Chemical Polymerization of Aniline in Hydrochloric Acid (HCl) and Formic Acid (HCOOH) Media. Differences Between the Two Synthesized Polyanilines

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Abstract   Conductive polyaniline (doped PAni) was synthesized by a chemical method in media containing, respectively, hydrochloric (HCl) and formic acid (HCOOH). The FT-IR and Raman results showed that the doping degree of PAni-HCOOH is greater than that of the PAni-HCl. Additionally, the Raman studies indicated that the oxidation degree of PAni-HCOOH is higher than that of PAni-HCl, and that polaron segments dominate the PAni-HCOOH structure. The thermogravimetric analysis (TGA) in oxidizing atmosphere also suggests that the doping level of PAni with HCOOH is higher than that of PAni with HCl. The DSC results confirm the differences of the thermal degradation mechanism, in non oxidative atmosphere, of the polymeric chain of both polyanilines. The electrical conductivity of the PAni-HCOOH was 7.51 S cm^{-1}, while that of the PAni-HCl was 0.143 S cm^{-1} confirming the results of FT-IR, Raman and TGA, i.e., the oxidation and the doping degree of PAni-HCOOH is higher than that of PAni-HCl.

Keywords   PAni-HCl, PAni-HCOOH, Thermal analyses

1. Introduction

Conducting polymers, polyaniline (PAni) among them, alone or mixed with conventional polymers, have been successfully applied in batteries[1], sensors[2], electrochromic devices, capacitors[3], solar cells, corrosion inhibitors, light emitting diodes, metallization[4], coating for metallic surfaces, etc[5–9]. The extensive range of applications of polyaniline can be ascribed to its ease of synthesis, reduced processing cost, chemical stability, and conductivity, which can be as high as 10 to 10^3 S cm^{-1}[10–16].

Polyaniline can be synthesized by electrochemical methods (potentiostatically or galvanostatically), by oxidation of the monomer using inert electrodes, such as stainless steel, platinum, gold, different types of carbon (vitreous or pyrolytic graphite), and glass covered with metal oxides[6]. Polyaniline can also be chemically synthesized in acidic media using an oxidizing agent, such as potassium dichromate, ammonium persulfate, hydrogen peroxide, cerium nitrate, etc[6].

PAni exists in three different forms: leucoemeraldine base (LEB, fully reduced form), emeraldine base (EB, partially oxidized form) and base Pernigraniline (PNB, fully oxidized form[17].

Among the different oxidation states of PAni, the emeraldine salt (ES) is the only one that presents electrical conductivity. Nonetheless, the emeraldine base (EB) can be converted to emeraldine salt (ES), and vice-versa, by protonation/ deprotonation with acid/base, as depicted in Figure 1[18] –19].
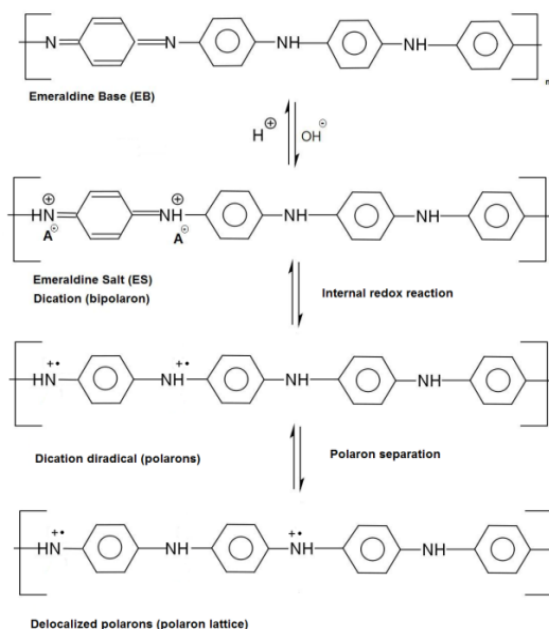

Figure 1.   Doping and de-doping processes of polyaniline (PAni) (Adaptation of[20, 21]) and Mechanism of formation of polaron structure of polyaniline (Adaptation of[22])

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In this work the synthesis of polyaniline in its doped state, in hydrochloric acid (PAni-HCl) and formic acid (PAni-HCOOH) media, was studied. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were used to study the thermal stability of the doped polyanilines. Infrared absorption (FT-IR) and Raman scattering were used to investigate composition changes of the corresponding emeraldine salts, (PAni-HCl and PAni-HCOOH), due to the synthesis process.

2. Experimental

2.1. Synthesis of Polyaniline Doped with Hydrochloric Acid (HCl)

Doped polyaniline (PAni-HCl) was chemically synthesized[23–24] using aniline, previously distilled under vacuum, and ammonium persulfate ($(NH_4)_2S_2O_8$) as oxidant in a 4:1 monomer/oxidant molar ratio. 20 mL of the previously distilled aniline was dissolved in 40 mL of 1 mol L^{-1} aqueous solution of hydrochloric acid in a 250 mL flask. During the dissolution the flask was kept inside a vessel containing a mixture of ice and salt at a temperature of ~ -10 °C. Separately, 12g of $(NH_4)_2S_2O_8$ was dissolved in 160 mL of 1 mol L^{-1} hydrochloric acid aqueous solution. The acid solution of $(NH_4)_2S_2O_8$ was slowly and carefully added into the flask containing the aniline acid solution during a period of 2 h and under constant stirring. During this entire process, the reaction medium was kept in ~ -10 °C. The reaction medium changed color, going through tons of brown, blue and green, and a solid deposit was formed at the bottom of the reaction flask. The green sediment was filtered, rinsed with a 1 mol L^{-1} HCl solution and dried under dynamic vacuum at room temperature for 72 h. Under these conditions the polymer obtained is in a doped state (PAni-HCl) slightly soluble in water[21].

2.2. Synthesis of Polyaniline Doped with Formic Acid (HCOOH)

Aniline was polymerized in formic acid (HCOOH) medium using $(NH_4)_2S_2O_8$ as oxidizing agent. In a typical procedure, 1 mL (0. 0107 mol) of previously distilled aniline was dissolved in 25 mL HCOOH (85% weight) at room temperature[26]. The obtained solution was cooled to about 2 °C in an ice bath. A solution of 2.44 g (0.0107 mol) $(NH_4)_2S_2O_8$ dissolved in 25 mL HCOOH (85% weight) was added dropwise into the cold aniline acid solution under constant stirring over a period of 30 min. The mixture was stirred over additional 2 h and its temperature was kept in 2 °C during this period. At the end of this period of time a dark green solid was formed in the reaction medium. This solid was filtered, thoroughly rinsed with deionized water and methanol. Under these conditions the polymer is obtained in a doped state (PAni-HCOOH).

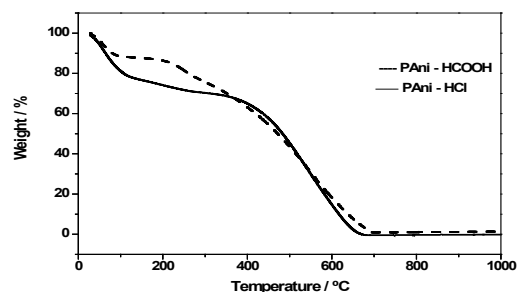## 2.3. Infrared Spectroscopy (FT-IR)

The compositions of the synthesized PAnis were characterized by infrared spectroscopy (FT-IR). KBr pellets were prepared for both, PAni-HCl and PAni-HCOOH. These pellets were used to obtain the FT-IR spectra in the range of 2000 - 500 cm^{-1}, performing 20 scans with a resolution of 4 cm^{-1}. The spectrometer used in this study was a Perkin Elmer, Spectrum One type spectrometer.
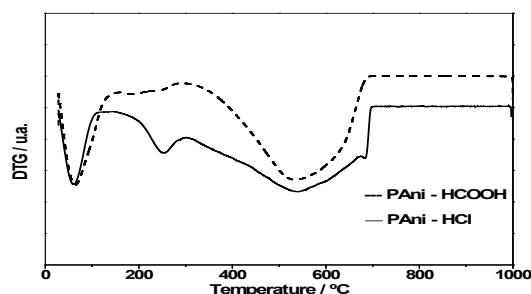
2.4. Raman Spectroscopy

Raman spectroscopy was used as a complement to characterize the composition of the synthesized polyanilines. A spectrophotometer Renishow model 2000 Raman was utilized for data acquisitions. Samples, in the powder form, were excited with a 514.5 nm Argon laser (0.5 mW), using a Spectra Physics equipment, model 127. 10 acquisitions of 10 s each were used to obtain every spectrum. All Raman data acquisitions were obtained at room temperature (± 25 °C).

2.5. Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) of the synthesized polyanilines was performed using a TGA-51 Shimadzu in the temperature range of 30 to 1000°C, under N2 and air atmosphere (flow rate: 50 mL min^{-1}), respectively. A heating rate of 10°C was used during the TGA tests. A crucible of platinum containing 15 mg of sample was used in the TGA analysis.

(a)

(b)

Figure 2.   (a) TGA and (b) DTG of PAni-HCl and PAni-HCOOH in oxidant atmosphere (air) (10 °C min^{-1})

2.6. Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) was carried out on a Netzch DSC 404 Pegasus in the temperature range of 25

to 590 °C, under helium atmosphere (flow rate: 50 mL min^{-1}). The heating rate was 20 °C min^{-1}. A crucible of aluminum containing 15 mg of sample was used in the DSC analysis.

2.7. Electrical Conductivity

Electrical conductivity measurements were made using a Cascade Microtech C4S-64 four probe system coupled to a source (Keithley 236), a multimeter and an ammeter. Circular plaque samples, ~ 2mm thick and with 15mm of diameter, were prepared by uniaxial pressing.

3. Results and Discussion

3.1. Thermogravimetric analyses (TGA) and Differential Scanning Calorimetry (DSC)

The results of TGA and DTG (first derivative of TGA curves) for samples of doped polyanilines (PAni-HCl and PAni-HCOOH), in an atmosphere of air, are showed in Figure 2.

At temperatures lower than 120 °C, PAni-HCOOH presents a weight loss of ~12% wt, much smaller than that of PAni-HCl (~23% wt) (Figures 2a and 2b). The weight loss in this temperature range has been attributed to volatilization of water absorbed by the polymer in the form of moisture[26–27]. In this case, one can infer that the absorption of water by the PAni-HCl is greater than that of the PAni-HCOOH.

In the temperature range of 85 – 215 ºC, PAni-HCOOH loses about 2% of its weight and ~ 19% wt more between ~ 210 – 365 ºC, losing in total ~ 21 % of its weight in the temperature range of 85 – 365 ºC. PAni-HCl loses ~ 7 % of its weight between about 105 and 260 ºC and another ~ 4% wt between ~ 260 – 365 ºC, losing in total ~ 11 % of its weight in the temperature range of 85 – 365 ºC.

The thermal stability of polyaniline in the temperature range of 85 to 215 ºC has been attributed to the formation of cross-linking bonds during heating, a process that involves no weight loss[28–30]. Weight losses of doped polyaniline at temperatures varying from 90 to 250 ºC have also been attributed to loss of water linked to the polymer structure as a dopant[31]. Therefore, the thermal stabilization observed for PAni-HCOOH in this temperature range (only ~2 % of weight loss) could be attributed to formation of cross-linking bonds during the heating process, while the weight loss observed for PAni-HCl (~ 7% wt) would be attributed to vaporization of water present in this polymer as a dopant. The presence of formic acid as a dopant in the polymer structure contributes for its structure stabilization at the temperature range of 85 – 215 ºC in oxidative atmosphere.

The additional weight loss observed for PAni-HCOOH (~ 19% wt) between 210 and 365 ºC was greater than the one observed for the PAni-HCl (~ 4% wt) between 260 and 365 ºC. Weight losses observed for polyanilines in this temperature range have been attributed to evolution of the dopant and/or smaller chain oligomers[31–32]. The fact that

PAni-HCOOH loses a greater weight than PAni-HCl in this temperature range suggests the doping level of PAni with HCOOH is higher than that of PAni with HCl.

For temperatures higher than ~ 365 ºC, a significant weight loss takes place for both polyanilines. PAni-HCOOH loses ~ 64% wt in temperatures between 430 and 675 ºC, while PAni-HCl loses ~ 66 % of its weight between 430 and 650 ºC. Weight losses in this temperature range have been attributed to thermal decomposition of the main molecular chain of the polymer[31].

The TGA and DTG (first derivative of TGA curves) results for PAni-HCl and PAni-HCOOH in inert atmosphere (N_2) are showed in Figure 3.
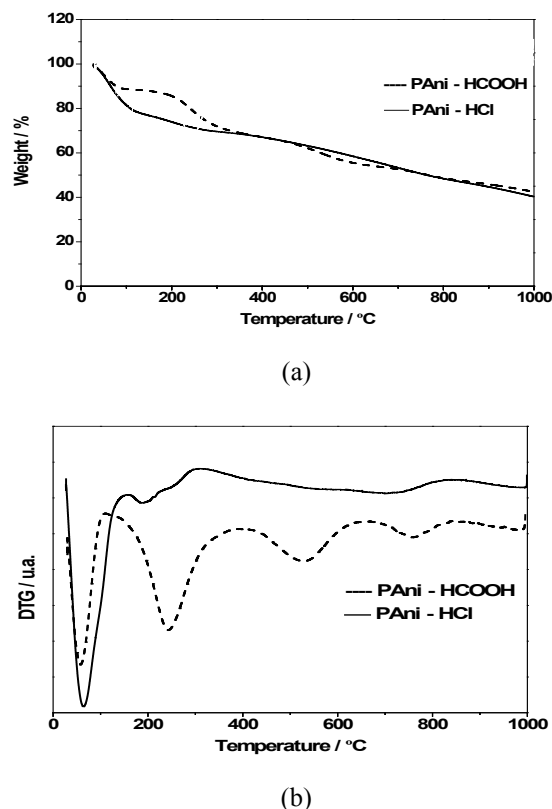

(a)

(b)

Figure 3. (a) TGA and (b) DTG of doped polyaniline (PAni-HCl) and (PAni-HCOOH) in an inert atmosphere (N_2) (10 ºC min^{-1})

Contrasting with the thermal behavior in oxidative (air) atmosphere, at which the doped PAnis were completely destroyed by oxidative changes at temperatures around 700 ºC, in nitrogen atmosphere, carbonization takes place leaving a marked amount of residue (47% wt)[23].

In N_2 atmosphere and temperatures lower than 100 ºC, the weight loss of PAni-HCOOH (~ 11% wt) is smaller than that observed for PAni-HCl (~ 21% wt). The weight loss of polyaniline in this temperature range has been attributed to the volatilization of water in the form of moisture absorbed by the polymer[26–27, 32–35] and it is hardly influenced by oxidative or inert atmosphere. These results confirm that the water absorption by PAni-HCl is much greater than that absorbed by PAni-HCOOH.

In N_2 atmosphere, PAni-HCOOH loses 2% wt between ~

90 – 185 ºC, plus 17% wt between 185 – 325 ºC and more 5 % wt between 325 and 450 ºC, losing a total of 24% wt, against 21% wt in air. PAni-HCl loses 3% wt between 110 and 165 ºC, 6% wt more between 165 – 255 ºC, and additional 5% between 255 and 450 ºC, making a total of 14% wt, against 11% wt in air. In this temperature range (~100 – 450 ºC), the weight loss in inert atmosphere is a little higher than in oxidative atmosphere, but the thermal processes are practically the same, i.e., PAni-HCl loses water linked to the polymer structure and dopant, while PAni-HCOOH changes its structure and loses dopant[32, 33, 36].

Significantly different from what occurs in oxidative atmosphere, the DTG curves show that, between 310 and 850 ºC, at least one stage is involved in the thermal degradation process of PAni-HCl, while two well defined stages, peaks with maximum at 530 and 760 ºC, respectively, are involved in the thermal degradation of PAni-HCOOH between 390 and 850ºC. PAni-HCl loses 17 % of its weight in the temperature range of 450 – 805 ºC, while PAni-HCOOH loses 10 % of its weight between 450 and 605 ºC, 3% wt more between 605 and 702 ºC, and plus 5 % wt between 702 and 820 ºC, losing 18 % wt in total in the temperature range of 450 – 820 ºC.

Thermal decomposition studies of doped polyaniline in non-oxidative atmosphere (He) using DSC\TGA\MS reveled that in temperatures between 450 and over 700 ºC the polymer chain break involves the following stages: elimination of many small fragments at 450 ºC; elimination of aromatic fragments and decarboxylation of extended aromatic structures, with CO_2 evolution and formation of coke at 550 ºC, and decomposition of the residue with elimination of substituted aromatic fragments and graphitization at temperatures over 655 ºC[37]. These three stages of polymer chain break are quite evident in the thermal degradation of PAni-HCOOH in non oxidative atmosphere and temperatures superior to 450 ºC, but they are not clear in the thermal degradation of PAni-HCl. It seems that PAni-HCl does not degrade into small fragments as PAni-HCOOH seems to do, but in temperatures superior to 310 ºC its chain might gradually break into more extended aromatic fragments that suffer further decarboxylation and graphitization at temperatures over 700 ºC, as observed in those DSC\TGA\MS studies for doped polyaniline[37]. This suggestion is supported in this work by the fact that the residual amount of PAni-HCl is higher than that of PAni-HCOOH in temperatures between 450 and 700 ºC. Since the thermal stability of intrinsically oxidized PAni is dependent of the dopant acid and generally decreases with the doping degree[38], the behavior of PAni-HCl in the temperature range starting from 310 up to 850 ºC might be a consequence of its smaller doping degree in comparison with that of PAni-HCOOH. PAni-HCOOH, on the other hand, might break into small fragments in temperatures between 390 and 650 ºC, with formation of aromatic and substituted aromatic segments, which decarboxylate and graphitize at temperatures around 650 and 700 ºC, respectively, as was observed in those DSC\TGA\MS studies for doped polyanilines mentioned

before[37]. Despite of these differences in the thermal degradation mechanism of the polymeric chain, both PAni-HCl and PAni-HCOOH synthesized in this work present practically the same residual weight at temperatures around 850 ºC.

The TGA (in N_2) and DSC (in He) results for PAni-HCl and PAni-HCOOH are showed in Figure 4.
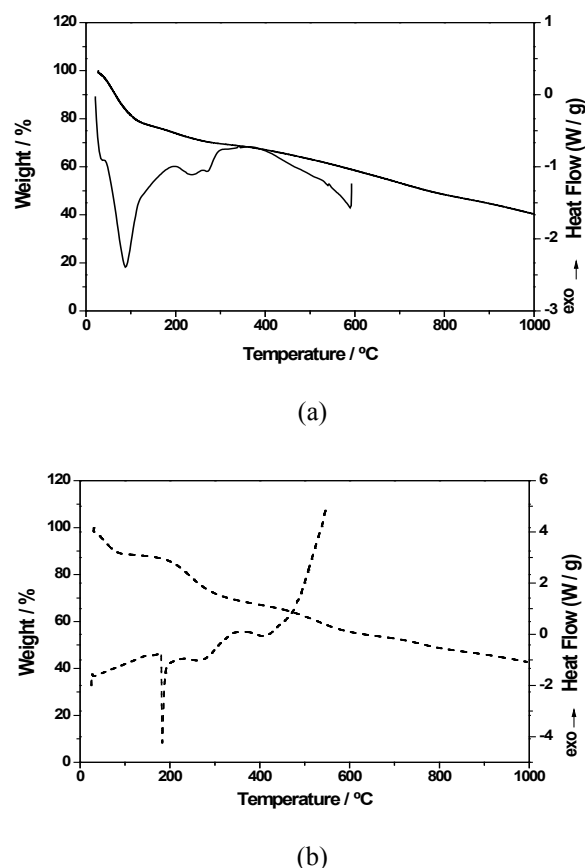

(a)

(b)

Figure 4.   DSC, in helium (20 ºC min⁻¹) atmosphere, and TGA, in nitrogen (10 ºC min⁻¹) atmosphere, of (a) PAni-HCl and (b) PAni-HCOOH

The DSC of PAni-HCl presents a very intense endothermic peak at 88 ºC (Figure 4 (a)). This peak can be associated to the evolution of water in the form of moisture absorbed by the polymer, which was observed in the TGA curve at temperatures lower than 100 ºC. Two less intense endothermic peaks appear, respectively at 235 and 270 ºC, in the DSC thermogram of PAni-HCl. The peak 235 ºC can be associated to evaporation of water linked to the polymer chain as dopant, as observed in the TGA curve o this polymer at temperatures between 90 and 250 ºC, while that peak at 270 ºC can be associated to the loss of the dopant observed in the TGA experiments in temperatures between 260 and 365 ºC. From 370 up to 590 ºC a new endothermic process starts, which can be associated to the beginning of the polymer chain break into extended aromatic fragments, as ascribed to the weight loss observed for this polymer in temperatures superior to 310 ºC in the TGA results of this polymer.

Figure 4 (b) shows de DSC (He) and the TGA (N_2) results for PAni-HCOOH. The DSC curve shows a very intense

endothermic peak at ~ 183 ºC, which can be related to the structural changes observed in the TGA results in temperatures between 85 and 215 ºC that provides thermal stabilization to PAni-HCOOH in this temperature range. A second endothermic peak of low intensity appears at ~ 261 ºC. This peak can be associated to evolution of the dopant[35], as ascribed to the weight losses observed in the TGA thermogram in temperatures between 185 and 325 ºC. A third endothermic peak appears at 405 ºC of the DSC thermogram. This peak does not appear in the DSC thermogram of PAni-HCl. It can be associated to the break of the PAni-HCOOH chain into small fragments ascribed to the thermal degradation process that was observed in the TGA results in temperatures between 390 and 650 ºC. Above 450 ºC up to 550 ºC, an exothermic process takes place, which was not observed in the DSC results of PAni-HCl. This exothermic process can be associated to the subsequent formation of aromatic and substituted aromatic segments, from the small fragments formed in the previous stage of the thermal degradation of the PAni-HCOOH, ascribed to the thermal degradation processes occurring in temperatures between 390 and 605 ºC in the TGA analysis. These two last observations confirm the differences in the thermal degradation mechanism of the two polyanilines prepared in this work.

3.2. Spectral Analysis (FT-IR)

Figure 5 shows the FT-IR spectra of PAni-HCl and PAni-HCOOH.
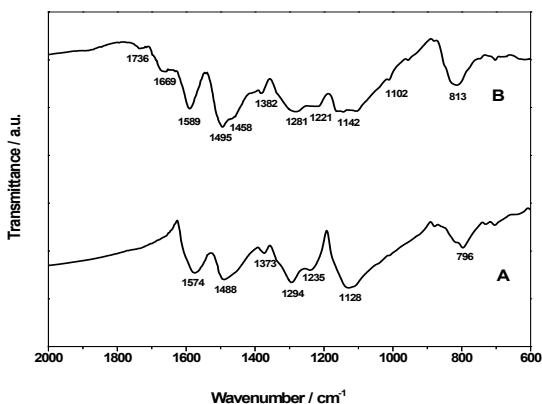

Figure 5. FT-IR spectrum of (A) PAni-HCl and (B) PAni-HCOOH

The bands with maximum in 1574 and 1488 cm^{-1} in the spectrum of PAni-HCl are assigned to stretching vibrations of quinoid ring (Q) and benzenoid (B), respectively. The ratio of the maximum intensity these two bands (I_Q / I_B) can be used to estimate the degree of oxidation on polyaniline[39]. The bands assigned to the stretching of the quinoid ring (Q) and benzenoid (B) also appear in the spectrum of PAni- HCOOH, in 1589 and 1495 cm^{-1}, respectively. The I_Q / I_B ratio of these two bands in the FT-IR spectrum of PAni-HCOOH is similar to that in the spectrum of PAni-HCl, indicating that, apparently, the oxidation degree of

PAni-HCOOH is somewhat similar to that of PAni-HCl.

The spectrum of PAni-HCl has a small intensity band at 1373 cm^{-1}, which is attributed to stretching of C – N bonds next to a quinoid ring (C – N = Q = N – C). The band at 1294 cm^{-1} in this spectrum is attributed to stretching of C – N bonds of secondary aromatic amines[31] and / or displacement of π electrons, induced by acid doping of the polymer. The band characteristic of the electrically conductive form of doped polyanilines is observed at 1235 cm^{-1} in the FT-IR spectrum of PAni-HCl. This band is attributed to the stretching of the C – N$^{+\bullet}$ polaron structure, formed as a result of the acid doping of the emeraldine base (EB) form of polyaniline, as schematically depicted in Figure 1[23]. The band at 1128 cm^{-1} is the most intense in the PAni-HCl (Figure 5 A) FT-IR spectrum and is attributed to vibration of the – NH$^+$= structure formed in the acid doping process of polyaniline, Figure 1.

The band, corresponding to the movement of π electrons induced by doping the polymer (1281 cm^{-1}), also appears in the spectrum of PAni-HCOOH. It appears shifted to lower wavenumber in relation to that of the corresponding band in the spectrum of PAni-HCl. This suggests that, the doping degree of the PAni-HCOOH might be greater than that of the PAni-HCl, which favors the movement of π electrons and justifies the displacement of the corresponding band to lower wavenumber. This last suggestion is reinforced by the finding that in the spectrum of PAni-HCOOH the ration between the intensity of the band in 1221 cm^{-1}, assigned to C – N$^{+\bullet}$ stretching of the polaron structure (Figure 1), and that of the band at 1281 cm^{-1}, corresponding to the delocalization of π electrons, is greater than the ratio of the intensity of the same bands in the spectrum of the PAni-HCl. Additionally, the band assigned to – NH$^+$= vibrations, band in 1142 cm^{-1}, in the spectrum of PAni-HCOOH is also one of the most intense in this spectrum. Therefore, these FT-IR results agree with the thermogravimetric analysis (TGA) in oxidizing atmosphere, which also suggests that the doping level of PAni with HCOOH is higher than that of PAni with HCl.

The region between 900-700 cm^{-1} corresponds to aromatic ring deformation and C – H bond vibrations out of ring plane[21].

The presence of formate anions in the PAni-HCOOH structure is indicated by the appearance of the peaks in 1736 and 1669 cm^{-1}, assigned respectively to vibration of carboxyl groups and C = O[26].

3.3. Spectral Analysis (Raman)

Fig. 6 shows the Raman spectra of doped PAni-HCl and PAni -HCOOH.

To facilitate the interpretation of the results, the Raman spectra of polyaniline obtained in this work (PAni-HCl and PAni-HCOOH) were splited in three regions of wavenumber: I) region corresponding to C – C ring stretching vibrations, between 1650 and 1520 cm^{-1}, II) region at which the different C – N stretch modes prevail, between 1520 and 1210 cm^{-1}, and III) region corresponding to the deformation of C – H
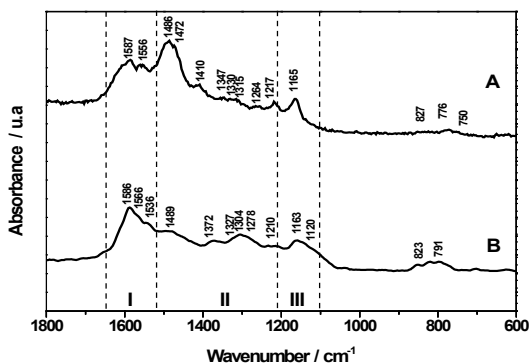
bond, between 1210 and 1100 cm^{-1}.

Figure 6.   Raman spectrum of (A) PAni-HCl and (B) PAni-HCOOH. emeraldine salt; EB: emeraldine base; PB: pernigraniline base (Adaptation of[41])

The Raman spectra of PAni-HCl and PAni-HCOOH show a peak at ~ 1165 cm^{-1}, which has been attributed to the deformation of the C – H bond in the ring plane of bipolaron structures[40]. This way, one can say that both polyanilines obtained in this study show segments of bipolaron structure in the polymer chain.

Only the spectrum of PAni-HCOOH shows a peak at ~ 1120 cm^{-1}, which appears as a shoulder in this spectrum. This peak is usually attributed to in plane deformations of C – H ring bonds in structures containing appreciable amount of segments of the more oxidized Pernigraniline base form (Figure 7)[40]. Therefore, one can say that the oxidation degree of PAni-HCOOH is, in fact, higher than that of PAni-HCl.
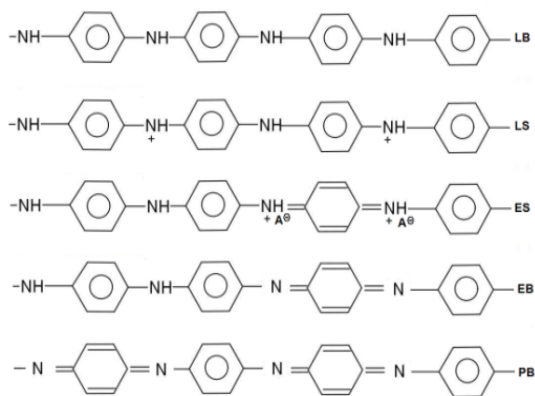

Figure 7.   Different forms of polyaniline - LB: leucoemeraldine base; LS: leucoemeraldine salt; ES: emeraldine salt; EB: emeraldine base and PB: pernigraniline base.

Four important aspects can be highlighted for region (II), between 1520 and 1210 cm^{-1}, of the Raman spectra:

a) The Raman spectra of both polyanilines synthesized in this work exhibit bands / peaks that can be associated to C – N$^{+\bullet}$ bond vibrations of delocalized polaronic structures and polaron segments in the polymer chains[40–43]. The Raman spectra of PAni-HCl present a broad band and two relatively weak peaks in 1347, 1330 and 1315 cm^{-1}, respectively,

which can be associated to vibrational modes of C – N$^{+\bullet}$ delocalized polaronic structures. The spectrum of PAni-HCOOH also present a peak in 1372 cm^{-1}, a shoulder in 1327 cm^{-1}, and a broad band in 1304 cm^{-1}, attributed to vibrations of delocalized polaronic structures (C – N$^{+\bullet}$). However, the relative intensity of the peaks corresponding to C – N$^{+\bullet}$ vibrations to the peak corresponding to C – H bonds deformation in the ring plane (peak in ~ 1165cm^{-1}) in the PAni-HCOOH spectrum is higher than similar intensity relation for the same peaks in the spectrum of PAni-HCl. This observation allows concluding that polaron segments are the main constituents of the polymer chain of PAni-HCOOH, i.e., the doping degree of PAni-HCOOH is higher than that of PAni-HCl, as was already suggested by the TGA and FT-IR results.

b) The Raman spectra of PAni-HCl presents an intense band in 1486 cm^{-1} attributed to C = N stretching in quinoid units (Q)[41–46] and vibration of imine group[40]. This peak also appears in the Raman spectrum of PAni-HCOOH at 1489 cm^{-1}, but its relative intensity to the peak corresponding to C – H bonds deformation in the ring plane (peak in ~1165cm^{-1}) is lower in this last spectrum. This last observation is an additional indication that polaron segments dominate the PAni-HCOOH structure.

c) The bands related to the amine groups appear in the Raman spectra of PAni-HCl as two bands at 1217 and 1264 cm^{-1}. Similar bands are present in the PAni-HCOOH spectra as a weak broad band in 1210 cm^{-1} and a shoulder in 1278 cm^{-1}[45–48].

d) The Raman spectrum of PAni-HCl shows a peak with relatively low intensity at 1410 cm^{-1}. This peak has been attributed to C – N bonds of tertiary amines on cyclic structures produced during the crosslinking of the polymer[37],[41–44]. It is noteworthy to point out that this peak was not observed in the Raman spectrum of the polyaniline obtained in formic acid, PAni-HCOOH.

The main features of the region corresponding to the stretch modes of C = C and C – C vibrations in quinoid and semi-quinone (B) (Q) rings are those bands that appear, respectively, in 1587 and 1556 cm^{-1} in the spectrum of PAni-HCl, and 1586 and 1566 cm^{-1} in the spectrum of PAni-HCOOH[39, 46–47]. The Raman spectrum of PAni-HCOOH shows a peak at 1536 cm^{-1} that is not present in the spectrum of PAni-HCl. This peak has been attributed to deformation of N – H bonds[39] and usually appears only in the Raman spectra of polyanilines containing segments bipolaron. This finding reinforces the conclusion that polaron segments dominate the PAni-HCOOH structure synthesized in this work.

3.4. Electrical Conductivity

The electrical conductivity values of the polyaniline (PAni-HCl and PAni-HCOOH) are presented in Table 1.

The electrical conductivity of the PAni-HCOOH (7.51 S cm^{-1}) is greater than that of the PAni-HCl (0.143 S cm^{-1}). This occurs because the oxidation and doping degree of the

polyaniline doped with formic acid is greater than that of that doped with hydrochloric acid.

Table 1. Electrical conductivity of PAni-HCl and PAni-HCOOH

Polyanilines	Electrical Conductivity (S cm^{-1})
PAni-HCl	0.143
PAni-HCOOH	7.51

4. Conclusions

The thermogravimetric analysis (TGA) in oxidizing atmosphere (air) shows that the absorption of water by the PAni-HCl is greater than the PAni-HCOOH and also suggests that the doping level of PAni with HCOOH is higher than that of PAni with HCl. The presence of formic acid as a dopant in the PAni-HCOOH structure contributes for its structure stabilization in oxidative atmosphere and temperature range of 85 – 215 ºC. In non oxidative atmosphere (N$_2$), three stages of polymer chain break seems to be involved in the thermal degradation of PAni-HCOOH: break into small fragments in temperatures between 390 and 650 ^{o}C, with formation of aromatic and substituted aromatic segments, which decarboxylate and graphitize at temperatures around 650 and 700 ^{o}C, respectively. In inert atmosphere, the polymer chain of PAni-HCl, on the other hand, seems to gradually break into more extended aromatic fragments that suffer further decarboxylation and graphitization at temperatures over 700°C. The DSC results confirm these differences in the thermal degradation mechanism in non oxidative atmosphere of the polymeric chain of both polyanilines, PAni-HCl and PAni-HCOOH, synthesized in this work.

The results of FT-IR spectra show that the doping level of PAni-HCOOH is somewhat higher than that of PAni-HCl. Therefore, these FT-IR results agree with the thermogravimetric analysis (TGA) in oxidizing atmosphere, which also suggest that the doping level of PAni with HCOOH is higher than that of PAni with HCl.

The Raman results show that both polyanilines present segments of bipolaron structure in the polymer chain, and that the polymeric chain of PAni-HCOOH contains appreciable amount of segments of the more oxidized pernigraniline base form. Therefore, one can say that the oxidation degree of PAni-HCOOH is higher than that of PAni-HCl and that polaron segments dominate the PAni-HCOOH structure.

The conductivity measurements showed that the polyaniline synthesized in formic acid medium has higher electrical conductivity than the polyaniline synthesized in of hydrochloric acid medium.

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