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Deprotonation, Raman dispersion and thermal behavior of polyaniline–montmorillonite nanocomposites

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ABSTRACT

In this work, for the first time, the deprotonation, soxhlet extraction, and thermal behavior of intercalated polyaniline (PANI) into Montmorillonite (MMT) clay layers were investigated by resonance Raman, X-ray absorption near nitrogen edge spectroscopy (N K XANES), High-resolution transmission electron microscopy (HR-TEM), and DFT calculations. The presence of new segments in intercalated PANI (named *m*-JGB units) is observed in all PANI chains (including the oligomers). The heating behavior monitored by *in situ* resonance Raman and N K XANES data shows the degradation of *m*-JGB units and formation of Oxazine-like structures during heating in air of the intercalated PANI. The Raman data indicates lower formation of Oxazine-like rings in intercalated PANI compared to the free one. It shows that clay act as a thermal barrier and precludes the thermal decomposition of PANI.

1. Introduction

Polyaniline (PANI) and its derivates have been widely studied since their discovery [1–4]. This class of polymers exhibits photoconductivity, electroactivity and electrocromism and as consequence made possible their use in a myriad of devices, such as solar cells, displays, lightweight battery electrodes, electromagnetic shielding devices, anticorrosion coatings, and sensors. PANIs can be obtained by oxidative polymerization of aniline and its derivates in a media having very strong oxidants (such as $(NH_4)_2S_20_8$, etc.) and acids (HCl, H_2SO_4, HNO_3, etc.). The morphological and crystalline aspects of PANIs are strongly influenced by polymerization conditions. In fact, in a media containing surfactants that acts simultaneously as dopant and template the polymer backbone can be forced to a self-organization at the nanoscale level [5,6]. Recently, the polymerization of monomer (aniline or its derivates) separated from the oxidant by a liquid–liquid interface has been employed as facile way to obtain PANI nanofibers [7,8]. A better morphological organization is acquired due to changing of the polymerization reaction rate.

The electronic structure of PANIs can be modulated by changing the oxidation and/or protonation levels [1–3]. The emeraldine forms of PANI have more environmental stability and its conducting state can be reached by protonation (see Scheme 1 for y = 0.5). Others forms can be prepared by protonation/deprotonation and/or oxidation/reduction processes [1–3]. However, many studies have verified the presence of new segments, generally denominated phenazine and/or oxazine-like units in the structure of PANI prepared in different synthetic paths or submitted to an external treatment.

Chemical, thermal and electronic properties of PANIs having higher phenazinic content will be very different from the other PANIs [9–14]. Higher amount of phenazine and/or oxazine-like rings can be formed in PANI chains during heating, solvent treatment or synthesis in confined environments, such as clays or zeolites [15–17]. In addition, Do Nascimento et al. [13,18] and Stejskal et al. [9,10] have been demonstrated that the phenazine and/or oxazine-like structures are also important in the formation and stability of the nanostructured shape of PANI particles.

Up to now, great efforts have been done to optimize the synthetic route of the PANIs, in order to form nanostructured materials with controllable shape, particle size, morphology, and crystallinity. However the structure of phenazine and/or oxazine-like structures must be better investigated in order to understand the stabilities of nanostructured PANIs. Our group has been used mainly the resonance Raman technique in the determination of the backbone features of PANIs and its derivates, as poly-*para*-phenylenediamine [19] and poly-*ortho*-phenylediamine [20]. Presence of phenazinic and/or oxazinic segments was observed for all investigated PANIs with nanostructured morphology [13,14,18] or confined in nanocavities [15,16].

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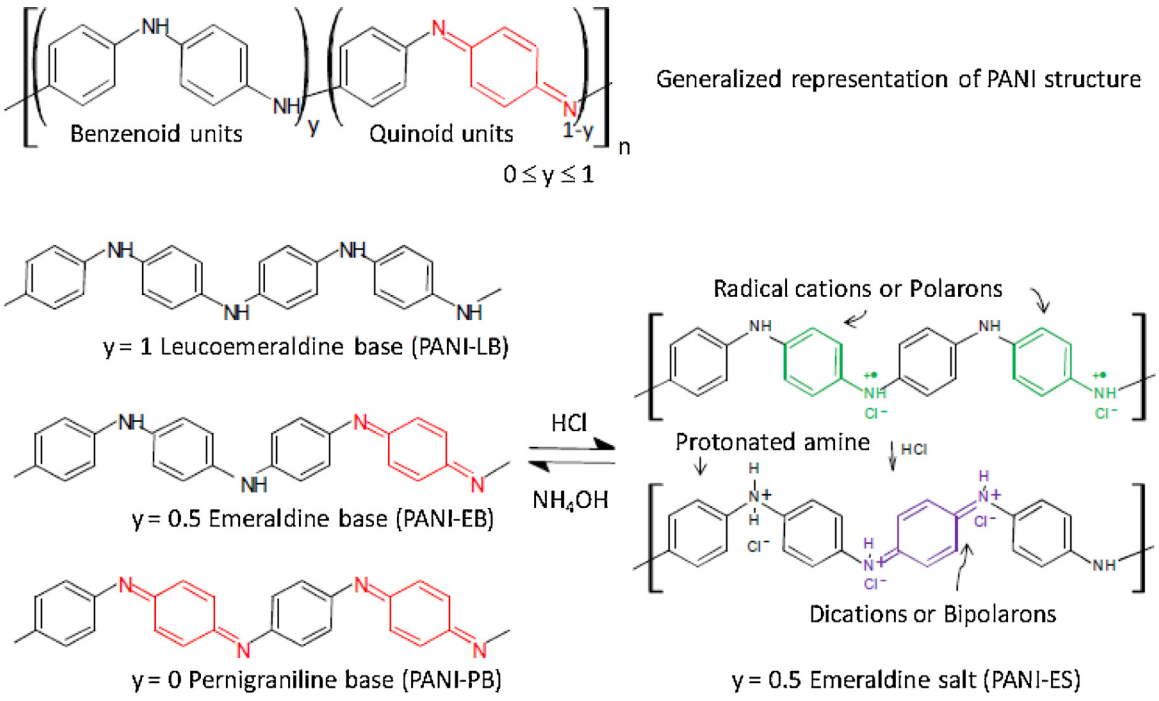

Scheme 1. Generalized representation of chemical structure of PANI and its most common forms.

In this work, for the first time, the neutralization, soxhlet extraction, and thermal behavior of PANI formed in Montmorillonite clay cavities are studied by *in situ* resonance Raman and UV–VIS–NIR spectroscopies. In addition, N K XANES spectroscopy and HR-TEM were also used for investigation of PANI-MMT after heating. All results are rationalized considering the presence of different phenazinic rings into structure of intercalated PANI.

2. Experimental part

2.1. Reagents

Aniline (Merck) was distillated under vacuum prior to use.

2.2. Preparation of standard PANI-ES

11.5 g of solid $(NH_4)_2S_2O_8$ (Merck) was dissolved in 200.0 mL of 1.0 mol L^{-1} of HCl aqueous solution and 20.0 mL of aniline was added in 300 mL of 1 mol L^{-1} of HCl aqueous solution [1,2]. Afterwards, the two solutions were refrigerated up to 2–5 °C in ice/water bath and mixed. After 1.5 h, a dark green solid was isolated by filtration, washed with 500.0 mL of 1.0 mol L^{-1} of HCl aqueous solution and dried in a desiccator.

2.3. Preparation of PANI-MMT composites

Swy2 Montmorillonite (MMT, from Clay Minerals Repository) was treated with sodium chloride and size fractioned to obtain homoionic Na^+-form free of main impurities. An aqueous suspension containing 2.6 g of Na^+-MMT in 100 mL was prepared and sonicated in ultrasonic bath for 1 h to promote interlayer swelling and clay exfoliation/delamination. A volume of 75.0 mL of Na^+-MMT suspension, and 25.0 mL containing 1 mol L^{-1} of camphorsulfonic acid, (−)HCSA (MERCK) aqueous solution and 0.5 mol L^{-1} of aniline were mixed under stirring at room temperature, and then 2.85 g of ammonium persulfate was slowly added to suspension. After 10 h a green solid was isolated by filtration (no washing of the composite was done after the isolation) and dried in desiccator.

2.4. Preparation of PANI-MMT composite by An^+-MMT polymerization

The important step of this procedure is the elimination of non-intercalated anilinium ions from An^+-MMT through exhaustive washing of the material with deionized water. Polymerization medium was an aqueous suspension of An^+-MMT at pH 2 and pH 5 (adjusted with HCl) and ammonium persulfate. After stirring for 12 h at room temperature, a dark green solid was isolated by filtration and dried in desiccator. The obtained CHN microanalysis of PANI-MMT there is 2.0 g of polymer/100 g of composite. A certain mass (see Table 1) of solid PANI-MMT was re-suspended in 25.0 mL of methanol under stirring. After 3–4 h of stirring, 10.0 mL of a methanolic solution having LiCl (1% w/w) was drop wise in the suspension and then was left under stirring for more 24 h [21]. During this, it exchanges between ions of the dissolved LiCl salt and the intercalated charged oligomers and polymers are expected.

Table 1
Values obtained from the Soxhlet procedure.

	PANI-MMT prepared at pH 2	PANI-MMT prepared at pH 5
m_1 = initial mass/g	0.1646	0.5000
m_2 = extracted mass/g	0.0435	0.0252
m_3 = final mass/g	0.1211	0.4748
Extraction yield/% $100 \times \left(1 - \frac{m_3}{m_1}\right)$	26.4%	5.04%