



Mechanochemical Synthesis and Characterization of Conductive Polyaniline Catalyzed by Maghnite-H⁺ (Algerian Montmorillonite)

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Abstract

Conductive polymers had been the topic of the large number of investigations during last decades because of their unique properties such as mechanochemical strength, electrical conductivity, corrosion and thermal stability. Maghnite-H⁺ is a montmorillonite sheet silicate clay, which exchanged with protons. Polyaniline (PANI), with unique electrical and optical properties, is a promising candidate for wide range of potential applications. So that, in the present paper we report:

1. Synthesis of polyaniline by chemical polymerization of aniline using montmorillonite (Mag-H⁺) as Protonic source.
2. Different oxidant such as (K₂S₂O₈, K₂Cr₂O₇, CuCl₂).
3. Characterization of different polyaniline by different technics.

With these easy synthesis associated good solubility, thermal stability and high electrical conductivity.

Keywords: Polyaniline salt; chemical synthesis; H-NMR spectroscopy; Maghnite-H⁺, composites, hybrid,

1 Introduction

In the recent year, polyaniline composite and nanocomposite suggest a great importance in the present nanotechnology, due to its easy synthesis, low cost, environmental stability and high conductivity [1]. These properties optical and electrical of polyaniline widen his application in several estate such as electronics devices (organo semi conductors, transistors), batteries and combustible piles. In many articles, preparation of polyaniline (PANI) soluble has been subjected [2], this very day, polymerization of aniline in montmorillonite (layered solid) by chemical methods have been reported [3]. The solubilization [4] of polyaniline is important parameter for studding, this physical properties depend on the route of the synthesis of polymer. Generally speak this parameter solubility after synthesis of polyaniline by oxidative polymerization of aniline in aqueous medium with ammonium persulfate (APS) solution and doping by different protonic acid such as (DBSA, CSA) [5]. Here we report a facile chemical method to high quality and solubility of polyaniline under the normal condition using mixture of (montmorillonite/oxidant), when oxidant (K₂S₂O₈, K₂Cr₂O₇, CuCl₂) is solid and water at low temperature. Another important parameter influencing the properties of the resulting polymer organo soluble hybrid (organic-inorganic) is the monomer, the catalyst and the molar ratio (oxidant/monomer) = 0,58. This dissertation describes chemical synthesis of novel composite material based a montmorillonite, oxidant soluble in various organics solvents. By TGA and under the moisture and protonic source (Mag-H⁺), the weight percentage of PANI Should have been round 38,83 % at 600⁰ C, and we obtained 6,65 % of aniline repeating units in 1 Molecule of PANI. By UV-vis spectra, on taking the soluble PANI in various solvents, we can calculate the band of energy by this equation.

$$\Delta E = h\nu = hc/\lambda$$

The solubility parameter (δ) is usually expressed in (cal/cm³)^{1/2} or preferably (J/cm³)^{1/2} units for many compound is defined from Hildebrand-Scotchard Solution theory is:

$$\delta = (\Delta E/V)^{1/2}$$

In ^1H -NMR spectra, the peak ($-\text{NH}-$) appear at 4,81ppm in different oxidant for EB-form PANI but not appear in ES-form Because it's protonated form. The resulting organo soluble polyaniline (PANI-Mag) has been characterized by various physico-chemicals techniques.

2 Experimental

Materials: Aniline 99%, potassium persulphate 98% (Aldrich), hydrochloric acid (35%–38%), Montmorillonite clay was obtained from ENOF Maghnia (Algeria). The MMT- H^+ (Mag- H^+) was prepared as described by Belbachir and al [6], and water ($\text{pH} < 7$) were used to synthesis émeraaldine salt (PANI-Mag- H^+) by emulsion polymerization. Some of the emeraldine base (EB), non-conducting form of polyaniline, was prepared by de-protonating PANI-ES in NaOH Solution (0, 5 M). A doping EB was carried out in aqueous medium of hydrochloric acid (HCl) [7].

2.1 Preparation of catalyst (Maghnite- H^+)

"Maghnite- H^+ xM" were prepared by a method similar to that described by Belbachir *et al.* [8]. Raw maghnite (20 g) was crushed for 20 min using a Prolabo ceramic ball grinder. It was then dried by baking at 105 °C for 2 h. The maghnite was then weighed and placed in an Erlenmeyer flask together with distilled water (500 mL) and magnetically stirred maghnite/water mixture was combined with sulfuric acid until saturation was achieved. After 2 days at room temperature the mineral was washed with water until it became sulfate free and then dried at 150 °C. Sulfuric acid solutions of 0.05M, 0.10M, 0.15M, 0.20M, 0.25M, 0.30M and 0.35M concentration were used to prepare "Maghnite- H^+ 0.05M", "Maghnite- H^+ 0.10M", "Maghnite- H^+ 0.15M", "Maghnite- H^+ 0.20M", "Maghnite- H^+ 0.25M", "Maghnite- H^+ 0.30M" and "Maghnite- H^+ 0.35M", respectively.

The best yield was obtained using "Maghnite- H^+ 0.25M", so for this reason this sample was used to study the effects of catalyst on polymerization. Acid treatment of "Raw-Maghnite" causes a reduction in octahedral content (Al_2O_3) and resulted in an increase in the proportion of silica (SiO_2) observed.

2.2 Synthesis of PANI-ES

This polyaniline salt (PANI-ES) was synthesized by the chemical oxidation of aniline with potassium persulfate ($\text{K}_2\text{S}_2\text{O}_8$), potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) or Silver chloride (CuCl_2), water and montmorillonite (Mag- H^+).

5,1 ml of (0.055 mol) aniline was added to 6% of (0.356 g) Mag- H^+ clay catalyst layered. The reaction was stirring for 30 mn at 0°C, after this time 3g of (0.013mol) oxidant was added slowly during 10 mn, after this we added drop by drop 15 ml of water. The reaction was continued for 1h 30 mn in the optimal condition (0°C).the precipitate product was filtered and washed with distilled water as far as neutralization, because this product contained traces of initiator, oligomer and monomer. In the end, we obtained black solid which be composed of (polymer-Mag). Whereas, the Mag- H^+ it's separate by filtration because it's insoluble in the solvents in which the polymer is soluble.

Eventually, the result it's black solution (polymer-solvent), after evaporation result a black powder it's (PANI-ES), washed several times with water and methanol, where dried at 60°C for 48 h for characterization.

2.3 Preparation of PANI-EB

The polyaniline base (PANI-EB) it's obtained by deal treatment of polyaniline salt (PANI-ES) with an solution of dilute NaOH (0,5 M). Then, the prepared ES-form PANI was converted to EB-form PANI by stirring with 200 ml of 0,5 M NaOH dilute solution at room temperature for (5 at 10) hours. At the end of the stirring, the PANI-EB was filtered, washed with water and methanol several times and dried under vacuum at 60°C for 48 hours by characterization. Finally, 1.53g of the dark black EB-form PANI powder was obtained (84. 14% yield).

3 Results and discussion

3.1 Polymerization and product characterization

The results of polymerization experiments of 0.055 mol aniline with 1.5 % of oxidant ($\text{K}_2\text{S}_2\text{O}_8$) induced by 6 % of catalyst "Maghnite- H^+ 0.25M" are reported. For all these experiments the temperature was kept constant at 0°C for 3hours.

3.2 FTIR spectral analysis

The FTIR spectra of the PANI-ES and PANI-EB under the same conditions were shown in Figure-1 and Figure-2. It was found that PANI had characteristic peaks at around 3631 cm^{-1} and 3288 cm^{-1} due to the characteristic free N-H stretching vibration suggests the presence of primary and secondary amino group ($-\text{NH}-$ and $-\text{NH}_2$), 1557 cm^{-1} , 1501 cm^{-1} (C-C stretching deformation of quinoid and benzenoid ring respectively), 1293 cm^{-1} (C-N stretching of secondary aromatic amine), 1168 cm^{-1} and 838 cm^{-1} (out-of-plane deformation of C-H in the 1,4- disubstituted benzene ring), which was similar with that of PANI sample without HCl under the same conditions. All of these peaks were identical to those of PANI synthesized by a common method [9].

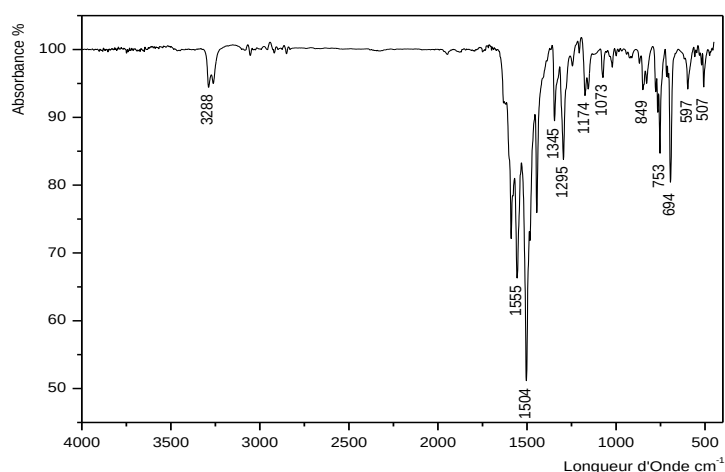


Fig. 1: Shows the characteristic FT-IR spectra of PANI-EB

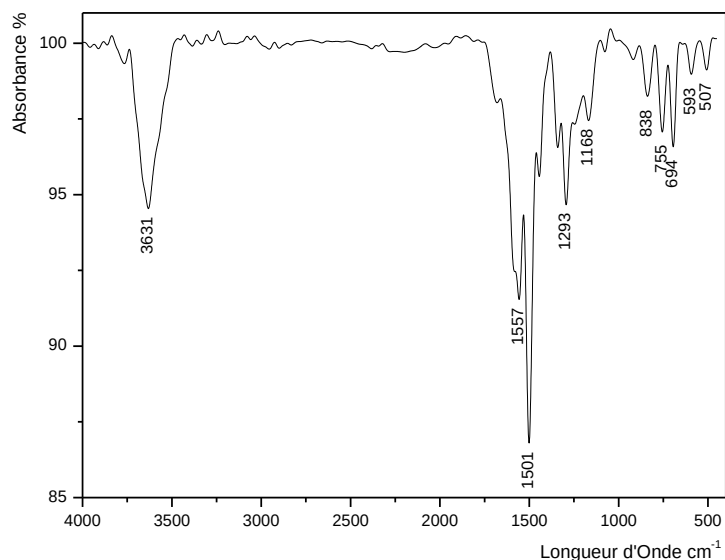


Fig.2: Shows the characteristic FT-IR spectra of PANI-ES

3.3 ^1H -NMR spectral analysis

The ^1H -NMR spectra of the PANI-ES and PANI-EB polymers exhibit strongest sharp peak centered at 7 ppm and 7,8 ppm due to protons on phenylene and disubstituted phenylene units, the weak peak at 4.81 ppm and medium broad peak at 6.22 ppm due to ($-\text{NH}-$ and $-\text{NH}_2$) end group respectively, another broad peaks centered at 1,78 ppm and 8

ppm may be due to the water protons bonded by ($-\text{NH}-$ and $-\text{NH}_2$) groups and ($\text{H}-\text{N}^+$) respectively, as show in Figure-3 and Figure-4 [10].

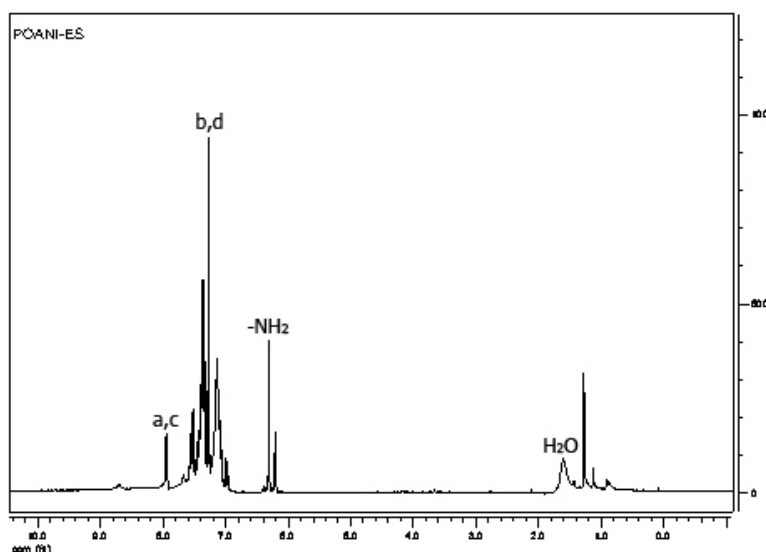


Fig. 3: ^1H NMR spectrum (300 MHz, CDCl_3 , Tetramethylsilane (TMS) was used as the internal standard) of polyaniline (PANI-ES) obtained by the polymerization of aniline with Mag-H^+ initiator system in CDCl_3 at 0°C .

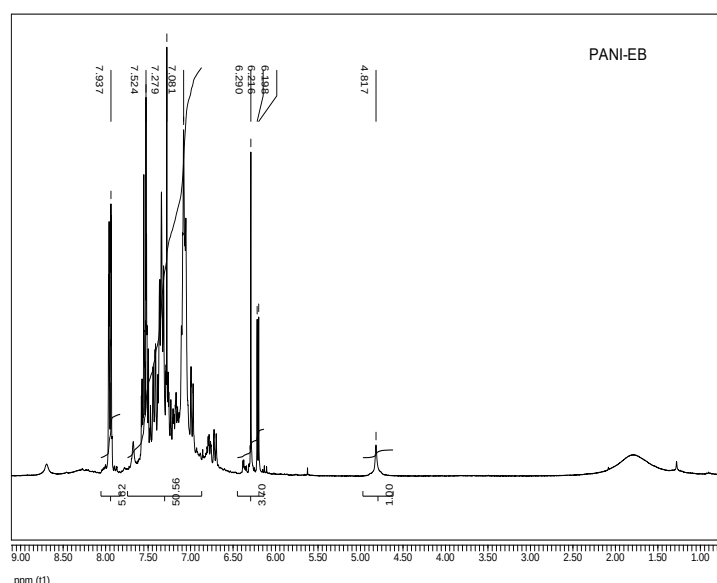


Fig. 4: ^1H NMR spectrum (300 MHz, CDCl_3 , Tetramethylsilane (TMS) was used as the internal standard) of polyaniline (PANI-EB) obtained by the polymerization of aniline with Mag-H^+ initiator system in CDCl_3 at 25°C .

3.4 Uv spectral analysis

Conductive polymers have a conjugated system of double bonds in a backbone polymer. These polymers show some conventional transitions in the UV region, such as $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$. The $\pi \rightarrow \pi^*$ transitions of conjugated double bonds are close to the visible region, associated with polaron and bipolaron states as well as solution conductive polymers [11]. The UV-visible spectral peak in the 250–300 nm region is due to the aniline groups and $\pi \rightarrow \pi^*$ is a conjugated couple system of the benzoic states in the 350–400 nm regions.

3.5 Solubility Studies

Solubility of PANI-ES composite was determined in a number of organic solvents **Table.1**. The PANI-ES composite in powder form was added to 100 mL of each solvent including: DMF, DMSO, Acetonitrile, toluene, dichloromethane, THF, and chloroform and stirred for 1 h before filtering. The dry weight of the filter paper was used to calculate the

solubility of the PANI-ES composite. It was found that, PANI-ES composite is relatively soluble in all above mentioned solvents [12]. The best solvents for PANI-ES composite are determined to be DMF and Toluene.

Table 1: Solubility of PANI-ES composite in different solvents (g/100 mL)

solvents	Solubilité (g/100ml)
Dimethylformamide	0,55
Toluène	0,54
Chloroforme	0,49
Dichloromethane	0,38
Acétonitrile	0,22
Tétrahydrofurane	0,14

3.6 Résultats of GPC

The GPC curves for PANI-ES, PANI-EB and PANI-HCL indicate a bimodal distribution [13]. The molecular weight distribution averages for the polymer are presented in Table-2 and Figure-5 and Figure-6.

Table 2: GPC of PANI-ES composite in THF

	Sample Name	RT	Area	% Area	Mn	Mw	Polydispersity
1	PANI-ES	17.973	1318425	6.01	644	746	1.158385
2	PANI-ES	23.638	20616395	93.99	33	114	3.413146

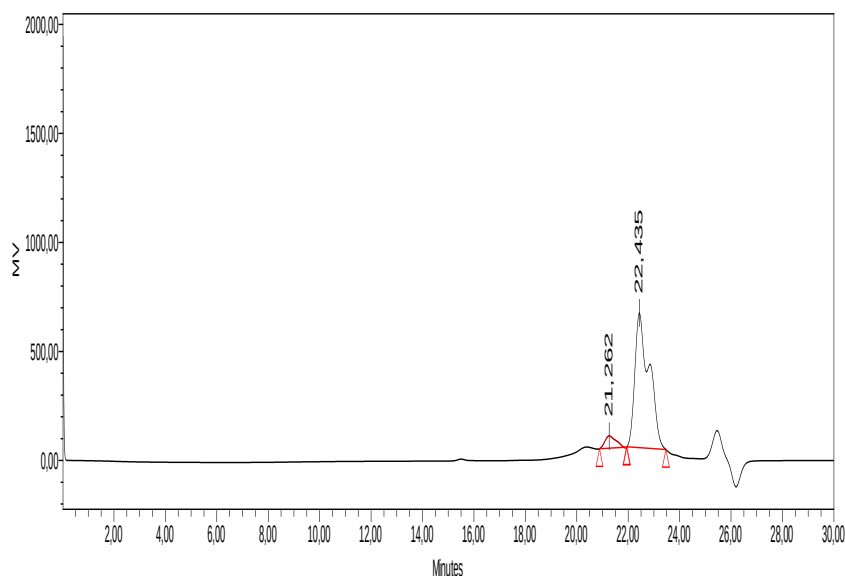


Fig 5: GPC chromatogram of PANI-ES with 6% Mag-H at 0°C for 1 h30 mn ; Number-average molecular weight = 644 g/mol, weight-average molecular weight=746 g/mol, and Polydispersity=1.15.

3.7 Conductivity

The conductivity of PANI-Mag depends on the molecular weight, oxidation state, interactions intrachain, degree of doping, ratio of oxidant/ monomer, content of catalyst (Mag-H⁺) and nature of (oxidant,solvent,dopant) [14] , etc....

In the present study, the PANI-Mag composite was prepared with K₂S₂O₈ as the oxidant, aniline as monomer and Mag-H⁺ as a catalyst, the relation between the content of catalyst and the conductivity was investigated. As shown in Table-3, the conductivity of the polymer is largest when ratio of oxidant/monomer = 0,58 and increases significantly with the addition of content of catalyst, the dc conductivity of PANI-Mag composite measured through a two probe method is 3.9 10⁻⁴ S/cm, same method shows conductivity in the range 10⁻⁶ only [15] , which proves the superiority of present method .

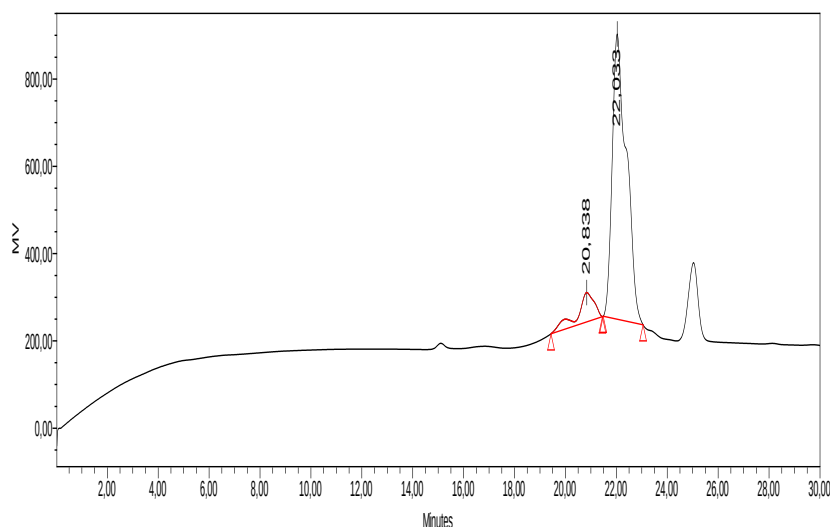


Fig. 6:GPC chromatogram of PANI-EB with 6% Mag-H at 0°C for 1 h30 mn .

Table 3:The conductivity values of PANI-Mag

Content of Maghnite-H ⁺ (%)	conductivity (S /cm)
10	$2,0. 10^{-4}$
50	$3,1. 10^{-4}$
100	$3,9. 10^{-4}$

3.8 Thermal Analysis

The thermogravimetry analysis and differential thermal analysis performed in the polyaniline; show the thermal stability of the polymer; the thermogram presented in the **Figure-7**. give the weight percentage of polyaniline determined in relation to temperature. First there is a low mass loss of less than 8.55% between 186.53°C and 252.51°C; resulted from the evaporation of moisture by cons there is significant drop in mass of about 19.61% between 390.16°C and 487.92°C, the main mass loss is associated with degradation of polymer [16]. Therefore, the weight percentage of PANI should have been around 38.83 % of initial mass is conserved. The residual mass is associated with the presence of polyaniline reticule, which is formed at high temperatures [17].

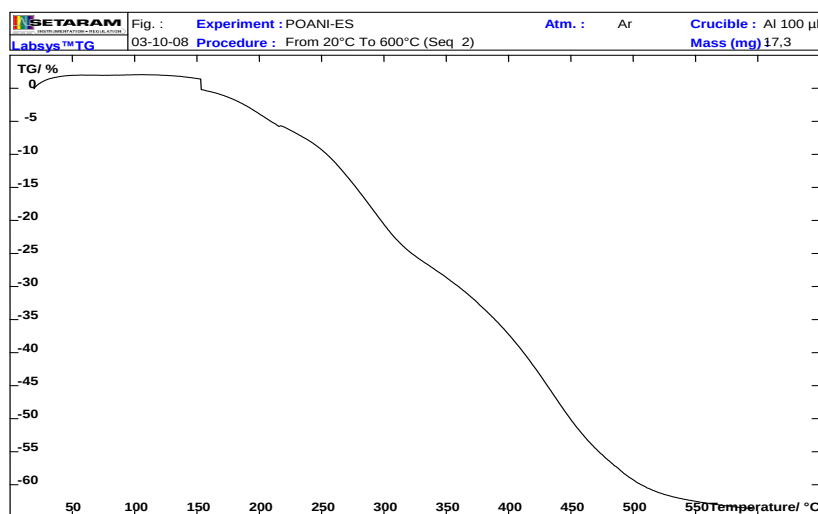


Fig. 7: TGA curves of a pure PANI-ES obtained in nitrogen atmosphere at heating rate of 10 °C/min

3.9 Kinetics studies

3.9.1 Effect of the amount of Mag-H⁺ on the yield of polymerization

As shown in **Figure-8**, a yield of 84,83 wt % was reached for 6 wt% of Mag-H⁺, and the use of a lower or higher amount of clay caused a decrease of the yield of the reaction. Similar results are obtained by Yahiaoui *et al.* [18–19] in the polymerization of epichlorhydrin, propylene oxide and cyclohexene oxide by Mag-H⁺ and the polymerization of styrene by montmorillonite, respectively. This phenomenon is probably the result of the number of initiating active sites responsible of inducing polymerization; this number is prorating to the catalyst amount used in reaction.

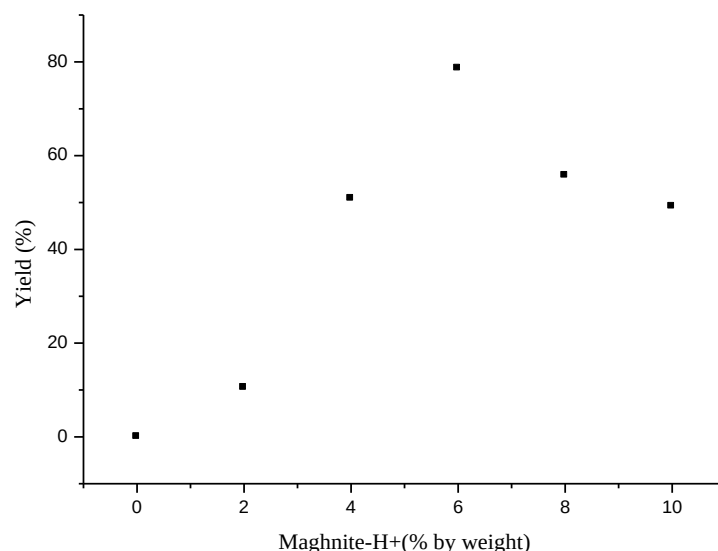


Fig. 8: Effect of the amount of Mag-H⁺ on the yield of the polymerization

3.9.2 Effect of temperature on the yield of the polymerization

In the presence of Maghnite-H⁺ at various weight ratios Maghnite-H⁺/monomer, the polymerization of aniline was carried out for 3 hours. The reaction was induced at different temperatures and the effect of temperature on polymerization was studied. The results are shown in Figure-9. The yield of polyaniline was found to increase with the temperature the temperature. The rate of polymerization at 0°C, however, was the small . A similar effect was shown in the polymerization of aniline initiated by chlorhydric acid [20].

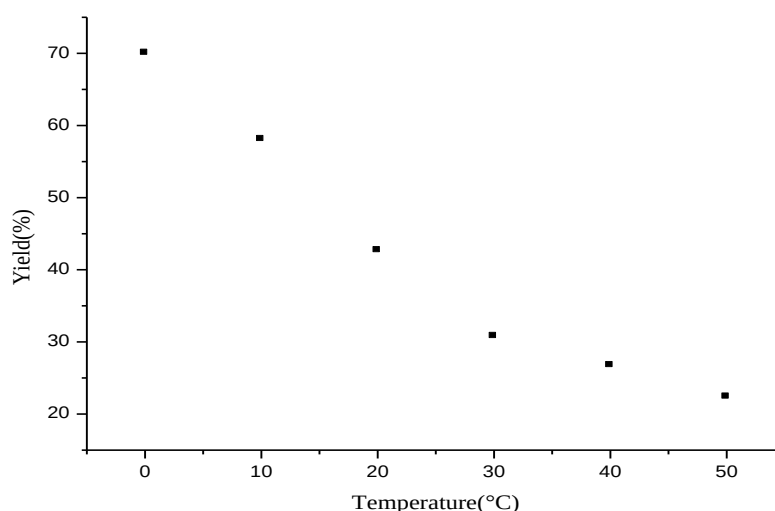


Fig. 9: Effect of the temperature on the yield of polyaniline (Maghnite-H⁺ = 6%, t=3h).

4 Conclusion

PANI/clay composite and nanocomposite were prepared using Mag-H⁺ (eco-catalyst Algerian) and K₂S₂O₈ as the oxidant, various analytical techniques prove the formation of conducting PANI-ES (éméraldine salt phase of the polymer). The FTIR spectroscopy evidence the formation of polyaniline structure containing 1,4-para-disubstituted linear chain, The ¹H-NMR spectroscopy evidence the (–NH– and –NH₂) end group respectively, UV-Visible spectra revealed the absorption peaks due to π - π^* transition of polyaniline, The results of differential scanning calorimetry (DSC) and thermogravimetry analysis (TGA) showed the improved thermal stability of the materials. Based on solubility studies, the composite is soluble in conventional organic solvents. Besides, this composite can be used as coating or molding material in many uses such as in anticorrosion protections, antistatic applications and photovoltaic cells.

References

- [1] MacDiarmid A G., and Epstein A., Synth Met, 1994, 65,103.
- [2] Chen S., and Lee H., Macromolecules, 1993,26,3254.
- [3] Zheng W., Angelopoulos M., Epstein A., MacDiarmid 1997, 30,2954.
- [4] Belbachir M., Bensaoula A., Composition and Method for Catalysis using Bentonites, US Patent. 2003/0069446 A1 (2003).
- [5] Belbachir M., Bensaoula A., US. Patent. 2001/6,274,527 B1 (2001).
- [6] Sinha Ray S, Biswas M. Preparation and evaluation of composites from MMT montmorillonite and some heterocyclic polymers: 3. a water dispersible nanocomposite from pyrrole-montmorillonite polymerization system. Mater. Res. Bull. 1999; 34: 1187–1194.
- [7] Gospodinova N;Mokreva P; Tsanov T; Terlemezyan L; Journal of Polymer ;38:743.(1997)
- [8] Rodriguez J, Grande H, Otero TF. Handbook of Organic Conducting Molecules and Polymers, vol. 2. Wiley: Chichester,1997; 415–468.
- [9] Viswanathan and al, US. Patent.2005/6,299,800 B1 (2005).
- [10] Rhee S B., Chang J L., Wang X., US Patents 1998/5,795,942 A (1998).
- [11] Omastova´ M, Pionteck J, Kosina S. In: Electronic and Optical Properties of Conjugated Molecular Systems in Condensed Phases, Hotta S (ed.). Research Signpost: Kerala, India, 2003; 153–186.
- [12] Hasegawa N, Okamoto H, Kawasumi M, Kato M, Tsukigase A, Usuki A. Polyolefin-clay hybrids based on modified polyolefins and organophilic clay. Macromol. Mater. Eng. 2000; 180/181: 76–79.
- [13] Kwan YA.,Succasunna J.,Elsenbaumer RL.,US Patents 1991/5,069,820A (1991).
- [14] Karna T., jukka L.,kalle L.,Savolainen E., US Patents 1999/5, 928,565 A (1999).
- [15] Wei.,Guang-Way Y., Scherr F., MacDiarmid A.G., Epstein E.,A J.,Polymer, 1992,33,3 14 .
- [16] Negi Y.S., Adhyapak P.V., J Macromol. Sci Polym. Rev. 2002,42,35–53.
- [17] Ryu K.S., Moon B.W., Joo j, Chang S.H., Polymer 42 -2001- 9355–9360
- [18] Yahiaoui A., Belbachir M., Soutif J. C., Fontaine L Materials Letters, 2005, 59, 759–767
- [19] Yahiaoui A., Belbachir M. Mendeleev Communications,2005, 15, 242–244.
- [20] J. Y. Kim, K. Lee, N. E. Coates, D. Moses, T.-Q. Nguyen, M. Dante, A. J. Heeger, Science 2007, 317, 222.