Acetylene polymerization in plasma of direct current

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Abstract. Plasma polymerization is a technique that allows obtaining polymer of any type of hydrocarbon, including the non-polymerizable by standard methods. This because of in the plasma state the activation energy can be reduced for the realization of reactions difficult to be presented under standard experimental conditions. For plasma polymerization only the implementation of different types of discharges in the radio frequency regime has been reported, leaving aside the application of direct current discharges for this process. The acetylene polymer consists of carbon chains with alternation of single and double covalent bonds. The formation of this polymer has been reported using radio frequency discharges in the abnormal regime. The paper reports the formation of polymer from acetylene using the abnormal glow discharge in the direct current regime, a novel process not yet reported in the literature. The deposition of the polymer is carried out at different times on a polycrystalline copper substrate previously treated in a glow discharge of argon and hydrogen. For the generation of this polymer an atmosphere of 60% Ar+35% H₂+5% C₂H₂ at 2 torr pressure and a temperature of 600 °C is used. The structural and morphological analysis of the deposits is carried out by infrared spectroscopy and scanning electron microscopy, respectively.

1. Introduction

The acetylene polymer or polyacetylene consists of a long chain of carbon atoms with single and double bonds alternating between them [1]. Polyacetylene is due to a chemical process generated by reagents, low molecular weight compounds that are chemically grouped together giving rise to a large weight molecule called three-dimensional macromolecule or a linear chain [2-4]. Another method for the formation of polymers is plasma polymerization which is commonly carried out by radio frequency [5]. In plasma polymerization, two opposing processes are presented that compete with each other: polymer formation, which has to do with the deposition of material, and ablation, which has to do with the removal of material. The ablation of materials by plasma is mainly due to two processes: physical sputtering and chemical etching. The formation of polymer and its properties are controlled by the balance between polymerization, induced by plasma and polymerization in the plasma, and ablation [6]. These polymers can have special properties dependent on the conditions of the polymerization process [7-12]. In the present research work we report the preliminary results of the acetylene polymerization process using the abnormal glow discharge (AGD) in direct current (DC). Although most of the work in the field of plasma polymerization using radiofrequency is performed at pressures of tens of millitorr [13,14], in this work the working pressure is of the order of a pair of torr.
2. Experimental setup
For the plasma polymerization process, a reactor with a confined anode geometry consisting of a cylindrical anode 50 mm in diameter and 60 mm in length was used, inside which the cathode of the discharge was placed. Both the anode and the cathode were manufactured in AISI 1020 steel. The polymer samples were produced by the AGD in an acetylene atmosphere on a copper substrate. The power supplied to the discharge was made through a pulsating DC signal obtained by rectifying the alternating current signal of the network. The temperature of the cathode, where the substrate was placed, was set at 600 °C through the discharge voltage (351 V y 85 mA). The substrate, 10 mm square side sheet made of electrolytic copper, was subjected to sputtering in a AGD of 75% Ar and 25% H2, at 2 torr of pressure, before the polymerization process. The cleaning step was carried out during heating, up to the polymerization temperature, at a rate of 100 °C/min. For the polymerization process an atmosphere of 60% Ar, 35% H2 and 5% C2H2 was used with a total flow of 100 mL/min at 2 torr of pressure. The polymerization time was established between 120 s and 5 s. The obtained polymer samples were analyzed by infrared (IR) spectroscopy and its surface observed by scanning electron microscopy (SEM).

3. Results and analysis
Figure 1 shows the results of the analysis by IR spectrometry of the plasma-polymer samples carried out in times between 5 s and 120 s. The IR spectra show absorbance and transmittance signals since the Kubelka-Munk method was used to transform the IR spectra from diffuse reflection to linear absorbance and transmittance [15,16], since the polymer deposits present a rough surface. These spectra are similar to each other and to those reported in the literature for the polymerization of acetylene in radiofrequency discharges. These radiofrequency discharges are usually carried out at pressures between 10 to 20 times lower than the one used here [17].

![Figure 1. IR spectrum for polymerization times of 5 s, 10 s, 20 s, 30 s, 45 s, 60 s, 78 s and 120 s.](image-url)

The IR spectra of Figure 1 show the C-H stretch at 2926.47 cm⁻¹ and 2852.7 cm⁻¹ and due to the absence of the C-H flexion bands the absence of CH2 and CH3 can be inferred. The stretch bands C=C are also observed at 1570.8 cm⁻¹ and the stretch C-C at 1390.3 cm⁻¹ and 1210.7 cm⁻¹. Due to the absence of the bands associated with the stretch C≡C in 2200 cm⁻¹ and 2100 cm⁻¹, corresponding to acetylene, it is deduced that this was completely dissociated by the impact of the energetic particles and the thermal energy present in the plasma. The presence of the bands in 1738.45 cm⁻¹ associated to the C=O and in 3603.3 cm⁻¹ associated with the O-H was already reported in other works as a product.
of the reaction of the oxygen of the environment with free radicals present in the polymer [5,17,18]. Finally, the band corresponding to the C-H stretch at 3008.2 cm\(^{-1}\) could be associated with the stretching of these sequential bonds, typical of poly-acetylene [19]. It is noteworthy that the formation of this structure was promoted by the modification of the substrate through the sputtering process described in the experimental part. This surface modification could provide greater reactivity of the substrate surface by the presence of larger anchoring sites for the formation of less ordered structures such as those of a polymer.

Figure 2 shows the micrographs, made with magnification 40,000 x, of the polymer deposits carried out for a time between 10 s (Figure 2(a)) and 120 s (Figure 2(b)). Thus, the evolution of the process of forming the polymer deposit over time can be observed. In the first instance at 10 s (Figure 2(a)), an aggregate has been deposited consisting of individual particles of the order of 200 nm that coalesce until forming a relatively porous layer 20 s (Figure 2(c)), on which continue to deposit particles that coalesce again 78 s (Figure 2(d)) to form a deposit granular continuous and free of pores 120 s (Figure 2(b)). This granular microstructure is composed of nanostructured grains of the order of 400 nm of equiaxial geometry and random orientation. The insulating character of this polymer was evidenced in the difficulty it presented to be focused at high magnifications with the electron microscope.

Figure 2. Images obtained by SEM with magnification 40,000 x, for polymerization times of (a) 10 s, (b) 120 s, (c) 20 s, (d) 30 s, (e) 60 s, (f) 78 s.
4. Conclusions
In atmospheres with 5% acetylene in the DC AGD, polymer deposits were created on copper substrates previously subjected to sputtering. This polymer corresponds to a polymer with a structure similar to that reported in works performed with radiofrequency discharges, demonstrating the potential of the DC discharges applied to the polymerization process at pressures higher than those commonly used.

The presence of oxygen as a constituent of the synthesized polymer suggests the reaction of the final deposit with the oxygen of the environment, after being removed from the reactor chamber. Through SEM it was possible to observe the evolution over time of the surface microstructure of the polymer during the polymerization process in the DC AGD, obtaining a nanostructure of randomly oriented equiaxed grains.

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References
[1] Saxman A M, Liepins R and Aldissi M 1985 Progress in Polymer Science 11(1-2) 57
[2] Chalifoux W A and Tykwinski R R 2010 Nature Chemistry 2(11) 967
[3] Clarke T C, Yannoni C S and Katz T J 1983 Journal of the American Chemical Society 105(26) 7787
[4] Yamabe T, Tanaka K, Terama-e H, Fukui K, Imamura S, Shirakawa H and Ikeda S 1979 Journal of Physics C: Solid State Physics 12(7) L257
[5] Chan C M, Ko T M and Hiraoka H 1996 Surface Science Reports 24(1-2) 1
[6] Yasuda H and Yasuda T 2000 Journal of Polymer Science Part A: Polymer Chemistry 38(6) 943
[7] Praveen K M, Pious C V, Thomas S and Grohens Y 2019 Non-thermal plasma technology for polymeric materials ed S Thomas et al. (Amsterdam: Elsevier) chapter 1 p 1
[8] Gulrajani M L 2013 Advances in the dyeing and finishing of technical textiles (Netherlands: Elsevier)
[9] Jacob M V, Olsen N S, Anderson L J, Bazaka K and Shanks R A 2013 Thin Solid Films 546 167
[10] Cakmak K, Bayram Ö, Solak K, Kaban G, Şimşek Ö and Mavi A 2019 Turkish: Journal of Chemistry 43(1) 323
[11] Cho E, Kim S H, Kim M, Park J S and Lee S J 2019 Surface and Coatings Technology 370 18
[12] Vandenbossche M and Hegemann D 2018 Current Opinion in Solid State and Materials Science 22(1) 26
[13] Peter S, Graupner K, Grambole D and Richter F 2007 Journal of Applied physics 102(5) 053304
[14] Guimond S, Hanselmann B, Hossain M, Salimova V and Hegemann D 2015 Plasma Processes and Polymers 12(4) 328
[15] Nobbs J H 1985 Review of Progress in Coloration and Related Topics 15(1) 66
[16] Hecht H G 1977 Proc. of a Workshop Seminar held at NBS 466 57
[17] Herrador J M H, Tišler Z, Hajková P, Soukupová L, Zárybnická L, & Černá K 2017 Acta Chimica Slovenica 64(3) 598
[18] Yasuda H, Bumgarner M O, Marsh H C, & Morosoff N 1976 Journal of Polymer Science: Polymer Chemistry Edition 14(1) 195
[19] Hudson B 2018 Materials 11(2) 242