

## Changes on electrical and structural properties of polyaniline and polypyrrol by mullite doping

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**Abstract.** In this work, the effect of mullite dopant (mull) on the structural and electrical properties of two conductive polymers: polyaniline (PAni) and polypyrrole (PPy), which have great interest in science and materials engineering, has been evaluated. Doped polymers were synthesized with different contents of mineral and at two polymerization times ( $t_p$ ) by an in situ chemical synthesis in acidic aqueous solution and using Ammonium Persulfate (APS) as the reaction initiator. Structural characterization was performed by X-Ray Diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FTIR). The conductivity values ( $\sigma_{ac}$ ) were estimated from Electrochemical Impedance Spectroscopy (EIS). It was found that, at concentrations of work, were obtained higher values  $\sigma_{ac}$  of conductivity at the highest concentration of the mineral, however, in some compounds the conductivity decreased. The variations in conductivity were attributed to PC-dopant interactions.

### 1. Introduction

Conductive polymers (PCs) are used as conductive glues, non-static textiles, organic compounds sensors [1,2], capacitors, and electrodes for rechargeable batteries [3] between many others. Recently, many studies have been focus on to optimize the structure and to improve electrical properties of PCs, which can be done by adding doping agents. It has been reported that before doping, PCs shows very low electrical conductivities (values  $\approx 10^{-10}$  S/cm), after doping this values can rise even in twelve magnitude orders ( $\approx 10^2$  S/cm) depending on polymeric matrix and dopant agent type [3-6].

The fundamental process of doping is a charge-transfer reaction between the organic polymer and a dopant. The dopants for conducting or semiconducting PANI include several types of molecules as acids, salts or mineral phases. In this study mullite mineral (mull) is used as dopant agent. Some outstanding properties of mullite are low thermal expansion, high temperature strength and good chemical stability. Besides mullite has been used recently as corrosion resistive coatings even at high temperatures [7,8].

The goal of this work is to present synthesize, structural and electrical characterization of doped PCs with a mineral phase. Studied PCs were polyaniline as emeraldine salt (PAni-ES) and protonated polypyrrol (PPy). These polymers were obtained by chemical polymerization in acidic medium. Both of these polymers were doped with mullite mineral ( $3Al_2O_3 \cdot 2SiO_2$ ) at three concentrations: 20, 40 and 60%. Doped PCs were analysed by XRD, FTIR and EIS.



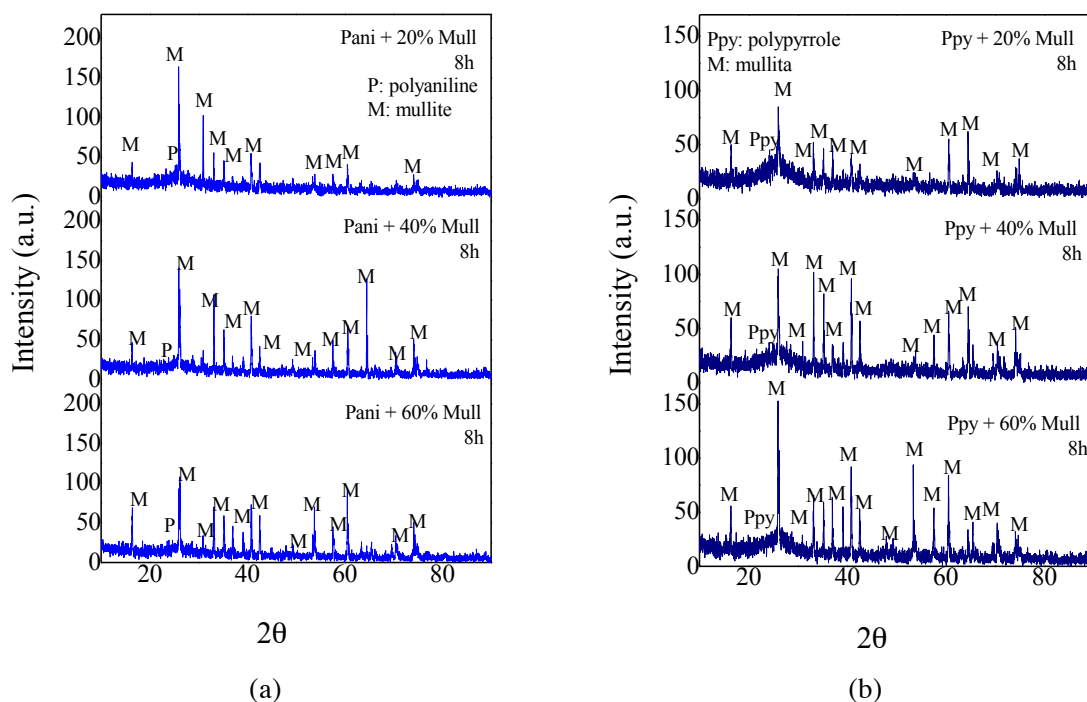
## 2. Experimental

PAni/mull and PPy/mull compounds were synthesised in oxidative polymerization in acidic medium with dopant agent in situ. Three quantities of mull were added to obtain mixtures of 20, 40 and 60% weight and reaction was performed at two polymerization times ( $t_p$ ) of 8 and 14 hours. General procedure was: 0.01mol of monomer (Ani or Py) were added to 100mL of HCl 2M. Precipitates formed were collected by filtration and washes with distilled water and the proper solvent (acetone for PAni and methanol for PPy) to discoloration. Later mull was added with continuous and vigorous stirring keeping temperature under 4°C. Then 0.01mol (2,28g) ammonium persulfate was slowly added (PSA)  $[(\text{NH}_4)_2\text{S}_2\text{O}_8]$ , as oxidant agent. Each mixture was allowed to react for 8 and 14h with continuous stirring. Doped PCs were dried at room temperature in a desiccator and then structurally and electrically studied.

## 3. Result and discussion

### 3.1. Structural characterization

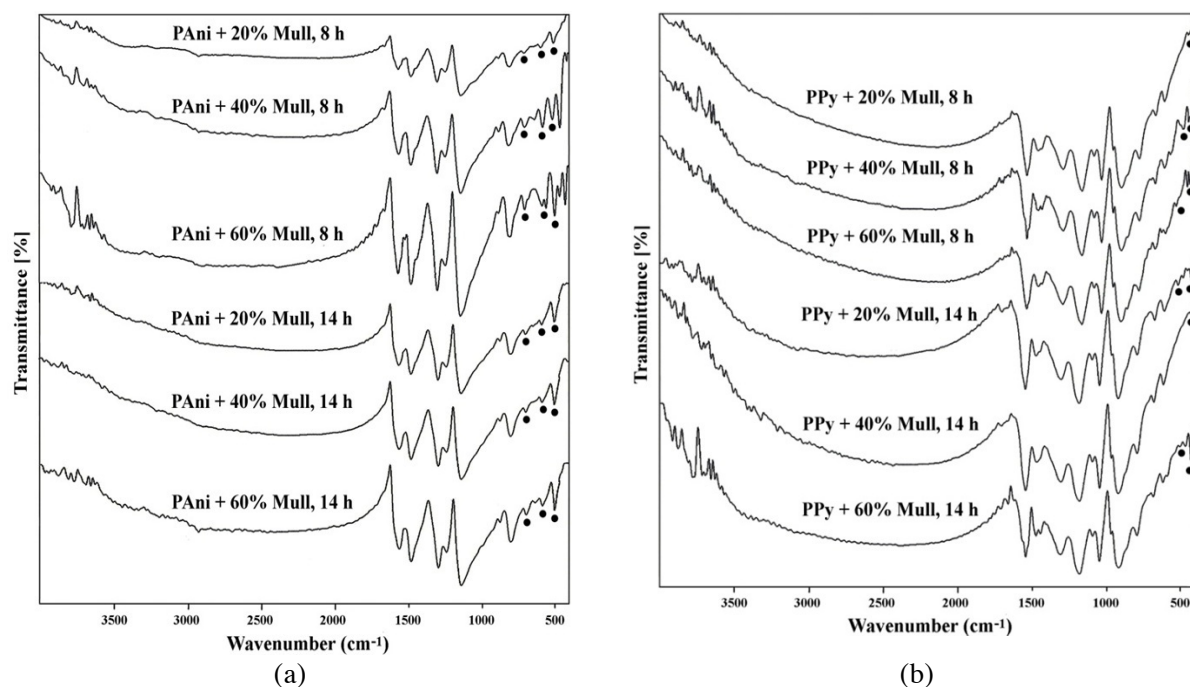
**3.1.1. XRD.** XRD for PAni/mull and PPy/mull are shown in Figure 1(a) and Figure 1(b) respectively, with 20, 40 and 60% of dopant and  $t_p$  of 8h. It is seen PAni characteristic signal at  $25.35^\circ$  and at  $25.47^\circ$  for PPy besides of mull typical peaks. XRD for both PCs at  $t_p$  of 14h has the same pattern (not shown here).



**Figure 1.** Ray diffraction patterns x of (a) PAni/mull and (b) PPy/mull at  $t_p$  of 8h.

Diffraction profile for doped PCs indicate that mineral phase is already incorporated into polymeric matrix: there is a principal peak, of low intensity, for each PC obtained ( $2\theta \approx 25.35^\circ$  for PAni and  $2\theta \approx 25.47^\circ$  for PPy); intense signals for mull also they appear. The most intense peak for mull is near to PCs peak at  $26^\circ$ . Mineral insertion to polymer chains causes and increase in crystallinity of PAni and PPy.

**3.1.2. FTIR.** FTIR spectra for PANi/mull and PPy/mull are shown in Figure 2(a) and Figure 2(b) respectively. All bands for PC and some key Mull bands prove the successful doping. In every PANi/mull FTIR spectra (Figure 2(a)), all PANi bands appear. Further it is observed a band next to  $704\text{cm}^{-1}$  related to stretching vibrations of Al–O bond in tetrahedral coordination and to flexion modes of Al–O–Al mull bond. Bands close to  $584\text{cm}^{-1}$  and  $497\text{cm}^{-1}$  are due to stretching vibrations of Al–O bond in octahedral structural units. In FTIR spectra for PPy/mull (Figure 2(b)) bands corresponding to PPy it seems and there are two bands at  $550\text{cm}^{-1}$  and  $426\text{cm}^{-1}$  associated with flexion modes of Al–O–Al bond in mull.



**Figure 2.** FTIR spectra of (a) Pani/mull and (b) Ppy/mull composites.

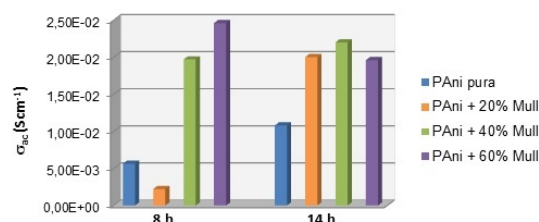
FITR spectra for doped PCs (Figure 2) shows that there are changes in intensity and number of bands that appear because of the mull adding. Those bands become more intense for more mineral concentration in most of the cases. Intensity alterations are presents no just in doping agent bands but in those for PC. This behaviour proves that the doping process involves a doping agent interaction with some specific places of polymeric chain, which carries out a structural modification. If it is true that this interaction it is not well known at molecular level, nevertheless it is know that this interaction is associated to changes in several properties as, for example, conductivity increase or decrease, depending on the electrical character of doping agent.

### 3.2. Electrical characterization (EIS)

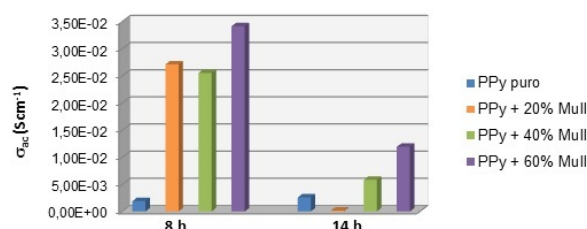
With the purpose of to appreciate the changes in conductivity for each PC/doping agent system, caused by the synthesis variables (mull concentration and polymerization time), results of EIS are shown in bar graphs. In Figure 3 variation of  $\sigma_{ac}$  as a function of mull content for both  $t_p$  for PANi/mull is plotted.

The 8h PCs sample with lowest mull content (20%), has a lower conductivity than that exhibited by non-doped PANi (pure emeraldine) synthesized at this  $t_p$ . On the other hand in PCs with 40% and 60% mull content  $\sigma_{ac}$  values increase according to increment of mineral doping. To 14h PCs every single sample with some mull content has higher  $\sigma_{ac}$  values that for non-doped PANi. The highest  $\sigma_{ac}$  value for PANi/mull it is exhibit by 60% mull PC at 8h.

In Figure 4 shift of  $\sigma_{ac}$  as a function of mull content for both  $t_p$  for PPy/mull is plotted. For 8h PCs  $\sigma_{ac}$  values are always higher than those of non-doped PPy. The highest conductivity it is shown for 40 and 60% mull concentration. For 14h sample with 20% mull, presents a  $\sigma_{ac}$  much less than  $\sigma_{ac}$  for non-doped PPy. The conductivity value for compounds 40 and 60% mull increase with increasing mineral quantity, but values were lower than those obtained for the same concentrations synthesized to 8h.



**Figure 3.**  $\sigma_{ac}$  versus composites PANi/mull  $t_p=8$  and 14h and  $f=1 \times 10^5$  Hz.



**Figure 4.**  $\sigma_{ac}$  versus % mullite composites PPy/mull  $t_p=8$  and 14h and  $f=1 \times 10^5$  Hz.

#### 4. Conclusions

From analysis of the diffraction patterns and FTIR spectra it was concluded that the addition of mullite to PCs involves a dispersion in the polymer dopant, which involves an increase in the crystalline behaviour of PCs. Similarly, there is an interaction between PC and dopant, possibly associated with PCs conductivity changes.

We found that in most PC-doped conductivity values increased relative to the values obtained for pure mullite and PCs. The highest value of conductivity for PANi/mull system was obtained for 60% mullite concentration synthesized during 8h. For the PPy /mull system is noted that for the compounds synthesized 8h, the conductivity values are always higher than that obtained for pure PPy, being the highest value for the sample with 60% of mullite. By comparing the two systems studied it was found that the interaction between the PANi and mullite and is less strong than between PPy and mullite, and so the increase in conductivity is lower. Therefore, the effect of doping on the electrical conductivity of the PCs depends on the nature of the dopant, the polymer and the interaction between them under certain conditions. Doping agents act as a charge carriers which is seems more efficient on PPy. Conductivity in PPy specifically is due to *p*-type (bipolar) conduction, in the inter-chain hopping of electrons and the motion of anions or cations within the material [9]. It is important also to keep present that the efficacy of doping is strongly dependent on external factors as pH and temperature. So, the values found in this study must be expanded to the same PC-doping composites but obtained and tested at different conditions.

#### References

- [1] Bhadra D, Khastgi D, Singha N and Hee Lee J 2009 *Prog Polym Sci* **34** 783
- [2] Pirsas S and Alizadeh N 2010 *Sens Actuators B* **147** 461
- [3] Armelin E, Meneguzzi A, Ferreira C and Aléman C 2009 *Surf Coat Technol* **203** 3763
- [4] Akasaki I, Sota S, Sakai H, Tanaka T, Koike M and Amano H 1996 *Electron Lett* **32** 1105
- [5] O'Leary S K, Foutz B E, Shur M S, Bhapkar U V and Eastman L F 1998 *J Appl Phys* **83** 826
- [6] Narayan H, Alemu H, Somerset V, Iwuoha E, Hernández M, Hernández J, Montañó A and Henao J 2009 *Fly ash composites with polyaniline synthesis, characterization and conductivity measurements* (New York: Nova Science Publishers) chapter 5 p 111
- [7] Tushar Kulkarni, Wang H Z, Basu, S N and Sarin V K 2011 *Surf Coat Technol* **205** 3313
- [8] Huang Jian-Feng, Zeng Xie-Rong, Li He-Jun, Xiong Xin-Bo and Huang Min 2003 *Carbon* **41** 2825
- [9] Richard Balint, Cassidy N J, and Cartnell, S H 2014 *Acta Biomater* **10** 2341