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Aniline-oriented polymerization over *nano*-SiO_2 particles

Wagner M. Picanço [a], Bianca de A. Feitosa [a], Noam G. da Silva [b], Greta T.A. Silva [b], Virgínia M. Giacon [c], Pedro H. Campelo [a, d], Sérgio M. de Souza [e], Kelson M.T. de Oliveira [b], Edgar A. Sanches [a, *]

[a] Laboratório de Polímeros Nanoestruturados (NANOPOL), Universidade Federal do Amazonas (UFAM), Manaus, AM, Brazil
[b] Laboratório de Química Teórica e Computacional, Departamento de Química, Universidade Federal do Amazonas (UFAM), Manaus, AM, Brazil
[c] Departamento de Engenharia Civil, Universidade Federal do Amazonas (UFAM), Manaus, AM, Brazil
[d] Faculdade de Ciências Agrárias, Universidade Federal do Amazonas (UFAM), Manaus, AM, Brazil
[e] Laboratório de Caracterização de Materiais (LabMat), Universidade Federal do Amazonas (UFAM), Manaus, AM, Brazil

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ABSTRACT

The goal of this paper is to report a systematic structural and morphological characterization of PANI-ES/*nano*-SiO_2 hybrid composite, which was synthesized in the bulk form by surface modification of *nano*-SiO_2 particles through *in situ* polymerization of aniline. The aniline-oriented polymerization was observed. XRD patterns of Polyaniline Emeraldine-salt form (PANI-ES) and PANI + *nano*-SiO_2 nanocomposite showed some differences. The intensities of peaks indexed as (1 1 0) and (4 3 0) decreased after polymerization in the nanocomposite form, while the intensities of the peaks (4 0 0), (0 0 1) and (0 3 0) remain unchanged. The unchanged planes are parallel to the unit cell axis and therefore parallel to the polymeric chains. This fact clearly indicates an oriented polymerization of aniline over the *nano*-SiO_2 particles. SEM images showed that the nanocomposite is made up of PANI-ES nanofibers deposited over the *nano*-SiO_2 particles. Furthermore, the PANI-ES morphology remains unchanged after polymerization in the presence of *nano*-SiO_2 particles. The theoretical quantum chemical calculations were performed to verify the effect of successive deposition of PANI on the regular SiO_2 surface. The participation of SiO_2, although weak, occurs in most of the vibrational modes. Furthermore, the MEPS of SiO_2 presents medium values of electrostatic potential, but of a mostly positive character, favoring the interaction with the polymer. The DC electrical conductivity of PANI-ES + *nano*-SiO_2 composite was found around 1.22×10^{-4} S cm^{-1} at 25 °C, which is 10% higher than pure polyaniline prepared under the same polymerization conditions. The better-aligned polyaniline chains over the *nano*-SiO_2 particles may improved the charge mobility along the polymer chains.

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1. Introduction

Polyaniline (PANI) has received great attention due to its range of electrical conductivity, chemical or electrochemical redox reversibility, good environmental stability, polar functional groups and ion exchange properties [1–3]. However, some technological applications of Polyaniline Emeraldine-salt form (PANI-ES) have been limited due to its low solubility and processability. For this reason, conducting polymer/inorganic hybrid materials have been extensively synthesized and represent important research topics [4]. Different methodologies to synthesize polyaniline-based inorganic nanocomposites have been developed for commercial applications [4,5].

Structural and morphological aspects in nanocomposite materials continue to be an interesting researched topic [6,7]. Hybrid composites composed of polyaniline and SiO_2 have been reported in the scientific literature. He et al. [8] have reported a strategy for preparation of functional SiO_2 nanofibers using post-electrospinning modification by *in situ* polymerization. Li et al. [9] have reported the properties of a polyaniline/nano-SiO_2 composite, which was prepared by surface modification of *nano*-SiO_2 particles using polyaniline. The authors have verified that *nano*-SiO_2 particles serve as the reaction core, and polyaniline macromolecules interacted on the surface of *nano*-SiO_2 particles. Liu et al. [10] have

* Corresponding author.
E-mail addresses: sanches.ufam@gmail.com, sanchesufam@ufam.edu.br (E.A. Sanches).

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synthesized semiconducting polyaniline nanoparticles through a solid-stabilized Pickering emulsion route using silica nanoparticles. Specific morphologies of the silica nanoparticle wrapped PANI particles were observed using electron microscopy. Nastase et al. [11] have explored the possibility of depositing polyaniline/silicon dioxide nanocomposite through a plasma polymerization route. Authors have verified that silica in the resulted polymer matrix changed the conduction mechanisms. Weng et al. [5] have reported gold decorated SiO_2/polyaniline core–shell microspheres (GDSP) synthesized by using silica spheres as core, polyaniline as shell, and $HAuCl_4$ as oxidizing agent.

A systematic structural investigation of the polymer molecular alignment, as consequence of the interaction between matrix and reinforcement was reported here. The evaluation of the molecular interaction between matrix and reinforcement using the Powder X-ray Diffraction Analysis (PXRD) data has not been reported in the scientific literature. For this reason, the ordered arrangement of the polymer chain and its interaction with the *nano*-SiO_2 reinforcement has been evaluated. Moreover, the goal of this paper is to report a systematic structural and morphological characterization of PANI-ES/*nano*-SiO_2 hybrid composite, which was synthesized in the bulk form by surface modification of *nano*-SiO_2 particles through *in situ* polymerization of aniline. *Nano*-SiO_2 particles were obtained from rice hull ash (RHA), an abundantly available waste material in rice-producing countries [12]. The synthesis method we have used here is very simple and has a great potential for commercialization. The PXRD technique was used to examine the long-range order produced as consequence of very short-range interactions, as well as to propose a mode of interaction between polymer chains and *nano*-SiO_2 particles in the nanocomposite form. The molecular geometries were fully optimized by the force gradient method using Berny's algorithm and the potential energy surfaces were characterized using standard analytical harmonic vibrational analysis. Scanning Electron Microscopy (SEM) was applied for the morphology evaluation. These results were then correlated with the DC electrical conductivity measurements.

2. Experimental

2.1. Nanocomposite synthesis

Nano-SiO_2 particles were obtained from rice hull ash (RHA) based on the method described elsewhere [13,14] with some modifications. Chloride salt of conducting polyaniline (PANI-ES) was synthesized by *in situ* polymerization in the presence of the recovered *nano*-SiO_2 (10% w/w). Two different solutions were prepared: Solution I was made by dissolving 2.16 g of hydrochloride aniline powder monomer and *nano*-SiO_2 in HCl (300 mL, 1.0 mol L^{-1}). Solution II was obtained by adding 3.42 g of APS in HCl (200 mL, 1.0 mol L^{-1}). Then, Solution II was added drop by drop to Solution I at room temperature. The system remained under constant stirring for 3 h. The PANI-ES/*nano*-SiO_2 hybrid nanocomposite was vacuum filtered and washed with acetone.

2.2. Powder X-ray diffraction analysis

XRD data were obtained in a PANalytical model Empryan diffractometer, operating with CuK_α, 40 kV and 30 mA. Powder diffraction patterns were obtained in the range $2\theta = 5–70°$, step of 0.02° and 5 s/step. The crystal parameters reported by Petkov et al. [15] (triclinic, P1; $a = 20.3170$ Å; $b = 10.9000$ Å; $c = 5.2000$ Å; $\alpha = \beta = \gamma = 90°$, and Konnert and Appleman [16] (triclinic, F1; $a = 9.932$ Å; $b = 17.2160$ Å; $c = 81.864$ Å; $\alpha = \beta = \gamma = 90°$) were used as input data for the aniline tetramer and *nano*-SiO_2 phases, respectively.

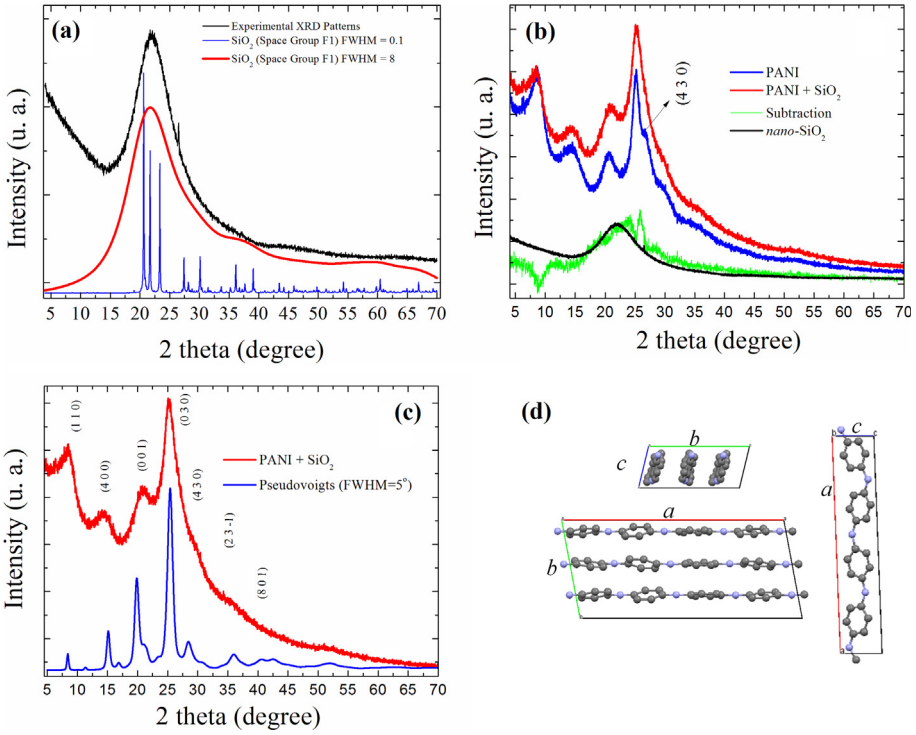

Fig. 1. (a) The PXRD of *nano*-SiO_2 phase (black curve); (b) The PXRD of PANI-ES and PANI + *nano*-SiO_2 nanocomposite in the blue and red curves, respectively; (c) The experimental PXRD of PANI + *nano*-SiO_2 composite (red curve) and the idealized PXRD of the modified Petkov's crystallographic information framework with FWHM = 5° and (d) The crystallographic information framework.

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