



Chemical Synthesis of Nanocomposites via Intercalative Polymerisation of 4-Aminobenzyl amine and Aniline using Exchanged Montmorillonite

F. Z. Zeggai¹, A. Hachemaoui^{1*}, A. Yahiaoui¹

*Mustapha Stambouli University. Laboratoire de Chimie Organique, Macromoléculaire et des Matériaux,
1Department of Material Sciences, Mustapha Stambouli University, Mascara, Algeria.
Bp 763 Mascara 29000 (Algeria).*

Received 24 Jan 2015, Revised 6 May 2015, Accepted 6 May 2015

*Corresponding author: E-mail: hachemaoui2002@yahoo.fr

Abstract

A detailed study about the synthesis, characterization and properties of poly(4-aminobenzyl amine)/ Chromium – montmorillonite (P4-ABzA/M–Cr) nanocomposites has been performed. We synthesized the nanocomposite by two methods of doping, first by the Ion–Clay as doped and the second by presence of acid HClO₄. Changes in the characteristics of the nanocomposites, depending on the intercalated cation between the clay layers before the synthesis, have been observed. The intercalation of P4-ABzA into the clay layers was confirmed by X–ray diffraction studies and FTIR spectra, particularly by the narrowing of the Si–O stretching vibration band confirmed the interaction between P4-ABzA and the clay. Thermal studies show an improved thermal stability of the nanocomposites P4-ABzA/M–Cr doped with ion-clay relative to the P4-ABzA/M–Cr doped with acid. The electrochemical behavior of the polymers extracted from the nanocomposites has been studied by cyclic voltammetry. Good electrochemical response has been observed for P4-ABzA/M–Cr grown into HClO₄ but not for the one polymerized without perchloric acid.

Keywords: Nanocomposite ; Conducting polymers ; Cation exchanged ; Montmorillonite Nanocomposite ; Conducting polymers ; Cation exchanged ; Montmorillonite .

1. Introduction

Polyaniline (PANI) has been known as one of the most technologically important conducting polymers because of its high electrical conductivity, easy producibility, environmental stability, easy preparation, and relatively low cost [1]. It has attracted much attention in recent years due to its potential applications in various hi-tech aspects, for example, in electrochemical displays, sensors, catalysis, redox capacitors, electromagnetic shielding as well as in secondary batteries [2–6].

Furthermore, PANI, commonly prepared through a chemical oxidative polymerization of aniline in acidic solution, is unique among inherently conducting polymers due to the fact that it can be rapidly converted between base and salt forms by a simple treatment with acid or base.

When the PANI is associated with clay to form nanocomposites, its original electrical properties can also be modulated. The electrically modified nanomaterials are possibly applied for various applications, including electrorheological (ER) fluids. The ER fluids, suspensions of polarizable particles in a nonconducting liquid in general, exhibit drastic changes in rheological properties under an applied electric field. By tuning fibrillar structures with controlled electric field strength, micro-structural transition from a liquid-like to solid-like state is generally obtained. Polarizable particles, under an external electric field, behave as electric dipoles, which attract each other to form chain and column structures aligned along the field direction [7–10]. The products, (PANI/4-ABzA)-MMT composites were characterized with FT-IR, Uv, TEM and XRD. In this study, a nanocomposite material, which consists of polyaniline (PANI) and poly(4-aminobenzyl amine-co-polyaniline) (PANI/4-ABzA) and inorganic Cr³⁺-montmorillonite called Maghnite (Mag-Cr³⁺), was synthesized through a chemical oxidative polymerization method [11]. The effect of comonomer proportion on the thermal and electrical properties of the copolymers is reported. The products, (PANI/4-ABzA)-Mag composites were characterized with FT-IR, Uv, TEM and XRD.

2. Materials and methods

2.1. Apparatus

The X-ray diffraction of the powder nanocomposites were taken using a Bruker CCD-Apex equipment with a X-ray generator (Cu Ka and Ni filter) operated at 40kV and 40mA. The scanning speed and the step size were 0.08°/min and 0.05°, respectively. X-ray fluorescence spectroscopy of the powder nanocomposites was made using a Philips PW1480 equipment with a UNIQUANT II software to determine elements in a semi quantitative way.

For recording the UV-Vis absorption spectra, a Hitachi U-3000 spectrophotometer was used. The solution of the homo- and co-polymer in N-methyl-2-pyrrolidone (NMP) was used for recording the spectrum. Fourier transform infrared (FT-IR) spectroscopy was recorded using a Bruker Alpha.

The electrochemical behaviour of the polymers was studied by cyclic voltammetry after their extraction from the polymer by dissolving in the N-methyl-2-pyrrolidone (NMP). It is known that this kind of conducting polymers is soluble in NMP [12], while the clay remains in solid state. Thus, both components can be separated by filtration. The electrochemical measurements were carried out using a conventional cell of three electrodes. The counter and reference electrodes were a platinum foil and a hydrogen reversible electrode (RHE), respectively. The working electrode was prepared as follows: after the polymer was extracted from the polymer using NMP, 50µL of this solution were cast over graphite carbon electrodes and the solvent evaporated to create polymeric films on the order of 25-30 µm. The electrolyte used was 1M HClO₄ and all experiments were carried out at 50mV/s.

For transmission electron micrographs (TEM) observations, the samples were dispersed in water and supported on TEM grids. The images were collected using a JEOL (JEM-2010) microscope, working at an operation voltage of 200 kV. The TEM is coupled with EDX for the elucidation of chemical composition of the samples.

2.2. Materials

Aniline (from Aldrich) was distilled under vacuum prior to use and 4-aminobenzyl amine (from Aldrich) was used as received. Perchloric acid (from Merck) was suprapur quality and the water employed for the preparation of the solutions was obtained from an Elga Labwater Purelab Ultra system. A natural sodium-montmorillonite clay (named as Maghnite) obtained from Tlemcen (Algeria) has been used.

2.3. Chemical synthesis

The clay, which has been used, is supplied by a local company known as ENOF Maghnia (Western of Algeria). The clay samples were washed with distilled water to remove impurities; the raw-montmorillonite (20g) were crushed for 20 min using a Prolabo ceramic balls grinder. The greatest proton saturation of the <2 mm fractions of clay were obtained by first saturating with Na⁺ ions using 1M NaCl solution. They were then dried at 423 K for 24 h and stored in tightly stoppered glass bottles for later use (samples M-Na). To obtain M-Na with Chromium intercalated (M-Cr), the M-Na was dispersed into a 1 M Cr(NO₃)₃·9H₂O solution and stirred for 24 h. Then the solid was recovered by centrifugation and washed with abundant water. The absence of chloride was confirmed using silver nitrate. The products were dried at 1100C, overnight and its composition was measured by X-ray fluorescence, obtaining the data in Table 1.

Polymer/M-Cr nanocomposites were prepared by the initial intercalation of M-Cr (1g) using 4-aminobenzyl amine and/or Aniline monomers (monomers were added with molar ratio 50/50 to a total concentration of 0.22M) and subsequent polymerization of monomers in the galleries as described previously [13-14].

Firstly, various amount of chromium-montmorillonite (M-Cr) was dispersed in 100 mL of deionized water using ultrasonication (a sonicated mixer "Haake Rheomix 600") at a fixed volume basis of 70% filling and at a temperature of 60° C. The rotor speed was set at 120 rpm and total mixing time including sonication was 5 h to allow swelling of the M-Cr. Then, 0.022 mol of 4-aminobenzyl amine or/and Aniline was added, followed by the addition of pre-cooled 1M perchloric acid HClO₄. The mixture was stirred for 24 h min until the monomers was fully intercalated into the M-Cr, and a clear dispersion was formed.

Then, pre-cooled 0.1M ammonium persulfate solution (dissolved in 1M aqueous HClO₄) was added drop wise, and the mixture was stirred magnetic for another 24 hours at room temperature. The obtained precipitate of the polymer/M-Cr nanocomposites was filtered out of the reaction mixture, and washed several times with deionized water and methanol to remove unreacted monomers and HClO₄ and dried under vacuum at 60°C for 24 h.

Table 1. Elementary compositions of Raw-Maghnite, Mag-Na and Mag-Cr clays

Sample	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	TiO ₂	Cr ₂ O ₃	Pert in fire
Raw-Maghnite	69.39	14.67	1.16	0.30	1.07	0.50	0.79	0.16	0.00	11.96
Mag-Na	70.75	14.46	1.05	0.19	1.01	2.61	0.78	0.14	0.00	09.01
Mag-Cr	71.00	14.06	1.00	0.14	0.98	0.00	0.71	0.15	2.61	09.35

3. Results and discussion

3.1. Procedure for lead determination method

3.1.1. DRX Spectroscopy

To confirm the intercalation of PANI into the layers of Cr³⁺-MMT, various kinds of analysis method can be applied. XRD was used to investigate the intercalation of P(4-ABzA-co-ANI) inside a MMT interlayer as shown in Fig. 1 and Table 1. The d-spacing values (d₀₀₁) were calculated from the peak position of XRD pattern using Bragg's equation $d = 2\pi/q$, where q is the magnitude of scattering vector defined as $q = (4\pi/\lambda) \sin(\theta)$; λ is the X-ray wavelength, and 2θ is the scattering angle [15]. The position of (001) peak, and corresponding d-spacing are shown in Table 2.

Table 2. Peak maximum, d-spacing and deference intensity peak of M, Mag-Cr, P(4-ABzA)/Mag-Cr, PANI/Mag-Cr and COPO(4-ABzA-co-ANI)/Mag-Cr.

Samples	Peak max, 2θ _{max} (deg)	Basal spacing d(001) (Å)	Interlayer spacing, Δd(A0)
Mag	6.07	14.64	//
Mag-Cr	5.59	15.89	1.25
PANI/Mag-Cr	5.07	17.5	2.86
P(4-ABzA)/Mag-Cr	4.91	18.09	3.45
COPO(4-ABzA-co-ANI)/Mag-Cr	3.53	23.69	9.05

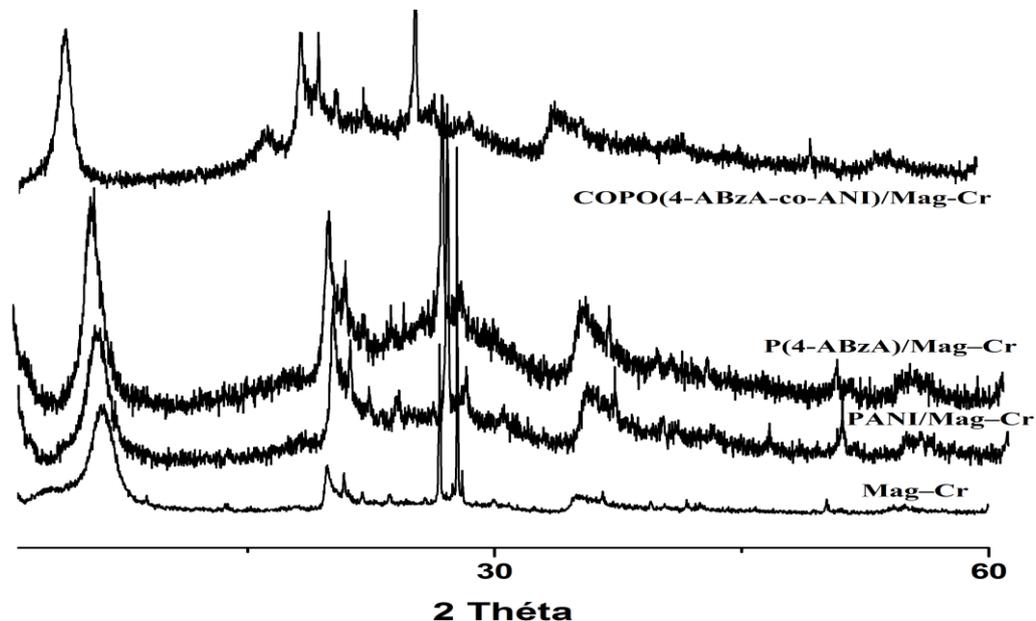


Figure. 1: XRD diffraction patterns of Sodium-Montmorillonite (M-Na), Chromium-Montmorillonite (M-Cr), poly(4-ABzA)/M-Cr, poly(4-ABzA-co-ANI)/M-Cr and PANI/M-Cr nanocomposites.

The degree of intercalation in synthesized intercalated poly(4-ABzA), poly(4-ABzA-co-ANI) and PANI nanocomposites in montmorillonite was confirmed by the X-ray diffraction pattern (Fig. 1). The peaks between 20-24° 2θ becomes clearer due to amorphous silica remaining from montmorillonite phase in all samples. A

sharp peak at $2\theta = 26.9^\circ$ due to SiO_2 in M-Cr was observed to be unchanged in all the polymer/M-Cr nanocomposites.

The XRD patterns show that the (001) diffraction peak between 3° and 7° changes depending on the inorganic cation intercalated. For the Cr^{3+} -MMT, a peak, which appears at $2\theta = 5.59^\circ$, corresponds to the d-spacing of 15.89 Å. The diffraction peak of P(4-ABZA-co-ANI)/M-Cr, which decreased to a lower angle of $2\theta = 3.53^\circ$, gave a d-spacing of 23.69 Å. The increase of d-spacing was demonstrated to be shifted due to the intercalation of the P(4-ABZA-co-ANI) between the M-Cr layers. In addition, the intensity of this peak reducing clearly with the increase in the amount of aniline (promotes polymerization of the polymer), this phenomenon shows the probability of the formation of exfoliated clay structures. The above result is also close to that reported for polyaniline with copper montmorillonite nanocomposite by many other researchers [16-18]. These XRD data are almost similar with our previous report, which represent the PANI/clay nanocomposite, representing that the intercalation state of P(Aniline-o-Toluidine)/clay nanocomposite was not changed by dedoping process of the P(Aniline-o-Toluidine) in this study.

3.1.2. FT-IR Spectra

FT-IR spectra of M-Cr and polymer/M-Cr nanocomposite are shown in Fig. 2. The analysis of the IR spectra of these nanocomposites is complicated because of the fact that in the region in which both the polymer and MMT are most sensitive to the structural and chemical changes like protonation, hydrogen bonding or intercalation, the characteristic bands of MMT, P(4-ABZA) and PANI overlap.

FTIR spectroscopy was used to investigate the chemical structure of the nanocomposites and interactions between the PANI, p4-ABZA, P(ANI/4-ABZA) and MMT. Figure 2 shows the FTIR spectra of Mag-Cr, PANI/Mag, P(4-ABZA)/Mag and P(4-ABZA-co-ANI)/Mag. The characteristic bands of Mag-Cr clay can be assigned according to the literature [19,20] as 3623 cm^{-1} ($\nu\text{O-H}$), 3367 cm^{-1} ($\nu\text{Mg-O}$), 791 cm^{-1} ($\delta\text{Al-OH}$), 524 cm^{-1} ($\nu\text{Si-O-Al}$). The broad absorption band in the 1,350–750 cm^{-1} region involves four Si–O stretching modes of the Mag clay [19]: three of them in plane (1,120; 1,048; and 1,025 cm^{-1}), and one out-of-plane mode (1,080 cm^{-1}). PANI/Mag is characterized by the vibrations at 1,292 cm^{-1} ($\nu\text{C-N}$ in secondary aromatic amine), 1,567 cm^{-1} ($\nu\text{C=C}$, quinoid ring), 1,492 cm^{-1} ($\nu\text{C=C}$, benzenoid ring), and 1,020 cm^{-1} (vibrational mode of B-N+=Q structure, which is formed spectroscopy for characterizing the state of the intercalation in polymer nanocomposites prepared from montmorillonite-based nanoclays. The authors stated that the Si–O-stretching band envelope is affected by both the chemistry of the montmorillonite and the presence of intercalant. It was shown that the shape of the clay band envelope in the 1,350–750 cm^{-1} region changes with the degree of processing because of the changes in the quality of intercalation. As shown on the FTIR spectra of copolymers, the peaks observed for both P(4-ABZA) and P(4-ABZA-co-ANI) films can be attributed as follows: the peaks at 1573 and 1499 cm^{-1} are attributed to the C=C stretching vibrations of the benzene ring and quinone ring vibrations. The peak at 2350 cm^{-1} is due to the C=N stretching of the polymer. The strongest band observed near 1000 cm^{-1} and the band at 1235 cm^{-1} are due to C-O stretching twisting, respectively, of the alkyl chain. The peak near 800 cm^{-1} is due to the N-H out-of-plane bending absorption. The peak at 3360 is attributed to the symmetric stretching of NH (hydrogen bonded) in aromatic amine. Especially, C-N stretching vibration was observed at 1301 cm^{-1} is consistent with study of Madakbas et al., [21]. These results point out that there was a transition from pernigraniline to emeraldine salt.

3.1.3. UV-Vis absorption measurement for the nanocomposites

The UV-Vis spectra (Figure 3) of the copolymers N-methyl-2-pyrrolidone (NMP) solution show the same bands observed for the PANI and P4-ABZA films, indicating that the same transitions observed in homopolymers occur in the copolymer. The UV-Vis spectrum of the copolymer is similar to that obtained for P4-ABZA films since both present a brown color. In copolymer/Mag-Cr nanocomposite, two major characteristics peaks can be observed at about 350 and 540 nm wavelengths. The absorption at 350 nm is due to polaron- π^* transition and the second band at 540 nm can be assigned to exciton transition between benzenoid and quinoid rings [22, 23]. The second band at 540 nm is slightly shifted to lower wavelength which indicated the interaction between poly(4-ABZA-co-ANI) and Mag-Cr. By cons, No observed the second peak in the case of poly(4-ABZA) and PANI, this results indicated that polymer is insoluble in NMP solvent used, because the intercalation and the enhancement may be attributed not only to the Van der Waals interaction between polymer and the cations, but also to the strong bonding of polymer on the inorganic cations.

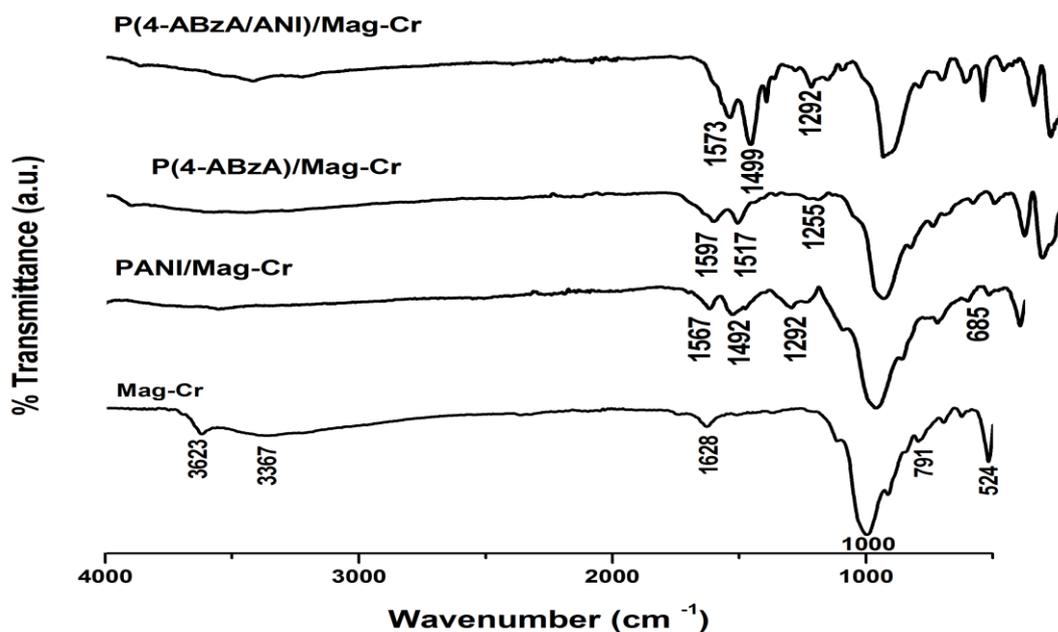


Figure. 2: FT-IR adsorption spectra of the Chromium-Montmorillonite (Mag-Cr) poly(4-ABzA-co-ANI)/Mag-Cr, poly(4-ABzA)/Mag-Cr and polyANI/Mag-Cr nanocomposites.

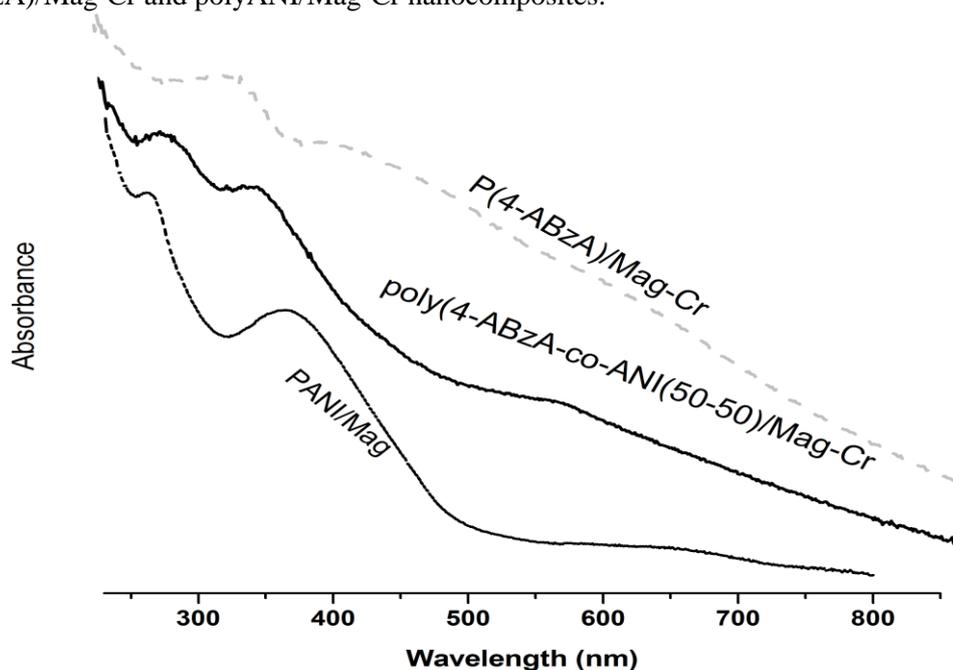


Figure. 3: UV-vis spectra of the : poly(4-ABzA-co-ANI (50/50))/Mag-Cr, poly(4-ABzA)/Mag-Cr and polyANI/Mag-Cr nanocomposites.

3.1.4. Electrochemical response

To study the electrochemical response of polymers and copolymers, a conventional cell of three electrodes was used. To separate the polymers from the catalysts, they were dissolved in N-methyl-2-pyrrolidone (NMP). Films of the polymers were made by casting a drop of a solution of them in NMP over the working platinum disk electrode and heating with an infrared lamp to remove the solvent.

To try to clarify all peaks observed, we have synthesized polyaniline and copolymer of amino-benzylamine/aniline with Mag-Cr as dopant. The cyclic voltammogram of these copolymers obtained by Mag-Cr is shown in Fig. 4. The voltammetric behaviour of copolymer poly(4-ABzA-co-ANI (50/50))/Mag-Cr is similar to those obtained in P4-ABzA/Mag-Cr. At higher concentration of aniline monomers (50/50), three pairs of anodic and cathodic current peaks are seen clearly, centered at around 0.48, 0.67 and 0.79 V. At lower

electrode potentials, not exceeding 0.48V, the reduced (leucoemeraldine) form prevail, whereas at high potentials, exceeding ca. 0.79V, the fully oxidized (pernigraniline) form exists, leaving a broad potential window, ranging from 0.48 to 0.79 V, where the conducting emeraldine form is most stable. In addition, for copolymers with high amounts of aniline (50/50) shows the same behaviour (three redox process). Therefore, besides that the properties of this kind of conducting polymers do not depend on the type of anion used in the synthesis [24], the electrochemical properties depend strongly on the dopant.

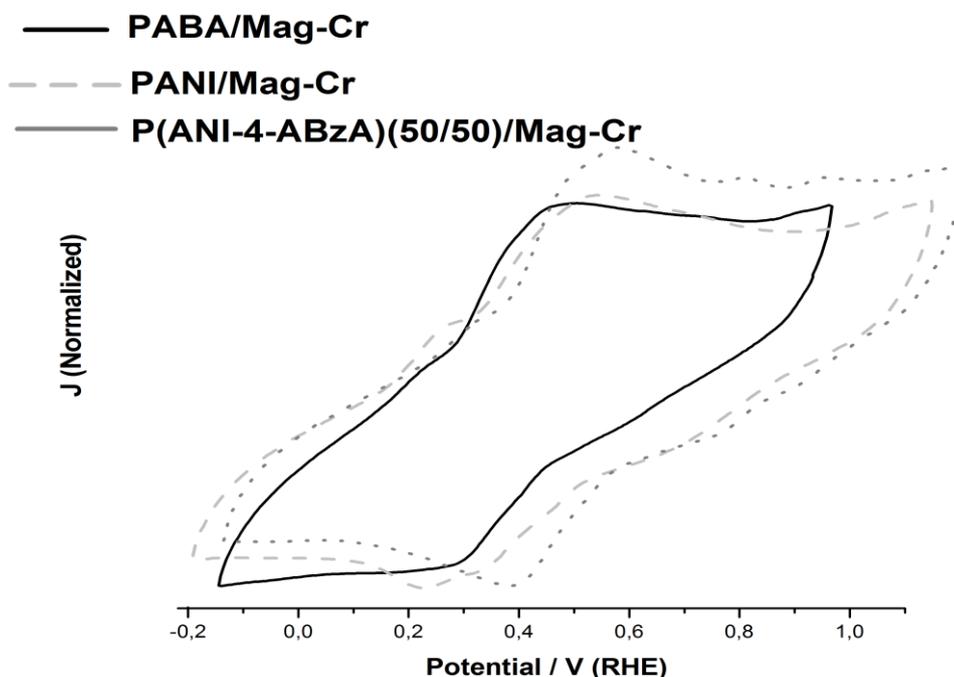


Figure 4: Cyclic voltammograms recorded for a graphite carbon electrode covered by poly(4-ABzA)/Mag-Cr, polyANI/Mag-Cr and copolymers poly(ANI-4-ABzA)(50/50)/Mag-Cr in 1M HClO₄ solution. Scan rate 50 mV s⁻¹.

3.1.5 Transmission Electron Micrographs (TEM)

To more clearly identify intercalated structures of the poly(4-ABzA-co-ANI)/clay nanocomposites, TEM images were done for the different nanocomposite formulations. It is clearly seen from 5, that the gray/white area represents the polymer matrix and dark stripes represent the clay layers. TEM image of poly(4-ABzA-co-ANI)/Mag-Cr (Fig. 5a and b) shows that the prepared nanocomposite has a considerable amount of stacked layers in which polymer chains are intercalated, which is reliable with the results of X-ray diffraction (Fig 1).

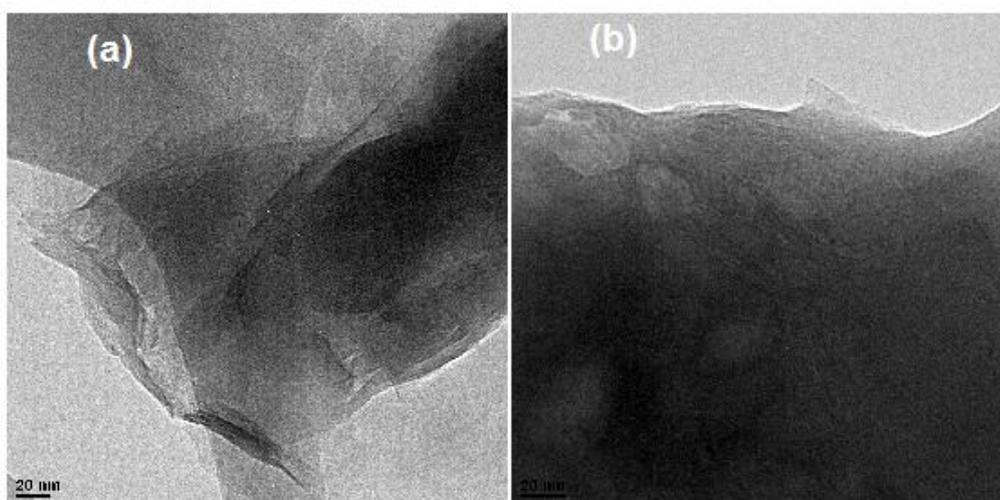


Figure 5: TEM image of (a) poly(4-ABzA)/Mag-Cr and poly(4-ABzA-co-ANI)/Mag-Cr

Conclusions

1. Polymers Aminobenzyl amine “poly(4-ABzA)” and Aniline (PANI), copolymer (2- Aminobenzyl amine and Aniline) “poly(4-ABzA-co-ANI) and polyaniline (PANI) with cromium-Montmorillonite (Mag-Cr) nanocomposites have been synthesised by solution polymerisation in the presence of perchloric acid and a substoichiometric amount of ammonium persulfate.
2. the monomer or/and comonomer was polymerised and largely incorporated into the Mag-Cr, which was confirmed by XRD, FT-IR Spectra and UV-Vis spectroscopy shows some peaks shifts, which indicate the formation of some new bonds and support the intercalation of polymer chains into the interlayer spacing of Montmorillonite M-Cr clay.
3. Electrochemical behaviour of poly(4-ABzA)/Mag-Cr is quite different from those observed for poly(4-ABzA-co-ANI)/M-Cr and PANI/Mag-Cr given broad peaks in the voltammogram that can be produced by the overlapping of two different processes.
4. The polymers synthesized using Mag-Cr could show a structure that is a mixture of conducting (polyaniline-type) and redox (phenazine-type) units.

Acknowledgements-This work was supported by the Agency Thematic Research Science and Technology (ATRST), the Directorate General of Scientific Research and Technological Development (DGRSDT) of Algeria.

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(2015) ; <http://www.jmaterenvirosci.com>