



New hybrid nanomaterial based on two polymers, one being an ion-conducting polymer and the other electron-conducting (PANI and PEO) in the interlayer galleries of an ecologic and friendly catalyst layered called Maghnite-H⁺ (Algerian MMT)

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ABSTRACT

Soluble and conducting block copolymer (PANI-PEO) nanocomposite was prepared by oxidative polymerization of aniline in non acid media and in different weight percentages in the presence of ecologic catalyst layered called (Maghnite-H⁺) and reactive polymer stabilizer such as poly(ethylene oxide) (PEO₂₀₀₀, M_n = 2000). The morphology, structure, solubility and electrical properties of PANI-PEO copolymer nanocomposite was characterized by FTIR, Uv-vis, 1H-NMR spectroscopy, dynamic scanning calorimetry (DSC), and thermogravimetric analysis (TGA). It was found that structure, solubility and conductivity of resulting PANI-PEO nanocomposite depended on the amount of catalyst, molecular weight and functionality of the reactive stabilizer (PEO) and molar ratio of monomers (PANI-PEO). The formation of the hydrogen bonding between PANI and PEO copolymer was predicted by the FT-IR spectra. DSC analysis showed only one (T_g = 16°C) for the blend copolymer implying compatibility of the two components

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Introduction

The conjugated macromolecules are primarily governed by the chemical structure of the polymer backbone itself; but a number of additional tools can be employed to further manipulate the bandgap of conjugated polymers [1]. Control of the effective conjugation length by the introduction of side chains which exhibit steric interactions and force the backbone to twist, along with the design of copolymers that comprise well-defined conjugated segments are illustrative examples of how emission color can be varied over a broad spectrum [2].

On the other hand, montmorillonite clay (MMT) have unique structural, mechanical, electronic and thermal properties [3] and are attractive building blocks for the development of novel polymer nanocomposite materials with enhanced functionality, especially if it comes to enhanced conductivity, thermal stability and solubility [4, 5].

Polyaniline (PANI), one of the most important conducting polymers, has received considerable attention due to its ease of synthesis [6], environmental stability [7], and unique acid/base doping/dedoping and oxidation/reduction chemistry [8]. Nanostructured PANI offers an opportunity to applications on sensors, actuators, supercapacitors, etc., due to its large specific surface area [9]. Many methods, including hard template, soft template and template-free methods, have been used to prepare nanostructured PANI as yet [10]. On the other hand, self-assembly of block copolymers is an effective method to synthesize various polymer or metal nanostructures because its morphology can be conveniently tuned into various nanostructures such as spheres, cylinders, tubules, and vesicles [11]. So, it is expected that various PANI structures could be produced by self-assembly of block copolymers containing PANI block [12].

Poly (ethylene oxide) (PEO) has been one of the most extensively studied synthetic polymers, because of not only its unique behaviors in solution but also its wide applications [13]. In particular is an exceptional polymer which dissolves with concentrations of a wide variety of salts to form polymer electrolytes [14]. Polymer electrolytes consist of polymer and ionizable salts. PEO is the most popular polymer used, due to its high solvating power with metal ions and outstanding mechanical properties [15].

Blending opens up a root for a combination of different properties. Some recent results indicate that conducting polymer composite materials may have significantly improved electronic and mechanical properties as compared to pure conducting polymer [16].

Interest in applications for polyaniline has motivated investigators to study its mechanical properties, the thermostability of its conductivity, its processibility, etc. and its use in polymer composites, nanocomposites or blends with common polymers [17]. As a result, several methods to produce composites and nanocomposites blends containing PANI have been developed [18]. In this present work authors have carried out the synthesis of new hybrid nanocomposites block copolymer based on Maghnite-H⁺ (Algerian ecologic catalyst MMT), in the interlayer galleries of which there are simultaneously the macromolecules of two polymers poly (ethylene oxide) and polyaniline, one being an ion-conducting polymer and the other electron-conducting, are obtained. It is found that the conductivity and solubility of PANI blends is more than pure PANI. The blends were prepared in order to combine the mechanical and physical properties of PEO with conducting properties of PANI.

Experimental

Materials and methods

Polyaniline (PANI) was prepared in our laboratory (laboratory of polymers chemistry, oran university, Algeria) by standard chemical intercalated method [19]. Polyethylene oxide (relative molecular mass of 2.10^3) was obtained from Sigma Aldrich, Potassium persulphate $K_2S_2O_8$ was analytical grade from Sigma Aldrich and dried under vacuum at 120°C for 24 h to remove water from the crystal, hydrochloric acid (35%–38%), MMT clay was obtained from ENOF Maghnia (Algeria). The MMT- H^+ (Mag- H^+) was prepared as described by Belbachir et al [20], and water ($\text{pH} < 7$) was used to synthesize emeraldine salt clay (PANI-ES / 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 (0.5M). A doping EB was carried out in aqueous medium of hydrochloric acid (1M).

The emeraldine base (50 mg) to dope it and dissolving it in (100 ml) of (2M) HCl. For two hour and the same time (PEO) 10 mg dissolving matrix (PEO) with (PANI) thin films of conducting polymer alloys PANI-PEO prepared by mixed different volume ratio of PANI with PEO [21].

Measurements

^1H nuclear magnetic resonance (NMR) measurements were carried out on a 300 MHz Bruker NMR Spectrometer equipped with a probe BB05 mm, in CDCl_3 . 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). Viscosity measurements were carried out with an Ubbelohde Capillary Viscosimeter (viscologic TI1, version 3–1 Semantec). Intrinsic viscosity, $[\eta]$, was measured at 30°C in benzene. 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. The purification of polymers were carried out by dissolving the product in chloroform (CHCl_3) and filtering to eliminate the Mag- H^+ . Then, chloroform was removed by evaporation.

Results and discussion

Infra red spectra

Fig 1. Shows the FTIR spectra of pure polyaniline (base form). The formation of polyaniline is confirmed by noticing the predominant peaks at the wave numbers of 1501 cm^{-1} corresponding to $\text{C}=\text{C}$ stretching of quinone ring, 1557 cm^{-1} for $\text{C}=\text{C}$ stretching of benzenoid ring, 1293 cm^{-1} for $\text{C}-\text{N}$ stretching, 755 cm^{-1} and 838 cm^{-1} for $\text{C}-\text{H}$ vibration of Para coupling benzenoid and benzene rings, $\text{C}-\text{H}$ bending is at 694 cm^{-1} , 593 cm^{-1} is corresponds to aromatic ring and 507 cm^{-1} is stretching at out of the plane. In pure PEO Spectrum a large broad band appears centered at 3442 cm^{-1} which is due to the hydration of PEO which confirms that PEO is highly hydrophilic and gets hydrated. Thus pure PEO shows a large broad band of CH_2 stretchings between 2950 and 2840 cm^{-1} . It is also been observed that CH_2 vibrational modes appear in PEO at 1467 cm^{-1} which corresponds to asymmetric CH_2

bending and 1344 cm^{-1} which corresponds to symmetric CH_2 wagging [22].

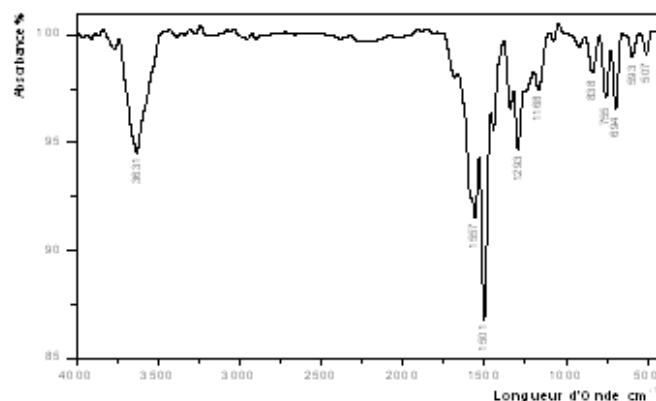


Fig 1. FT-IR spectra of polyaniline base (PANI-EB) obtained by the intercalated method between Aniline and Maghnite- H^+ (black powder) at 0°C .

The infra red spectra for PANI-PEO nanocomposite is also shown in Fig.2. There are significant changes in both the intensities and the frequencies in the product (PANI-PEO). There are more pronounced between 690 and 1574 cm^{-1} . The bonds also show doublet and triplets. This may indicate that there is significant interaction between the oxygen of the ether group of polyethylene oxide and the nitrogen in the aniline of polyaniline [23].

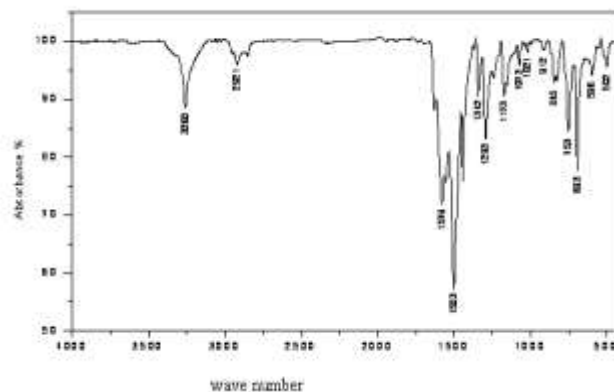


Fig 2. FT-IR spectra of block copolymer polyaniline-polyethylene oxide (PANI-PEO) obtained by the intercalated method between Aniline, polyethylene oxide and Maghnite- H^+ (black powder) at 70°C .

^1H NMR Spectra

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 (Fig.3). The down field signals centered at 7.2 ppm to 7.5 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 ^1H -NMR spectra with slight shift of the peak positions (i.e. NH protons appear at 4.81 ppm and aromatic protons centered at 7 ppm to 8 ppm) [24].

An investigation was devoted to the analysis of the polyethylene oxide (PEO) by ^1H NMR spectroscopy at 300MHz (Fig. 4). According to the work published by *Yahiaoui et al* [25], ^1H NMR spectroscopy at 300 MHz (Solvent CDCl_3) (Fig. 4) showed different peaks: (a) the methylene groups (CH_2 -) at 2.6 ppm, and (b) the methylene (CH_2O -) at 3.7ppm.

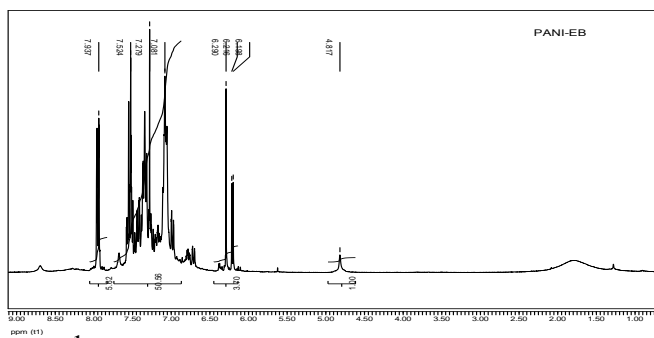


Fig 3. $^1\text{H-NMR}$ spectra of the polyaniline base (PANI-EB) obtained by the intercalated method between Aniline and Maghnite- H^+ (black powder) at 0°C .

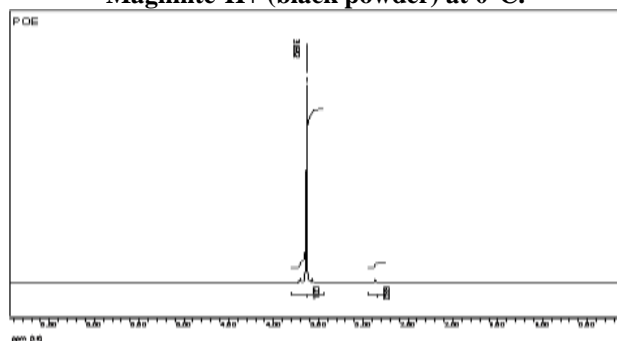


Fig 4. $^1\text{H-NMR}$ spectra of pure poly ethylene oxide (PEO) $^1\text{H-NMR}$ data for the product consisting on polyaniline and polyethylene oxide (Fig 5). In the $^1\text{H-NMR}$ spectra of the product, a wide signal in the region of 6.8 to 8 ppm was assigned to benzenoid hydrogen of polyaniline already reported by MacDiarmide *et al* [26]. Three peaks in these region was assigned to para position of polyaniline is linked for the polymerization. Doublet signal at 3.25 to 3.75 ppm indicate peak of $\text{CH}_2\text{O-}$ and $\text{CH}_2\text{CH}_2\text{O-}$ hydrogen of polyethylene oxid reported by Yahiaoui *et al* [27]. Peak at 1.5 to 2 ppm is due to CH_2 hydrogen respectively. The shift of the CH_2 peak to highly shielded region is due to polymerization. Integral ratio of the NH proton signal of polyaniline in PANI-PEO appeared at 4.25 ppm, to note that the chemical displacement of this peak was changed from polyaniline (4.81 ppm) to PANI-PEO copolymer (4.25 ppm) which shows the modification of PANI by the PEO.

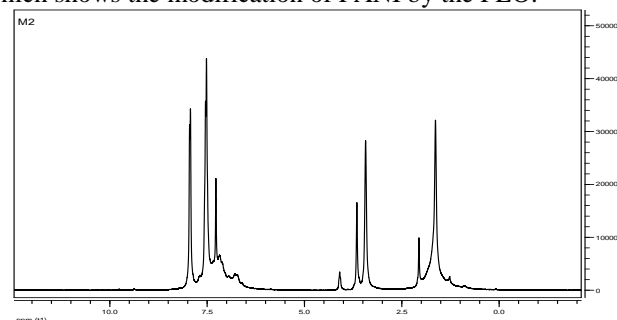


Fig 5. $^1\text{H-NMR}$ spectra of the product polyaniline-co-poly(ethylene oxide) (PANI-PEO) obtained by the intercalated method between Aniline, poly(ethylene oxide) and Maghnite- H^+ (black powder) at 70°C .

Thermophysical properties

The thermophysical properties of PANI-PEO were studied by TGA and TDA. The weight loss (%) was recorded as function of temperature for both PANI-PEO using TGA (SDT Q600 V20.9 Build 20). The samples weighing about 2.0 mg

were scanned in the temperature range of $0-800^\circ\text{C}$ under nitrogen atmosphere at a heating rate of $10^\circ\text{C}/\text{min}$.

Fig 6. Presents the curves of weight loss versus temperature showing the behaviour of PANI-PEO sample. The first significant weight loss occurs already at temperature between 50°C and 100°C . It is known, that PANI-PEO is hygroscopic and during the heating to 100°C the residual water evaporates. Then the main mass loss, which corresponds to polymer degradation starts at about 200°C and 500°C [28].

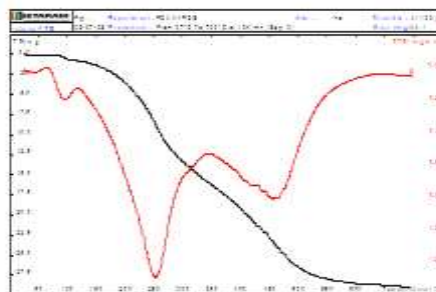


Fig 6. TGA curves of pani-peo prepared in the presence of maghnite-h+ (25M)

Conclusion

In the present work pure PANI and its blend with PEO_{2000} was prepared by intercalative polymerization of aniline and poly(ethylene oxide) in the interlayer galleries of Maghnite- H^+ (Algerian MMT). The copolymer electrolyte based on polyethylene oxide complexed with conducting polyaniline in galleries of catalyst has been prepared in different weight percentage ratios. The complexation is confirmed by Ftir And $^1\text{hnm-R}$ Spectroscopy.

Intercalation, structure and morphology of the copolymer nanocomposite is confirmed by physicochemical analysis. It is found that The predominant peaks appeared in composites at 2922.42 cm^{-1} , 2363.01 cm^{-1} , 1581.77 cm^{-1} , 1467.96 cm^{-1} , 1342.58 cm^{-1} , 1294.35 cm^{-1} , 968.35 cm^{-1} and 482.25 cm^{-1} fully confirms the formation of (PANI-PEO) nanocomposites, the conductivity, solubility and thermal stability of PANI blends is more than pure PANI. The blend was prepared in order to combine the mechanical properties of PEO with conducting properties of PANI.

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