, which make a good candidate for plasma treatment due to its high melting point and its catalytic action for the formation of organic deposits on its surface [8]. Some innovative contribution in the production of polymeric coatings have resulted from the use of abnormal direct current glow discharge technique in an acetylene atmosphere, which has led to shorter film formation times [9].

This has led us to delve into the formation of polyacetylene films on a copper substrate using AGD in direct current under an acetylene/argon/hydrogen atmosphere. The formation of the polymeric acetylene film was evaluated at different discharge times (5, 30, 78 and 120 s), while the structural and morphological characteristics of these polymeric deposits were analyzed by Infrared (FTIR) Spectroscopy and Scanning Electron Microscopy (SEM), respectively. Additionally, a corrosion resistance analysis was performed on these polymeric/copper systems.

2. Methodology

The plasma polymerization process was carried out in a steel reactor with a confined anode geometry, which consisted of acylindrical anode with a diameter of 50 mm and a length of 60 mm, inside wich the cathode is also located. Both the anode and cathode were made of AISI 1020 steel. The polymer samples were produced by the abnormal glow discharge method in an acetylene atmosphere on a copper substrate. During the formation of the polymer films on a copper substrate, dynamic atmosphere composed of argon (60%), hydrogen (35%) and acetylene (5%) was used, with a total flow of 100 mL/min at 2-torr pressure. The amounts of the constituent gases of the polymerization atmosphere were obtained empirically. The polymerization time was set between 5 and 120 s, as illustrated in Figure 1. Before the polymerization process, the metal substrate, consisting of an electrolytic copper foil with a square geometry of 100 mm^2, was subjected to cathodic sputtering cleaning by abnormal glow discharge with reducing atmosphere of argon (60%) and hydrogen (20%). The sputtering cleaning was done during the heating stage up to the polymerization temperature at a rate of 100 °C/min.

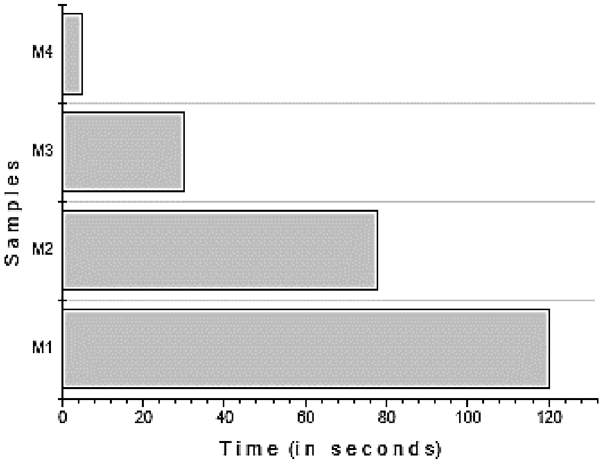


Figure 1. Deposition time used for the production of polymer samples in an atmosphere of 60% Ar + 35% H_2 + 5% C_2H_2 at a pressure of 2 Torr and a temperature of 600 °C using the AGD. M4 (5 s), M3 (30 s), M2 (78s), and M1 (120 s).

Temperature of the cathode, where the substrate was located, was set at 600 °C using a discharge voltage (351V and 85 mA) and with a discharge power of a DC signal. The characterization of the composition of each polymeric sample obtained was carried out by Infrared (IR) Spectroscopy using a Shimadzu Prestigie-21 spectrophotometer with Fourier Transform (FTIR), equipped with a Michelson-type interferometer, a KBr/Ge beam-splitter, a ceramic lamp, and a DLATGS detector. The FTIR spectra were measured in the range of 4000–500 cm^{-1} with a resolution of 3.0 cm^{-1} and 30 scans using the techniques of attenuated total reflectance/reflection (ATR).

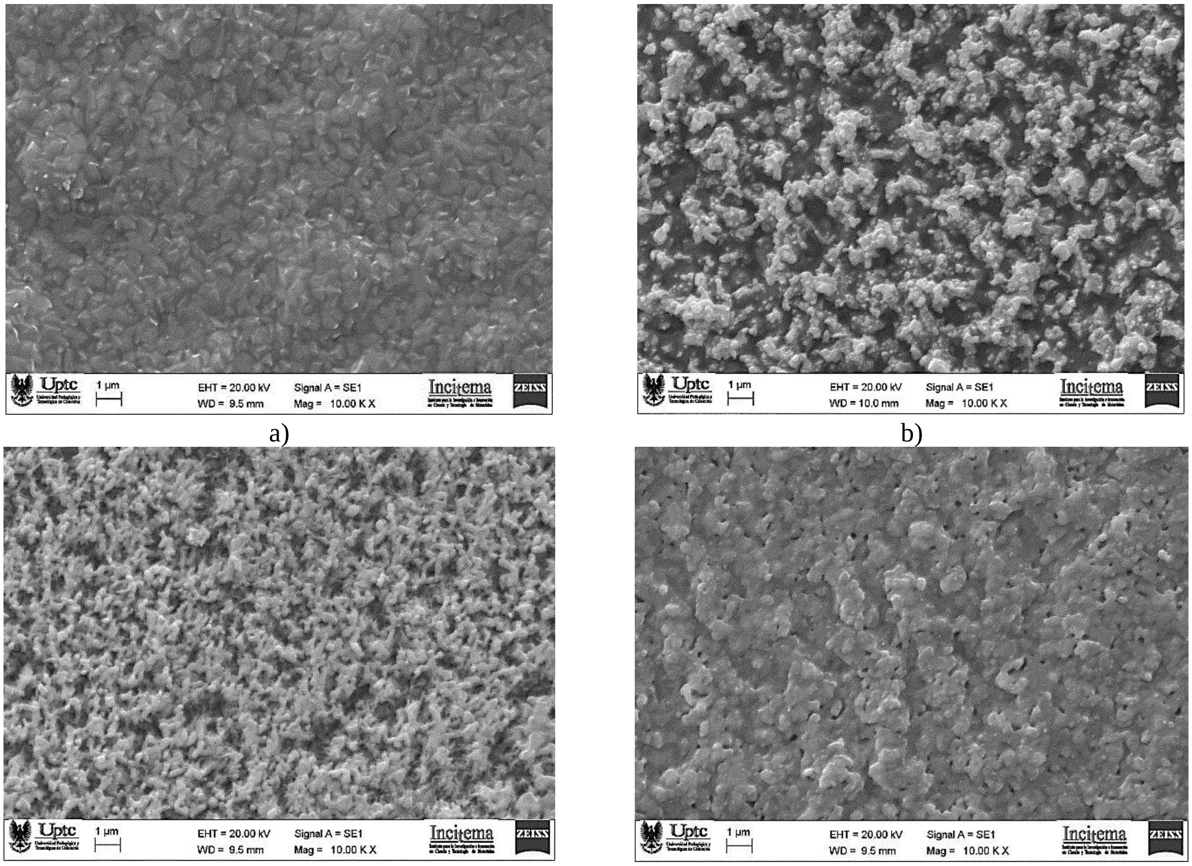
The microscopic morphology of the polymeric films was evaluated by scanning electron microscopy (SEM) using an EVO MA 10-Carl Zeiss equipment (Oberkochen, Germany) operating at 20 kV. All samples were coated by gold–palladium sputtering before their examination. Finally, a corrosion resistance test was performed on the samples obtained using a copper sulfate solution.

3. Results and Analysis

Figure 2 shows the SEM images taken at 10,000x magnification of polymer films formed at plasma discharge times of 5s (a), 30s (b), 78s (c), and 120s (d). The evolution of the polymer deposit formation process over time is shown. In the first stage of formation, i.e., at 5s (Figure 2 (a)), the deposition of a continuous polymeric aggregate, composed of equiaxial grains of the order of 200 nm, was observed. By increasing the deposition time to 30s, the continuity of formation of aggregates of the order of nanometer on the initial surface is also observed (Figure 2 (b)). As the deposition time increased to 78s, the polymeric film continued to progressively densify (Figure 2 (c)). At a time, greater than 120s, the densification of the deposits increased in such a way that a relatively irregular continuous surface was formed with the presence of nanometric-sized pores (Figure 2(d)). The insulating character of this latter polymeric film was indirectly evidenced due to difficulty to be focused at high magnification with the electron microscope.

Since the polymer deposits on the Cu substrate presented a rough surface and their IR spectra were taken in ATR mode [9], [10]. These IR spectra presented a profile similar to those reported in the literature for the polymerization using acetylene in radiofrequency discharges [11], the latter corresponding to a regime where the treatments were carried out under pressures between 10 and 20 times lower than that used in this study.

Figure 3 shows the IR spectra of the polymer samples on copper support at deposition times of 5, 30, 78, and 120s.



a) b)

c) d)

Figure 2. Scanning electron microscopy images of the polymer films deposited on a copper surface using AGD at times ranging from (a) 5 s, (b) 30 s, (c) 78 s, and (d) 120 s, in an atmosphere of 60% Ar + 35% H2 + 5% C2H2 at a pressure of 2 Torr and a temperature of 600 °C.

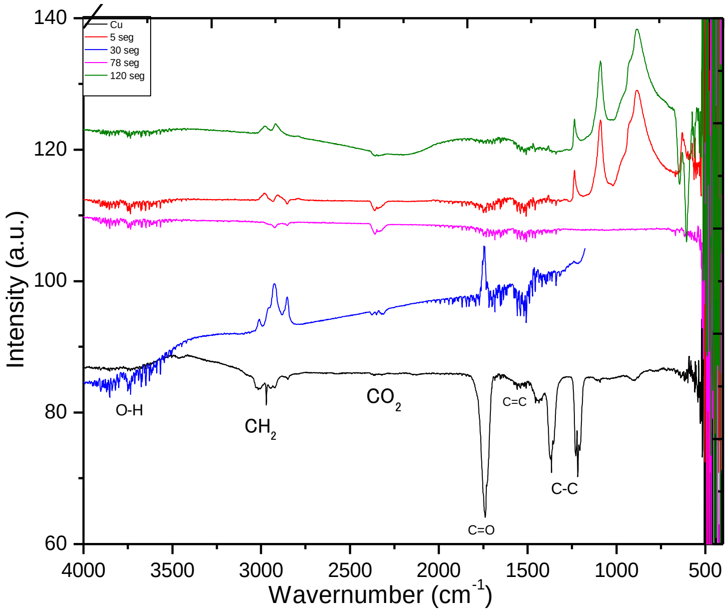


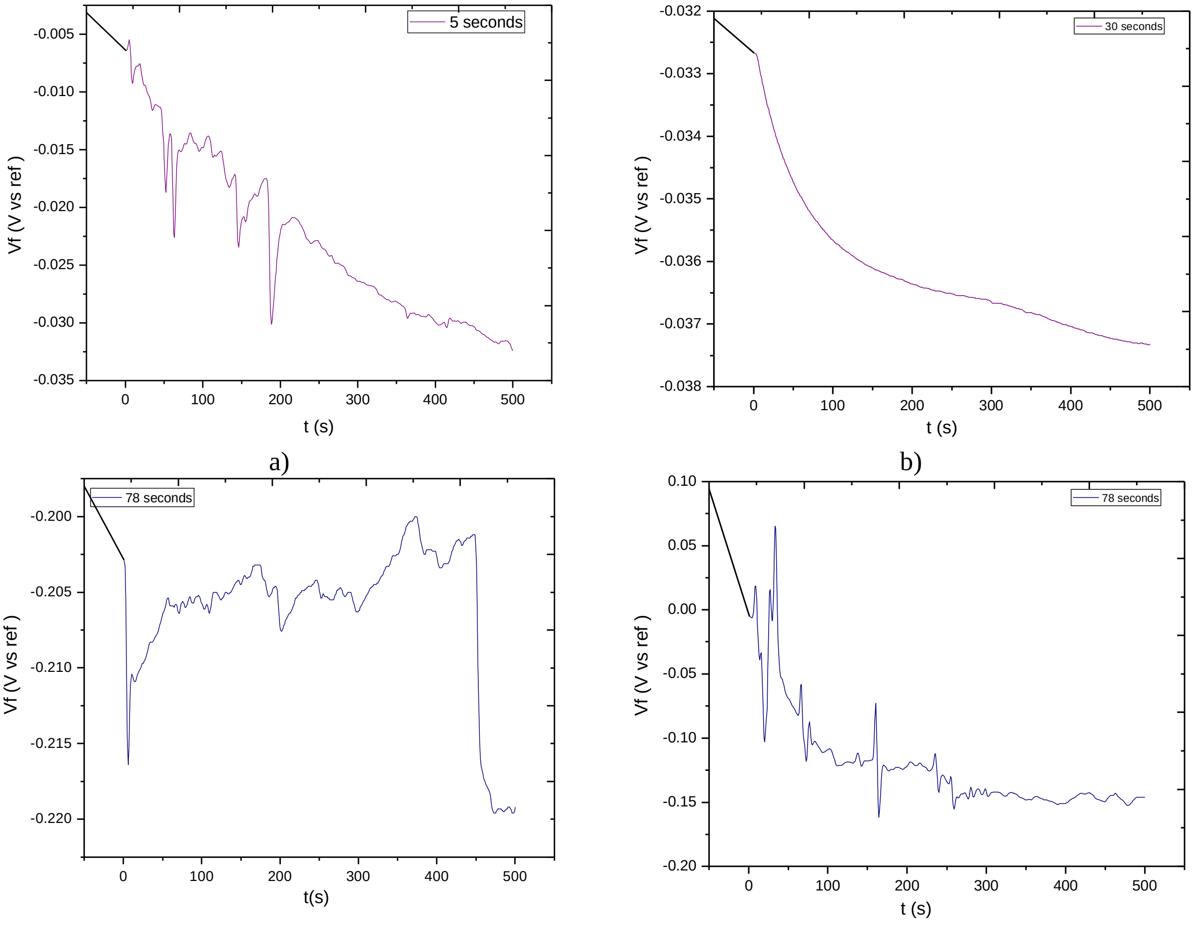
Figure 3. IR spectroscopy of the polymer samples from 120 s to 5 s of formation, in an atmosphere of 60% Ar + 35% H_2 + 5% C_2H_2 at a pressure of 2 Torr and a temperature of 600 °C.

The main signals detected in these spectra correspond to C=C stretching at 1604.00 cm^{-1}, C-C stretching at 1390.30cm^{-1} and 1210.70 cm^{-1} and C-H stretching at 2926.47cm^{-1} (asymmetric) and 2852.70cm^{-1} (symmetrical). Due to the absence of the C-H bending band, the absence of CH2 and CH3 moieties could be deduced.

While from the absence of the bands associated with the C≡C stretching at 2200.00cm^{-1} and 2100.00cm^{-1}, the complete dissociation of acetylene was deduced, this as a consequence of the impact of energetic particles and thermal energy present in the plasma [12]. The presence of bands at 1743.00cm^{-1} associated with C=O and at 3603.3cm^{-1} associated with H-O-H bond, have already been reported in other works as a product of the reaction of ambient oxygen with the free radicals present in the polymer [12], [14]. The band corresponding to the C-H stretching at 3008.2cm^{-1} could be associated with the stretching of the sequential C-H bonds, characteristic of polyacetylene [15], [16].

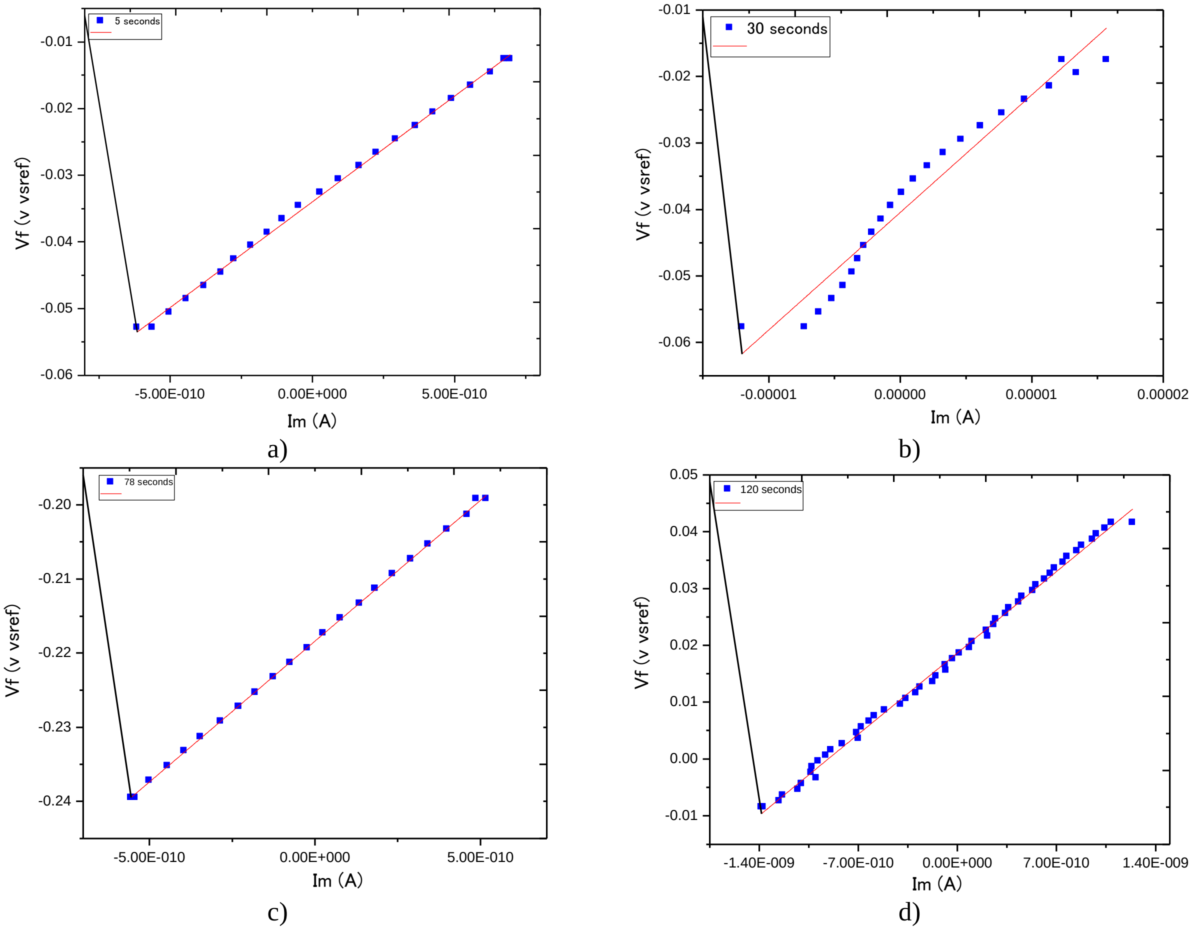
Relating the results of the infrared analysis shown in Figure 3 with the electron microscopy images shown in Figure 2, it can be seen that for the less compact microstructure, corresponding to 30s of deposition (see micrograph in Figure 2(b)), there is a greater signal for C-H stretching (see Figure 3), which allows us to infer that for shorter and longer times, a more cross-linked compact structure is obtained. The formation of this structure was promoted by the modification of the substrate by the process of the discharge described in the methodology, such surface modification could provide a higher reactivity of the substrate surface due to the presence of larger anchoring sites for the formation of structures less ordered, like those of a polymer.

Figure 4 and 5 show the results of the behavior of the polymer films in a corrosive solution of copper sulfate of 1000 ppm, from which measurements of open circuit potential and corrosion resistance were obtained.



a)
b)
c)
d)

Figure 4. linear polarization resistance of polymer films with (a) 5s, (b) 30 s (c) 78 s to (d) 120s formation in an atmosphere of 60% Ar + 35% H_2 + 5% C_2H_2 at a pressure of 2 Torr and a temperature of 600 °C.



a) b)

c) d)

Figure 5. Polarization resistance of polymer films with (a) 5s, (b) 30 s (c) 78 s to (d) 120s formation in an atmosphere of60% Ar + 35% H_2 + 5% C_2H_2 at a pressure of 2 Torr and a temperature of 600 °C.

These measurements allow us to gather information about the corrosion rate of the polymer film [17], [18]. Figure 4(a) presents the corrosion potential as a function of time.

Figure 4 shows the polarization resistance of the polymer films formed at times from 5s to 120s. These graphs illustrate corrosion resistance behavior in a copper sulfate solution. Table 1 shows the corrosion rate and corrosion resistance data obtained by this method of analysis. As can be seen in Table 1, the polymer coating formed at 120s has higher corrosion resistance compared to those obtained at 78s, 30 s and 5s.

It is reported in the literature that an increase in the corrosion potential and a decrease in the corrosion current, with respect to the untreated sample, are parameters that indicate that a material has improved its corrosion resistance [19], [20], [21]. As shown in Table 1, two coatings meet both premises, the 5 s and the 120s. However, for the case of the sample with a time of 78s, the corrosion current and the corrosion potential decrease, unlike the 30-s sample whose corrosion current increases by one order of magnitude while the corrosion potential increases slightly. Thus, only the coatings at 5s and 120s presented a better behavior to the corrosive process with respect to the untreated sample.

Corrosion analysis can be correlated with microscopic images of the polymer films taken by SEM. The film formed at 5 s presents a homogeneous coating since there was only the formation of a very thin layer, while at 30 s, a surface with irregular deposits was observed that increased with time, as corroborated in the sample treated for 78 s (Figure 2c). These surface irregularities could decrease the corrosion resistance of the samples treated for 30 s and 78 s due to the ease with which the corrosive agent can interact with a rough surface. In the same way as for the sample treated for 5 s, the sample treated for 120 s (Figure 2d) presented a homogeneous surface, but was thicker due to the longer treatment time.

Table 1. Polarization Resistance analysis of polymer films at a formation time 120s-5s, in an atmosphere of 60% Ar + 35%H_2 + 5% C_2H_2 at a pressure of 2 Torr and a temperature of 600 °C

Sample	I_{corr}(pA)	E_{corr} (mV)	R_p(KΩ)	V_{corr}(mpy)
Substrate (Cu)	194100	-87.30	134.2	1.250×10^{-1}
120 s	1260.0	18.58	20680.00	3.383×10^{-3}
78 s	666.5	-219.30	39.09	67.490×10^{-5}
30 s	1588000.0	-86.13	16.41	4.263
5 s	832.5	-32.58	31.19	845.570×10^{-5}

Thus, the homogeneity presented in the surface microstructure of the samples treated for 5s and 120s seems to be responsible for their better behavior against corrosive phenomena, compared to the untreated substrate.

4. Conclusions

Using the abnormal luminescent glow technique in direct current, under an atmosphere of acetylene (5%)/hydrogen (35%)/argon (60%) at 600 °C, it was possible to form thin polymeric coatings on a surface of copper. The structural, morphological and anticorrosive properties of the films formed at discharge times of 5 s, 30 s, 78 s, and 120 s were analyzed. The polymeric coatings formed presented structural and physicochemical characteristics similar to the films prepared in other studies using radiofrequency discharges.

Through SEM images it was possible to observe the evolution in time of the surface microstructure of the coating during the polymerization process using DC glow discharge. During the first stage of polymerization, a nanostructure consisting of randomly oriented equiaxial grains was formed, on which structures were superimposed and densified with increasing polymerization time.

The IR spectroscopy analysis, contrasted with the images of the polymeric films observed by SEM, allowed inferring the formation of a crosslinked polymeric structure in the samples treated for times greater than 3s. The presence of C=O and OH functional groups as components of the synthesized polymer suggests the reaction of the final deposit with ambient oxygen after being removed from the reactor chamber.

The corrosion analysis was consistent with the micrographs obtained from SEM, since the samples with a more regular surface showed a better behavior against the corrosion phenomenon compared to the untreated substrate.

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Autor Contributions

A. Sarmiento-Santos: Investigation, Conceptualization, Methodology, Writing – original draft. J. A. Gómez-Castaño: Methodology, Writing – review & editing. B. Alvarez-Luna: Writing – review & editing. W. Redondo-Lancheros: Conceptualization, Supervision, Writing - review & editing. J. Garcias-Zuniga: Writing – review & editing.

All authors have read an agreed to the published version of the manuscript.

Conflicts of Interest

The authors declare no conflict of interest.

Institutional Review Board Statement

Not applicable.

Informed Consent Statement

Not applicable.

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