

# Synthesis and Characterization of HY Zeolite-doped Poly(aniline) by Chemical Oxidation Method

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*HY zeolite (solid acid) doped poly (aniline) has been synthesized through oxidative polymerization of aniline with ammouim peroxydisulfate used as an oxidant in aqueous medium. The influence of HY zeolite contents (5wt %, 10 wt %, 15wt %, 20wt % and 50 wt %) on the conductivity characteristic, thermal stability, and specific surface area of poly (aniline)/ HY zeolite composites was performed. All samples were characterized by FTIR, UV-Vis, XRD, TGA and SEM techniques. The electrical conductivity was measured using a four-probe method and it was found to be equal to 2.2 S/cm. FTIR spectra has confirmed the presence of poly (aniline) in the form of conducting emeraldine salt and suggest significant interaction of poly(aniline) with HY zeolite.*

**Keywords:** conducting polymer, PANI, doping, HY zeolite, conductivity

In recent years, conducting polymers such as polyaniline, polypyrrole, polythiophene have received much attention because of their potential applications including anticorrosion coatings, batteries, supercapacitors, photovoltaic devices, photoluminescence devices and sensors [1-4].

Among these polymers, PANI has attracted significant attention because of its commercial viability, good electrical conductivity, and easy synthesis. However, there are also some disadvantages such as low chemical stability and mechanical strength that are unfavorable for PANI-related applications. It has been reported that organic-inorganic hybrid materials can synergize or complement the properties of the pure organic or inorganic materials [5,6].

Strong protonic acid solid such as HY zeolite lowered both the work function and increase the conductivity of poly (aniline) according to the known protonic form of doping mechanism, zeolites are nanoporous aluminosilicate materials in which the presence of aluminium atoms introduces charge defects that are compensated by non-framework cations [7,8]. One important topic in the search of zeolites is the characterization of Brønsted and Lewis acid centers. Zeolites are also well known as environmentally friendly acid solid [9-14].

In the present work, we have investigated structural, optical and electrical properties of chemically synthesized HY zeolite (acid solid) doped PANI composites.

## Experimental part

### Materials

All chemical were used as they are received, aniline purchased from Merck (purity > 99%), zeolite  $\text{NH}_4\text{Y}$  [ $\text{Na}_{138}(\text{NH}_4)_{52}33\text{Al}_{53}33\text{Si}_{138}67\text{O}_{384}$ ], zeolite international,  $\text{SiO}_2/\text{Al}_2\text{O}_3 = 5.2$ ;  $\text{Na}_2\text{O} = 0.2\%$ ,  $\text{Si}/\text{Al} = 2.6$  (ZEOLIST<sup>®</sup>) were distained from Sigma Aldrich, Ammonium peroxide sulfate (APS) (purity >99%) was supplied by Panerac, Chloroform (purity >99.9%) and ammonia solution (with concentration fraction of 25% concentrated) were purchased from Fisher scientific. Methanol was obtained

from Biochem, and N-methyl-2-pyrrolidone (NMP) were purchased from Biochem.

### Synthesis of zeolite doped PANI

Pure PANI was synthesized at 0-5 °C by in-situ chemical oxidative polymerization method, described in several reports [15, 16]. The PANI/HY composite was also prepared by an in-situ chemical oxidation polymerization of aniline using different weight of HY zeolite acid solid (5%wt, 10%wt, 15%wt, 20%wt, 50%wt) as a doping agent, HY was prepared using thermal treatment of  $\text{NH}_4\text{Y}$  according to the method described in [17] and the oxidizing solution of APS ( $(\text{NH}_4)_2\text{S}_2\text{O}_8$ ) APS prepared into a ratio of [oxidant]/[aniline] equal to 1.15. The 0.1 M of aniline was dissolved in 100 mL of distilled water solution and then mixed with 10 mL of HY zeolite for 30 min, the oxidizing solution was added drop wise under continuous mechanical stirring. After four hours, a good degree of polymerization is achieved and the dark green precipitate was recovered. The solution was left in undisturbed position over the night for the completion of chemical reaction. The produced precipitate in the reaction was removed by filtration, washed repeatedly with distil water, and dried under vacuum oven for 48h.

### Characterization

Fourier transform infrared (FT-IR) spectra were obtained using a spectrometer type SHMADZU 8400S with a resolution of 1  $\text{cm}^{-1}$ . All powders measurements were performed according to the absorption mode in spectroscopic grade KBr pellets. UV-Visible spectra of the deprotonated and protonated samples dissolved in N-methyl-2-pyrrolidone (NMP) were recorded using a UV-Vis Spectrometer type SHMADZU UV-2401, in the wavelength range of 290–900 nm. Electrical conductivity of compressed pellets of the samples is measured using a Four-Point Probe (Model: RST-8 China) with a DC current source, at ambient temperature. Thermal stability of sample was performed on a thermogravimetric analyzer (Model: TG 209 F1 NETZSCH German). XRD patterns were recorded in the range of 5°–70°, 2 $\theta$  region counting at every 0.02° with a PANalytical, X PerPRO X-ray diffractometer.

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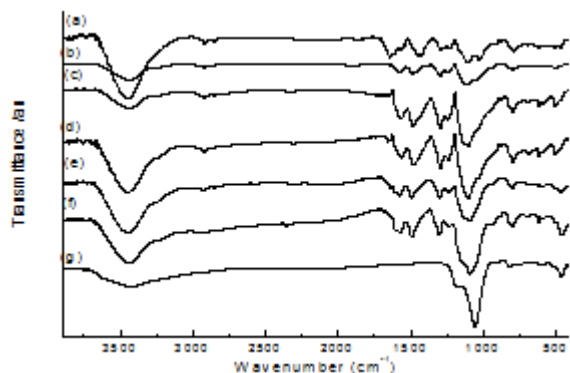


Fig. 1. FTIR spectra of composite PANI/Zeolite (a) pure PANI, (b) PANI/5HY, (c) PANI/10HY, (d) PANI/15HY, (e) PANI/20HY, (f) PANI/50HY, (g) pure zeolite HY

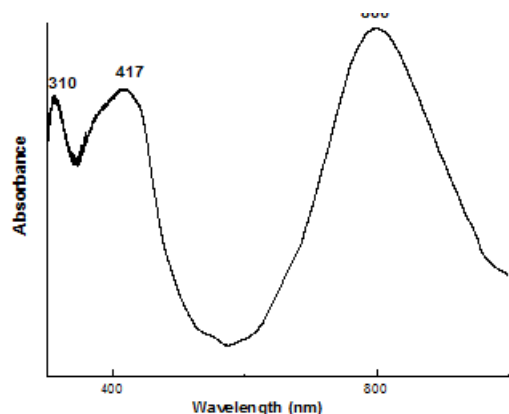


Fig. 3. UV-visible spectra of the protonated form of PANI/5HY

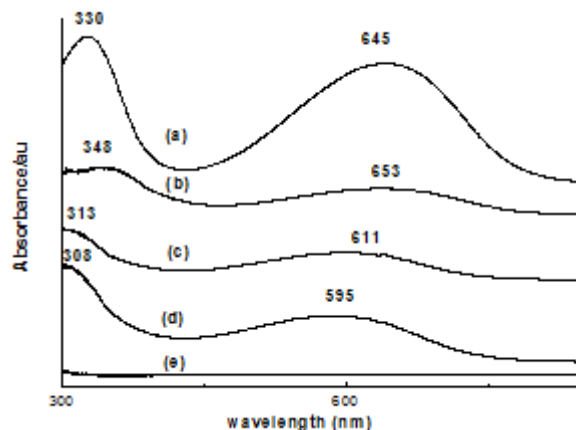


Fig.2. UV-Vis spectra of the deprotonated form of poly(aniline) composite (a) pure PANI, (b) PANI/5HY, (c) PANI/20HY, (d) PANI/50HY, (e) HY

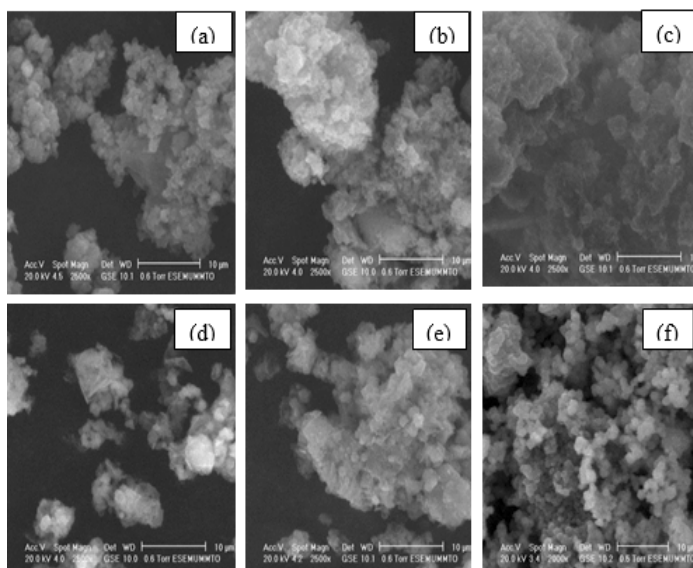


Fig. 4. SEM image of poly(aniline) /zeolite composite (A) pure PANI, (B) PANI/5HY, (C) PANI/10HY, (D) PANI/20HY, (E) PANI/50HY, (F) pure zeolite HY

The morphological observations were carried out using the SEM apparatus type PHILIPS XL40.

## Results and discussions

### Infrared Spectroscopy

Figure 1 shows the FTIR spectra of PANI-zeolite HY composite, in which some vibration bonds are described. The characteristic bands of 3447 and 3252  $\text{cm}^{-1}$  correspond to the O-H and N-H bonds stretching vibration [14], of the emeraldine salt at 1581  $\text{cm}^{-1}$  stretching vibration of quinonoid ring and band 1508  $\text{cm}^{-1}$  stretching vibration of benzenoid ring are related to vibrations of the C = C of the system (N = Q = N) and system C-C (N-B-N) ring deformation respectively. These two bands are very important because they result in qualitative information on the oxidation of polyaniline; the peaks near 2924  $\text{cm}^{-1}$  and 2852  $\text{cm}^{-1}$  are assigned to stretching vibrations of C-H band contained in the PANI structure [18-20].

The characteristic bonds of the zeolite appeared at 1237  $\text{cm}^{-1}$ , 1033  $\text{cm}^{-1}$  corresponds to the stretching group O-T-O and the elongation of the early group T-O-T [21], two bonds at 1298  $\text{cm}^{-1}$  and 1146  $\text{cm}^{-1}$  are due to the vibrations of the C-N system (N-B-N) and C = N system (N = Q = N) of aryl secondary amine [22]. The bands characteristics of C-H at 506  $\text{cm}^{-1}$  and 695  $\text{cm}^{-1}$  are out of range for the ring deformation vibration [23].

The bonds can be observed in the region 626  $\text{cm}^{-1}$  and 468  $\text{cm}^{-1}$  the symmetric stretch of the early group T-O-T and the bonds can be observed in the region between strains (TO). We note that the incorporation form of the HY, characteristic bonds of the zeolite, including the bonds are

located at 1175  $\text{cm}^{-1}$  and 1049  $\text{cm}^{-1}$ , these bonds are assigned to stretching vibrations of groups T-O-T and O-T-O which are increased with the increase of weight [24].

### Ultraviolet-Visible (UV- Vis) spectroscopy

The UV-Visible spectra of the deprotonated PANI/HY composites and pure deprotonated PANI are illustrated in figure 2. Two absorption maxima in NMP. The UV-visible spectrum of pure PANI emeraldine base consists of two bands at 330 and 643 nm. The band at 330 nm has been assigned to the  $\pi \rightarrow \pi^*$  electronic transition and its position corresponds to that observed for standard PANI emeraldine base at ~330-340 nm [25]. This band is sensitive to the number of aniline units. The band at 645 nm corresponds to the *exciton* band which has been attributed to a charge transfer from the highest occupied energy level, centered on the benzenoid ring, to the lowest unoccupied energy level, centered on the quinonoid ring [26]. The exciton band can be used as a measure of the oxidation state of PANI, and it is observed at 637 nm for the *standard* emeraldine base [27]. The UV-visible spectra of PANI/HY composites exhibit two absorption maxima, which show blue-shifting with the increase of the zeolite content in composites: from 348 and 653 nm for 5HY to 313 and 611 nm for 20HY, and to 308 and 595 nm for 50HY.

The UV-Vis spectra of chemically synthesized PANI-Emeraldine salt is dissolved in solvents, generally exhibits

Samples	PANI	PANI/HY					
Percentage of zeolite HY	0	3	5	10	15	20	50
Electrical conductivity (S/cm)	1.12	1.55	2.2	0.127	0.166	0.013	$3.57 \cdot 10^{-3}$

**Table 1**  
CONDUCTIVITY OF PURE PANI, PURE ZEOLITE HY, AND PANI/HY

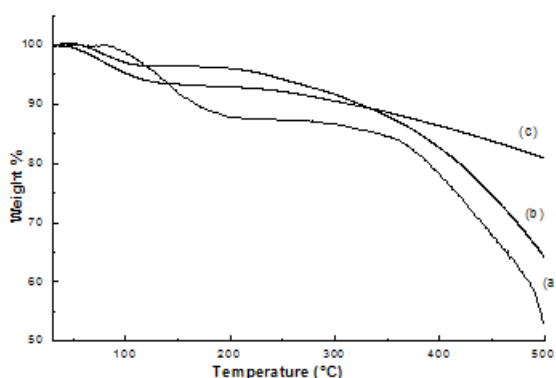


Fig.5.TGA curves for poly(aniline)/zeolite HY (a) PANI, (b) PANI/zeolite 5% and (c) 50%, recorded in air stream

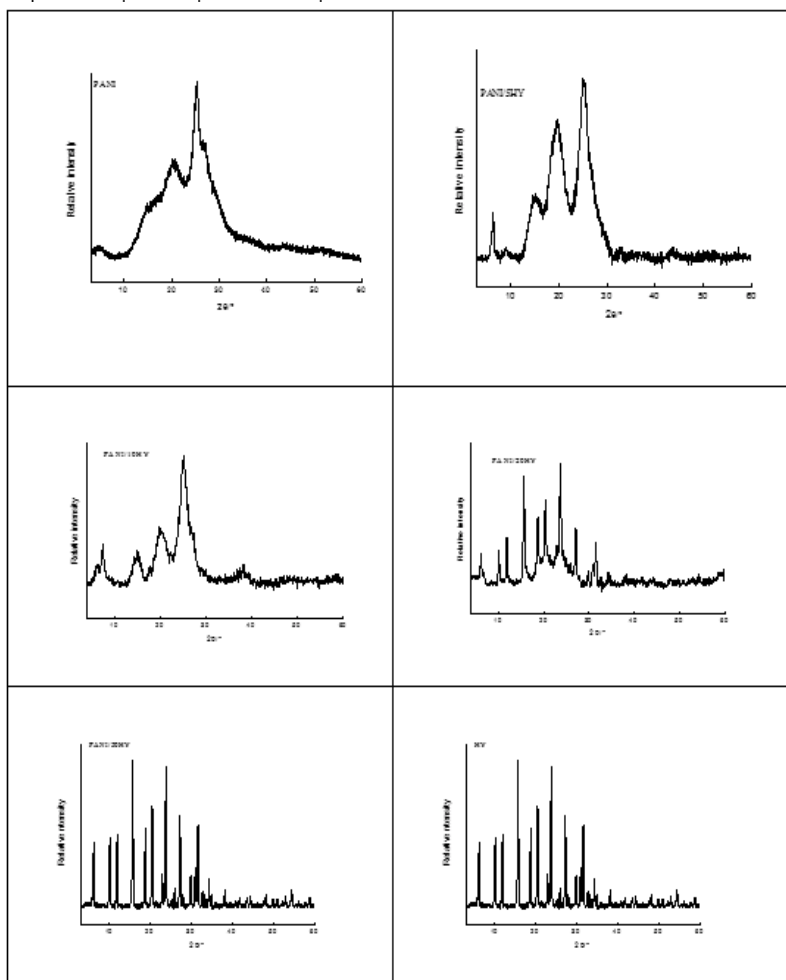


Fig. 6. DRX of parent pure PANI, PANI/5HY, PANI/10HY, PANI/20HY, PANI/50HY and HY pure zeolite

three bands at 730–800 nm, 430 nm (both originating from polaron transitions) and 350 nm ( $\pi^* \leftarrow \pi$  transition) [28]. These three transitions are also present in PANI/5HY dispersions in DCA (dichloroacetic acid). Figure 3 shows the growth of the band at The UV-Vis spectrum of PANI/5HY exhibits three bands at 800 nm, 417 nm and 310 nm.

#### Scanning electron microscopy observations (SEM)

SEM image shows the crucial influence of the initial zeolite weigh ratio on the morphology of PANI/zeolite (fig. 4). According to the above micrographs they reveal the formation of particle agglomerates in the form of different sizes.

#### Thermogravimetric analysis

The weight ratio of PANI and PANI/HY in composites was determined by thermogravimetric analysis (TGA), (fig. 5). Taking into account that the combustion of PANI in air stream is completed at 500 °C, and the residual weight refers to the content of zeolite in the composite, as well as that the weight loss from 25 to 200 °C corresponds to the release of residual water.

#### Electrical conductivity at room temperature

The results of the electrical conductivity measurements at room temperature are summarized in table 1.

The results of electrical characterization (measurement of conductivity) of the processed samples indicate that composites PANI-HY zeolites 5wt% is showing a high conductivity compared to other composite which are

difference observed decrease in conductivity depending on the content of HY.

#### X-ray diffraction (XRD)

The presence of simple peaks in the XRD pattern recorded for PANI/HY, confirms the presence of HY in the composite. The intensity of the XRD pattern peaks can be influenced by crystallinity or by poly(aniline) chains order in composite structure. According to figure 6, XRD pattern of poly(aniline) suggests that it has relatively amorphous structure, but by encapsulation of poly(aniline) in the HY channels, the alignment and arrangements of poly(aniline) chains were significantly improved and as a result, the intensity of the peaks related to the composite were increased.

The average crystallite size was estimated from the integral intensity of the XRD using the Scherrer's equation [29]:

$$D = \frac{K\lambda}{\beta \cos\theta}$$

where  $K$  is the shape factor for the average crystallite (expected shape factor is 0.9),  $\lambda$  is X-ray's wavelength for  $K_{\alpha}$ ,  $\beta$  is full width at half maximum of the diffraction line, and  $\theta$  is Bragg's angle.

Adopting the Scherrer formula, the calculated size based on the XDR results, it is estimated that the mean size of HY nanoparticles is 43.8 nm and nanocomposite content 5% of



Samples	HY	PANI	PANI/5HY	PANI/10HY
S <sub>BET</sub> (m <sup>2</sup> /g) BET	643.96	6.22	15.79	18.65

Abbreviation: BET Brunauer, Emmett and Teller method; PANI/HY poly(aniline)/zeolite

**Table 2**  
THE SPECIFIC SURFACE AREA OF MATERIALS  
ACCORDING TO THE BET

HY is 16.7 nm, 10% of HY is 27 nm, 20% of HY is 39.8 nm and 50% of HY is 43.8 nm. X-ray powder diffraction analysis proved that the crystallinity of zeolite HY in the PANI/50 HY is the same as that of the original HY.

#### Porosity characterization

In table 2, Brunauer–Emmett–Teller (BET) surface areas of different samples are given. The results revealed an increase in specific surface area of the increase of weight percentage of HY zeolite.

The decrease of specific area and specific pore volume with the increase of PANI content in PANI/zeolite composites is caused by the blockade of the zeolite HY pores with PANI [30].

#### Conclusions

The in-situ polymerization of aniline was confirmed by the use of both FTIR and UV-vis spectroscopy which leads to the formation PANI emeraldine base, known by its conductivity and this matter reduces significantly the porous aspect of zeolite HY which was confirmed by the use of BET method. The presence of zeolite HY attributes the amorphous structure to the elaborated composites, in which the SEM images confirm the formation of aggregates regions. From the previous investigations of PANI/zeolite HY composite, it is found that the threshold content of HY as a minor phase was equal to 5 wt % that should be enough to increase electrical conductivity till 2.2 S/cm and then all properties goes with.

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