

## Conducting polymers doped with a mineral phase: structural and electrical study

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**Abstract.** This work reports the results obtained of a series of novel doped conducting polymers (CPs) of polyaniline/hematite (PANI/HEM), which were synthesized in acidic aqueous solution by the *in situ* chemical oxidative polymerization, using ammonium peroxydisulfate as oxidant reagent. The synthesis was carried out with 20, 40 y 60 % (weight percent) contents of hematite (HEM) at 8 and 14 h of polymerization times (tP). These composites were structurally characterized by X-ray diffraction (XRD) and Fourier-transform infrared spectroscopy (FTIR). An electrochemical analysis was made by Electrochemical impedance spectroscopy (EIS). Results of this study allow to evaluate the influence of hematite on the improvement of the structural properties and in the increase of the electric conductivity ( $\sigma$ ) of the doped polymers compared to CPs without dopant agents.

### 1. Introduction

Nowadays conducting polymers (CPs) are an interesting research area because of these several applications as low impact environmental devices with longer half life time. It has been used in batteries manufacturing, muscles and artificial nervous, intelligent optical (windows, mirrors) parts, electromechanical devices and as additives against corrosion process, between many others [1-5]. Besides it has been proved that CPs improves its optical, mechanical and electrical properties by addition of doping agents as fly ashes [6-8]. The goal of this study is to evaluate the effect on structural and electrical properties of emeraldine, Poly-aniline (PANI), a widely used CP, by doping it with hematite mineral (HEM).

### 2. Experimental

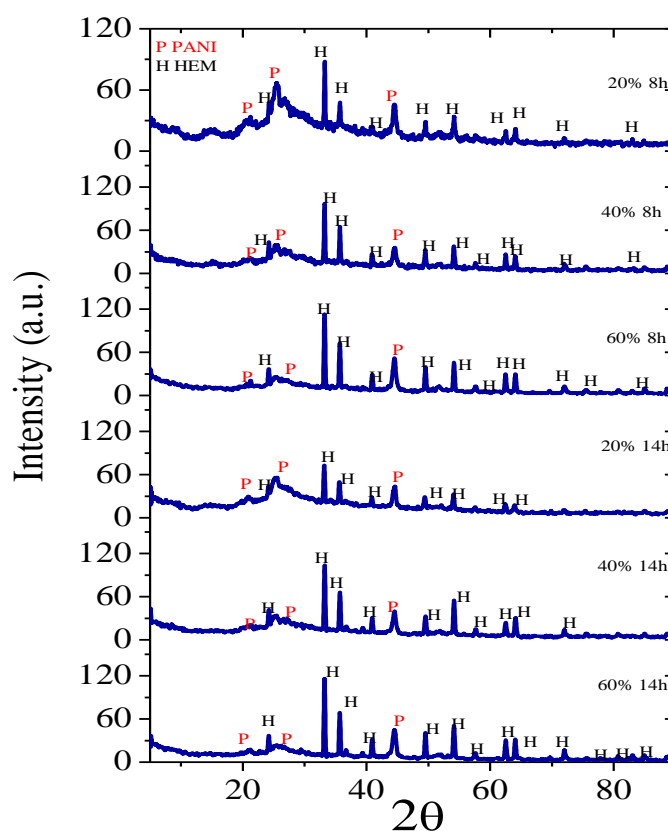
PANI/HEM composites were synthesized through oxidative polymerization adding ammonium peroxydisulfate in acidic media with doping agent *in situ*. HEM was added at 20, 40 and 60% in weight. Mix reactions were keeping during 8 and 14 hours as polymerization time. Samples of doped PANI were characterized by XRD, FTIR and EIS.

### 3. Results and discussions

In all PANI/HEM diffractograms the doping achieved is seen figure 1. By comparing diffraction patrons it is also possible to affirm that during polymerization there are not structural changes in



polymer or in dopant mineral, as PANI/HEM does not show new reflections compared with precursors. Doping could be seen as dopant dispersion at polymer matrix. This dispersion produces an increase in crystal degree of doped CPs. Reached doping is also affected by polymerization time. Diffraction pattern of the PANI/HEM with same HEM concentration, it has some variations at intensities at 8 and 14 h of  $t_p$  for both, PANI and HEM signals. In figure 2, intensity for peak at  $25,35^\circ$  of PANI/HEM as function of HEM concentration for both  $t_p$  is shown. By increasing of dopant mineral, intensity of same peaks for PANI/HEM has trend to decrease, however, this tendency is lightly major when polymerization reaction is carried out at 14 h. This fact could mean that at this  $t_p$  a higher doping is produced and therefore, a greater degree of crystallinity.

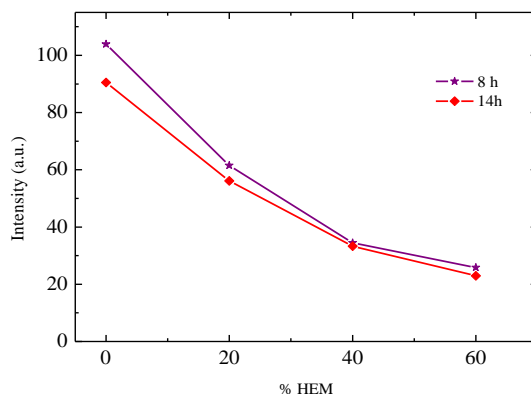


**Figure 1.** X- ray diffraction patterns for PANi/Hem polymers doped.

FTIR spectra for PANI, HEM and PANI/HEM composites are shown in figure 3. PANI FTIR spectra shows its eight characteristics bands. At  $3416\text{ cm}^{-1}$  it is seen tension vibrations of N-H of amine groups, at  $2923\text{ cm}^{-1}$  is due to C-H stretching vibration of aromatic rings. Signal attributed to quinolinic rings presented on the oxidation state of emeraldine salt (PANI), is at  $1574\text{ cm}^{-1}$ . while the band close to  $1482\text{ cm}^{-1}$  is assigned to C=C stretching vibration of aromatic ring. The doublet at  $1298$  y  $1243\text{ cm}^{-1}$  corresponds to stretching vibration of C-N bond of secondary amine. Band at  $1139\text{ cm}^{-1}$  is the flexion vibrations on aromatic plane for C-H, while deformations C-H out of plane of a 1,4-disubstituted system it appears at  $799\text{ cm}^{-1}$ .

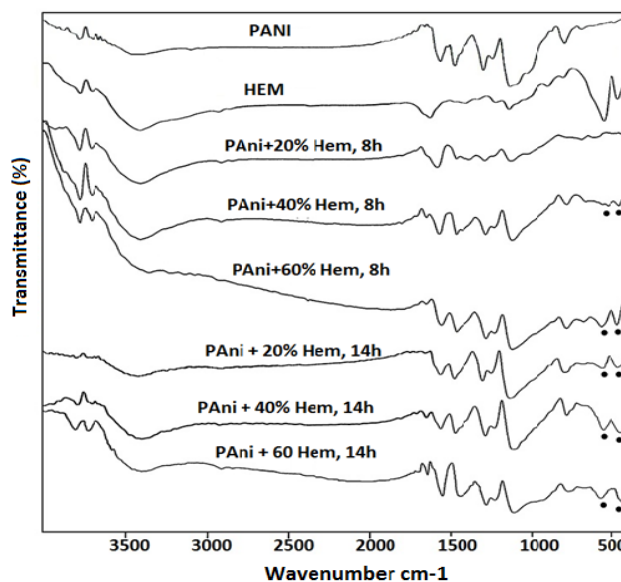
HEM FTIR presents seven characteristics bands. At  $3411$  y  $1629\text{ cm}^{-1}$  are bands of stretching and bending vibration of water of HEM hydration. Band at  $1220\text{ cm}^{-1}$  is due to Si-O-Si bonds vibrations of quartz. At  $1138$ ,  $898$  y  $798\text{ cm}^{-1}$  there are bands corresponding to the stretching metal-OH bond

vibrations for the iron and silice compounds like SiOH, FeOH and goethita ( $\alpha$ -FeOOH). Finally, the most intense bands for HEM at  $551$  y  $462\text{ cm}^{-1}$  are keys to identify doped PCs.



**Figure 2.** PANI peak ( $25, 35^\circ$ ) intensity against HEM percentage at 8 y 14 h tP. (Solid lines are a visual guide to the trend).

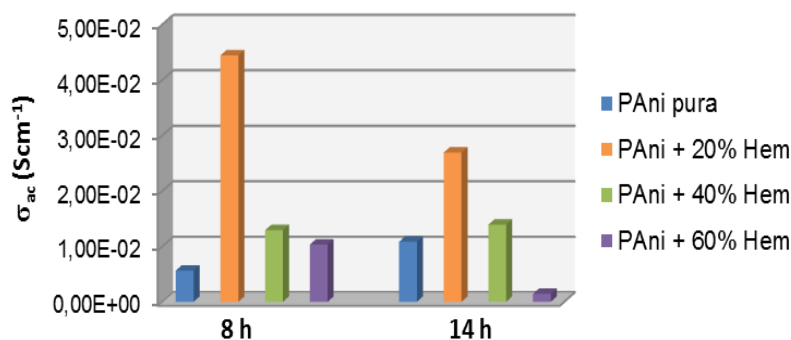
FTIR spectra for PANI/HEM composites show every single PANI bands. About HEM, in these spectra it is possible to identify bands at  $552$  y  $480\text{ cm}^{-1}$  at 8 h tP and  $568$  y  $461\text{ cm}^{-1}$  at tP of 14 h, intensity of all signals increases with increasing HEM concentration on polymer matrix. Rising dopant percentage results in a growing of almost all bands at right end of the spectrum (for both PANI and HEM) in relation to the broad band at  $3416\text{ cm}^{-1}$  corresponding to N-H bond of PANI. In general, HEM bands at 14 h are most intense that those at 8h tP. It is seen for example, that with HEM 20%, mineral characteristics bands are almost imperceptible at 8h tP whereas at 14 h are visible clearly.



**Figure 3.** FT-IR Spectra. From top to bottom: pure PANI, pure HEM, doped CPs 8 h tP, doped CPs 14 h tP.

Based on the conductivity measurements it is possible to establish that PANI/HEM composite at 20% HEM with 8h tP has the higher  $\sigma_{ac}$ , its value is four times the conductivity of PANI without

doping. There is an optimal dopant concentration with which the maximum  $\sigma_{ac}$  for doped CPs is achieved (20% HEM), an increase in dopant content above this value has a contrary effect on conductivity, from this point  $\sigma_{ac}$  diminish to values even lower than those for pure PANI. Its behavior for both reaction times is schematized in figure 4.



**Figure 4.**  $\sigma_{ac}$  values PANI/HEM against HEM percentage ( $t_p = 8$  y 14 h;  $f = 1 \times 10^5$  Hz).

#### 4. Conclusions

Experimental techniques XRD and FTIR allowed to confirm the presence of HEM on doped CPs and also to follow doping process by changes in dopant concentration and reaction time. It was found that, the rise in CPs doping degree and crystallinity is proportional to the concentration increase of doping agent, being higher in PANI/HEM compounds synthesized at 14h  $t_p$ . It was determined that the biggest increment of Cps conductivity is reach at 20% of dopant agent, what can be said that there is an optimal concentration of HEM which leads to a maximum value of conductivity. Any additional amount of HEM produces a negative effect on PANI/HEM conductivity.

#### References

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