Synthesis and characterization of copper coatings on polyimide membranes (PIR 003)

P. E. Velarde Loayza[a,b,*], E. A. Brocchi[c], R. N. C. de Siqueira[d]

[a]*Department of Chemical and Materials Engineering, Pontifical Catholic University of Rio de Janeiro, RJ, Brasil*
[b]*Universidad Tecnológica del Perú*
[c]*Department of Chemical and Materials Engineering, Pontifical Catholic University of Rio de Janeiro, RJ, Brasil*
[d]*Department of Chemical and Materials Engineering, Pontifical Catholic University of Rio de Janeiro, RJ, Brasil*

The formation of stable metallic/polymeric joints is a huge challenge in the materials sciences. Adhesion requires interphase that is able to specifically interact with the metallic phase. The primary amino groups exhibit copolymers as highly reactive to metal surfaces. This article will give a better understanding of the mechanisms of chemo-absorption by chemical functionalization of polyimides, as well as in the wet development of metallization of materials based on H_2 reduction in polymers. And it will be evidenced by comparisons by measures of polymer/metal characterization.

1. Introduction

The development and application of composites consisting of polymeric matrices and metallic coatings can have wide application when it comes to weight reduction, for example in the medical field (medical implants), aeronautical area (coatings) [4]. While the polymer allows for weight reduction, the metallic phase allows for the incorporation of differentiated properties, such as mechanical strength, which is directly correlated with grain size.

Rodríguez, J. A.; Fernández G., M, [10], studying the application of polyimide, including in the form of thin coatings, was recently used as gas separation membranes (selective permeability) by incorporating high thermal stability and adequate mechanical properties. [6].

In polyimides, the glass transition temperature (tg) is approximately 300°C and the thermal decomposition temperature (400°C), showing much higher values when compared to those of typical polymers. [1]. Allowing the use of polyimide as a substrate for the production of metallic coatings via in situ reduction to a temperature below 300°C.

To evaluate the polymer concentration parameters for the coating, membranes were previously developed with 2.5%, 7.5% and 12.5% of the polyimide PIR 003, dissolved in dimethylformamide (C_3H_7NO), which developed an optimal homogeneous surface for the covering was in its composition of 7.5%.

All metallization processes require a pre-treatment of polymer substrates to allow for metal deposition. The challenge of the present study is to generate good adhesion of the metal, but chemical functionalization tests were developed, using different chemical reagents, to activate some functional groups (primary amino groups) of the polyimides, which allow and facilitate the adhesion of the metal [12]. The chemical agents used are: palladium chloride ($PdCl_2$), silver nitrate ($AgNO_3$), sodium hypochlorite (NaClO), and solvents (xylene and toluene) to activate the primary amino groups. To determine how much influence the chemical treatments on polyimides, it was

necessary to carry out measurements of the contact angle, to determine in which of them there was a decrease in surface energy to favor the effect of adhesion on the metallic coating produced.

Interactions between the metallic coating and the polymer surface are established and determined in layers of adjacent atoms along the interface. Noble metals in polymers have a strong tendency to aggregate due to their high cohesive energy and their metal-polymer interaction is relatively weak [5]. In this sense, nanocrystalline grains allow to achieve expressive strength gains. Metals will configure different surface properties in relation to the polymer used, among them, particularly when in the nano dimension, the use as absorbents for gases can be mentioned (eg. CO), copper is included among them [9].

Within the methods of synthesis of polymer-metal coatings, there is chemical vapor deposition, ion track technology and sputtering, but the present work will develop it, by reduction via H_2, wet method, for the synthesis of copper coatings in PIR 003 polyimide matrices, with $CuSO_4$ and $CuCl_2$ precursors at 200°C. The characterizations of the coverings were carried out by measurements of SEM-EDS and XRD.

2. Polymeric membrane technology

Polymeric membrane technology is widely applied in several industries, such as water treatment, molecular separations, biomolecule purification, environmental remediation, and gas separation. It has high flexibility, low energy requirements, and relatively low preparation cost. The use of nanoparticles in polymeric structures is considered to be an effective way to address the mentioned challenges to produce membranes with greater reliability. [8]. These nanoparticle modified membranes are categorized into four categories: conventional nanocomposites, thin-film nanocomposites, thin-film composites with nanocomposite substrate, and nanocomposites located on the surface (Fig. 1) and are described in the following item. [15].
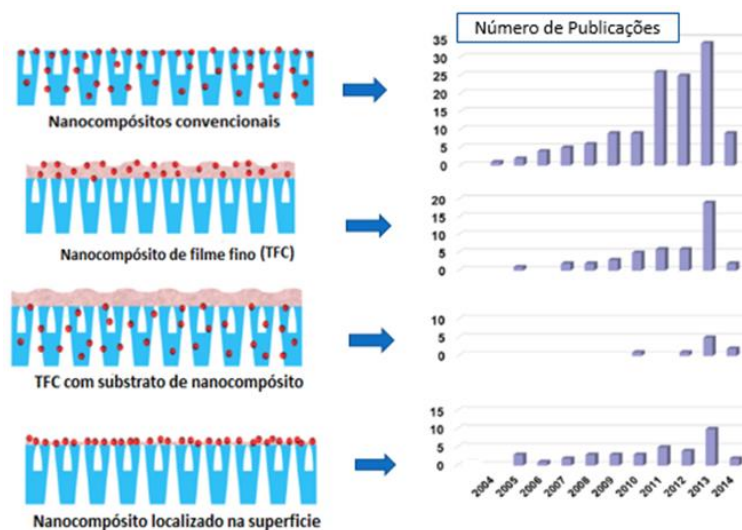

Fig. 1. Types of nanocomposite membranes and corresponding publication numbers related to water treatment applications [14].

2. Adhesion of particles to the metal-polymer membrane

The adhesion of polyimide to metals is usually quiet poor, this is probably due to it's rigid molecular structure and the fact that the low surface energy component (aromatic rings) dominates the high surface energy component (polar groups) in the surface phase. Regardless of the nature of

the metallization process used (dry chemicals or physical methods), the surface of the polymeric substrates (PI substrates in this work) has to be chemically functionality. (Fig. 2).

Electrolytic metallization or chemical deposition consists of a redox process in which the ions of the metal to be deposited (usually Ni or Cu) are chemically reduced to a metallic state on the substrate surface due to the presence of a strong reducer. Palladium-based catalysts are commonly used to initiate the redox reaction and several experiments show that only Pd^0 species operate as the catalyst in a chemical deposition. Cu electrolytic films deposited on PI substrates involve the functionalization of the surface in a nitrogen atmosphere, and a subsequent "activation" through the $PdCl_2$ route, the metal/polymer systems exhibit good adhesion and gas permeabilization characteristics. [3].
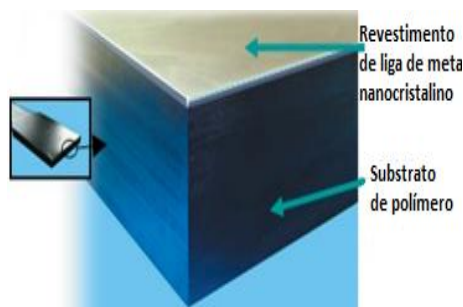

Fig. 2 Hybrid system showing the nanometal coating on the polymer substrate. [4]

3. Surface-free energy (SFE)

Adhesion is related to surface phenomena, which occur spontaneously and result from decreased surface energy. Free surface energy (SFE) is a characteristic parameter of a material strongly associated with the equilibrium state of atoms on the surface and its value depends on the nature and aggregate state of the material. It is fundamental because it is a function of the response of the conditions of the formation of adhesive joints, serving as an equivalent for characteristics of resistance of the adhesive joint to external action. [13]. SFE is defined as the work required to produce a new material surface, and is given as energy/ surface area; the units are mJ/m^2. In a solid-liquid interface, the forces of interaction are determined by the forces of cohesion and adhesion. The relationship between these two forces allows the determination of SFE in solids. By measuring the contact angle between the tangent of the contour surface of a liquid drop and the surface (Fig. 3). [14].
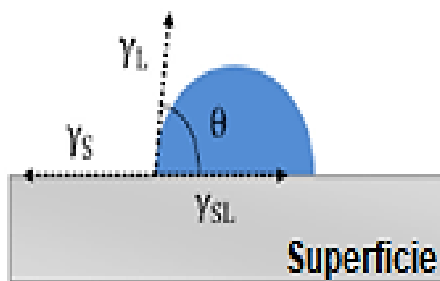

Fig. 3. Scheme of a drop of liquid showing the quantities in Young's equation. [11].

4. Methodology

In order to evaluate the parameters that influence the adhesion of copper to the polyimide in the synthesized film, the surface energy measurements of the functionalized membranes were evaluated, after the film synthesis, the XRD and SEM measurements were performed.

4.1. Functionalization of the polyimide

Regardless of the nature of the metallization process used (dry chemicals or physical methods), the surface of the polymeric substrates (polyimide PIR 003) has to be chemically modified, by activating the membrane with chemical solutions.

4.1.1. Materials

To carry out membrane functionalization, the following reagents were used, showed in the Table 1:

Table 1. Reagents used in the functionalization of PIR 003 polyimide.

Reagent	Formula	Origin	Purity (%)
Tin chloride II	$SnCl_2.2 H_2O$	ISOFAR	98
Palladium chloride	$PdCl_2$	ISOFAR	99
Silver nitrate	$AgNO_3$	ISOFAR	99
Sodium hipochlorite	NaClO	ISOFAR	4 - 6
Xylene	C_8H_{10}	ISOFAR	98.5
Toluene	$C_6H_5CH_3$	ISOFAR	99.5
Hydrochloric acid	HCl	ISOFAR	36.5 - 38

4.2. Functionalization with $SnCl_2$ and $PdCl_2$

Species like, Sn^{+2} have a strong chemical affinity in relation to oxygenated functional groups and no chemical affinity for nitrogen functionalities. In addition, the Pd^{+2} species have a strong chemical affinity in relation to the nitrogen functionalities, present in the polyimide surfaces, generating the functionalization of the surface of nitrogenous species, grafted by means of Pd^{+2} ion chemisorption, in the presence of Sn there is a redox reaction, leading to the formation of covalent bonds of CO-Sn (Pd) [3]. With this bibliographic premise, the membranes were immersed for 3 min in a solution containing 0.1 g/l of $SnCl_2$ and 0.1 ml/l of HCl, rinsing them in deionized water (sensitization step). Then, immersed in a solution of 0.2 g/l of $PdCl_2$ and 3.5 ml/l HCl and rinse (activation step). It was also functionalized with a more concentrated solution containing 0.2 g/l $SnCl_2$ and 0.6 g/l $PdCl_2$ with the same acid dilution as HCl.

4.3. Functionalization with $AgNO_3$

As an alternative to functionalization in view of the fact that $PdCl_2$ is a high-cost input, if you had the initiative to test functionalization with $AgNO_3$, preparing a solution of 0.1 g/l of $SnCl_2$ and 0.1 ml/l of HCl, rinsing them in deionized water (sensitization step). Then, it was dipped in a solution containing 0.06 g/l of $AgNO_3$ and 3.5 ml/l of concentrated HCl and rinse (activation step). It was also functionalized with a more concentrated solution containing 0.2 g/l $SnCl_2$ and 0.6 g/l $AgNO_3$ with the same acid dilution as HCl.

4.4. Functionalization with NaClO

Awaja, F. et al. [2], showed that the immersion of a high density polyethylene in NaClO, mixed with acid increased the surface adhesion in polymers. They used XPS to show that chlorine atoms were added to the surface. In view of this, this functionalization based on NaClO was also considered, solutions at 5%, 15% and 30% were prepared in a 0.2 M HCl medium, the polyimide membranes were immersed for 5 min of each concentration.

4.5. Methodology to determine the surface energy (Angle of contact)

Direct measurement of surface energy (SFE) in the solid is not possible, its calculation is based on measurements of contact angle of liquids deposited on the solid surface as shown in Figure 1; this value is used in Young's well-known equation.

And Young's equation is:

$$\Upsilon_s = \Upsilon_{sl} + \Upsilon_l \cos\theta \tag{1}$$

where Υ_l and Υ_s are the SFE of the liquid and solid respectively, Υ_{sl} is the solid-liquid inter-facial energy and Θ is the contact angle. Both Υ_l (experimental surface tension) and Θ can be easily determined, but the value of Υ_{sl} must be known to calculate Υ_s. There are different theoretical models to calculate Υ_{sl} and Υ_s, the geometric mean method was the one used in the present work. [11].

4.5.1. Geometric Average Method (GM)

The GM model is based on the fact that intermolecular interactions between two substances have two main components; the dispersive component or London and the polar component due to the contributions given by the forces of Keesom and Debyee. Therefore, SFE arises from these contributions of interactions as the sum of two components, the dispersive (ɣd) and the polar components (ɣp) as:

$$\Upsilon_i = \Upsilon_i^d + \Upsilon_i^p \tag{2}$$

which combined with Young's equation results in:

$$\gamma_{SL} = \gamma_S + \gamma_L - 2(\sqrt{\gamma_S^d \cdot \gamma_L^d} + \sqrt{\gamma_S^p \cdot \gamma_L^p}) \tag{3}$$

And to calculate the values of ɣsd and ɣsp, the equation is linearized in:

$$\frac{0.5\,\gamma_L\,(1+\cos\theta)}{\sqrt{\gamma_L^d}} = \sqrt{\gamma_S^p}\left(\frac{\gamma_L^p}{\gamma_L^d}\right)^{1/2} + \sqrt{\gamma_S^d} \tag{4}$$

4.5.2. Contact angle

The contact angle was measured using the sessile drop method with a micro-syringe, in a goniometer of the Dataphysics model and the Labcontrol brand, the photos and measurements were processed with the SCA20 software, the contact angle in each drop is the average value the angle measured on the left and right sides of the drop image. If a minimum of three contact angle tests were performed, they were recorded on different surface areas to obtain an average result.

To estimate the non polar (gdl) and polar (gABl) dispersive component of the solid's surface energy, contact angle measurements with non polar and polar liquids are performed. For the present study, it was used; deionized water, which has a predominant polarity over the dispersive component; glycerol dispersive component slightly larger than the polar component and diiodomethane, as a predominant dispersive component over the polar component, for the case of distilled water (72.2 mJ/m^2) and diiodomethane (52.2 mJ/m^2) the droplet was 1 µl and glycerol (63.7 mJ/m^2) was 5 µl. [13].

4.6. Methodology of the synthesis of the polyimide-copper film

In the functionalized PIR 003 polyimide, 0.0240g of CuO powder is added and 1 drop of distilled water (0.05 ml approx.) Is add and spread with a spatula along the membrane, then placed in the oven at 200 ° C in a flow of 10 ml/s of air and 50 ml/s of H$_2$ for 1 hour, then cool in an inert argon medium of 10 ml/s to room temperature, to avoid re-oxidation of the sample. The following Fig. 4, shows the scheme of the H$_2$ reduction process in the synthesis of polyimide-copper films.
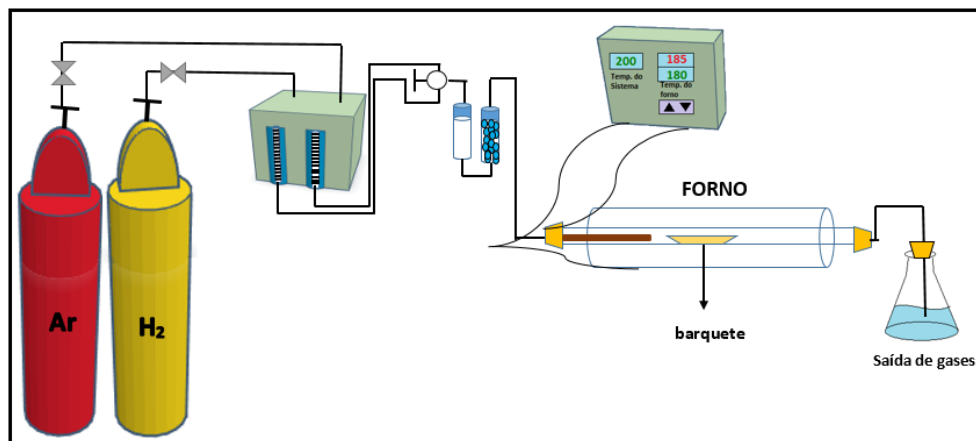
Fig. 4 Scheme of the H$_2$ reduction process in the synthesis of PIR-copper polyimide films.

4.7. X-ray Diffraction Methodology (XRD)

The X-ray diffraction technique is of great importance in determining the structural parameters of the materials. X-rays have a wavelength in the same order as the diameter of the atoms in crystalline materials, thus allowing to obtain valuable information about these materials when diffracted. X-ray diffraction is a technique that can be applied to both films and poly-crystalline materials (powder diffraction). For the present study, the XRD of the film precursors (CuSO$_4$.5H$_2$O), converted to CuO, was evaluated to identify the predominant phase. Measurements were also made of the synthesized polyimide films PIR 003-copper, to evaluate the influence of the functionalization of the polyimides compared to the predominant phase of metallic copper.

The X-ray diffraction equipment used was of the X´Pert PRO model and the PANalytical brand, used in CBPF laboratories. The data from the DRX spectra were refined with the aid of the Profex 4.0 software, and designed using the OriginPro 2015 software. The anode used is copper with a wave length of: Λ = 1.54 Å, the start position is 20 ° C and the end is 100 ° C, the step size is 0.0250 and the counting time was 2 min.

4.8. Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) is an electron beam technique in which electron scattering is used to evaluate the topography image of the sample surface under investigation. It has the potential to generate images with a few nanometers of resolution, a relatively large depth of field, which in today's microscopes can reach a million times. [2]. The SEM images that were obtained in this work were made through a Scanning Electron Microscope model JSM-6510LV (Jeol), equipped with EDS, model Noran System 7, Thermo Scientific brand, and the Scanning Electron Microscope bench top TM3000 from HITACHI, belonging to the Microscopy Center of PUC-RIO. will be measure the thickness of the samples, elementary chemical composition and morphology of the films, as well as the correct and continuous formation of the film layers.

5. Results and discussions

5.1. Contact angle in polyimides

The contact angle of three different liquids was measured, deionized water, as the predominant polar component over the dispersive component, glycerol as the dispersive component slightly greater than the polar component, and diiodomethane as the predominant dispersive component [1]. The contact angles measured for the PIR 003 polyimide case, with the different functionalities, for the three liquids are listed in Table 2.

Table 2. PIR 003 polyimide contact angle measurements for various liquids (in degrees).

	Água destilada		Glycerol		Diiodometano	
	Ẍ	SD	Ẍ	SD	Ẍ	SD
Sem tratamento	78.4	1.42	87.8	0.52	28.2	2.37
Sn/Pd 0.1 0.2 (g/l)	92.8	0.64	80.1	0.50	42.8	1.26
Sn/Pd 0.2 0.6 (g/l)	85.1	0.37	78.2	0.77	40.8	0.74
Sn/Ag 0.1 0.06 (g/l)	91.7	0.15	79.6	0.30	36.8	1.35
Sn/Ag 0.2 0.6 (g/l)	91.8	1.21	76.3	1.00	38.3	0.75
NaClO ao 5%	74.4	2.40	70.1	0.76	32.2	1.21
NaClO ao 15%	78.3	0.43	69.1	2.08	31.4	3.74
NaClO ao 30%	82.0	0.80	79.6	0.93	46.4	0.79
Solvente ao 10%	92.0	0.50	82.5	0.59	45.7	0.76
Solvente ao 20%	92.3	0.34	81.7	0.68	36.8	1.62
	Ẍ = valor principal			SD = desviação estándar		

5.2. Surface energy for polyimides

As has already been pointed out, adhesion is related to surface phenomena because the result of this formation of adhesive joints, the value of surface energy (SFE) decreases. With the measurements of the contact angles measured for each polyimide with the three liquids, the dispersive and polar energies were determined in addition to the surface energy and was used to obtain the best fit using the least squares method. As can be seen in Fig. 5, the graph of the surface energies of the different chemically functionalized treatments on the polyimide membranes PIR 003 is presented, in which the treatments that gave a noticeable decrease in surface energy were treated with Sn/Pd (0.2/0.6 g/l), Sn/Pd (0.1/0.2 g/l) and 5% NaClO, and what gave a greater surface energy with a strong contribution of polar component was with the solvent treatment at 20 %.
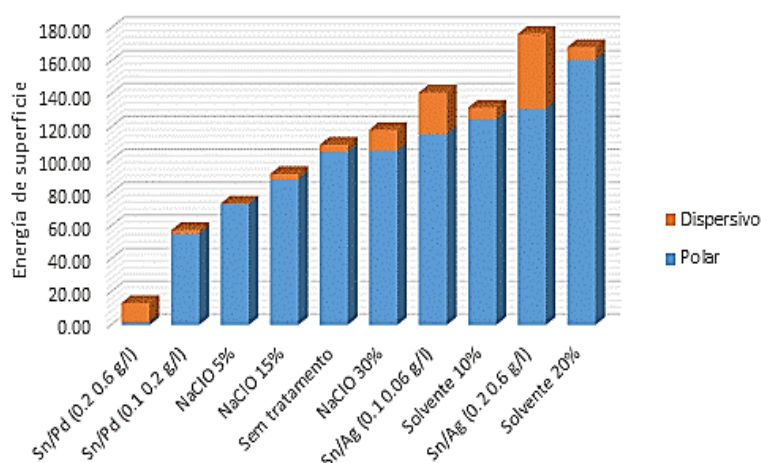

Fig. 5. Surface energy of the different chemically functionalized treatments on the polyimide membranes PIR 003.

5.3. XRD of Cu-polymer films in polyimide PIR 003

In the following figures, the structures show Bragg reflections at the following angles: 2Θ = 43.3°, 50.3°, 74.1° and 90° which identifies the crystalline planes of Cu°. And the structure that shows Bragg reflections at the following angles: 2Θ = 36.2°, 42.3°, 61.4° and 73.8°, identifies the crystalline planes of Cu_2O.

The representation of Figures three and eight, you can see a comparison of the experimental results of XRD, of a reduction process made with H_2 to obtain metallic Cu, for each of the functionalization treatments on the membrane with PIR 003, with three being the treatments of functionalization in different concentrations, submerging in solutions of Sn/Pd, Sn/Ag and NaClO, and a surface modification treatment was applied using solvents already described in the methodology part.

For the case of Figure 6, the XRD spectrum, the precursor used was CuSO4, for comparative purposes, the measurement of the XRD, the reduction of CuO without treatment or without functionalization was performed, where it shows a slightly visible peak of the presence of metallic Cu at the position of 2Θ = 43.3, while the peaks referring to the Cu of the Sn/Pd treatments at that same peak position are clearly defined and representing the largest peak for the Sn/Pd treatment at 0.1/0.2 g/l. In the case of the treatment with Sn/Ag the peaks referring to Cu are also well defined, except that the intensity is greater in the case of Sn / Ag treatment at 0.1/0.06 g/l, and decreasing the intensity for the case of treatment of Sn / Ag at 0.2/0.6 g/l, in the case with the treatment of NaClO, present different behaviors in the three cases, with the treatment of NaClO at 5% representing the highest peak intensity referring to the metallic Cu in the position of 2Θ = 43.3, with the treatment of NaClO at 15% the intensity at that same peak is lower and with the treatment of NaClO at 30% the marked presence of Cu_2O was verified in the position of 2Θ = 36.2, showing that the reduction was incomplete and is an oxide thermodynamically more stable than CuO, and having a decrease in peak intensity in the presence of the Cu phase at the peak of 2Θ = 43.3. And finally, with the surface modification treatments using solvents, there is a notable difference with respect to the 10% solvent treatment, where it shows the clear peaks referring to Cu in the four positions of 2Θ = 43.3°, 50.3°, 74.1° and 90°, while with the 20% solvent treatment, the peak intensity of the Cu is decreased. (Fig. 6).
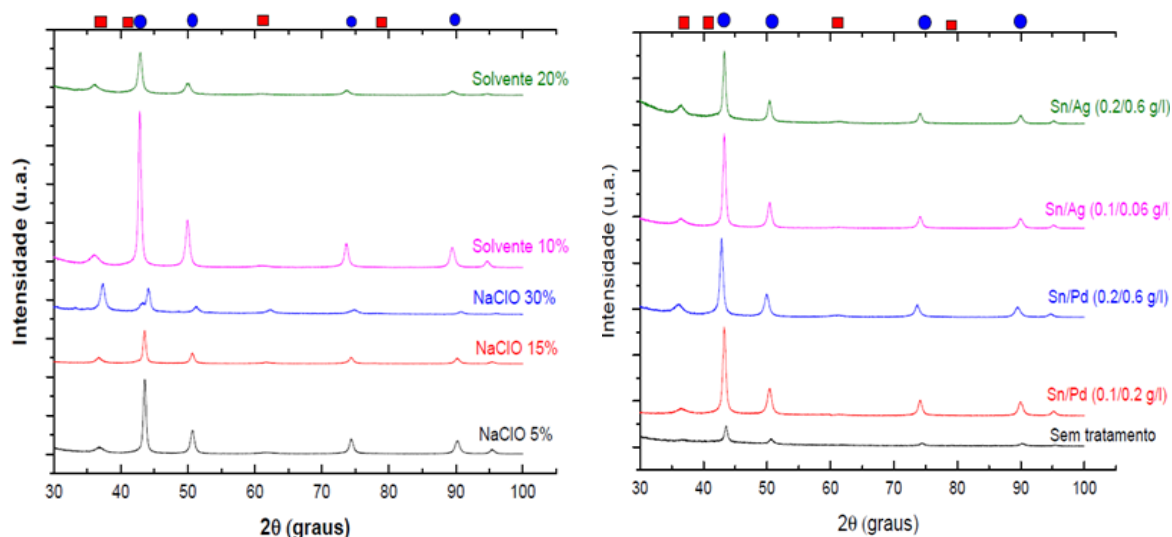

Fig. 6 Comparison of the diffraction profiles obtained by XRD of the films in polyimide PIR 003 with precursor of $CuSO_4.5H_2O$, of the different functionalities. At the top, marked with red squares are the positions of the Cu_2O peaks, and blue circles are the positions of the metallic copper peaks.

As can be seen in Table 3, quantitative data were obtained regarding the polymer-copper film using the polyimide PIR 003, with the precursor of CuSO4, and depending on the type of treatment, in some cases a conversion greater than 80% was obtained of Cu, and the presence of

Cu_2O oxide can also be seen, showing an incomplete reduction, and almost without the presence of CuO, in the

Rietveld refinement, the Rwp adjustment is the weighted R standard (weighted R-pattern) which is minimized by procedure of square minima, Rep is the expected R, and the results are normalized and expressed in terms of the GOF, which is expressed in terms of Rwp/Rexp and when it gives a value of 1, indicating a perfect fit.[7].

Table 3. Quantitative data of the XRD spectrum for the treatment of the copper-polymer film, in the polyimide (PIR 003), with the precursor of CuSO4.

Tratamento	Componente (%)			Estimativas residuais de ajuste			
	Cu	Cu2O	CuO	Rwp	Rexp	X2	GOF
Sem tratamento	72.2	12.08	1.64	8.96	8.2	1.19	1.09
Sn/Pd (0.1 g/l, 0.2 g/l)	85.94	14.06	0	11.5	8.12	2.01	1.42
Sn/Pd (0.2 g/l, 0.6 g/l)	75.42	24.58	0	10.09	7.75	1.7	1.3
Sn/Ag (0.1 g/l, 0.06 g/l)	81.44	18.56	0	11.49	8.25	1.94	1.39
Sn/Ag (0.1 g/l, 0.6 g/l)	68.89	27.6	3.51	8.68	6.76	1.65	1.28
NaClO 5%	83.35	16.24	0.41	10.96	8.54	1.65	1.28
NaClO 15%	71.15	28.26	0.59	12.89	11.44	1.27	1.13
NaClO 30%	48	51	0.58	9.27	7.48	1.54	1.24
Solvente 10%	80.29	19.71	0	10.51	6.5	2.61	1.62
Solvente 20%	65.5	34.5	0	11.44	8.48	1.82	1.35

As can be seen in the Fig. 7, it was the functionalization treatments with less concentration, of the different 4 types of functionalization, which gave a greater conversion to 80% of metallic Cu, as they are: Sn/Pd (0.1/0.2 g/l), Sn/Ag (0.1/0.06 g/l), NaClO at 5% and with solvent at 10% and the treatment that obtained less Cu conversion was with the treatment of NaClO at 30%.
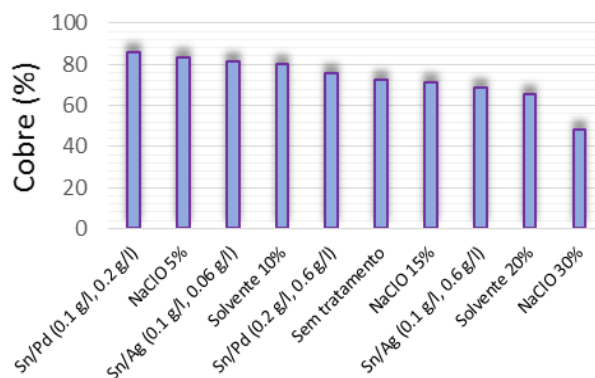

Fig. 7. Percentage of copper in the Cu-polymer films in the polyimide PIR 003, (precursor to $CuSO_4$), as a function of its functionalization.

6.4. Surface SEM for PIR 003-Cu polyimide film with CuSO4 precursor
6.4.1 Film SEM without treatment

In Fig. 8, the image shows the amplitude of 2 mm, it can be seen that the polyimide film PIR 003-Cu without treatment of functionalization in the polymer, the surface presents several fissures, it is very likely that it is due to the lack of adhesion at the interface, in the image with a

greater magnification of 30 um it can be seen that the metallic copper present on the surface is evenly distributed.
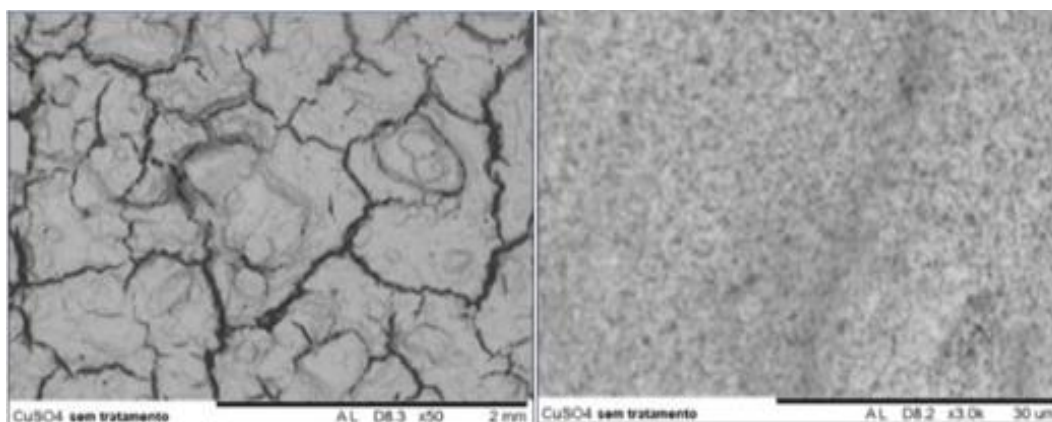

Fig. 8. SEM of polyimide film PIR 003-Cu (without treatment).

6.4.2 Film SEM with Sn/Pd functionalization (0.1/0.2 g/l)

In the case of Fig. 9, the 2 mm amplitude image shows that the polyimide film PIR003-Cu with Sn/Pd treatment (0.1/0.2 g/l) the morphology is more homogeneous compared to the film without treatment, presenting scarce fissures, showing a probable good adhesion along the interface, and in the image with amplitude of 30 um, an equitable formation of metallic layer can also be observed.
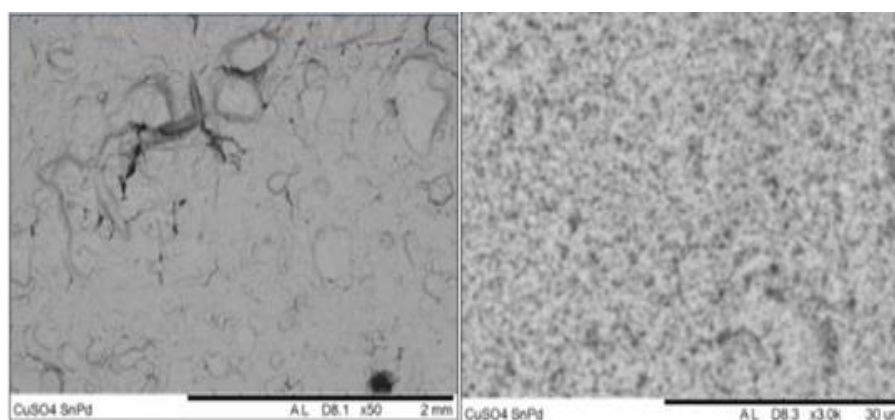
Fig. 9. SEM of the polyimide film PIR 003-Cu (Sn/Pd (0.1/0.2 g/l).

6.4.3. Film SEM with Sn/AgNO3 functionalization (0.1/0.06 g/l)

The behavior of the morphology in the PIR-Cu polyimide film, for the case of the Sn/Ag treatment (0.1/0.06 g/l), as can be seen in Fig. 10, in the 2 mm scope, presents striking and others not so striking, it is likely that it does not present good adhesion, and in the image of greater amplitude a light fissure is observed, forming a light layer of Cu and a homogeneous morphology, and in a semi-quantitative way it indicates a greater presence at 75% of metallic Cu in the film .
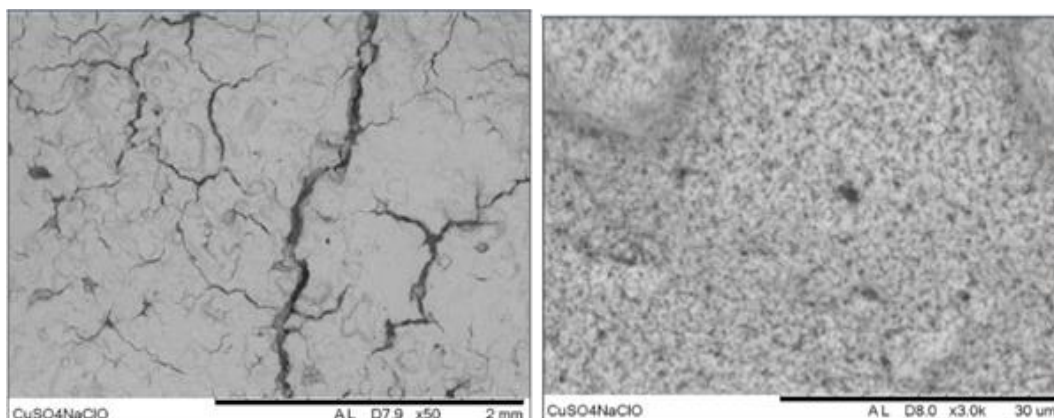
Fig. 10 SEM of the polyimide film PIR 003-Cu (Sn / AgNO3 (0.1 / 0.06 g / l)).

6.4.4. Film SEM with 5% NaClO functionalization

The behavior of the morphology in the polyimide film PIR-Cu, for the case of treatment with NaClO 5%, as can be seen in Fig. 11, in the magnitude of the image of 2 mm, presents marked and lighted fissures, already in the image of magnitude of 300 one, these fissures can be observed better, and from the image of 30 um the copper coating in the polymer has a homogeneous morphology with some light bumps, and in a semi-quantitative way it indicates a greater presence at 82% of metallic Cu in the film.
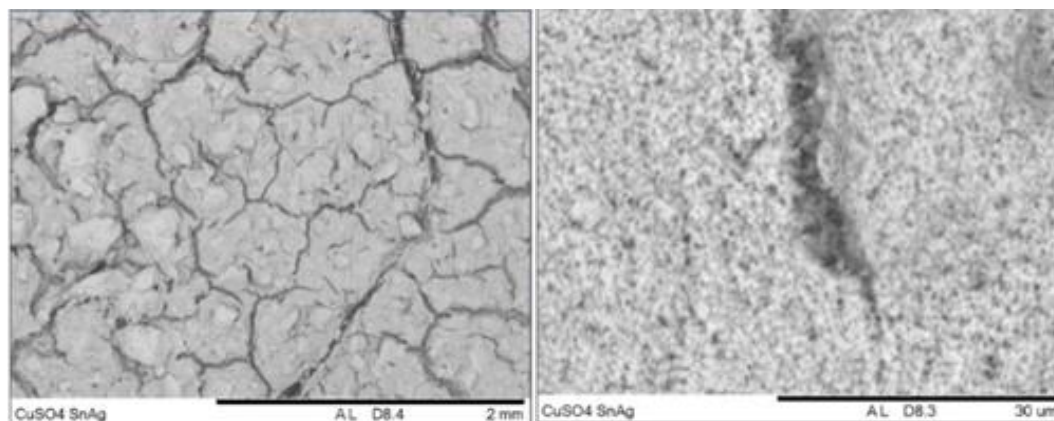

Fig. 11. SEM of the polyimide film PIR 003-Cu (5% NaClO).

6.4.5. Film SEM with 10% solvent functionalization

For the case of the PIR-Cu polyimide film, for the 10% solvent treatment, as can be seen in Fig. 12, in the general magnitude of the 2 mm image, it presents a general layer of homogeneous copper plus also some cracks striking, and from the 30 um image the copper polymer coating has a homogeneous morphology with some light bumps, and in a semi-quantitative way it indicates a greater presence at 91% of Cu.
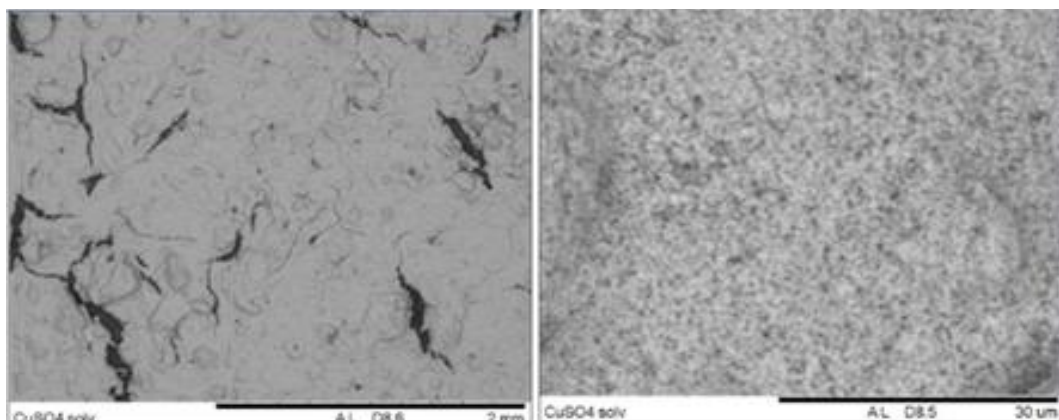
Fig. 12 .SEM polyimide film PIR 003-Cu (10% solvent).

6.4.6. Cross-sectional SEM for PIR 003-Cu polyimide film with CuSO$_4$.5H$_2$0 precursor

As can be seen in the Fig. 12, the treatment that obtained the greatest metallic copper film thickness was with the treatment of NaClO at 5%, of 182 um, the second treatment with greater film thickness was with the Sn/Pd (0.1/0.2 g/l) of 96 μm, solvent treatment and Sn / Ag (0.1 / 0.06 g / l) gave the thinnest thickness of 39 μm and 27 μm respectively. And in all cases, a homogeneous layer is observed.
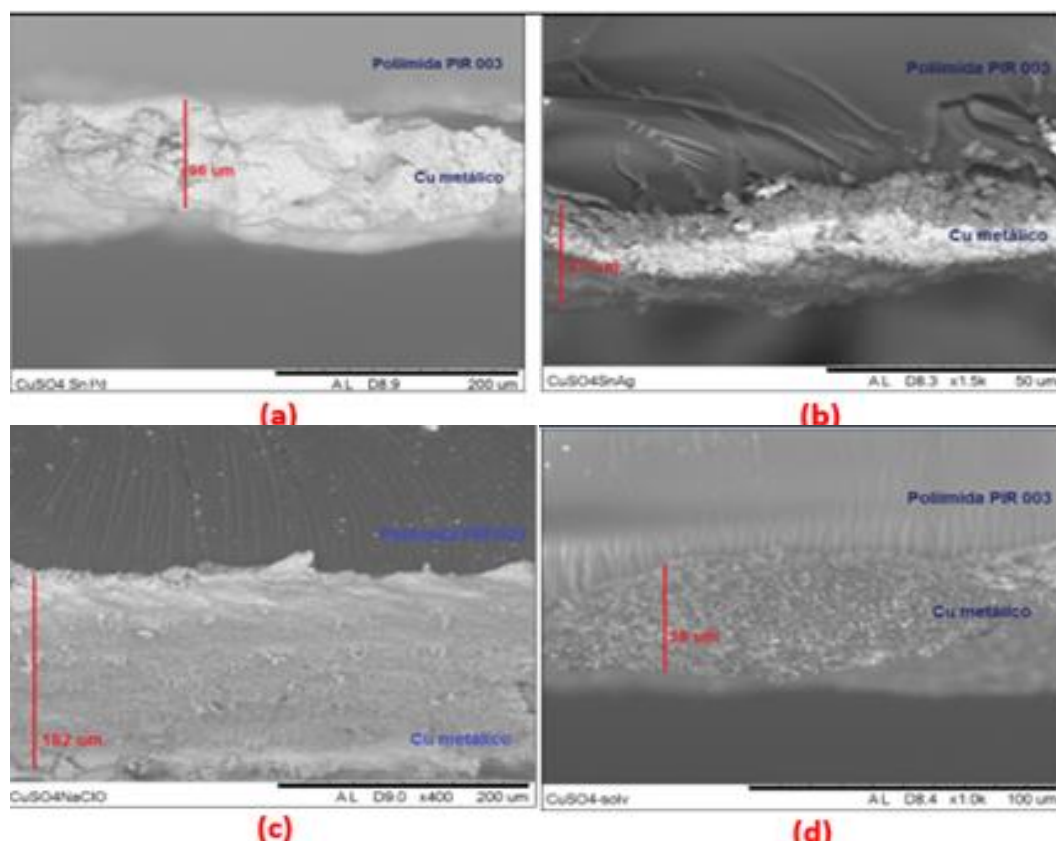

Fig. 13. Cross section of the polyimide film PIR 003-Cu with the precursor of CuSO4.5H20.

7. Conclusions

The response variable under the effect of membrane functionalization chemically, was evaluated by surface energy measurements, in which the treatments that gave a noticeable decrease in surface energy were treated with Sn/Pd (0.2/0.6 g/l), Sn/Pd (0.1/0.2 g/l) and 5% NaClO, this is reflected in the percentages of copper obtained in the synthesized polyimide-copper films, where in the treatment of Sn/Pd (0.1/0.2 g/l) if 85.94% metallic copper was obtained and NaClO at 5%, 83.35% metallic copper was obtained, which means that it did influence the chemical functionalization in the polymer-copper adhesion. It is also confirmed by the measurements made on the SEM, which reflects a thickness of 182 μm for the case of treatment with NaClO at 5% and 96 μm for the case of treatment with Sn/Pd (0.1/0.2 g/l), being the two treatments with greater thickness of metallic copper.

Acknowledgments

References

[1] ABADIE M. J., et al., ¨Practical Guide to Polyimides, Processable Aromatic Polyimides Base Non-traditional Raw Materials¨, first edition [s.n], UK, (2007)

[2] AWAJA, F. et al. Adhesion of polymers : Progress in Polymer Science, v 34, n 21, p. 948-968, 28 may. (2009); https://doi.org/10.1016/j.progpolymsci.2009.04.007

[3] CHARBONNIER. M., et al., ¨New developments in the adhesion promotion of electroless Ni or Cu films to polyimide substrates¨, Vol. 2, pp. 289-314, Ed. K.L. Mittal, (2003).

[4] DAY M. R., ¨Nanometal- Polymer Hybrid¨, ADVANCED MATERIALS & PROCESSES, Michigan, (2008).

[5] FRIEDRICH, J., ¨Metal-Polymer Systems, Interface Design and Chemical Bonding. Germany¨: [s.n], (2018); https://doi.org/10.1002/9783527679898

[6] ISMAIL. A. F. et al., ¨Gas Separation Membranes Polymeric and Inorganic¨, Switzerland: [s.n], (2015); https://doi.org/10.1007/978-3-319-01095-3_6

[7] MACÍAS, M. A.; ¨Cálculo e implementación de la función de resolución instrumental en el refinamiento estructural para el cálculo de la microestructura, cuantificación de fases y caracterización estructural por difracción de rayos-X de muestras policristalinas¨.[s.l.], Universidad Industrial de Santander, Bucaramanga, (2009).

[8] MONFARED. J. S. Z., et al., ¨Polymer Composites Containing Functionalized Nanoparticles and the Environment¨, Faculty of engineering and natural sciences, materials science and nano engineering, Sabanci University, Tuzla, Istanbul, Turkey, (2019).

[9] NICOLAIS L., CAROTENUTO G., ¨Metal-Polymer Nanocomposites¨, Institute of Composite and Biomedical Materials National Research Council Naples, Italy, (2005).

[10] RODRÍGUEZ, J. A.; FERNÁNDEZ G., M. ¨Synthesis, properties, and applications of oxide nanomaterials¨. New Jersey: John Wiley and Sons, (2007); https://doi.org/10.1002/0470108975

[11] SCHUSTER, J.M., et al., Analysis of the results of surface free energy measurement of Ti6Al4V by different methods. Procedia Materials Science V 8, p 732-741, (2013); https://doi.org/10.1016/j.mspro.2015.04.130

[12] SPANGE, S., et al. Adsorption of Poly(vinyl formamide-co-vinyl amine) (PVFA-co-PVAm) onto Metal Surfaces. Progr Colloid Polym Sci. 132: 110-116, (2006); https://doi.org/10.1007/2882_023

[13] STAROSTINA, I. et al., ¨Polymer Surfaces and Interfaces: Acid-Base Interactions and

Adhesion in Polymer-Metal Systems¨. AAP Research Notes on Polymer Engineering Science&Technology: [s.n.], (2014); https://doi.org/10.1201/b17028

[14] VICENTE., C.M.S, et al., Simple measurement of Surface free energy using a web cam, Revista Brasileira de Ensino de Física v. 34, n. 3, 3312, (2012); https://doi.org/10.1590/S1806-11172012000300012

[15] YIN J., DENG B., Polymer-matrix nanocomposite membranes for water treatment, v 479, p 256-275, (2014); https://doi.org/10.1016/j.memsci.2014.11.019