

Synthesis of Nanocomposites Based Semiconductors of PPy(Cl)/Zeolite HY

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This research is based on the study of the chemical polymerization of nanocomposites based conductors polypyrrole PPy(Cl) and the HY Zeolite type Faujasite as reinforcements, at room temperature and atmospheric pressure using FeCl₃ as initiator of the reaction and dopant at the same time. After characterization commodity we methods primarily on the polymerization of pyrrole with different molar ratios of [FeCl₃] / [Pyrrole] in an aqueous medium, followed by a series of characterizations for the polymers obtained. Won the right ratio was used for the preparation of nanocomposites PPy (Cl) / HY Zeolite. After each synthesis, the developed product is characterized by FTIR, SEM, UV-Vis, XRD, and electrical conductivity in order to confirm the success of the process of synthesis and study their properties to specific applications envisaged.

Keywords: nanocomposite, polypyrrole, zeolite HY, conductor polymer

The materials have always occupied a key position in the history of mankind. For a long time, the selection of a material for a structural or functional application was bound to only one of its properties [1].

The idea to improve material properties has always existed. Indeed the man continually seeks to improve the properties of the surrounding materials or manufactures associating them or combining them in different ways, which is commonly called, composite materials [2].

From the fifties, the need for new materials led to the development of materials combining the mechanical properties of insulating polymers and electrical properties of metals [3]. After the discovery of a new polymer type in the 1970 which led in 2000 to the award of the Nobel Prize in chemistry to Alan J Heeger, Alan G MacDiarmid and Hideki Shirakawa for their revolutionary discovery that a polymer is at first the insulating state, could become driver if he alternately included single and double bonds between the carbon atoms and if he was doped by oxidation (removal of electrons) or reduction (adding electrons). The "holes" or extra electrons can then move throughout the molecule which becomes electrically conductive [4, 5].

Among these materials, polypyrrole (PPy) is the first commercially available conductive polymer due to its good stability in air and heat, as well as its low cost with various potential applications such as electromagnetic shielding, capacitors, sensors, antistatic packaging, anticorrosion coating, etc. .

The need arose from the current trend of miniaturization, to understand the laws governing the behavior of matter at the nanoscale and learn to control them to produce nanostructured objects [6]. Nanotechnology is now a social phenomenon worldwide. This new discipline falls challenges both economic and political, for it is as a future science at the interface of several scientific areas [7].

The work presented in this manuscript is to explore other avenues for the synthesis of nanocomposites based conductive polypyrrole as a template, the HY zeolite faujasite type as reinforcements with the optimization of

operating conditions in order to increase the value of the electrical conductivity.

Experimental part

Pyrrole (C₄H₅N) 99% iron (III) chloride 97%, 98% Zeolite NH₄Y were purchased from Sigma Aldrich. Pyrrole monomer was purified by distillation under reduced pressure and stored at 4°C in the absence of light.

Pretreatment of Zeolite NH₄Y

In this part, described the preparation of an HY zeolite sample from the base zeolite NH₄Y, provided the ammonium form by Sigma Aldrich.

The chemical formula was established on the basis of data XRF, SiO₂ / Al₂O₃ = 2.6 and Na₂O = 2.54% and the assumption that the number of silicon and aluminum mesh is 192. The chemical formula of the mesh, having a Si/Al ratio of 2.6, is: Na₄(NH₄)_{52,33}Al_{53,33}Si_{138,67}O₃₈₄

To eliminate the amount of ammonia present in the zeolite NH₄Y, we developed a désammonisation in a muffle furnace (static reactor) type Nabertherm 30-3000°C, the ammonia removal by heat treatment (désammonisation) by solid route we will detail later. A preliminary study showed that the thermal treatment in static or dynamic mode has no influence on the textural properties of the zeolite.

For this, 2 g zeolite NH₄Ysont heated to 500°C stepwise at a rate of 2°C / min. A holding time of one hour at 100°C is needed to allow maximum water safe disposal desaluminatation. The overall reaction of désammonisation is:



As the following figure 1 shows, the crystal structure of the zeolite mother N₄HY is virtually identical to that after calcination, so that we register a slight decrease in the intensity of the characteristic peaks.

The thermal treatment of the zeolite by NH₄Y temperature stages is as follows:

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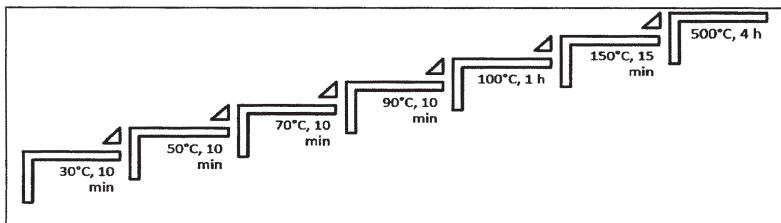


Fig. 1. Désammonisation programmée température Zeolite NH₄Y

Analysis by FTIR spectroscopy

The following figure shows the superposition of the infrared spectra of Zeolite and Zeolite HY NH₄Y:

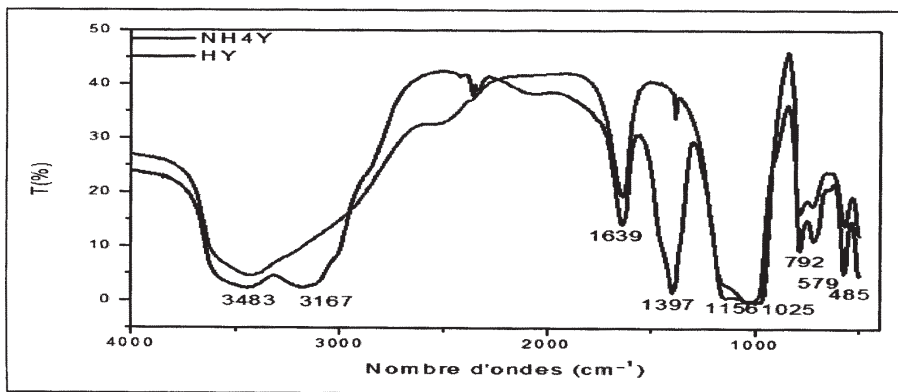


Fig. 2. Overlay infrared spectra for NH₄Y Zeolite and Zeolite HY

Broadband 3483 cm⁻¹ corresponds to the elongation of the O-H group, 3167 cm⁻¹ corresponds to the elongation of the N-H group and at 1639 cm⁻¹ to H-O-H deformation;

A band at 1397 cm⁻¹ corresponds to the elongation of the N-H group, at 1156 cm⁻¹ corresponds to the asymmetrical stretching of the O-T-O group and at 1025 cm⁻¹ corresponds to the elongation of the T-O-T group;

The bands observed in the region 579 cm⁻¹ corresponding to the symmetrical stretching of the T-O-T group and in the region between 485 and 792 cm⁻¹ are due to symmetric vibration n(T-O) structure. These vibrations are said to internal and external tetrahedra.

According to infrared analysis, the disappearance is observed of the band 3167 and 1397 cm⁻¹ corresponding to the ammonium (NH₃), thus deamination NH₄Y is completed [9].

X-ray diffraction analysis

The Scherrer method was used to calculate the mean particle size, that is expressed by the following formula:

$$D_{Scherrer} = \frac{k\lambda}{\beta \cos\theta} \quad (1)$$

where λ is the wavelength of the X-ray radiation ($\lambda = 0.154056$ nm), K is the Scherrer constant ($k = 0.89$), θ is the diffraction angle and β is the line width at half-maximum height of the most intense peak [9].

The average crystallite sizes of each sample calculated by Scherrer formula are shown in the following table 1.

Syntheses of nanocomposites based on PPy(Cl)/Zeolite HY

In a 100 mL flask, we prepared a mixture of Pyrrole / reinforcement in 50 mL of distilled water under stirring for one hour, with a report of mass [Zeolite HY] / [Pyrrole] =

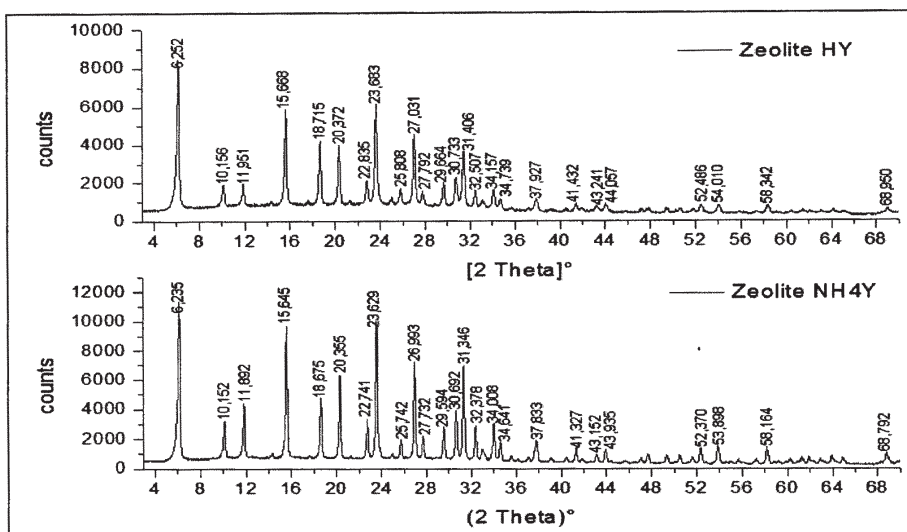


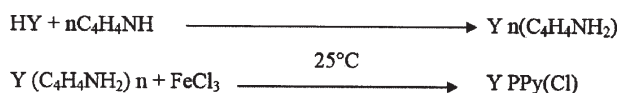
Fig. 3. Overlay DRX for Zeolite NH₄Y and Zeolite HY

Material	2θ	d[Å]	Miller Indices			β [Å]	D _{Scherrer} (nm)
			h	k	l		
Zeolite NH ₄ Y	5.887	15	1	1	1	0,1632	98,2 nm
Zeolite HY	5.887	15	1	1	1	0,1836	78,0 nm

Table 1
AVERAGE SIZES OF THE NANOPARTICLES OF ZEOLITE NH₄Y AND ZEOLITE HY

0.1 - 0.2 - 0.3 -0.4 -0.5. We then added 1.4 mL of pyrrole, under agitation also during 4h. We see the emergence of a creamy solution in both cases. The polymerization is initiated by the injection drop wise 50 mL of a solution of oxidizing FeCl_3 in mid aqueous prepare in temperatures of 25°C (using the best molar ratio $[\text{FeCl}_3]/[\text{Pyrrole}]$ obtained according to the results of characterizations of PPy(Cl)). After 3 h of polymerization, the nanocomposites obtained were filtered, washed completely with water to remove the oxidant and the traces of pyrrole not reacted, then with methanol to remove the remaining oligomers. Finally, the nanocomposites obtained are made dry in an oven between 60 to 70°C for eight hours. The polymerization is made according to the following flowchart:

The general reaction of synthesis of the zeolite HY and pyrrole is the following:



Characterizations of nanocomposites based semi-conductors of PPy(Cl)/ Zeolite HY

Analyze par spectroscopy FTIR

The following figure shows the spectra of transmittances in infrared of PPy(Cl)/Zeolite YH prepared with the report $[\text{FeCl}_3]/[\text{Pyrrole}] = 2.5$ and different mass percentages of the zeolite HY (fig. 4).

We observed in $1390, 1028, 779, 579 \text{ cm}^{-1}$ the emergence of bands of vibrations of the zeolite HY. In contrast, the bands that appear in $1547, 1452, 1307, 1190, 1028$ and 910 cm^{-1} is due to vibration of the connections PPy(Cl) [8, 9]. This means that the zeolite HY channeled into our case is the PPy(Cl). By suggesting this, the zeolite is involved only to compensate the positive charge on PPy(Cl) [10]. The main bands of vibration in infrared allowing the identification of PPy(Cl) and of the zeolite HY were observed, which confirms the correct process of polymerization.

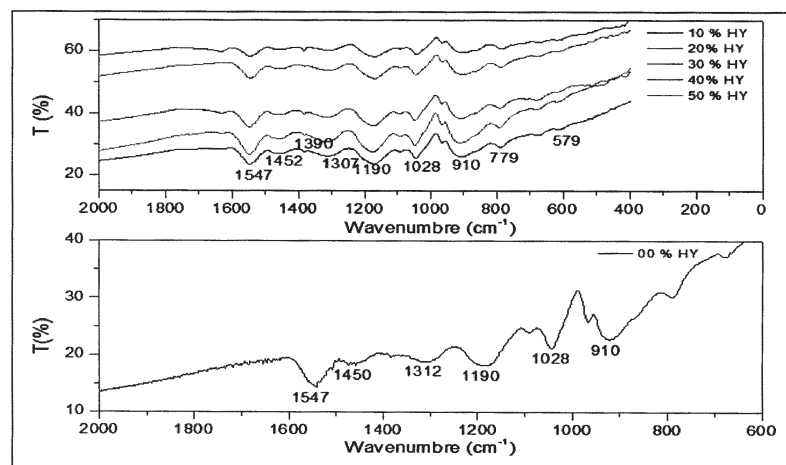


Fig. 4. Superposition of infrared spectra of the nanocomposites synthesized with the report $[\text{FeCl}_3]/[\text{Pyrrole}] = 2.5$ and different mass percentages of the Zeolite HY

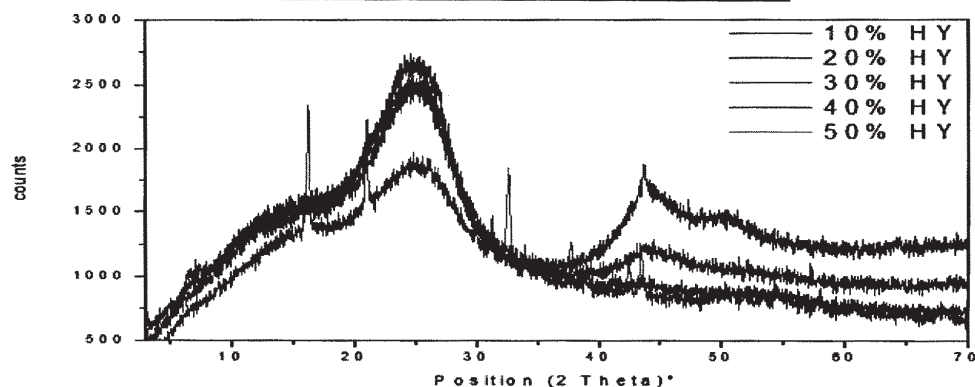


Fig. 5. Superposition of spectral XRD of nanocomposites synthesized with the report $[\text{FeCl}_3]/[\text{Pyrrole}] = 2.5$ and different weight percentages of the Zeolite HY

Analysis by X-ray diffraction

The results obtained by X-ray diffraction (XRD) performed on the powders of PPy(Cl)/Zeolite HY have enabled us to conclude that they are of amorphous structures, therefore the zeolite HY is fully coated by the PPy(Cl) until a report of 50% Zeolite HY or there was the emergence of a semi crystalline, there is an excess of zeolite HY not coated by the PPy(Cl).

The Zeolite HY has a character of non acid fort, therefore there is an interaction between the zeolite HY and the pyrrole, which reveals a superficial adsorption limited leading to a polymerization in-situ which has as result, PPy(Cl) hooked to the pores, therefore the formation of envelope by the PPy(Cl) [11] on the zeolite HY. The following figure illustrates a proposal of mechanism for the polymerization of pyrrole on the surface of the HY zeolite.

Measurement of the electrical conductivity

Applying a pressure on four points spaced by a distance of the sample surface allowed us give a precise resistivity measured in samples having different shapes, which can be expressed by the following formula:

$$\varphi = \frac{\rho}{G^7(W/S)} (\Omega \cdot \text{cm}) \quad (2)$$

$$\varphi_0 = \frac{V}{I} 2\pi S \quad (3)$$

$$G^7(W/S) = \frac{2S}{W} \ln 2 \quad (4)$$

Where φ is an electrical resistivity with the correction coefficient, S is a distance between the centers ($s = 2.0 \text{ mm}$), W is a thickness of the wafer and φ_0 is an Electrical resistivity without correction coefficient.

The nanocomposites based semiconductors of PPy(Cl)/Zeolite HY, as can be seen on the figure 4, although the PPy(Cl) is amorphous, the structure of the cavities of the

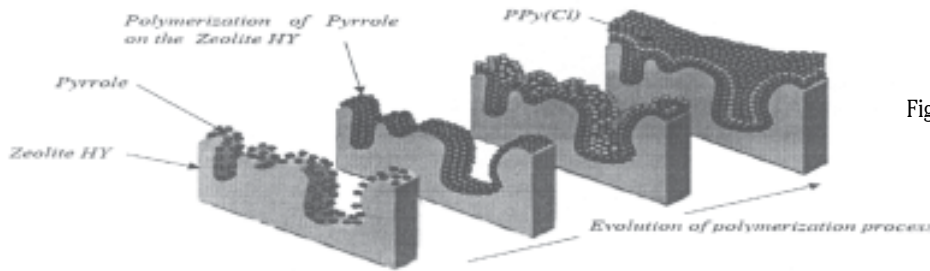


Fig. 6. Adsorption mechanism of pyrrole on the Zeolite HY with its polymerization in-situ

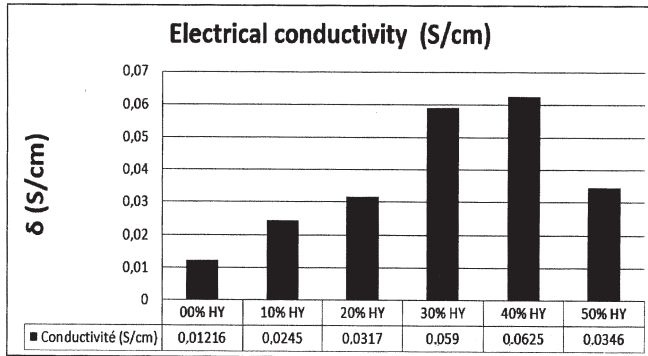


Fig. 7. Evolution of the electrical conductivity of nanocomposites synthesized with the report of $[\text{FeCl}_3]/[\text{Pyrrole}] = 2.5$ and different mass percentages of Zeolite HY

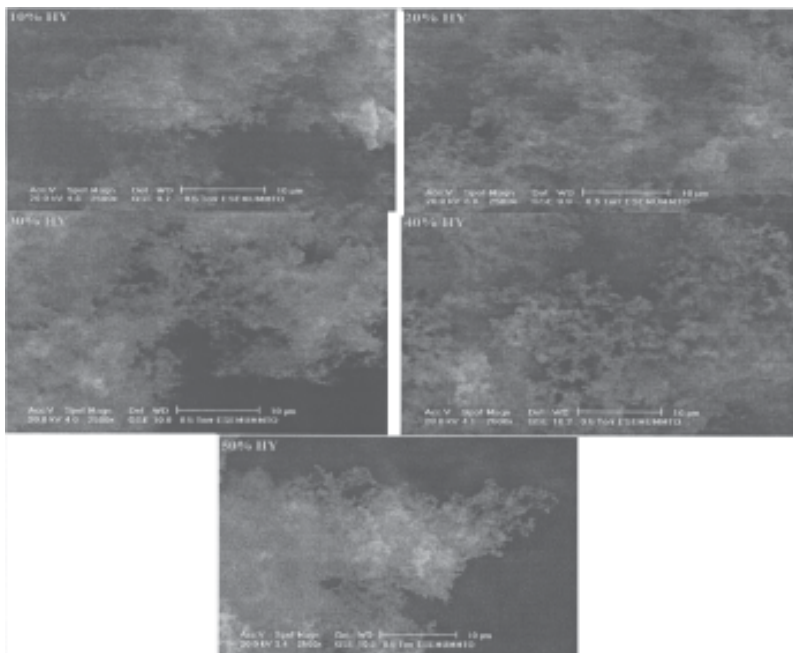


Fig. 8. The SEM images of the nanocomposites synthesized with report $[\text{FeCl}_3]/[\text{Pyrrole}] = 2.5$ and different percentages weights of Zeolite HY

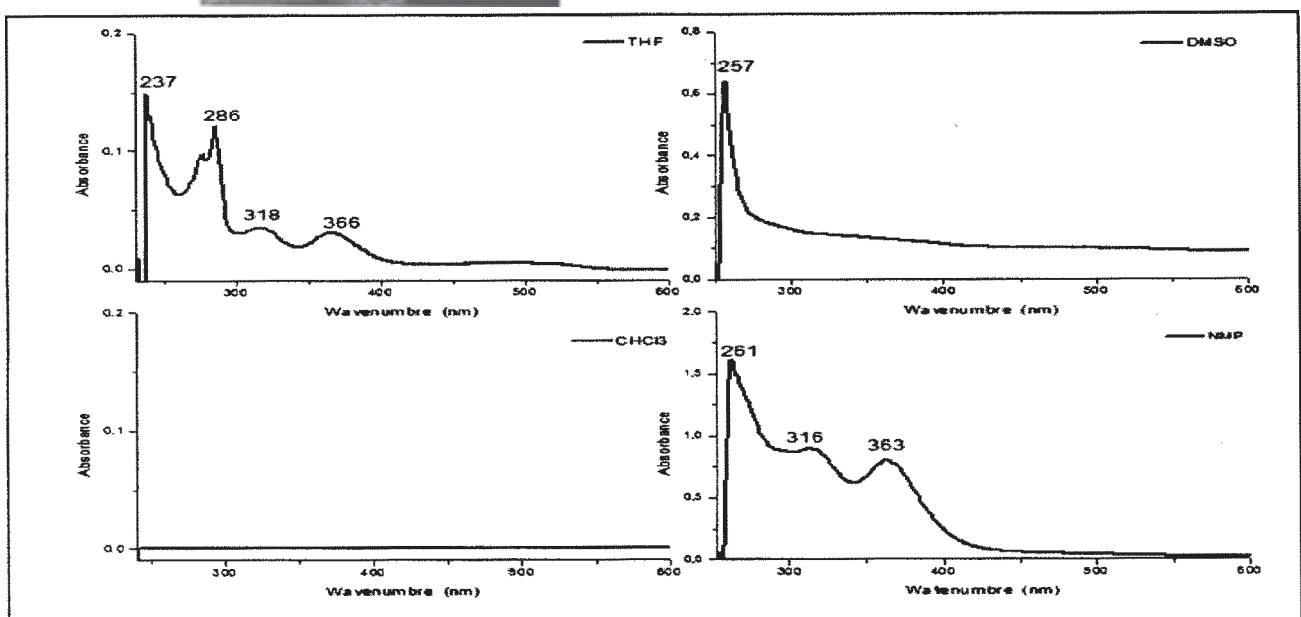


Fig. 9. UV-Vis spectra- of the Nanocomposite synthesized with the report of $[\text{FeCl}_3]/[\text{Pyrrole}] = 2.5$ and 40% mass of Zeolite HY, Put in different solvent

Solvent	Wavenumber (nm)	Assignment
THF	237	$\pi \rightarrow \pi^*$ (Pyrrole)
	285-318	$\pi \rightarrow \pi^*$ (Polypyrrole)
	366	Polaron
DMSO	257	$\pi \rightarrow \pi^*$ (pyrrole)
NMP	261	$\pi \rightarrow \pi^*$ (pyrrole)
	316	$\pi \rightarrow \pi^*$ (Polypyrrole)
	363	Polaron

Table 2
ASSIGNMENT OF THE CHARACTERISTIC BANDS
BASED NANOCOMPOSITE PP_y(CL) / ZEOLITE
HY ANALYZED BY UV-VISIBLE [15, 16]

zeolite HY improves the alignment of the chains of PPy(CI) by the adsorption of the latter on the surface of the grain, which increase the conductivity mounting and coasts the aging [12].

We note that the electrical conductivity depends on the ratio of the zeolite HY added. The entire quantity is well covered by the conductive polymer, up to the ratio of 50 %, or we observed the emergence of the semi crystalline, by consequence, a declination of the electrical conductivity.

Analysis by Scanning electron microscope (SEM)

According to the micrographs, below, there is a marked evolution of the morphology of nanocomposites conductors in function of the rate of zeolite HY incorporated [13]. The particles of the zeolite HY are covered by the PPy(CI) with a spherical nature dispersed in the polymeric matrix, forming clumps of different distributions with significant proportions.

Analysis by spectroscopy UV-Visible

The spectra UV-Visible of the Nano composite driver's control center basis of PPy(CI)/ Zeolite HY with [FeCl₃] / [Pyrrole] = 2.5 (molar) and 40% mass of the zeolite HY dissoute in THF, DMSO, CH₃Cl and NMP are shown on figure 10 The nanocomposite is insoluble in chloroform and partially soluble in other solvents used.

Has share similar bands observed with the PPy (CI), one notes the appearance of a band at 318 nm with the solvent THF, and approximately 360 nm with solvents NMP and THF, which can be assigned to a strong absorption of energy in a stat doped of PPy(CI) [14].

Conclusions

In this part, there has been a clear evolution of the properties of nanocomposites as a function of the ratio mass [Zeolite HY] / [Pyrrole] added.

- Spectroscopy IRTF has confirmed the coexistence of PPy(CI) and of the zeolite HY in the nanocomposites ;
- electrical conductivity increases as a function of the quantity of the zeolite HY added, up to a report of 40% mass, or there is the threshold of saturation PPy(CI) by the zeolite HY (the stability of the conductivity);
- the DRX shows that the nanocomposites are amorphous, c-t-d that the zeolite HY is coated by the PPy(CI) until a report of 50% or there was the emergence of a semi crystalline, which indicates the presence of a part of the zeolite HY non-coated;
- images SEM attest to the evolution of the electric conductivity obtained (presence of a regular morphology);
- the analysis by spectroscopy UV-Visible we have confirmed an improvement in the status of doping of PPy(CI).

The structure of the zeolite HY contains pores, channels and cages of different forms and nanoscale dimensions, which is used to protect the polymer from a few oxidants and air humidity. The adsorption of the conductive polymer on the surface of the zeolite HY improves the alignment of strings and decelerates the aging, therefore, you get an

increase in the electrical conductivity of nano. In addition, the acidity of the zeolite HY to the surface provides the excellent accession of the two materials, and given a system PPy(CI)/ Zeolite HY which has a quick electronic mobility with the ability to exchange of cations in the structure of the zeolite HY [13, 17, 18].

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