



## Studies on the conducting nanocomposite prepared by polymerization of 2-aminobenzoic acid with aniline from aqueous solutions in montmorillonite

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### ARTICLE INFO

#### Article history:

Received 28 June 2012

Received in revised form 20 August 2012

Accepted 22 August 2012

Available online 11 October 2012

#### Keywords:

Conducting polymers

Nanocomposites

Intercalation

Exfoliation

Montmorillonite

o-Aminobenzoic acid

Aniline

### ABSTRACT

A simple and facile method was used to synthesize poly(o-aminobenzoic acid) (PoABA) and polyaniline (PANI) nanocomposites with sodium montmorillonite (M-Na) using in situ intercalative oxidative homo-, and co-polymerization by a substoichiometric amount of ammonium persulfate. The conductive emeraldine salt form of all polymers used is inserted into the layers of M-Na to produce the hybrid with high conductivity. The properties of the hybrid are characterized by X-ray diffraction (XRD), Fourier transform Infrared (FT-IR), thermogravimetric (TG), X-ray photoelectron spectroscopy (XPS), and electrochemical response; the results show that what we obtain is really a nanocomposite.

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### 1. Introduction

Intercalation polymerization is a promising strategy to study the confining polymer chains in the nanometer size inorganic galleries. As conjugated polymers usually have high electric conductivity with many of potential applications, the insertion of conjugated polymers in the layered (two-dimensional) or microporous (three-dimensional) inorganic hosts has received extensive attention over the past few years and many conjugated polymer/inorganic host hybrid composites have been synthesized and studied, such as polymer/clay nanocomposites [1–5] and polymer bronzes [6] through intercalative polymerisation of speciality monomers like pyrrole, aniline, thiophene or *N*-vinylcarbazole in host matrices such as FeOCl [7], xerogels [8] or zeolites [9]. Biswas and SinhaRoy [10] reported that cationic polymerisation of *N*-vinylcarbazole could be initiated by clay in solid phase at melting temperature of *N*-vinylcarbazole (>64 °C) or in benzene solution at 50 °C. By repeated benzene extraction of nanocomposite reaction product, an intercalate of polymer in clay was isolated and duly characterised. However, attempts to polymerise pyrrole or aniline under such conditions by montmorillonite unaided by FeCl<sub>3</sub> or (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> were unsuccessful.

More recently, Choi and co-workers [11] reported preparation of nanocomposite of polyaniline and Na<sup>+</sup>-clay by emulsion polymerisation using dodecylbenzenesulfonic acid as an emulsifier and (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> as the oxidant. Intercalated polypyrrole/Na<sup>+</sup>-clay nanocomposite was prepared by Choi and co-workers [12] through inverted intercalative pathway using (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>. Besides the above nanocomposites of speciality polymers, several other nanocomposites of clay with fundamental polymers were also reported [13,14].

Commonly, there are three types of methods to prepare a polymer/clay based nanocomposite. The first type is to mix clay (maybe modified clay) and polymers or prepolymers or precursor polymers in a common solvent to obtain a molecular level mixing [15]. The second type concerns about mixing the clay with monomers with or without solvent (maybe a dispersing agent) and the clay can be swollen with monomers, followed by the polymerization, which is also called in situ method. Finally, the third type is to melt-mix the modified clay with neat polymers in a mixer [16,17].

The hydrophilic clay cannot be easily mixed with the organic polymers unless some hydrophobic groups are introduced into the clay. This can be done by exchanging the cationic ions in the interlamellar spaces with organic alkyl ions to improve its compatibility with organic polymers and to increase the mechanical, heat-resistant, gas barrier properties of the polymers [15,18,19].

Polyaniline and derivative of polyaniline, which is the most popular type of conducting polymers because of its easy production and processing, has been used to insert into various types of clays

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to obtain conducting nanocomposites via the modification of the hydrophilic clay into an organic clay [20–25,19,26].

In this study, we will use in situ method letting the water-borne clay swell with anilinium monomers in an aqueous solution. It is slightly different from the second type since the clay used is pristine and water-borne with no modification and the monomers are hydrophilic as well [27,28]. Therefore, the slow and tedious process to insert the modifiers into clay galleries by ion exchange can be avoided. In other words, it is more feasible and easier to prepare a derivative of polyaniline/clay nanocomposite by dispersing the pristine clay with the aniline monomers in the aqueous solution and start the polymerization.

For this purpose, in this work we report the synthesis of nanocomposites of poly(*o*-aminobenzoic acid) (PoABA) with a natural montmorillonite clay modified with inorganic cations (i.e., H<sup>+</sup>) and the properties of the nanocomposites and the polymers extracted from them.

## 2. Experimental

### 2.1. Reagents

The monomer *o*-aminobenzoic acid (*o*ABA) employed for the polymerization reaction was of reagent grade supplied by Merck. The aniline (ANI) was purchased from Aldrich and used as received. Perchloric acid (from Merck) was suprapure quality, ammonium persulfate (from Merck). All solutions were prepared with bi-distilled water was obtained from Elga Labwater Purelab Ultra system.

### 2.2. Preparation of montmorillonite (M-Na)

The clay was obtained from Algeria a montmorillonite from Tlemcen. The clay sample was washed with distilled water to remove impurities; the raw-montmorillonite (M-raw) 20 g was crushed for 20 min using a Prolabo ceramic balls grinder. They were then dried at 423 K for 2 h and stored in tightly stoppered glass bottles for later use. The montmorillonite sample (M-raw) was treated with a 2 M NaCl solution under continuous stirring, and washed several times with bi-distilled water, to remove Cl<sup>-</sup>, and finally dried at 105 °C [29]. The sample so obtained was delaminated clay labeled as M-Na. The chemical composition of the different clays is included in Table 1.

### 2.3. Preparation of nanocomposite polymer/M-Na

To obtain the nanocomposites, 0.22 mol of monomers *o*-aminobenzoic acid (*o*ABA) or aniline (ANI) were added to 1 g of the modified montmorillonite with Na<sup>+</sup> and the mixture was kept under magnetic stirring for 1 h. The chemical polymerization began when 100 ml of 0.1 M ammonium persulfate solution was slowly added to the mixture. Thus, the final concentration of (*o*ABA or ANI) was 0.22 M. The reaction was carried out under magnetic stirring for 1 h at 5 °C. The nanocomposites were isolated, washed with 1 M hydrochloric acid (soluble oligomers were eliminated) and water. The products were dried under a dynamic vacuum for 24 h.

The same procedure was used for the copolymer/M-Na synthesis at feed ratio from (50/50) (*o*ABA/ANI), keeping always the concentration of the aniline units equal to 0.22 M (aniline units come from ANI and *o*ABA).

### 2.4. Characterization

Fourier Transform Infrared (FT-IR) spectroscopy (Bruker Alpha) of the nanocomposites, in the transmission mode. The dry PoABA and ground into powders in a mortar with a pestle. The scanning

was performed with from 4000 to 400 cm<sup>-1</sup> for 64 times with a resolution of 4 cm<sup>-1</sup>.

The sample preparation for wide angle X-ray diffraction (XRD) was similar to that of Fourier transform infrared (FT-IR). The X-ray diffraction of the powder nanocomposites were taken using a Bruker CCD-Apex equipment with a X-ray generator (Cu K $\alpha$  and Ni filter) operated at 40 kV and 40 mA.

X-ray fluorescence (XRF) spectroscopy of the powder nanocomposites was made using a Philips PW1480 equipment with a UNIQANT II software to determine elements in a semi quantitative way.

The XPS spectra were measured with a VG-Microtech Multilab electron spectrometer using non-monochromatised Mg K(1253.6 eV) radiation from a twin anode source operated at 300 W (20 mA, 15 kV). Photoelectrons were collected into a hemispherical analyser working in the constant energy mode at pass energy of 50 eV. The binding energy (BE) of the Cls peak at 286.4 eV was taken as internal standard. Peak analysis was done with mixed Gaussian/Lorentzian function lineshape by using the Peak-fit program implemented in the control software of the spectrometer. The pressure in the analysis chamber was always lower than  $2 \times 10^{-9}$  Torr. Thermal degradation of the samples does not occur because the time required to collect the XPS spectra is low. The XPS measurements have been performed in the PoABA/M-Na samples. That is, the polymer has not been separated from the catalyst.

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.

The electrochemical behavior of the polymers was studied by cyclic voltammetry after their extraction from the nanocomposites by dissolving in the *N*-methyl-2-pyrrolidone (NMP). It is known that this kind of conducting polymer is soluble in NMP [30], 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 immersed in the same electrolyte, respectively. The working electrode was prepared as follows: after the polymer was extracted from the nanocomposite using NMP, 50  $\mu$ l of this solution were cast over platinum disks and the solvent evaporated to create polymeric films. The electrolyte used was 1 M HClO<sub>4</sub> and all experiments were carried out at 50 mV/s.

## 3. Results and discussion

### 3.1. Fourier transform infrared (FT-IR)

Fig. 1, of the FT-IR spectra of PoABA/M-Na present similar bands as those reported for montmorillonite (M-Na) [31]. The characteristic infrared bands of M-Na present in polymer/M-Na are listed in Table 2. An additional band is detected in the low specters of montmorillonites mainly carbonates (band at 1664 cm<sup>-1</sup>) and quartz (bands at 798 cm<sup>-1</sup>) and a broad band of (O–H–O) at 3432 cm<sup>-1</sup>. The presence of kaolinite is justified by the band that appears at 3720 cm<sup>-1</sup> and by the band which appears around 695 cm<sup>-1</sup>. The vibration bands of (Al–OH) stretching at 3657 cm<sup>-1</sup> and deformation at 915 cm<sup>-1</sup> indicate that this clay is dioctahedral and are characteristic of dioctahedral smectite [32]. The bands 1552 and 1009 cm<sup>-1</sup> is characteristic of stretching vibrations (Si–O) network of clay. The deformation bands appear around 530 cm<sup>-1</sup> for vibrations (Si–O–Mg) (Fig. 2).

Regularly, the intercalation of a polymer with clay materials comes from the H-bonding of the amine with hydroxyl groups

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