

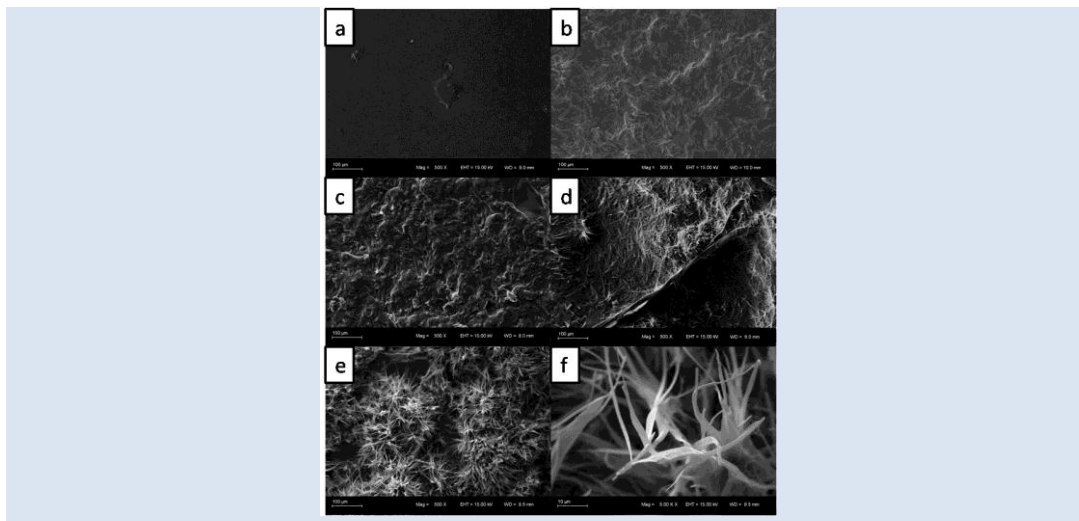
CONDUCTIVE COATINGS FOR STATIC CHARGE DISSIPATION IN AN ELECTRICAL INSULATING POLYMER

Alexandros Aravanis¹, Álvaro Meneguzzi¹, Rodrigo Sanchotene Silva^{2*}

1: Laboratory of Corrosion, Protection and Recycling of Materials - LACOR, Department of Materials - DEMAT, School of Engineering - EE, Federal University of Rio Grande do Sul - UFRGS, 91501-970, Porto Alegre, RS, Brazil

2: Laboratory of Materials Recovery and Treatment - State University of Rio Grande Sul - UERGS, 90010-191, Porto Alegre, RS, Brazil

* e-mail: rodrigo-sanchotene@uergs.edu.br



ABSTRACT

This study aims to evaluate the efficiency of conductive coatings on an insulating substrate, such as Acrylonitrile-Butadiene-Styrene (ABS), for shielding and dissipation of the static charge. This way the coatings were characterized by the chemical composition of the mixture between Polyaniline (PAni/DBSA) and acrylic resin, to analyze if there were reactions that resulted in new chemical bonds. The distribution of polyaniline fibers and the roughness of the coatings were evaluated to verify if these characteristics influence the conductivity. Conductivity measurements were carried out at four points and the influence of the degradation on the conductance of these coatings was evaluated. With the results obtained it is possible to indicate that conductive coatings, as PAni/DBSA for shielding and dissipation of the static charge of non-conductive materials.

Keywords: Polyaniline, Coatings, Conductivity, Antistatic.

RECUBRIMIENTOS CONDUCTORES PARA LA DISIPACIÓN DE CARGA ESTÁTICA EN UN POLÍMERO DE AISLAMIENTO ELÉCTRICO

RESUMEN

El objetivo de este estudio es evaluar la eficiencia de los recubrimientos conductores sobre un sustrato aislante, como el acrilonitrilo-butadieno-estireno (ABS), para proteger y disipar la carga estática. De esta manera, los recubrimientos se caracterizaron por la composición química de la mezcla entre polianilina (PAni/DBSA) y resina acrílica, para analizar si hubo reacciones que dieron como resultado nuevos enlaces químicos. La distribución de las fibras PAni/DBSA y la rugosidad de los recubrimientos se evaluaron para verificar si estas características influyen en la conductividad. Las mediciones de conductividad se llevaron a cabo en cuatro puntos y se evaluó la influencia de la degradación en la conductancia de estos recubrimientos. Con los resultados obtenidos es posible indicar que los recubrimientos conductores, como PAni/DBSA, para el blindaje y la disipación de la carga estática de materiales no conductores.

Palabras Claves: Polianilina, Recubrimiento, Conductividad, Antiestático.

1. INTRODUCTION

Conductive materials that have antistatic properties that arouse interest in the technological applications, enabling the electrostatic shielding in the of the external materials that make up of electronic equipment, through the dissipation of the static charge, and substituted in the use of flammable chemical products, which are used to prevent the formation sparking in the event of electrostatic discharges, which may result in explosion or damage to electronic equipment [1][2].

Polyaniline (PAni) is one of the most studied intrinsically conductive polymers (ICPs) due to several characteristics: high stability to the environment, relatively high electrical conductivity, ease of synthesis, good reversibility in redox reactions and low cost monomer. The only disadvantage of the use of ICPs is in processability due to degradation occur below the melting temperature [3].

The conductivity of ICPs, unlike metals that occurs due to the free electrons present in the crystalline structure, is explained through the electrical conduction capacity is attributed to the presence of conjugated double (or alternating double) bonds along its chain, which when exposed to the action of a doping agent, occurs the resonance with delocalization of electrons present in the bonds π to along the polymeric chain. This will provide the mobility necessary for weakly bonded electrons (π bonds) to move along the polymer chain, causing the polymer's electrical conduction capacity to increase [4].

The aniline monomer, which gives rise to the polyaniline polymer, can be processed by a chemical synthesis using a functionalized protonic acid (DBSA) in a one step emulsion process; the result of the reaction is the formation of polyaniline fibers protonated with DBSA (PAni/DBSA) [5].

The mixtures of conductive charges in polymeric matrices have required several studies in the academic field [6]. Thus, these blends offer materials with the characteristics of the desired polymeric matrices and at the same time static electricity dissipation and electromagnetic shielding [7]. In most of the works proposed, this mixture is given in the processing of the insulation matrix with the addition of conductive charges. Therefore, it leads to an obstacle in the use of PAni/DBSA as a

conductive additive, since it is a polymer that degrades at low melt temperatures, which is necessary in the processing of the matrices [8].

The proposal of this work is may be the application of a conductive coating on the insulating substrate without the need for adding conductive charge during the matrix processing step. As the mixing PAni/DBSA in polymeric resins produces a conductive paints that when applied on the insulation matrices, produced the static electricity dissipation and electromagnetic shielding. Moreover, the PAni/DBSA coating formed structure and insulating polymer substrate has the advantage of not suffering the interference of high temperature degradation in the processing of insulating polymeric substrate, enriched in its polymeric matrix with ICPs, which makes it impossible to dissipation properties of static electricity and electromagnetic shielding.

The indicators of satisfactory conductivity values for the antistatic materials used for dissipation and electrostatic shielding are above 10^{-5} S/cm [9][10][11].

Therefore, materials with antistatic properties, coupled with the desired characteristics such as the mechanical properties and lightness of the polymers, can be achieved with a coating of conductive paint on the surface of an insulating substrate.

2. MATERIALS AND METHODS

2.1 Materials

In this work we used aniline from the brand Nuclear, with 99% of purity, dodecyl benzene sulphonic acid ($\text{CH}_3(\text{CH}_2)_{11}\text{C}_6\text{H}_4\text{SO}_3\text{H}$) -DBSA - from Kintran Chemical Industry Co., limited with 96% of purity, Toluene ($\text{C}_6\text{H}_5\text{CH}_3$) from brand Synth with 99.5% purity, Ammonium Persulfate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$) - APS - 98% purity, Suvinil Acrylic resin and Acrylonitrile-Butadiene-Styrene (ABS) processed at Metalsinos company with the proportion of acrylonitrile: 30%; butadiene: 15%; styrene: 55%.

ABS was chosen because it is a material that creates roughness when attacked the nodules of butadiene by the solvent toluene, increasing the adhesion of the resin on the substrate [12].

2.2 Polymerization of PANi by Emulsion

Polymerization of PANi/DBSA was carried out in a step where 0.06 mol of aniline was added in an emulsion previously prepared of 200 ml of distilled water, 0.1 mol of DBSA and 50 ml of toluene, cooled to 0°C. After one hour stirring the mixture under these conditions, 0.04 mol of the APS initiator, previously solubilized in 50 ml of water, was slowly dripped into the solution, for one hour. The reaction was then maintained for a further 5 hours.

After, 200 ml of toluene was added to the solution aniline+DBSA+APS to terminate the polymerization process. This mixture was allowed to stand for one day and after forming a homogeneous solution the separation occurred in two phases: water and solvent+PANi/DBSA. The polyaniline obtained, doped with DBSA, remained solubilized in the solvent phase and the unreacted DBSA and APS remained in the water phase.

The PANi/DBSA was separated from the water in a separatory funnel and transferred to a wide-mouth erlenmeyer flask.

2.3 Paint Preparation

A 10 ml PANi/DBSA sample was collected on watch glass and exposed to room temperature for solvent evaporation, subsequent was analysis only of the existing amount of PANi/DBSA. In this process was obtained 1.2469 g of PANi/DBSA, in 10 ml solution of PANi/DBSA.

The acrylic resin was also exposed to atmospheric action and room temperature for the evaporation of the solvent, which resulted in 2.61g of acrylic resin for 10ml in solvent solution.

From these data, base acrylic paints pigmented with PANi/DBSA in solution with toluene solvent were produced. Table 1 shows the composition of the different paints produced with acrylic resin that will be part of the study and analysis of the necessary properties.

Table 1. Composition of paint of acrylic resin with PANi/DBSA.

Acrylic Resin (mL)	PANi/DBSA/Toluene (mL)	%Percentage of PANi/DBSA
10	2.070	9
10	4.2871	17
10	8.9705	30
10	13.954	40
10	20.937	50

Blends were performed with PANi/DBSA in a toluene solution. The PANi/DBSA obtained in the process diluted in toluene is easier to homogenize in the resin, because it has a lower viscosity. Since the acrylic resin has a viscosity of 500 mPas, this means that as the amount of PANi/DBSA diluted in solvent is increased in the blends, the viscosity of the paints will be reduced due to the additional toluene solvent.

2.4 Paint Application

PANi/DBSA paint was applied on ABS samples by dip coating method. Immersion of the polymer substrate in the paints was at a constant rate of 0.5m/s. Immersion lasted 1 minute to avoid the toluene solvent present in the PANi/DBSA attacking the ABS, which could promote the dissolution of the polymer. Exposure of ABS to the solution containing toluene is intended to increase substrate roughness via chemical treatment in order to

increase the adhesion of the paint to it.

2.5 Physical-chemical characterization

The 9% PANi/DBSA paint produced according to Table 1 was characterized by Fourier Transform Infrared Spectroscopy (FT-IR), on a Thermo Nicolet Nexus Tm spectrometer equipment to analyze if the polymeric blend, resin and PANi/DBSA in a toluene solution did not result in possible new chemical bonds.

Were evaluated the dispersion of the PANi/DBSA pigmented coating along the substrate by the technique of Scanning Electron Microscopy (SEM) and X-ray dispersive spectroscopy (XR-DS) in a ZEISS MEV EVO MA 10 electron microscope. The thickness of the coating was evaluated by optical microscopy Axio LAB ZEISS. Rugosity was performed by an RP-200 digital measuring rugosimeter from the brand Instrutherm.

2.6 Conductivity Analysis and degradation effects on an accelerated test in the UV Ultraviolet Fluorescence Chamber

Was performed the measurements of the films widths and lengths on the substrate ABS, also the distances between the tips of the conductivity measuring equipment of four-point, with the use of caliper. The average thickness values of the films for each composition of Table 1 were measured by optical microscopy, except for the substrate without resin, for which the thickness of the polymeric substrate itself was used, shown in Table 2.

With the equation 1, it is possible to calculate the resistivity of the samples and after the average of these values. Thus, the resistivity being the inverse of the conductivity, conductivity values were

calculated as a function of the percentage of PAni/DBSA in the acrylic resin.

$$V = (\rho \cdot I \cdot \left(\frac{\ln 2}{w}\right) \cdot \frac{1}{\pi}) \cdot Cpo \quad (1)$$

In equation “V” is the potential, “ρ” is the resistivity, ‘w’ is the average film thickness for each composition and the correction factor is represented by the acronym Cpo, shown in Table 2. The correction factor is calculated by crossing the data of the length and width of the ABS substrates with the distances between the tips of the meter [13].

Through the four-point analysis, were measured currents (A) and potential (V) on the surface of substrates ABS coated with paints produced, whose compositions were presented in Table 1.

Table 2. Substrate measurements.

0% de PAni/DBSA					9% de PAni/DBSA				
	Sample 1	Sample 2	Sample 3	Sample 4		Sample 1	Sample 2	Sample 3	Sample 4
a (mm)	27	27	19	32	a (mm)	25	25	21	32
d (mm)	11	11	13	10.2	d (mm)	17	17.19	12	22
w (mm)	2	2	2	2	w (mm)	1.31E-02	1.31E-02	1.31E-02	1.31E-02
s (mm)	12	12	12	12	s (mm)	12	12	12	12
Cpo	0.9429	0.9429	0.9692	0.9815	Cpo	0.9692	0.9692	0.9429	0.8584
17% de PAni/DBSA					30% de PAni/DBSA				
	Sample 1	Sample 2	Sample 3	Sample 4		Sample 1	Sample 2	Sample 3	Sample 4
a (mm)	31	22	29	19	a (mm)	32	27	23	21
d (mm)	19	12	12	12	d (mm)	17	12	21	12
w (mm)	9.15E-03	9.15E-03	9.15E-03	9.15E-03	w (mm)	1.50E-02	1.50E-02	1.50E-02	1.50E-02
s (mm)	12	12	12	12	s (mm)	12	12	12	12
Cpo	0.9287	0.9429	0.9287	0.9815	Cpo	0.9692	0.9287	0.9429	0.9287
40% de PAni/DBSA					50% de PAni/DBSA				
	Sample 1	Sample 2	Sample 3	Sample 4		Sample 1	Sample 2	Sample 3	Sample 4
a (mm)	21	25	18	19	a (mm)	20	28	25	25
d (mm)	13	11	11	13	d (mm)	18	11	11	11
w (mm)	7.71E-03	7.71E-03	7.71E-03	7.71E-03	w (mm)	1.35E-02	1.35E-02	1.35E-02	1.35E-02
s (mm)	12	12	12	12	s (mm)	12	12	12	12
Cpo	0.9558	0.9429	0.9815	0.9692	Cpo	0.9692	0.9429	0.9424	0.9429

With these measurements it is possible to determine the correction factor value for each analyzed sample. The correction factor is calculated by

crossing the data with the Table 3 [13].

Table 3. Correction Factors [13]

$\frac{d}{s}$	$a/d = 1$			$a/d = 1.25$			$a/d = 2$			$a/d = 4$		
	C_H	C_{p0}	C_{pB}	C_H	C_{p0}	C_{pB}	C_H	C_{p0}	C_{pB}	C_H	C_{p0}	C_{pB}
$\sqrt{2}$				0.85665	0.9815	-0.0185	0.7500	0.9429	-0.0571	0.7391	0.9376	-0.0624
1.5	0.9047	0.9960	0.0040	0.7715	0.9692	0.0019	0.6746	0.9287	-0.0185	0.6647	0.9235	-0.0216
1.75	0.6863	0.9558	0.0442	0.5808	0.9161	0.0686	0.5065	0.8749	0.0771	0.4990	0.8700	0.0775
2	0.5341	0.9012	0.0988	0.4501	0.8584	0.1327	0.3921	0.8201	0.1519	0.3863	0.8158	0.1536
2.5	0.3467	0.8011	0.1989	0.2912	0.7626	0.2338	0.2534	0.7322	0.2564	0.2496	0.7289	0.2586
3	0.2420	0.7276	0.2724	0.2030	0.6960	0.3022	0.1766	0.6724	0.3221	0.1740	0.6700	0.3240
4	0.1366	0.6392	0.3608	0.1145	0.6184	0.3810	0.0995	0.6036	0.3946	0.0981	0.6021	0.3959
5	0.0875	0.5926	0.4074	0.0733	0.5783	0.4214	0.0637	0.5684	0.4309	0.0628	0.5674	0.4318
6	0.0608	0.5657	0.4343	0.0509	0.5554	0.4445	0.0443	0.5483	0.4514	0.0436	0.5476	0.4520
7	0.0447	0.5489	0.4511	0.0374	0.5411	0.4588	0.0325	0.5359	0.4640	0.0321	0.5353	0.4645
8	0.0342	0.5377	0.4623	0.0286	0.5317	0.4682	0.0249	0.5276	0.4723	0.0245	0.5272	0.4727
10	0.0219	0.5244	0.4756	0.0183	0.5205	0.4795	0.0159	0.5178	0.4821	0.0157	0.5176	0.4824
20	0.0055	0.5062	0.4938	0.0046	0.5052	0.4948	0.0040	0.5045	0.4955	0.0039	0.5044	0.4956
∞	0.0000	0.5000	0.5000	0.0000	0.5000	0.5000	0.0000	0.5000	0.5000	0.0000	0.5000	0.5000

Conductivity measurements were carried out at four point in at least 5 ABS samples immersed in each ink of Table 1 and the influence of the degradation effects on an accelerated test in the UV Ultraviolet Fluorescence Chamber. After each degradation acceleration test on the materials a new conductivity measurement is carried out to verify the effect of degradation on the conductivity.

Analysis of the mechanical adhesion properties and impact coatings will be explained in the following topics concerning the results.

3. RESULTS AND DISCUSSIONS

3.1 FT-IR of Acrylic Base Paint with composition of 9% PANi/DBSA

Infrared analyses were used to characterize the existence of chemical bonds between the acrylic resin and PANi/DBSA mixtures. The spectra are of the acrylic resin, PANi/DBSA and the acrylic base paint with composition of 9% PANi/DBSA, shown in Figure 1.

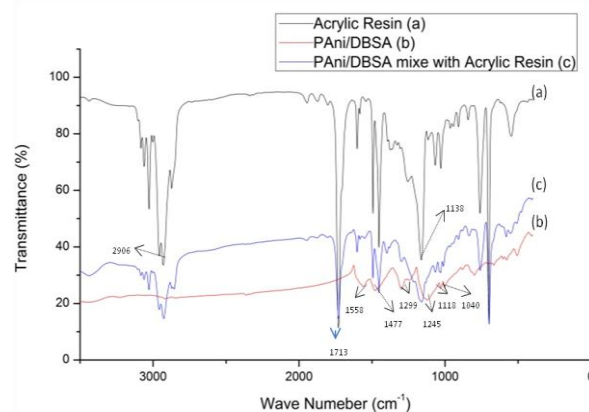


Figure 1. (a) Acrylic Resin; (b) PANi/DBSA; (c) Mixture of PANi/DBSA and Acrylic Resin.

In the spectrum of the acrylic resin, the bands of 3000 to 2800 cm^{-1} correspond to the stretching of the CH_3 bonds of the polymethacrylate structure. The 1713 cm^{-1} band corresponds to the stretching of the $\text{C}=\text{O}$ bond characteristic of the methyl polymethacrylates. The peak present at the 1138 cm^{-1} wave number corresponds to the absorption of the $\text{C}-\text{O}$ bonds. Peaks below 1000 cm^{-1} may be related to the stretching vibrations of $\text{C}-\text{O}$ bonds [14].

The spectra of oxidation level of PANi/DBSA can be qualitatively estimated by the ratio of the intensities

of the absorption bands, $\sim 1558\text{ cm}^{-1}$ (stretching of the kinetic ring) and $\sim 1477\text{ cm}^{-1}$ (stretching of the benzenoid ring). Refer when these two peaks have a ratio approximately equal to 1 if the corresponding emeraldine form, wherein the PANi is 50% oxidized and 50% reduced [5][15][16]. The ratio of PANi/DBSA synthesized in this work was 1.054, that is it, the highest concentration of kinoid groups and near the ideal emeraldine salt form, 50% oxidized with a ratio of 1.

The same spectra of PANi/DBSA show a peak 1299 cm^{-1} that is attributed to C-N stretch and C-C angular strain. The 1245 cm^{-1} band is attributed to C-N stretch and C-C stretch. The peak around 1118 cm^{-1} may be associated with high electrical conductivity and a high degree of electron delocalization, since it is attributed to a plane that doubles the vibration of the CH bond, which is formed during protonation [15][16]. The peak present at the 1040 cm^{-1} wave number is attributed to S=O, which is the sulfur characteristic of the protonation produced by DBSA [5].

The spectra obtained for Acrylic resin pigmented with PANi/DBSA showed a result which is very close to the virgin resin spectrum. It was not possible to verify the appearance of new bands in the PANi/DBSA spectrum mixed with acrylic resin, indicating a possible occurrence of new chemical bonds. And there was also a superimposition several bands of the Acrylic resin and the PANi/DBSA conducting additives are superimposed.

3.2 Roughness

The measurement is performed according to the variation in micrometers of the peaks in the substrate surface relief. Therefore, the larger the peak variation, the greater the roughness [17]. Figure 2 shows a graph of the roughness of the samples according to the PANi/DBSA composition in the paints.

There is an increase in roughness according to the amount of PANi/DBSA added in the resin. That is an expected result, as the amounts of fibers of the conductive additive in the substrate increased. The increase becomes more significant from the 20% composition and stabilizes after 30%. This may be due to an overlaps of fibers occurring from the paints with higher PANi/DBSA composition on the substrate.

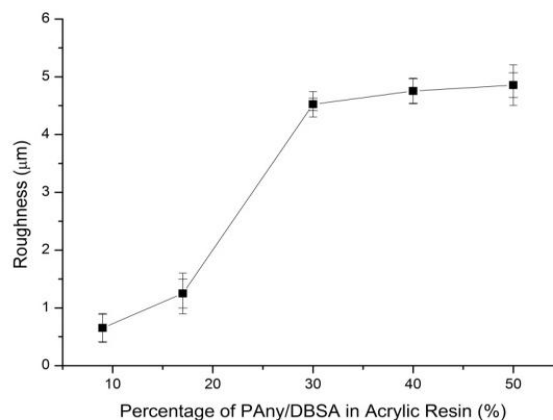


Figure 2. Analysis of the roughness according to the PANi/DBSA percentage in the acrylic resin.

3.3 Scanning Electron Microscopy (SEM)

Figure 3 presents images (a), (b), (c), (d) and (e) of the SEM with a magnification of 500 times for the samples surface immersed in acrylic resin mixed with PANi/DBSA in toluene solvent. The image (f) corresponds to a magnification of 1000 times of the paint with a 50% PANi/DBSA composition in the blend.

The emulsion process resulted in the production of a fibrillar conductive polymer, as shown in Figure 3. The surface morphology of polyaniline may present two structures depending on the dopant used: granular or fibrillar. In the one-step emulsion process with functionalized protonic acid, PANi/DBSA polymerizes in a fibrillar morphology [18].

The images show an increase in the amount and distribution of the fibers as the composition of PANi/DBSA in the resins increases. In this semi-qualitative analysis it was possible to evaluate the homogeneous distribution of fibers on the substrate surface.

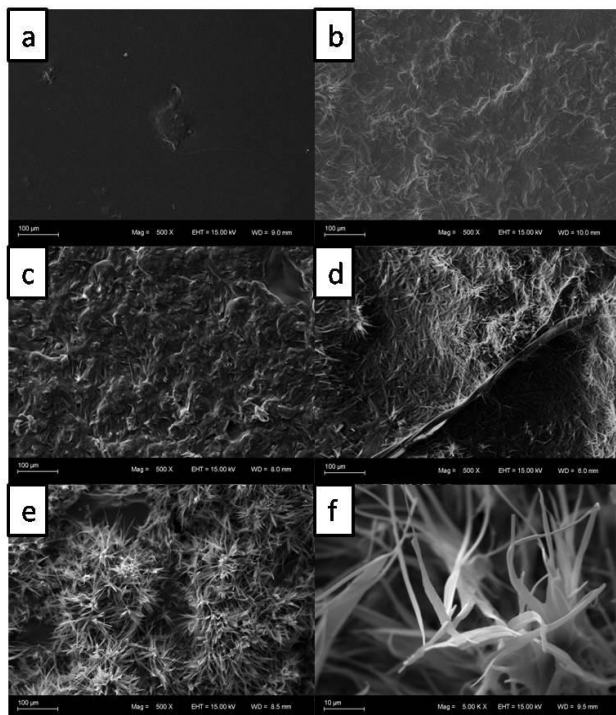


Figure 3. ABS immersed in acrylic based paint with (a) 9% PANi/DBSA; (b) 17% PANi/DBSA; (c) 30% PANi/DBSA; (d) 40% PANi/DBSA; (e) 50% PANi/DBSA; (f) Image magnified 1000 times for ABS immersed in acrylic based paint with 50% PANi/DBSA.

3.4 X-ray dispersive spectroscopy (XR-DS)

Through XR-DS it is possible to perform a semi-quantitative analysis of the sulfur element present in the DBSA (doping agent) in the polyaniline structure. Figure 4 represents the semi-quantitative analysis of the percentage in sulfur weight relative to the amount of PANi/DBSA in the acrylic resin.

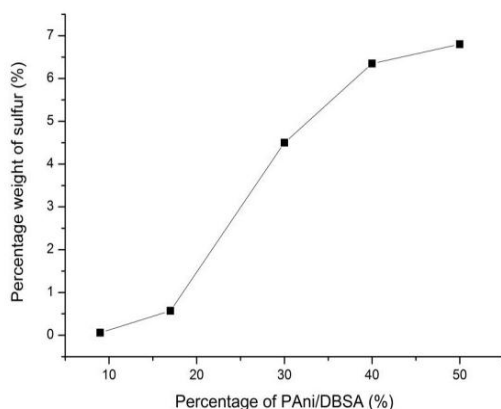


Figure 4. Percentage of PANi/DBSA in the paint compositions of table 1 relative to weight percentage of sulfur.

Figure 4, based on the analysis of the samples with a 500 times increase in magnitude and the scale of 100 μm , shows an increase in percentage of sulfur element as the amount of PANi/DBSA in the acrylic resin increases. That is an expected result, since DBSA is a functionalized protonic acid dopant, and is present in the structure of PANi as reported in FTIR, through the characteristic band of 1040cm^{-1} of the bond $\text{S} = \text{O}$. The sulfur element, which is present in the DBSA structure, appears in larger amounts as the conductive additive is added.

Figure 4 shows a more effective increase in the amount of sulfur between 20 to 40% of PANi/DBSA. The disparities found in the fact that the increase in PANi/DBSA in the mixture is not proportional to the increase in the amount of sulfur is due to the fact that these are semi-quantitative analyses, which depend on the point where the electron microscope analyzed the sample. In the compositions with 40% PANi/DBSA there is a possibility of overlapping PANi/DBSA polymer chains, which may difficulty to analyze the percentage of sulfur weight. However, this result is further evidence of the PANi/DBSA presence on the surface of the substrates which were immersed in the formulated paints, according to Table 1.

The mapping of sulfur by EDS along the surface of the substrate provides an interesting indication of the amount of PANi on the polymer substrate and the homogeneity of its distribution. Figure 5 shows this indication.

The result shows an increase in the distribution and homogeneity of the PANi fibers as the amount of PANi/DBSA is increased in the resins composition. The white dots represent the bond $\text{S}=\text{O}$, which is the sulfur characteristic of the protonation produced by DBSA.

This result is an indication that with a higher distribution of PANi/DBSA along the substrate, the samples tend to be more conductive; which will be treated in the four-point conductivity analysis, since there will be a greater number of contacts between PANi/DBSA fibers on the surface of the substrate.

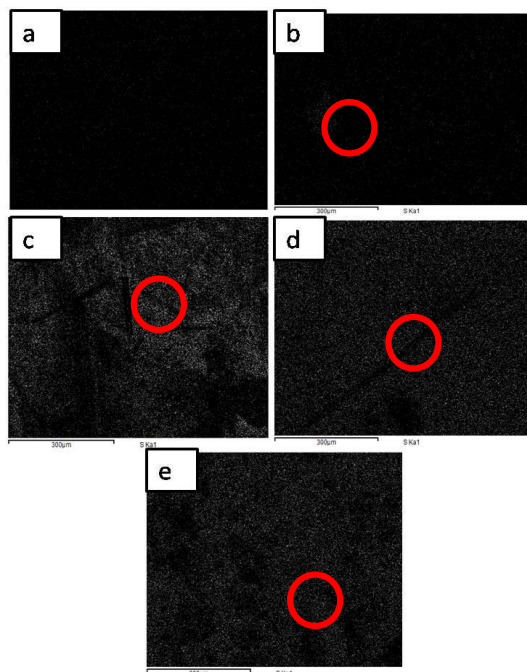


Figure 5. Mapping of sulfur in ABS substrate immersed in acrylic resin paints with (a) 9% PANi/DBSA; (b) 17% PANi/DBSA; (c) 30% PANi/DBSA; (d) 40% PANi/DBSA; (e) 50% PANi/DBSA

3.5 Optical microscopy

The thickness of the coatings, formulated according to the paints of table 1, on the surface of the ABS substrate, were measured by an Optical microscope.

Figure 6 shows the average of the thicknesses according to the percentage of PANi/DBSA in the composition of acrylic resin paints.

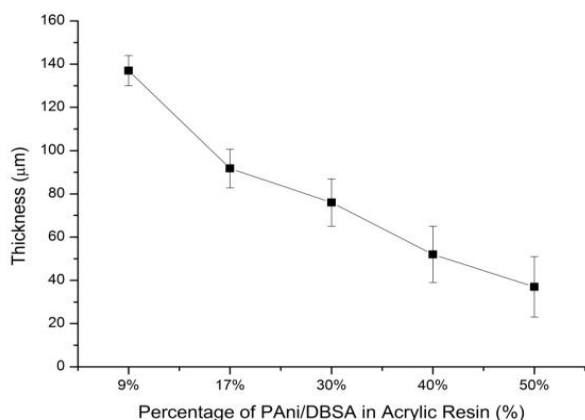


Figure 6. Thickness of Coating on the substrate surface according to PANi/DBSA percentage in the resin.

There is a constant reduction in the coating thickness on the polymeric substrate as the percentage of PANi/DBSA in the acrylic resins is increased. This is due to the reduction of viscosity according to the increase in the amount of toluene solvent in the paints.

3.6 Coating Conductivity Analysis

Conductivity measurements performed on each ABS sample immersed in the paints produced according to table 1 are shown in the graph of figure 7.

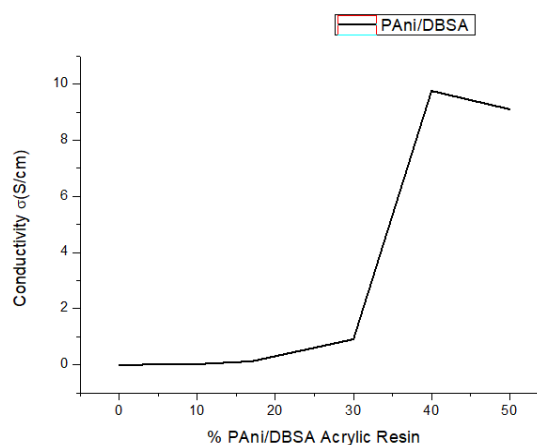


Figure 7. Conductivity according to the percentage of PANi/DBSA in the Acrylic resin.

Figure 7 shows an increase in conductivity as the PANi/DBSA composition in the acrylic resin is increased. This is because it increases the number of contacts of the polyaniline fibers in the coating, consequently increasing conductivity. The graph also shows that the thickness values of the coatings as well as the roughness were not as efficient as the influence of the higher PANi/DBSA composition in the resin.

The increase in conductivity is more efficient from the composition with 30% PANi/DBSA on, this occurs because the number of contacts of the fibers is more effective from this composition, due to greater homogenization and distribution presented in the SEM, indicating the percolative threshold of the resin.

After the conductivity test the samples were sent to a humid chamber, where they were exposed to UV radiation in three time intervals of 250, 500 and 1000 hours, that is, according to ASTM G154-12a. At each interval the samples were removed from the Chamber and a new conductivity measurement was performed.

Figure 8, shown below, presents the log of conductivity analysis performed in samples which were not tested in the UV Fluorescence Chamber and in the samples tested at intervals of 250, 500 and 1000 hours.

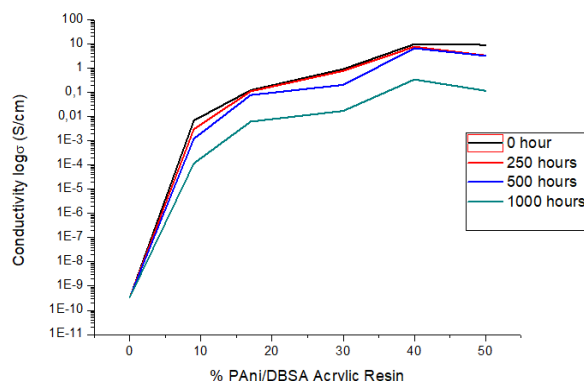


Figure 8. Conductivity of the samples for different PANi/DBSA compositions.

The degradation effect reduced the conductivity of the coatings at all time intervals analyzed; Mainly in the samples after a 1000 hour test. This is due to the fact that there is a reduction of PANi/DBSA charge carriers as long polymeric chains break.

It is also possible to notice a reduction of the most pronounced conductivity in the 50% PANi/DBSA paints, in shorter intervals of degradative tests, which may be related to the fact that there is a lower proportion of resin quantity in this mixture and thus a greater degradation in the PANi/DBSA which is less protected by this resin.

Mitzakoff and De Paoli obtained satisfactory results in his research with direct polyaniline filled polymeric matrix, but they used different matrix polymeric. The values of conductivity in his work, in the range of 10^{-7} S/cm for blends containing only 5% of polyaniline (v/v). Materials with conductivity in this range are used for the production of plastic parts which are able to dissipate electrostatic electricity [7].

Another work, with polypyrrole-coated amorphous silica short fibers (PPy-ASF) hit a conductive layer on the ASF surface which was responsible for electrical conductivity of 0.32 S/cm, similar to that found for pure PPy [10].

Carbon Black when used as polymer matrix loading showed proximal conductivities of 10^{-3} S/cm [19]. The results of the proposed work with coating were

very promising. A conductivity of 10^{-3} S/cm for 9% and 9 S/cm for inks with 50% PANi/DBSA was achieved.

3.7 Evaluation of mechanical adhesion properties

A pull-off adhesion test was performed with different samples immersed in the paints with the compositions of table 1.

As the amount PANi/DBSA was increased in the resins there was a reduction in the cohesion of the paint. The adhesion values were satisfactory, especially in the PANi/DBSA with compositions between 9% and 30%, reaching adhesion values similar to the ones found in metallic substrates. This is also due to the attack of toluene in the ABS substrate, creating micropores that increase adhesion by anchoring.

3.8 Evaluation of Mechanical Impact Properties

For all the impact tests there was a rupture of the ABS insulating polymer sample due to the drop of the indenter, which consequently caused the rupture of the coating. The films with acrylic resin had an adequate impact resistance, greater than the ABS substrate.

4. CONCLUSIONS

It was not possible to determine whether there was chemical bonding between the PANi/DBSA and the resin due to the energy bands overlap in the FTIR analysis.

As the amount of PANi/DBSA increased, the amount of fiber in the PANi/DBSA increased on the substrate. Consequently it reduced the thickness of the paints and increased roughness. The results showed that the conductivity is mainly related to the amount of PANi/DBSA in the polymeric blend of the conductive additive and not with the thickness and roughness of the film on the substrate. The degradation effect was higher in conductivity with a 50% PANi/DBSA composition at shorter time intervals in the Fluorescence Ultraviolet camera due to the lower amount of resin, which protects the conductive fibers from the degradation effects. In the 1000 hour test there was a significant reduction in conductivity in all compositions due to the lower number of charge carriers in the PANi/DBSA mixed with resin and as a result of degradation.

The adhesion tests of the paints exhibited a more cohesive break as the amount of PANi/DBSA in the blend was increased. On impact, all the paints presented good results, and the paint was damaged only when the polymeric substrate was ruptured.

The results were satisfactory in relation to the conductivity and mechanical properties of the films on the substrate, showing conductivities greater than the expected indicators in the range of 10^{-1} to 10^{-7} S.cm⁻¹ [7][10][19]. The surface conductivities with the coatings applied on the polymer substrate are also above the conductivities of other work in which the polymer matrix received conductive charge in the processing step.

This may be the way to solve problems related to the applicability of the polymers to enabling electrostatic shielding in the packaging of electronic products, and at the same time allowing the dissipation of the static charge in processes where the operation requires the use of flammable chemical products.

5. ACKNOWLEDGMENTS

National Council for Scientific and Technological Development (CNPq) and Coordination for the Improvement of Higher Education Personnel (CAPES).

6. REFERENCES

- [1]. Kuester S, Demarquette NR, Ferreira J C, Soares B G, Barra, GMO. *Europ. Pol. Jour.* 2017; 88: 328-339.
- [2]. Ramôa SDAS, Barra GMO, Oliveira RBV, Oliveira MG, Cossa M, Soares BG. *Pol. Intern.* 2018; 62 (10): 1477-1484.
- [3]. Roth S, Graupner W. *Synth. Met.* 1993; 57 (01): 3623-3631.
- [4]. Silva RS. *Tinta inteligente na proteção anódica de aço carbono*, Tesis Ph.D. Porto Alegre (Brazil): Universidade Federal do Rio Grande do Sul, 2016.
- [5]. Kim J, Kwon S, Ihm D. *Curr. Appl. Phys.* 2018; 7 (1): 205-210.
- [6]. Barick AK, Tripathy DK. *Mater. Scien. and Eng.: B.* 2011; 173 (18): 1445-1447.
- [7]. Mitzakoff S, De Paoli MA. *Europ. Pol. Jor.* 1999; 35 (10): 1791-1798.
- [8]. Martins CR.; De Paoli MA. *Europ. Pol. Jour.* 2005; 41 (12): 2867-2873.
- [9]. Al-saleh MH, Sundararaj U. *Carb.* 2009; 47 (01): 2-22.
- [10]. Merlini C, Rosa BS, Müller D, Ecco LG, Ramôa S.D.A.S, Barra GM.O. *Pol. Test.* 2018; 31 (08): 971-977.
- [11]. Oliveira LB, Graeff CZ, Faria PV, Backes EH, Cristovan FH, Passador FR. *AIP Conf. Proc.* 2016; 1779 (01): 1-10.
- [12]. Shuyng Y, Castilleja JF, Barrera EV, Lozano K. *Polym. Degrad. and Stab.* 2004; 88 (03): 383-388.
- [13]. Green MA, Gunn MW. *Solid-Stat. Eletr.* 1972; 15 (05): 577-584.
- [14]. Nakamoto K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*. New Jersey: John-Wiley & Sons, 2006.
- [15]. Armelin E, Meneguzzi A, Ferreira CA, Alemán C. *Surface and Coatings Technology* 2009, 203(24), 3763-3769.
- [16]. Baldissera AF, Ferreira CA. *Prog. in Org. Coat.* 2012; 75 (03): 241-247.
- [17]. *Manual de Instruções Rugosímetro de superfície digital modelo RP-200*. Instrutherm, 2016.
- [18]. Zhang Q, Jin H, Wang X, Jing X. *Synth. Met.* 2001; 123 (3): 481-485.
- [19]. Rebeque PV, Cena CR, Nagashima HN, Malmonge JA, Kanda DHF. *Pol. Comp.* 2019; 40 (01): 7-15.