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Full Length Research Paper

Maghnite-H^+, an eco-catalyst layered (Algerian Montmorillonite) for synthesis of polyaniline/Maghnite clay nano-composites

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Nanocomposites Polyaniline/Maghnite clay (PANI-Mag) were synthesized by solution polymerization of aniline in the presence of sulfuric acid using potassium persulfate (PPS) as oxidant. Using molar ratio of monomer to oxidant of 2:1, the aniline was polymerized and largely incorporated into the Maghnite, which was confirmed by FTIR, ^{1}H-NMR spectra and UV-Vis spectroscopy. These methods show the shifting of some peaks, which indicate the formation of some new bonds and support the intercalation of PANI chains into the interlayer spacing of Maghnite MMT clay. That, the morphology of the PANI-Mag composites changed according to the proportion of clay. The conductive emeraldine salt form of polyaniline PANI-ES is inserted into the layers of maghnite clay to produce the hybrid with high conductivity and solubility in various organic solvents. The resulting organic-inorganic hybrid material, PANI-Mag has been characterized by various physicochemical techniques

Key words: PANI-ES, GPC, nanocomposite, maghnite, H-NMR, emeraldine base.

INTRODUCTION

For commercial applications, polyaniline (PANI) is the best promising material in conducting polymers, because of environmental stability [Joo et al., 1998], easy processing [MacDiarmid et al., 1985], and economical efficiency [Joo et al., 1994]. PANI has been used for electrode of light emitting diode [Yoshimoto et al., 2005], Li ion rechargeable battery [Yoshimoto et al., 2004] and corrosion protection [Bedre et al., 2009]. Among organic-inorganic nano-composite-sites, PANI-Mag nanocomposites are the most prevalent and interesting due to the special properties as well as wide uses of polyaniline [Yoshimoto et al., 2004], the nature, abundance, low cost of Mag and attractive features such as a large surface area and ion-exchange properties [Ray and Okamoto, 2003]. Clay minerals especially the members of smectite group are the most suitable candidates for synthesis of polymer nano-composites, because these possess a unique structure and reactivity together with high strength. In general, the structures of polymer/clay nanocomposites are classified according to the level of intercalation and exfoliation of polymer chains into the clay galleries [do Nascimento et al., 2004]. Various parameters including clay nature, organic modifier, and polymer matrix and preparation method are affective on the intercalation and exfoliation level. Therefore depending on the nature and properties of clay and polymer as well as preparation methodology of nanocomposites, different micro-structure composites can be obtained [Stejkal and Gilbert, 2002].

The series of nanocomposites namely Polyaniline/Maghnite clay (PANI-Mag) were synthesized by solution polymerization of aniline in the presence of sulfuric acid and amount of potassium persulfate (PPS), with molar ratio of monomer to oxidant of 2:1, the aniline was polymerized and largely incorporated into the Mag, which was confirmed by FTIR, ^{1}H-NMR spectra and UV-Vis spectroscopy. These methods show the shifting of some peaks, which indicate the formation of some new bonds and support the intercalation of PANI chains into

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the interlayer spacing of Maghnite (Mag-H+) clay [Palaniappan, 2004].

EXPERIMENTAL

Materials

Aniline 99%, potassium persulfate 98% (Aldrich), hydrochloric acid (35 to 38%), MMT clay was obtained from ENOF Maghnia (Algeria). The MMT-H^+ (Mag-H^+) was prepared as described by Abdryim et al. [2005], and water (pH<7) were used to synthesis éméraldine salt (PANI-Mag-H^+) by emulsion polymerization. Some of the emeraldine base (PANI-EB), the non-conducting form of polyaniline, was prepared by de-protonating PANI-ES in NaOH solution (0.5 M). The doping of EB was carried out in aqueous medium of hydrochloric acid (HCl) [Yahiaoui and Belbachir, 2006].

Preparation of catalyst (Maghnite-H^+)

Maghnite-H^+ was prepared according to the process reported in our previous study [Belbachir and Bensaoula, 2001]. Raw-Maghnite (20 g) was crushed for 20 min using a prolabo ceramic balls grinder. It was then dried for 2 h at 105°C. The Maghnite was placed in an Erlenmeyer flask 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 material was then washed with distilled water to become sulfate free and then dried at 105°C.

Procedures of synthesis

The present study provide process for preparing of polyaniline or another polymer conductors such as (polypyrole, plythiophene) or substituted polyaniline (o-anisidine, o-methoxy-aniline, o-toluidine, etc), which comprises dissolving of the oxidizing agent (solid) slowly in mixture of catalyst and monomer (Mag-H^+, aniline) after 30 min at ranging temperature (0 to 4°C) and during 10 min , after this time we added drop by drop 15 to 20 ml of water , the reaction mixture was stirred for 1 h 30 min at the optimal conditions. At the end of polymerization, we obtained the polyaniline/clay nanocomposites (PANI- Mag-H^+). Eventually, the result it's black solution (polymer-solvent), after evaporation result a black powder it's (PANI-Mag), washed several times with water and methanol and dried at 60°C for 48 h before characterization.

Polymer characterization

Measurements of ^1H NMR spectra were conducted in D_2O solution, under ambient temperature using an AM 300 FT Bruker spectrometer and tetramethylsilane (TMS) as internal standard. IR absorption spectrum was recorded on an ATI Matson FTIR No 9501165 spectrometer using the KBr pressed disc technique. Gel permeation chromatography (GPC) was performed with a Spectra-Physics chromatograph, equipped with four columns connected in series and packed with Ultrastyragel 103, 104, 105, 106 Å. Tetrahydrofuran (THF) was used as solvent and the instrument was calibrated to a first approximation with polystyrene of known molecular weights. Viscosity measurements were carried out with an Ubbelohde capillary viscosimeter (viscologic TI1, version 3-1 Semantec). Intrinsic viscosity, [η] (ml/g), was measured at 25°C in THF.

RESULTS AND DISCUSSION

Montmorillonites have both Bronsted and Lewis acid sites and when exchanged with cations having a high charge density, as protons, produce highly active catalysts for acid-catalysed reactions [Chen et al., 2005]. It have been demonstrated that intercalated organic molecules on the surface of Montmorillonite are mobile and can be highly polarized when situated in the space between the charged clay layers [Yang et al., 2007; Zeng and Ko, 1997]. The present study examines the catalytic activity of Algerian proton exchanged montmorillonite clay (Maghnite-H^+). It was demonstrated that there is an excellent correlation between the acid treatment and the catalytic activity of Maghnite [Shang et al., 2002].

FTIR spectra of catalyst (Mag–H+)

FTIR spectra have been widely used to characterize the polymer–clay nanocomposites [SinhaRay and Biswas, 1999] and are also used in this work. The FTIR spectra (Figure 1) show the presence of characteristic peaks of Maghnite from the extracted nanocomposites. In addition, absorption bands related to silicate are also found, such as OH stretching of lattice water (3630 cm^{-1}), H–O–H bending (1635 cm^{-1}), Si–O–Si stretching (1043 cm^{-1}), and Si–O stretching and Si–O bending (600 to 400 cm^{-1}).

FTIR spectra of nanocomposite PANI–Mag

The formation of polyaniline–Mag nanocomposites is confirmed from the infrared spectroscopy. The FTIR spectrum (Figure 2) of the product shows the characteristic vibration peaks of polyaniline, which agrees well with that of chemically synthesized polyaniline. They exhibit all the bands observed for polyaniline and the swollen Maghnite. 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 838 cm^{-1} and the C–N bond stretching vibrations at 1293 cm^{-1}. 1501 and 1557 cm^{-1} represents the absorption peaks of benzene- and

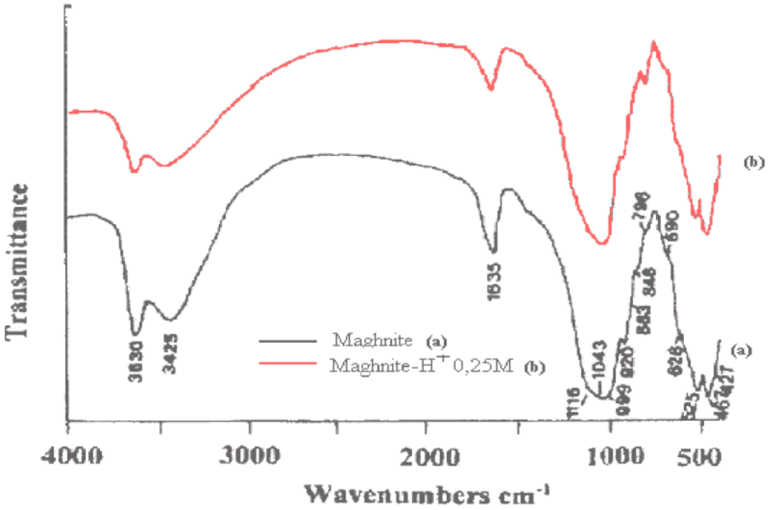

Figure 1. Infra red spectra of raw maghnite and maghnite active 0.25 M.

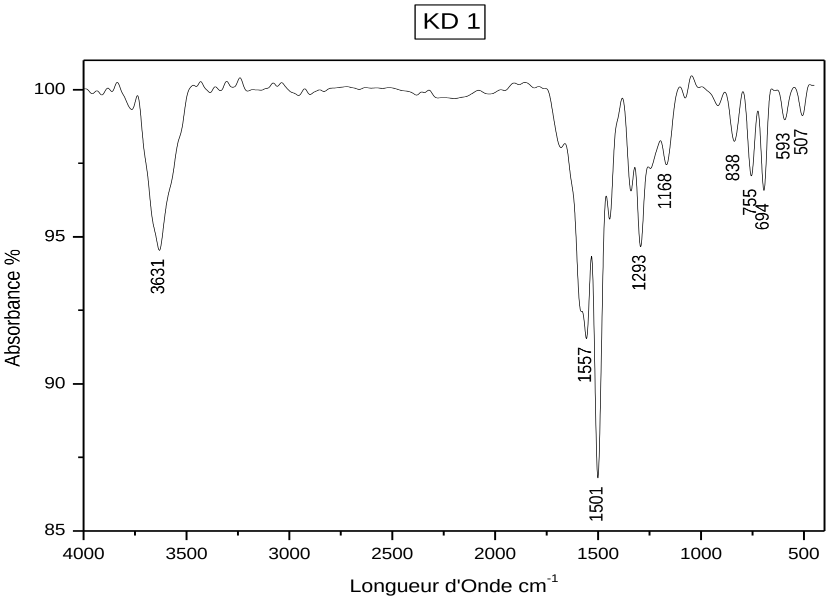

Figure 2. FT-IR spectrum of the polymer (PANI-Mag) obtained by the intercaled method between Aniline and Maghnite (black powder) at 0°C.

quinoide-type in polyaniline chain.

H-NMR spectra of nanocomposite PANI–Mag

The ^{1}H-NMR spectra of the PANI-ES and PANI-EB polymers exhibit strongest sharp peaks centered at 7 and 7.8 ppm due to protons from phenylene and disubstituted phenylene units, the weak peak at 4.81 ppm and medium broad peak at 6.22 ppm due to (–NH– and –NH_2) end group respectively, another broad peaks centered at 1.78 and 8 ppm may be due to the water protons bonded by (–NH– and –NH_2) groups and (H-N^+) respectively, as show in Figure 3 [Stejkal and Gilbert, 2002] .

Optical characterization

Polyaniline nanocomposites synthesized by oxidation of aniline in montmorillonite (maghnite) are characterized also by the UV spectra. The spectra exhibit typical PANI-ES, including the transition from the black color of protonated PANI-ES in maghnite to black dark color corresponding to PANI-EB in alkaline ones. The UV-

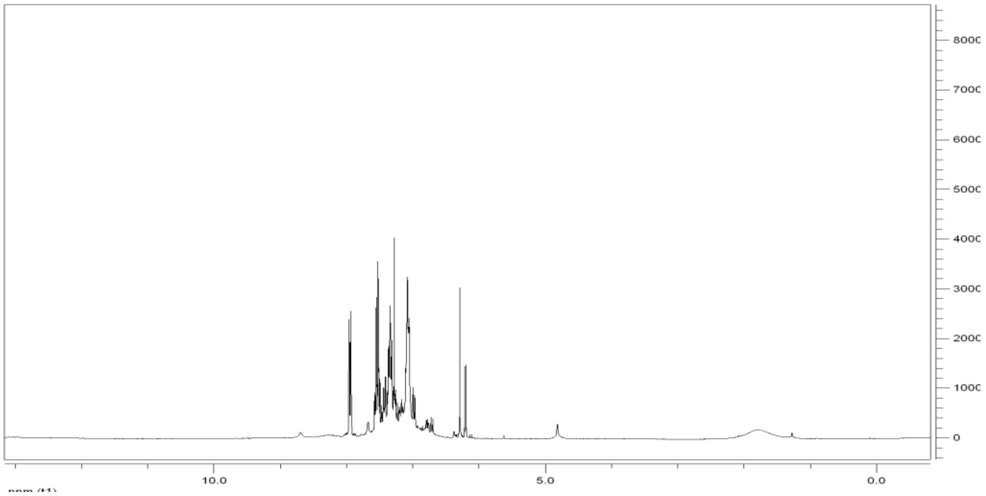

Figure 3. ^{1}H NMR spectrum (300 MHz, $CDCl_3$, Tetramethylsilane (TMS) was used as the internal standard) of polyaniline-Maghnite (PANI-EB-Mag) obtained by the polymerization of aniline with Mag-H+ initiator system in $CDCl_3$ at 0°C.

Table 1. 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	1.15
2	PANI-ES	23.638	20616395	93.99	33	114	3.41

visible spectrum of PANI solution in chloroform has three absorption peaks 300, 400 and 565 nm. It should be mentioned, however, that the absorption maxima are black by about 1 hour compared with the PANI-MMT spectra reported in the literature [Palaniappan, 2004]. This especially applies to PANI-EB, where absorption maximum of dispersions in *N*-methyle-2-pyrrolidone solutions were located typically at 610 and 635 nm, respectively [Abdryim et al., 2005]. Based on the UV spectra, we now know that polymer chains have different electronic structures in chloroform and *N*-methyle-2-pyrrolidone. This difference in electronic structures can be attributed only to their difference in conformational structures. Specifically, polymer chains of PANI have a more extended conformation and hence a longer conjugation length in *N*-methyle-2-pyrrolidone than in chloroform.

Results of GPC

Gel permeation chromatography (GPC) was performed with a Spectra-Physics chromatograph, equipped with four columns connected in series and packed with Ultrastyragel 10^3, 10^4, 10^5, 10^6A˚, tetrahydrofuran (THF) was used as solvent and the instrument was calibrated to a first approximation with polystyrene of known molecular weights. The GPC curves for PANI indicate a bimodal distribution. The molecular weight distribution averages for the polymer are presented in Table 1 and Figure 4.This bimodal distribution has been reported previously for PANI in N-methyle-2-pyrrolidone.The molecular weight of the polymer shows the growth of PANI on PAN-Maghnite. Several reactions were done for many summers to follow the influence of physicals chemicals properties on the molecular weight of polymer. The yield of polymerization and the molecular weight of polyaniline were determined in dependence on the ratio of aniline, amount of catalyst, temperature, reaction time and a volume of water added. It was found that polymerization yield and molecular weight decrease with the increasing ratio catalyst to aniline, water and temperature. This result shows the cationic nature of the mechanism put into play results. Similar have been observed with other polymerization reactions catalyzed by Maghnite-H $^+$ [Yahiaoui and Belbachir, 2006; Belbachir and Bensaoula, 2001].

Thermodinamics properties

Completely soluble polyaniline-Maghnite clay (Mag–PANI) composite with enhanced conductivity, improved thermal stability, and solubility, has been synthesized. Here, polyaniline exists in its soluble non-conducting and conducting form as shown in Table 2.

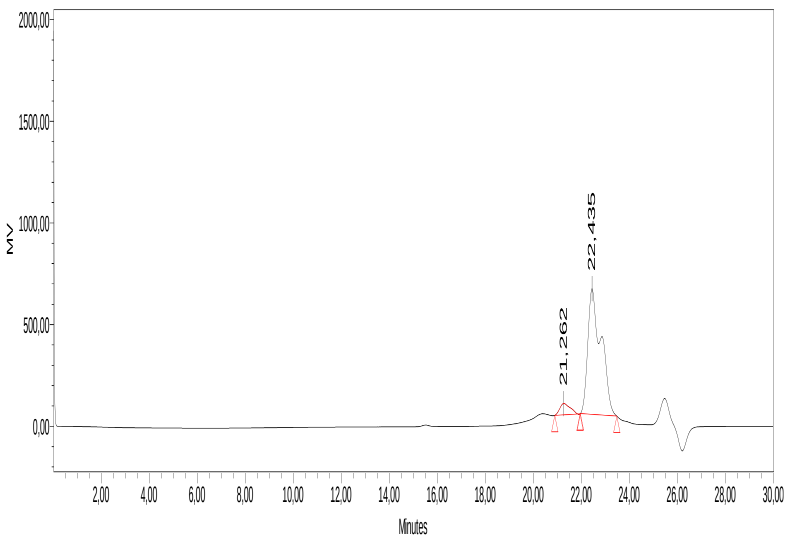

Figure 4. GPC chromatogram of PANI-ES with 6% Mag-H at 0°C for 1 h30 min; Number-average molecular weight = 644 g/mol, weight-average molecular weight = 746 g/mol, and polydispersity = 1.15.

Table 2. Thermodynamics properties of different forms of polyaniline-Mag 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-Mag	55.99	103.46	X	74.06	4.3161	20.5363	X	0.311
PANI-ES-Mag	50.34	140.10	221.07	103.75	167.6042	4.4617	10.7719	0.154
PANI-HCl-Mag	100.45	163.09	218.57	126.89	1.9678	8.7614	16.8337	0.180

Table 3. Effect of the catalyst (Mag-H^+) on the yield of polymerization and viscosity.

Maghnite-H^+ 0.25 M (%)	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

Kenetics studies of the reaction

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

The effect of the amount of Maghnite-H+ on the yield of polymerization was examined (Table 3). It can be noted that the yield increases with increasing “Maghnite- H+ 0.25 M” proportion 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 et al. [2001]. Indeed, using various amounts of Mag-H+, 2, 4, 6, 8 and 10 % by weight, the yield increases from 49.12% until 84.03% while the viscosity decreases from 1.85 dl/g to 0.98 g/dl, respectively.

Effect of the temperature on the polymerization

Table 4 shows the experimental results for the polymerization of aniline (0.022 mol) induced by (6% of Maghnite- H^+ 0.25 M) in bulk at different temperatures. It

Table 4. Effect of reaction temperature on the yield of polymerization.

T (°C)	Yield(%)	η (dl/g)
0	80.53	1.32
5	76.45	1.21
10	50.19	0.95
20	42.02	0.83
30	33.27	0.57
40	25.11	0.30

[Aniline] = 0.022 mol/l ; 6% of Maghnite-H+; Reaction time 3 h; determined in $CDCl_3$ at 25°C.

Table 5. Results of measuring the conductivity of different forms of polyaniline.

Sample	e (cm)	R (Ω)	ρ (Ω. Cm)	σ (S/cm)
PANI-ES-Mag	0.1	0.609	0.584	1.712
PANI-EB-Mag	0.1	1.880	25.792	0.038
PANI-HCl-Mag	0.1	0.976	0.163	6.134

was found that Maghnite- H+ by itself possesses good activity as catalyst for the polymerization. The yield of polymerization and the intrinsic viscosity reach maximum values around 0 to 5°C. On the other hand, with the increase in the reaction temperature above 5°C the intrinsic viscosity and the yield of the obtained polymers decrease progressively suggesting the possible occurrence of thermal degradation [Zeng and Ko, 1997; Shang et al., 2002].

Conductivity measurements

The electrical conductivity of the samples was measured by the four-point method. Four points aligned and spaced at the same distance are applied by simple pressure on the sample. A current I is injected through the outer tips with a current source, thus creating a potential variation. Voltage U can be measured between two points connected to internal voltmeter [SinhaRay and Biswas, 1999; Yang and Chen, 2003].

$$\rho = R\,(\pi . r^2 / e)\ (\Omega.cm) \qquad (1)$$

$$\sigma = 1/\rho\ (S/cm) \qquad (2)$$

The measured value of the transverse strength of the polyaniline is converted to volume resistivity, using Equation (1), and then the electrical conductivity is calculated from the Equation (2). In applying these equations, the value of (σ) presented in Table 5.

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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