Structure and Physicochemical Properties of Polyaniline Synthesized in Presence of Maghnite clay Catalyst layered (*Algerian Montmorillonite*)

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Abstract

In order to prepare conducting polyaniline composite and nanocomposite soluble in various organic solvents before and after doping, and we based on these experimentally resultants finding, the present study relate to a new process for preparing conducting polyaniline with controlled molecular weight, high solubility in various organic solvent .In a more specific aspect of the present study, the polymer is formed in non acid medium. Another embodiment, the polymer is formed by layered catalyst MMT (Mag-H$^+$). Another embodiment the polymer is formed by oxidizing agent powder (solid) contained alkali metal salt. In another specific aspect, the polymer is formed by intervention of deferent's reactors and water in three steps: (a)between MMT and monomer (b)between mixture of (MMT-monomer) and oxidizing agent (c)between second mixture (MMT-monomer-oxidant) and water.

Keywords: Polyaniline, oxidative polymerization, 1H-NMR spectroscopy, Maghnite-H$^+$, structure.

Introduction

Polyaniline has attracted much attention as a promising material for electrodes of batteries[1], electric and optical devices[2], and electrochromic displays[3]. Recent studies on polyaniline revealed several molecular structures of the polymer depending on the oxidation state and on the degree of protonation.

Maghnite-H$^+$ an Algerian montmorillonite were prepared according to the process reported in our previous study[4]. Raw-Maghnite (20 g) was crushed for 20 mn using a prolabo ceramic balls grinder. It was then dried for 2 h at 105ºC. The Maghnite was placed in an Erlenmeyer flask together with 500 ml of distilled water. The Maghnite/water mixture was stirred using a magnetic stirrer and combined with 0.25 M sulfuric acid solution, until neutralization was achieved over 2 days at room temperature, the mineral was then washed with distilled water to become sulfate free and then dried at 105ºC.

Many papers on conductive polymer/clay nanocomposites were available in the literature[5], but there is little work about preparation, characterization and properties of intercalated polyaniline/Na-montmorillonite nanocomposites using unmodified smectic clay. In this paper, we described the synthesis of PANI/Na-Mag (Algerian montmorillonite) nanocomposites via oxidative polymerization using potassium persulfate as an oxidizing agent. The synthesized polymer was characterized by Fourier transform infrared spectroscopy (FTIR), ^{1}H-NMR spectroscopy, thermogravimetric analysis (TGA), and GPC.

Material and Methods

Materials: Aniline 99%, potassium persulphate 98% (Aldrich) , hydrochloric acid (35%–38%),MMT clay was obtained from ENOF Maghnia (Algeria). The MMT-H$^+$ (Mag-H$^+$) was prepared as described by Belbachir and al[6], and water (PH<7) were used to synthesis éméraldine salt (PANI-Mag-H$^+$) by emulsion polymerization. Some of the emeraldine base (PANI-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].

Table-1
Elementary compositions of Protons exchanged samples "Maghnite" (Compositions wt%). PF* : Pert in Fire

Sample	SiO$_2$	Al$_2$O$_3$	F$_e$2O$_3$	CaO	MgO	Na$_2$O	K$_2$O	TiO$_2$	SO$_3$	PF*
Raw-Mag	69.39	14.67	1.16	0.30	1.07	0.50	0.79	0.16	0.91	11
Mag-H	71.70	14.03	0.71	0.28	0.80	0.21	0.77	0.15	0.34	11

Activation of Maghnite-Na⁺: Maghnite-H⁺ was prepared according to the process reported in our previous study[8]. Raw-Maghnite (20 g) was crushed for 20 mn using a prolabo ceramic balls grinder. It was then dried for 2 h at 105°c. The Maghnite was placed in an Erlenmeyer flask together with 500 ml of distilled water. The Maghnite/water mixture was stirred using a magnetic stirrer and combined with 0.25 M sulfuric acid solution, until neutralization was achieved over 2 days at room temperature, the mineral was then washed with distilled water to become sulfate free and then dried at 105°C . The Table-1 show elementary compositions of Protons exchanged samples.

Catalyst structure: The x-ray powder diffraction profiles shown in Fig.1 exhibited the presence of other crystalline phases such as quartz, feldspath and calcite in (raw-Maghnite). Under acid treatment, all trace of calcite was removed in "H-Maghnite". The increase in basal spacing from 12.5 Å in "raw-Maghnite", characteristic of a single water layer between the sheets, to a 15.02 Å value in "Maghnite"— for two interlamellar water layers — reflects the changes in interlayer cation and its associated hydration state as a result of the acid treatment[9].
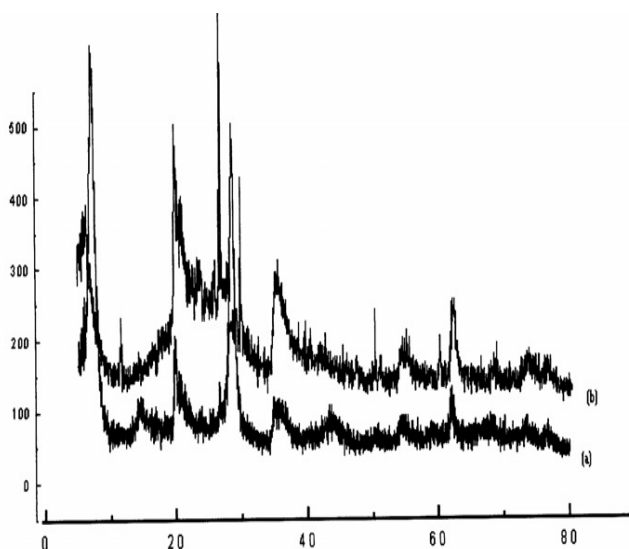

Figure-1
X-ray powder Diffraction of (a) Maghnite-Na⁺; (b) Maghnite- H⁺ 0.25M

The thermal characterizations of the composites include thermogravimetric analysis (TGA). Figure-2. Show the weight losses (%) versus temperature (°C) curves for pure Maghnite–Na⁺, The TGA of pure Maghnite–Na⁺ show two stages of weight loss. The first weight loss in Na⁺-Mag below 100 °C is a result of the release of free water. The second weight loss around 600 °C is associated with the dehydroxylation of silicate structure[10-11]. The total weight loss is only 13.94% up to 800 °C. As can be expected, Maghnite–Na⁺ shows a high thermal stability.
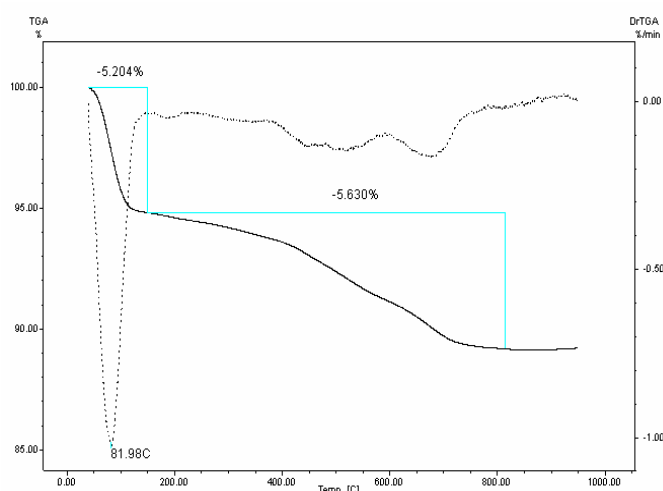

Figure-2
TGA curves of a Maghnite–Na⁺ obtained in nitrogen atmosphere at heating rate of 10°C/min

Procedures : The present study provide process for preparing polyaniline or another polymer conductors such as (polypyrole , plythiophene) or substituted polyaniline (o-anisidine, o-methoxy-aniline, o-toluidine …….), which comprises dissolving oxidizing agent (solid) slowly in mixture of catalyst and monomer (Mag-H⁺, aniline) after 30 mn at ranging temperature (0°C to 4°C) and during 10 mn , after this time we added drop by drop 15 ml to 20 ml of water, the reaction mixture was stirred for 1h 30 mn at the optimal conditions. At the end of polymerization, we obtained the emeraldine salt /clay (PANI-ES / Mag-H⁺). 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. The polyaniline base (PANI-EB) was obtained by deal treatment of polyaniline salt (PANI-ES) with an solution of dilute NaOH (0, 5M). A doping EB was carried out in aqueous medium of hydrochloric acid (1M). Approximately 1,5 g of fine powder of polyaniline base was suspended in 200 mL of appropriate acid solution. After stirring at room temperature for 5 h, the black polymer salt was collected by filtration followed by drying under dynamic vacuum for 48 h at 60°C.

Measurements: ¹H nuclear magnetic resonance (NMR) measurements were carried out on a 300 MHz Bruker NMR Spectrometer equipped with a probe BB05 mm, in CDCl3. Tetramethylsilane (TMS) was used as the internal standard in these cases. Fourier transform infrared spectroscopy (FTIR) spectra were obtained between 900 and 4000 cm⁻¹ on an ATI Matson FTIR No 9501165. Ten scans were averaged at a resolution of 4 cm⁻¹ for the solid tested samples of modified and unmodified montmorillonite prepared as KBr pellets (ca. 3% by mass in KBr).

DSC measurements were carried out on a TA instrument, according to the following program: the specimens were first heated from ambient temperature to 250∘C at 10∘C/min maintained at this temperature during 5 minutes then cooled to 25∘C at 20∘C/min.The tests were performed on a TA instrument (TGA Q500) by heating the samples from 20 to 550∘C at 20∘C/min. DTG thermograms giving the variations of the weight loss derivative as a function of temperature.

GPC measurements of the samples were carried out using a WISP 712, Waters Associates chromatograph, THF was used as solvent and the instrument was calibrated to a first approximation with polystyrene of known molecular weights.

The flow rate of tetrahydrofuran was 10 ml/min. intrinsic viscosity measurements were performed on SEMATECH Viscologic TI 1 apparatus at 25°C using THF as solvent.

Results and Discussion

Spectroscopic characterizations: Figure-3 and 4 shows the characteristic FT-IR spectra of Na^+-Mag, H^+-Mag and polyaniline (PANI) sample obtained at different amount of Maghnite. The characteristic absorption peaks of MMT are assigned to the Si–O–Si skeleton vibration at 1037–1098cm^{-1}, the strong absorption bands of Si–O and Al–O bending vibration at 600–640 cm^{-1} and the OH stretching vibration at 3445 cm^{-1}. In addition, for polyaniline, the literature data indicated that the characteristic absorption peaks are assigned to the C–H aspect bending vibration on the replaced benzene ring at 832cm^{-1} and the C–N bond stretching vibrations at 1308 cm^{-1}. 1498 and 1590 cm^{-1} represent the absorption peaks of benzene- and quinine-type in polyaniline chain[12].
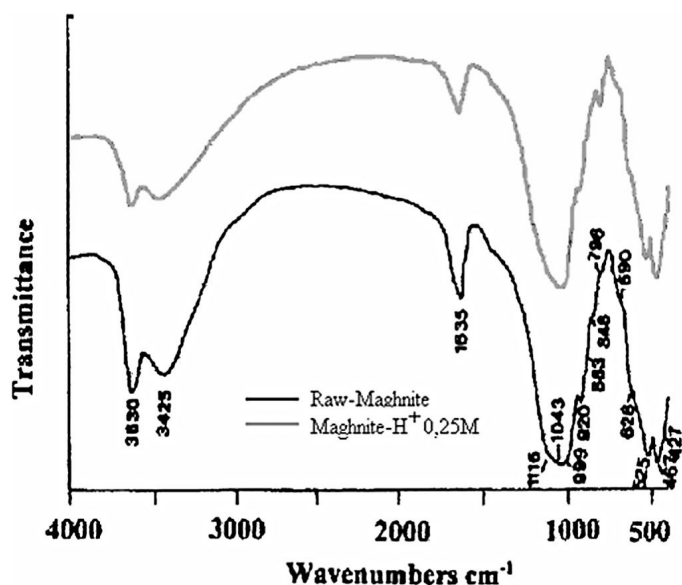

Figure-3
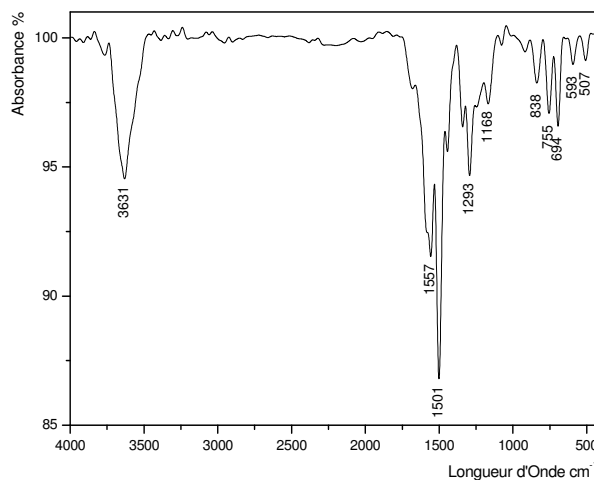**FTIR spectra of Raw-Maghnite and H-Maghnite-H+0.25M**

Figure-4
FT-IR spectra of the polymer (PANI-Mag) obtained by the intercaled method between Aniline and Maghnite (black powder) at 0°C

The product (obtained by room temperature reaction in 3 days) which was reduced with 100 mL of hydrazine solution (20%) displays two groups of signals in the 1H-NMR spectra Figure-5. The down field signals centered at 7.2 ppm are due to four aromatic protons of the pure reduced form (leucoemeraldine base). Integral ratio of the NH proton signal appeared at 3.55 ppm .Whereas non-reduced form of the product (Emeraldine base) gave a ^{1}H-NMR spectra with slight shift of the peak positions (i.e. NH protons appear at 4.81 ppm and aromatic protons centered at 7.3 ppm)[13].
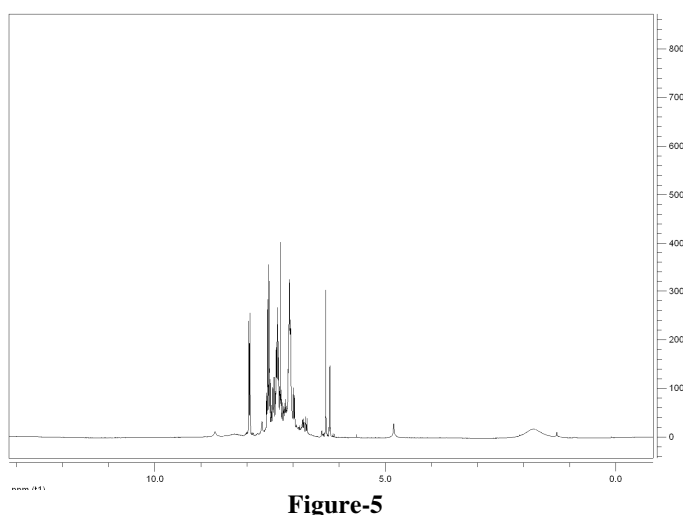

Figure-5
1H NMR spectrum (300 MHz, CDCl3, Tetramethylsilane (TMS) was used as the internal standard) of polyaniline-Maghnite (PANI-Mag) obtained by the polymerization of aniline with Mag-H+ initiator system in CDCl3 at 0°C

These polymers show some conventional transitions in the UV region, such as n →π∗ and π →π∗. The π → π∗ transitions of conjugated double bonds are close to the visible region, associated with polaron and bipolaron states as well as solution conductive polymers[14]. The UV-visible spectral peak in the 250–300 nm regions is due to the aniline groups and π →π∗ is a conjugated couple system of the benzoic states in the 350–400 nm regions[15].
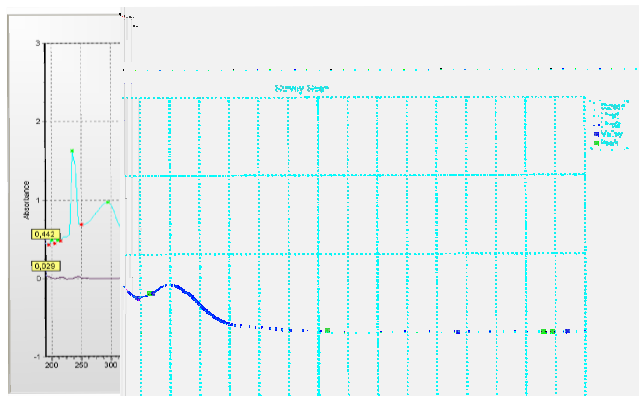

Figure-6
UV-vis spectrum of polyaniline salt (PANI-ES) in CDCl₃

Effect of the amount of Mag-H⁺ on the yield of polymerization: The effect of the amount of Maghnite-H+ on the yield of polymerization was examined (table 2). It can be noted that the yield increases with increasing "Maghnite- H+ 0.25 M" proportion. Indeed, using various amounts of Mag-H+, 2, 4, 6,8 and 10 % by weight, the polymerization was carried in bulk at 0 °C. The polymerization rate increases with the amount of Mag-H+, In contrast, the intrinsic viscosity (η) is inversely proportional to the amount of Mag-H+, in which the effect of Mag-H+ as a catalyst is clearly shown. This phenomena is probably the result of number of "initiating active sites" responsible of inducing polymerization, this number is prorata to the catalyst amount used in reaction. Similar results are obtained by Belbachir and al[16-17].

Table-2
Effect of the catalyst (Mag-H⁺) on the yield of polymerization

Maghnite-H⁺ 0.25M (%)	Yield (%)	η (dl/g)
2	49.12	1.85
4	59.61	1.68
6	66.94	1.49
8	75.86	1.07
10	84.03	0.98

Effect of the reaction time on the polymerization : Polymerization using 6 % of Maghnite- H+ 0.25 M was carried at 0 °C and the reaction was monitored at various times. The results are given in (table 3) shows the evolution of the yield and the intrinsic viscosity of the polymer with reaction time.

The intrinsic viscosity increases with polymerization time. On the other hand, the yield increases with the time and it can be noted that initially the polymerization proceeds very slowly; this can be considered as an induction period (3 h). At the end of this period the polymerization process becomes faster[18].

Table- 3
Effect of the time on the yield and intrinsic viscosity of polymerization [Aniline] = 0,055 mol; [K₂S₂O₈] = 0,013 mol; 6% of Maghnite-H+ 0.25 M, T=25°C, in CDCl3.

time (h)	Yield (%)	η (dl/g)
1	39.37	1.73
2	51.64	1.56
3	63.91	1.28
4	70.83	1.01
5	82.09	0.85

Thermal analysis: The TGA thermogram of the polyaniline (PANI–ES) at a heating rate of 10°C/min in nitrogen is shown in Fig–7. It can be found that at the temperature range of 187—600 °C the weight loss amounted to 61, 17%, which can be reasonably attributed to the weight loss of the polymerized polyaniline (PANI–ES) and to thermal decomposition of the polyaniline chains.

Polyaniline is known to be a hygroscopic polymer[19] some authors[20] assigned the endothermic effect registered by (DSC) in the range from ambient temperature up to approximately 120°C to the evaporation of water.
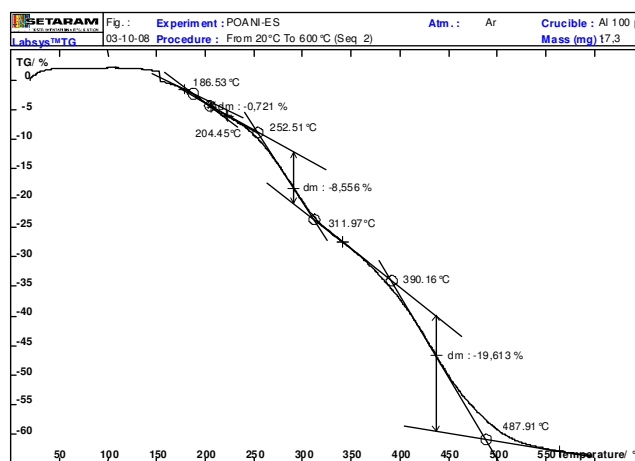

Figure-7
TGA curves of a pure PANI-ES obtained in nitrogen atmosphere at heating rate of 10 °C/min

First run and second run in figure-8 show the DSC cooling trace of the PANI-ES. It can be observed two remarks. (a) Three endothermic peaks. These peaks were most likely due to the evaporation of water, evaporation of dopant and degradation of the polymer respectively (b) higher glass transition temperatures Tg than their Counterpart PANI-EB.

Table- 4
Thermodynamics properties of different forms of polyaniline T (°C), ΔH (J/g), ΔCp (J/g*°C)

Sample	T_1	T_2	T_3	Tg	ΔH_1	ΔH_2	ΔH_3	ΔCp
PANI-EB	55.99	103.46	X	74.06	4.3161	20.5363	X	0.311
PANI-ES	50.34	140.10	221.07	103.75	167.6042	4.4617	10.7719	0.154
PANI-Cl	100.45	163.09	218.57	126.89	1.9678	8.7614	16.8337	0.180

The Tg of the polymer increases slightly with the increasing of the conductivity. For example, the Tg of PANI-EB is around 74.03°C, whereas the Tg is shifted to around 103.75°C for PANI-ES and 126.89°C for PANI-HCL. These observations are well in agreement with the results reported by other research[21].
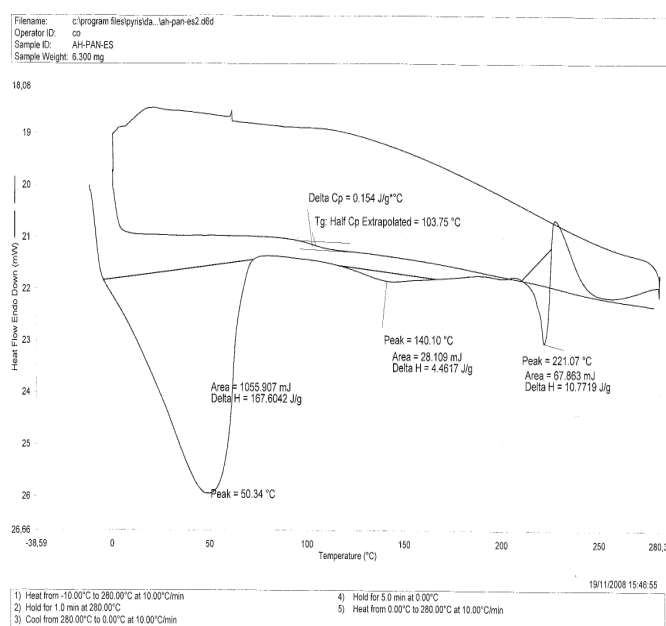

Figure-8
DSC Curve of the PANI-ES composite obtained in nitrogen atmosphere at heating rate of 10 °C/min

For more information such as stability, conductivity, solubility, chemically structure and morphology of different form of polyaniline the table-4 shows the thermodynamics properties of different states of polyaniline.

Conclusion

Polyaniline-maghnite nanocomposites containing different polyaniline contents were prepared by intercalation and oxidative polymerization of aniline into interlayer spacing of maghnite (Mag-H$^+$) layers. Fourier Transform Infra Red analyses and UV-vis spectroscopy confirmed the successful synthesis of polyaniline chains, particularly by the narrowing of the Si–O stretching vibration band confirmed the interaction between PANI and the clay.

Maghnite-H$^+$, proton exchanged montmorillonite clay is an effective initiator for the polymerization of aniline. In the polymerization, the solid catalyst was thought to act as an acid to generate cation species. Actually, the efficiency of the polymerization reflected the Lewis acidity of maghnite-H+. Two main advantages were shown in the polymerization system using the solid acid maghnite-H$^+$, that the catalyst could be removed from the mixture of the products by simple filtration and recycled without a loss of catalytic activity.

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