Polyaniline Synthesis Using Hydrofluoric Acid as Doping Agent: Comparative Evaluation with Polyaniline Doped with Sulfuric Acid

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ABSTRACT: This work focuses on the comparison between the morphological, chemical, and electrical properties of polyaniline doped with fluoridric and polyaniline, and doped with sulfuric acid. The FT-IR, XRD, and SEM/EDS results indicate that the use of hydrofluoric acid as doping agent does not provide meaningful changes in the crystalline and morphological structure of polyaniline. Although, the inclusion of F^- type counter-ions from the doping process with HF provide more compact, denser, and with higher electrical conductivity polymeric matrices. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

Conducting polymers containing conjugated p-electron systems have been the subject of a great deal of attention in the last few decades.[1] They have made a significant impact upon a number of different technologies, since the discovery that, the semiconducting polyacetylene could be converted into a highly conducting form by proper chemical doping.[2] They are known as conducting polymers and possess the electronic, electrical, and optical properties of a metal, while retaining the processability and mechanical properties usually associated with a conventional polymer.[3]

With the advent of electronics, along with a better comprehension of conducting polymers, new technologies and applications were developed, making possible the application of these polymers in a wide range of products. There are many different areas of application of conducting polymers; however, we can highlight the application in electronics, with its thermoelectric, electroluminescence, and electromagnetic properties, and also, a wide application in membranes and sensors.[4]

Polyaniline (PANI), although well studied nowadays, was discovered in 1834, when Runge synthesized it looking for new dyes for cotton.[5] A better understanding of PANI emerged in 1971, with many studies about the special properties of PANI, published by Jozefowicz and Cols.

The electrical properties of PANI can be changed within a range of factors. It is possible to highlight the effect of synthesis adopted (chemical or electrochemical synthesis), oxidation percentage, pH solution during the synthesis, humidity, operating temperature, the kind of doping agent and the protonation degree. All these factors control and lead to changes in the isomerism, density of structural defects, or in the morphology of the polymeric chain, thus causing changes in the electrical resistance of the polymer.[6–9]

In PANI, the doping process occurs by the protonation of nitrogen (N-type doping), promoting consistency in the number of electrons associated to the polymeric chain. This process happen when polyaniline is in contact with the Bronsted acid HX, and some nitrogen atoms are protonated, creating positive charges that are moved in the conjugated chain. At the end of the process, the resulting polymer is a salt form.[8,10] The doping process is important because it changes the optical, morphological, and electrical characteristics of PANI. These characteristics are interfered by the kind of acid used in the doping process.[8–12] Because of its variants, the electrical conductivity of PANI can change since very low values (as an insulating material) to values close to some metals (a conductive material).

Because of the interesting properties many works has been studied about redox mechanisms and electrochemical behavior with
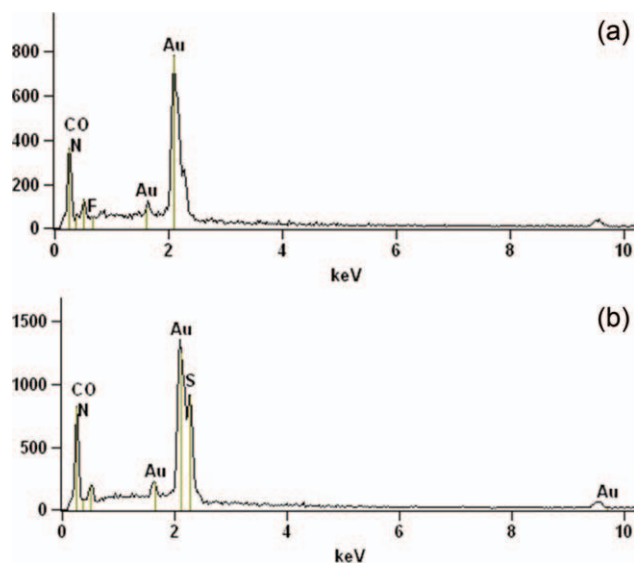
polyaniline and its reprotonation[13,14] and application to development of the rechargeable battery of the type polyaniline/propylene carbonate-LiClO$_4$/Li-Al.[15]

Most studies have applied in the synthesis of polyaniline with sulfuric acid and hydrochloric acid as doping agents.[16–19] These studies have evaluated the effect of these acids in the mechanisms of conduction and electric properties of PANI.[20–23] But few studies have used hydrofluoridric acid as doping agent. Grzeszczuk et al. in 1993 studied the mechanistic-kinetic scheme for the ionic ejection/injection in redox process. These studies indicated the preferred route for the reduction process in hydrofluoric acid.

Recently, many studies have applied the hydrofluoridric acid in the synthesis of the polyaniline.[24–26] Prokes et al. showed that polyaniline synthesized with hydrofluoridric acid have higher stability on its electrical conductivity at high temperature and Jayamurugan et al. showed that polyaniline doped by hydrofluoridric acid could present high photoluminescence efficiency.[27]

This work focuses the synthesis of PANI using hydrofluoric acid as doping agent and the comparison of morphological, chemical, and electrical characteristics with the PANI doped with sulfuric acid.

MATERIALS AND METHODS

PANI was obtained by chemical polymerization with controlled temperature of 5.0°C. The reactional medium for all the samples

were prepared with 25.0 mL of 1N solution of doping acid, 2.0 mL of aniline (Vetec Química Fina, 99.0%), and 5.0 g of oxidant agent (ammonium persulfate, Vetec Química Fina, 98.0%). Two types of reaction were carried out, differing only by the kind of doping acid used. As doping acids, they used sulfuric acid (Vetec Química Fina and 95.0%) and hydrofluoric acid (F. Maia Ind. and Com. and 40.0%). The samples of PANI were filtered through vacuum system, washed with distilled water, and dried in vacuum oven (MA 030/12, Marconi).

PANI-H$_2$SO$_4$ and PANI-HF showed aspects of a fine and green powder after drying. The samples were cold pressed at 8700 kgf cm^{-2} in an uniaxial hydraulic press with a circular template of 23 mm of diameter.

The samples of PANI-H$_2$SO$_4$ and PANI-HF were submitted to Fourier transform infrared spectroscopy—FTIR (IR Prestige-21, SHIMADZU). The samples were prepared with same mass percentage with 2.0 wt % of PANI polymers and 98.0 wt % of KBr. The samples were produced in a mechanical press (SHIMADZU) with press of 70 kN and cylindrical format with diameter of 13 mm.

The samples were submitted to analyses by X-ray diffraction—XRD (XRD-6000, SHIMADZU), scanning electron microscope—SEM (JSM-6390, Jeol), and energy dispersive X-rays spectrometer—EDS (5L, Thermo). The electrical behavior was evaluated by I vs. V curves.

To analyze the dependence of density in the properties of PANI, the samples of PANI-H$_2$SO$_4$ and PANI-HF were pressed with 8700 kgf cm^{-2} and different mass values. The samples were produced with 500, 700, and 900 mg, and the density was determined by the ratio of mass and final bulk.

RESULTS AND DISCUSSION

Figure 1 shows the EDS results to the samples of PANI-HF and PANI H$_2$SO$_4$. The EDS spectra indicate the presences of Carbon (C), Nitrogen (N), and Oxygen (O). Also shows the presence of sulfur (S) and fluor elements (F). Table I shows the atomic percentage of these elements.

To the PANI-HF samples are observed peaks with low magnitude in energies of 1.0 keV that correspond to values of (0.50 ± 0.71) at % of fluor species. Even with low magnitudes and being statistically uncertain, this information is an indicative of the presence of these species in the polyaniline structure synthesized in media containing hydrofluoric acid. The spectra show also peaks with low magnitudes in energies of 2.3 keV that are characteristics of sulfur elements. These peaks have high statistical uncertainty, but can be a indicative of the presence of (0.52 ± 0.60) at % of sulfur species in PANI-HF samples.

This information indicates the possibility of introducing counter-ions of F$^-$ and HSO$_4^-$ in the polyaniline structure during

Table I. Atomic Perceptual of the Chemical Specimens in the Samples of PANI-HF and PANI-H$_2$SO$_4$

Samples	C and N (at.%)	O (at.%)	S (at %)	F (at %)
PANI-H$_2$SO$_4$	89.56 ± 0.54	7.34 ± 1.20	3.10 ± 0.62	0.0
PANI-HF	85.64 ± 0.99	13.34 ± 1.70	0.52 ± 0.60	0.50 ± 0.71

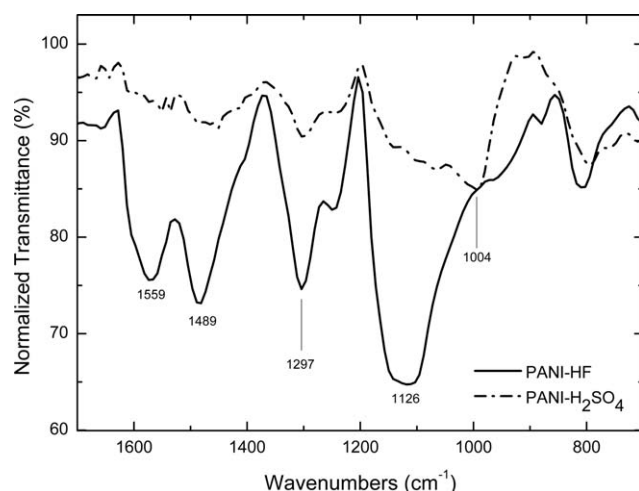| Samples	Area % of pore and superficial irregularities
PANI-HF	11.6%
PANI-H_2SO_4	14.8%

the synthesis process in the solutions containing HF. The counter-ions of HSO_4^- are formed due to a probable reduction of ammonium peroxydisulfate present in the synthesis solution.

In turn, the EDS spectra from PANI-H_2SO_4 samples show peaks in energy values of the order of 2.3 keV corresponding to an average value of (3.10 ± 1.48) at % of sulfur species. To this synthesis condition the EDS results confirm the presence of this element in large amount in the PANI-H_2SO_4 samples, that can be directly associated with the presence of large amounts of counter-ions of HSO_4^-.

The EDS results also indicate greater quantity of oxygen in samples of PANI-HF than in samples of PANI-H_2SO_4. Because the quantity of sulfur species is much lower in samples, PANI-HF cannot associate the increased quantity of oxygen with the increased amount of species of HSO_4^-. But these results can be a strong indicative that the increase of oxygen species can be associated with oxidation of polyaniline molecules by oxygen or due the formation of fluorides of oxygen in the structure of PANI molecules.

Figure 2 shows the results of FT-IR analysis for the samples of PANI synthesized with the two different doping acids. The results indicate the formation of a typical polymeric structure of polyaniline molecules in both synthesis procedures. The spectra are similar, with few changes in the region near the wave number 1000 cm^{-1}, but with different magnitude of the transmittance signals. The transmittance signals are more intense for PANI-HF than PANI-H_2SO_4.

The FT-IR spectra presented the characteristic peaks related to PANI. The peak of 1559 cm^{-1} is assigned to the stretching of C=C bonds present in the quinoid rings of PANI. The peak in 1489 cm^{-1} is corresponding to the vibration mode of C=C bonds present in the benzenoid ring.[28] The mole ration of quinoid to benzenoid rings in PANI chains indicates the oxidation states of the PANI and its change can facilitate the transition between a conductive form (emeraldine) to insulating form (leucoemeraldine).[29]

The peaks related to the vibration modes of single bonds between carbon and nitrogen (C—N), present in polyaniline molecules, are shown at 1297 cm^{-1} and the double bonds C=N in 1126 cm^{-1}.[30] In the spectra of the samples doped with sulfuric acid it is observed a peak near to 1004 cm^{-1}, corresponding to the vibration mode of double bonds between sulfur and oxygen (S=O), which may be attributed to the HSO_4^- counter-ions present in the polyaniline molecules.[31]

The difference in the magnitude of the FT-IR peaks, obtained for same mass of PANI-HF and PANI-H_2SO_4, can be indicative of the formation of PANI matrices with different densities by the difference between crystallizations degree of the polymeric compounds. The FT-IR spectra for PANI-HF showed a greater magnitude probably due the formation of a polymeric matrix with greater crystallization degree than PANI matrix synthesized with sulfuric acid. The increase of the crystallization degree can promote regions containing great amounts of polyaniline molecules per volumetric unit and the effective density of the polyaniline matrices can be increased.

The large amount per unit of volume of quinoid and benzenoid groups indicated by FT-IR spectrums suggest that the incorporation of F$^-$ from HF does not change the molecular structure of PANI, although can provide higher crystalline degree and can promote differences on the morphological aspects of the polyaniline matrices.

Figure 3 shows the comparison of XRD for the samples of PANI-HF and PANI-H_2SO_4. The diffractograms show diffraction patterns characteristic of the crystalline structure of conductive polyaniline. The diffractograms do not show changes in the angular positions of diffraction peaks for the PANI
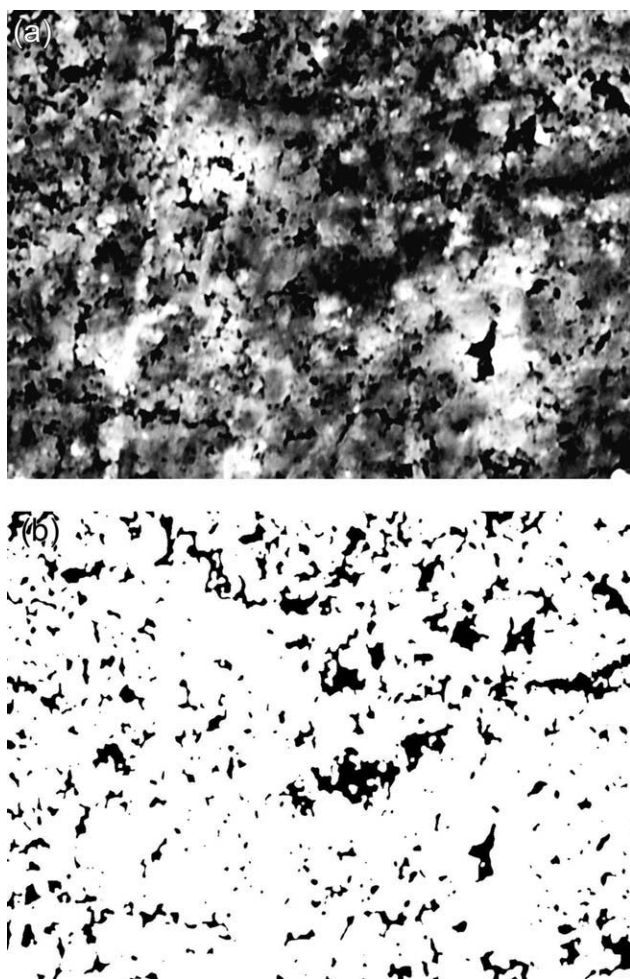

Figure 2. FT-IR of PANI-HF and PANI-H_2SO_4.
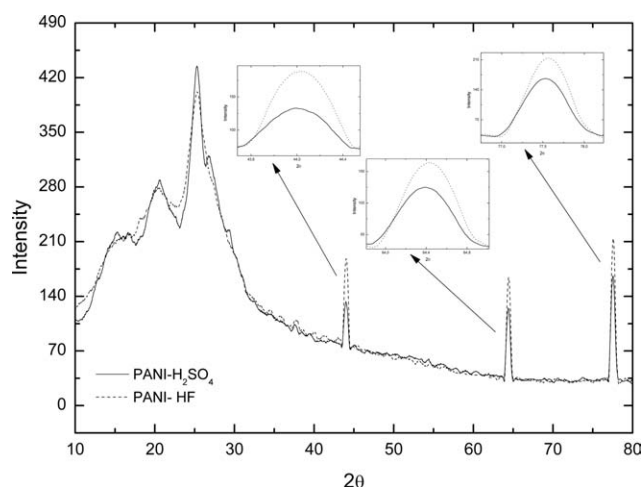
**Figure 3.** Diffractograms of XRD for PANI-HF and PANI-H_2SO_4.
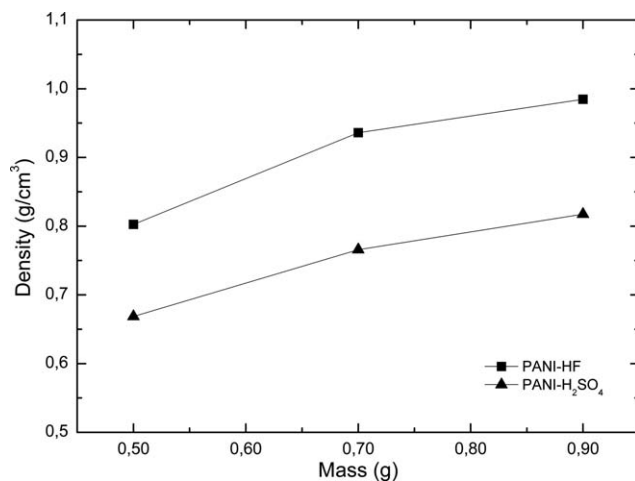
Figure 4. Density of PANI-HF and PANI-H$_2$SO$_4$ a function of mass.

synthesized with both acids, and shows that the synthesis with hydrofluoric acid does not modify the molecular structure of polyaniline.

Figure 5. The ×2000 magnification of MEV micrograph of PANI-HF. (a) MEV Micrograph (b) Binary form of the micrograph.
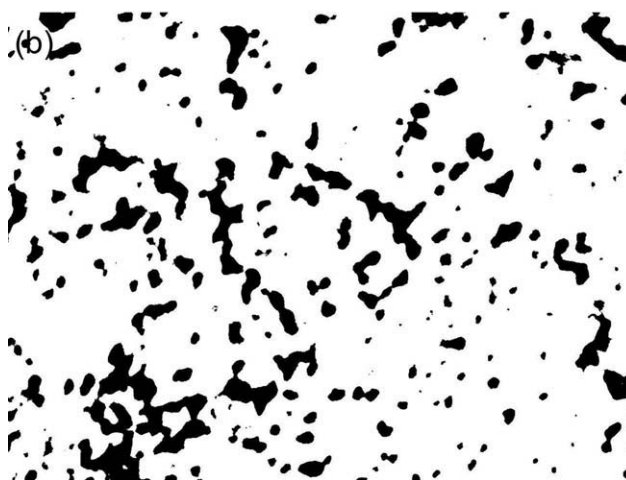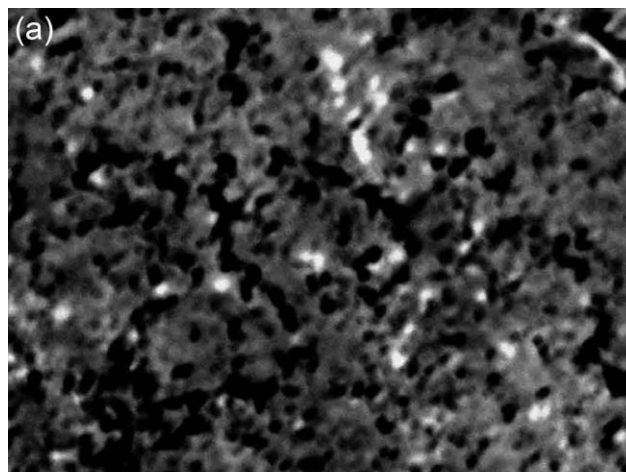

Figure 6. The ×2000 magnification of MEV micrograph of PANI-H$_2$SO$_4$. (a) MEV micrograph and (b) binary form of the micrograph.

The XRD results also show that the samples of polyaniline synthesized from hydrofluoric acid (PANI-HF) have larger magnitudes in the diffraction peaks. The increase in magnitude is associated with the increase of amount of diffraction planes per unit of volume in the polyaniline matrix. The diffractogram indicate that the matrices of polyaniline containing F$^-$ as counter-ions have higher volume fraction of crystalline phases or conductive phases, thus the higher degree of crystallinity when compared to the matrices of polyaniline synthesized with sulfuric acid.

The combination of the results of FT-IR and XRD corroborate with the possibility that counter-ions with higher electrical affinity and with smaller ionic radius promote polyaniline matrices with higher crystallinity degree, i.e., the samples of PANI-HF are denser and more conductive than the samples of PANI-H$_2$SO$_4$.

Figure 4 shows values of density for the samples of PANI-HF and PANI-H$_2$SO$_4$, pressed at 8700 kgf cm^{-2} and different values of mass. The results indicate that the density of PANI increases with the mass and it is dependent on the type of doping acid used.

For the same mass, the density is higher to the samples of PANI-HF. According to the results of FT-IR and DRX the
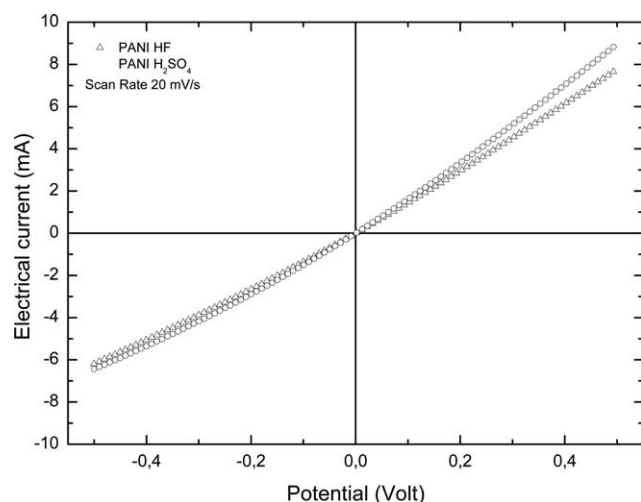
Figure 7. I vs. V curve obtained from the surface of PANI-HF e PANI-H_2SO_4 samples.

counter-ions F^-, present on the PANI-HF molecules, are more electronegative that the counter-ions HSO_4^- and proportionate higher crystallinity degree to polyaniline. Thus, PANI-HF has higher amount of mass per unit of volume higher density.

The dependence of the density with the amount of mass and same pressure is associated to the formation of different amount of pores or irregularities in the matrix of polyaniline. PANI-HF molecules, which present counter-ions with more electrical affinity, provide polymeric matrices with higher crystallinity degree and smaller amounts of pores and irregularities and, consequently, higher density.

Figures 5 and 6 show the micrographs of SEM and its corresponding binary images. These results were applied for the evaluation of the amount of pore and irregularities in the surface of the samples of PANI-HF and PANI-H_2SO_4. Table II shows the percentages of pore on the total surface of the samples PANI-HF and PANI-H_2SO_4.

The micrographs show that the type of doping acid used in the synthesis of PANI provides meaningful changes in the size and number of pores on the surfaces. For the samples of PANI obtained with F^- counter-ions (PANI-HF), the surfaces show a large compact regions and smaller pores. In turn, the samples of PANI doped with sulfuric acid showed larger pores and smaller compact regions. The estimated values, obtained by the analysis of the images, indicate amounts of 11.6% of superficial areas occupied by pores, while for the samples of PANI-H_2SO_4 the value is that of 14.8%.

The results of electronic microscopy corroborate with the results of FT-IR and XRD. The presence of F^- counter-ions promotes the increase of the amount of polyaniline molecules per unit of volume, which provides the higher degree of crystallinity and density in the matrices of PANI, providing so, more compact surfaces.

Figure 7 shows I vs. V curves (current versus electric potential difference) obtained in the surfaces of the samples of PANI doped with the different acids. The results indicate a linear

behavior, characteristic of the conduction mechanisms of an Ohmic-type polymer in the range of 0.5 to -0.5 V. I vs. V curves show that PANI-HF has the higher electrical conductivity when compared to PANI-H_2SO_4. The presence of F-type counter-ions in PANI-HF, favor the formations of matrices of polyaniline with higher crystallinity degree and smaller amount of pores and superficial irregularities. The increase of the crystallinity degree is a result of the increase of the polyaniline crystals volumes in the polymeric matrix. The crystallinity structures has high electrical conductivity, so F^- counter-ions provides the increase in the electrical conductivity of PANI-HF and higher compared to PANI-H_2SO_4. Yet, the decrease of the amount of pores decrease the quantity of the scatter center and these characteristics favor the increase of the electrical conductivity too in the PANI-HF.

CONCLUSION

The use of hydrofluoric acid as doping agent does not provide change in the molecular and crystalline structure of polyaniline. However, the incorporations of F^- counter-ions, with high electrical affinity and small size provides more compact, denser, and with higher electrical conductivity polymeric matrices for PANI-HF.

ACKNOWLEDGMENTS

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