

Preparation of conducting polymers in organized systems

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Abstract

One way to obtain orientation of polymer chains is to grow them inside a structurally organized host framework. In this work we report on the preparation of nanocomposites by encapsulating polyaniline in three different hosts: (a) Tin IV 2-carboxyethyl phosphonate (lamellar host), (b) porous glass (Vycor – Corning 7930) and (c) sol-gel silica. The hosts and respective composites were characterized by X-Ray Diffractometry, Cyclic Voltammetry and Scanning and Transmission Electron Microscopy. Each organized host determined the growth of the conductive polymer and the results obtained confirm the enhanced molecular order of polyaniline chains.

Keywords: Conducting polymers; Composites; Template synthesis.

Preparação de polímeros condutores em sistemas organizados

Resumo

Uma maneira de obtenção de cadeias poliméricas orientadas consiste na síntese do polímero no interior de hospedeiros organizados estruturalmente. Neste trabalho reportamos a preparação de nanocompósitos por meio do encapsulamento da polianilina em três diferentes hospedeiros: a) 2-carboxietil fosfonato de estanho (IV) (hospedeiro lamelar); b) vidro poroso (Vycor-Corning 7930) e c) sílica sol-gel. Os hospedeiros e respectivos compósitos foram caracterizados por Difractometria de Raios X, Voltametria Cíclica e Microscopia Eletrônica de Varredura e Transmissão. Cada hospedeiro organizado determinou o crescimento do polímero condutor e os resultados obtidos confirmaram o aumento da ordem molecular das cadeias de polianilina.

Palavras-chave: Polímeros condutores; Compósitos; Sistemas organizados.

Introduction

Electronically conductive polymers (ECPs) have potential applications as electrode materials in batteries (Kaneto et al., 1982), electrochromic displays (Yoneyana et al., 1985) and molecular electronic circuit elements (Trackeray et al., 1985). In all applications, the ECPs must switch reversibly and rapidly between the conductive and the insulating states. This switching process requires that counter-ions be incorporated into (insulator-to-conductor transition) and subsequently expelled from the polymer film (conductor-to-insulator transition). In general, the rate of counter-ion diffusion within the polymer limits the overall rate of the switching process (Triverdi, 1997). Morphology determines the facility of ion-transport (Kaneto et al., 1982) and the most important consideration from a chemical viewpoint is that enhanced electronic transport is obtained if polymers with enhanced molecular and supramolecular order can be prepared (Lei et al., 1995). Polymers with enhanced molecular order contain fewer conjugation-interrupting defects,

such as sp³-hybridized carbons or twists and kinks in the polymer chain (Martin, 1995). One way to obtain orientation of the polymer chains would be to grow them inside a structurally organized host framework. The framework could be either three-dimensional (3D), with large oriented tunnels, or two-dimensional (2D), with accessible interlayer space. These compounds can undergo *chimie douce* reactions resulting in the incorporation of a guest species into their structure. The synthesis of these well-ordered systems has demonstrate a self-assembly process distinctive to the starting materials and conditions of the reaction (Ozin, 1992). In this work we also propose to use spatial restriction, by synthesizing the polymer in the empty spaces of three different hosts: (a) Tin IV 2-carboxyethyl phosphonate (α -SnP-C – lamellar host) (Maia et al., 1997), (b) porous Vycor glass (PVG – Corning 7930) (Maia et al., 1995), and (c) sol-gel silica film (Neves, 1999), both 3D – hosts. The properties of these (nano)composites were investigated by SEM, TEM, XRD and Cyclic Voltammetry.

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Experimental

The synthesis of the Tin IV 2-carboxyethyl phosphonate was made as described in the literature (Medeiros et al., 1992). The conductive emeraldine form of polyaniline was chemically synthesized in the interlayer space of α -SnP-C by exposure of the Fe (III) containing host, to an aqueous acid solution of aniline. The transition metal ion was previously intercalated in the host by ionic exchange (Maia et al., 1997).

The conductive emeraldine salt form of polyaniline was chemically synthesized in the pores of PVG using the following method (Zarbin et al., 1999): treated PVG plates (1.0 x 1.0 x 0.1 cm) was immersed for 2 h in 20 mL of a 2 Mol.L⁻¹HCl aqueous solution containing 7 mL of distilled aniline, at room temperature. After this time the glass was copiously washed with distilled water to remove the aniline adsorbed on its external surface, and immersed in a (NH₄)₂S₂O₈ acid solution (0,15 g of (NH₄)₂S₂O₈ in 20 mL of 2 mol.L⁻¹HCl aqueous solution).

Sol-gel solutions were prepared by mixing of tetraethyl ortosilicate (TEOS), 1,1,3,3-tetramethyl-1,3-diethoxydisiloxane (TMDES), methanol (1:1:2, w/w) and 0.3 mL of 0.15 M HCl. This solution was spin-coated (3.000 rpm) on an ITO glass plate and after evaporation of methanol a thin sol-gel film was obtained. The polymerization of PANi on silica sol-gel film was carried out in the potentiodynamic mode by cycling the potential from 0.1 to 0.85 V vs Ag|AgCl (15 cycles).

The samples were characterized by X-ray diffractometry (Shimadzu XD-3A, 2KCPS, $\tau_c = 2.35$

kV, 25 mA) and cyclic voltammetry in a three-electrode one-compartment cell. The reference electrode was a saturated calomel electrode (SCE), the counter electrode a Pt plate and the working electrode was an indium-tin oxide (ITO)-glass coated plate, modified with the composite. A PAR 263A potentiostat interfaced to a PC-computer was used.

The transmission electron microscopy data was obtained in a Zeiss IN 902 microscope, at 80 KV in the filament. The sample was crushed and a small amount of the powder was first suspended in water and allowed to settle for 15 min. Then a drop of the supernatant dispersion was placed onto a parlodium film supported by a copper grid. One layer of carbon was deposited on the samples by sputtering.

The scanning electron microscopy data were obtained in a JEOL JSM T-300 microscope, after coating the dispersed samples with gold by sputtering.

Results and discussion

The first evidence of the formation of the composite is the appearance of the green color in the all hosts, characteristic of the protonated emeraldine form of polyaniline. The emeraldine salt formation was confirmed by Raman, FTIR and UV-Vis-NIR spectroscopies of the samples (Maia et al., 1997; Zarbin et al., 1999), that show bands characteristics of the conducting form of polyaniline. The X-ray diffractograms of the host (α -SnP-C) and respective composite are presented in Figure 1 where a peak in the low angle region is characteristic of the host material ($2\theta = 6.07^\circ$).

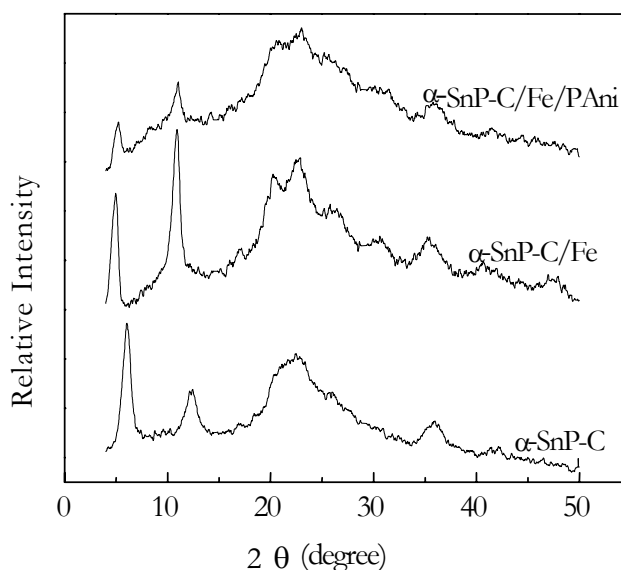


Figure 1 – X-ray diffractograms of the host (α -SnP-C), the host after reaction with FeCl₃ (α -SnP-C/Fe) and the respective composite (α -SnP-C/Fe/PAni)

A shift of this peak is assigned to changes in the interlayer distance, direction "c" perpendicular to the lamellae. The shift to lower 2θ values after the exchange reaction with iron indicates an increase in the interlayer distance ($2\theta = 5.02^\circ$) for the host containing Fe^{3+} . The interlayer distance of $\alpha\text{-SnP-C/Fe}$ is large enough to accommodate the polyaniline and after the formation of the composite there is a slight decrease in this distance.

Cyclic voltammetry experiments were done to

test the electroactivity of the $\alpha\text{-SnP-C/Fe/PAni}$ composite. The electroactivity of the pure host material deposited on the surface of a platinum electrode and in the same electrolyte was previously tested (Maia et al., 1999). It presents no redox process at the potential range studied. In Figure 2 we show the voltammogram of the composite obtained in aqueous LiClO_4 0.1 M/ HClO_4 0.1 M.

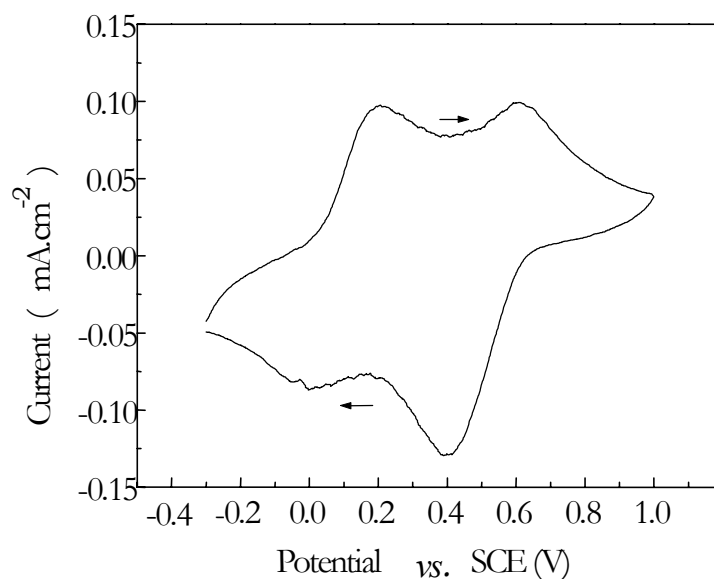


Figure 2 – Cyclic voltammogram of the composite $\alpha\text{-SnP-C/Fe/PAni}$. Electrolyte: 0.1 M HClO_4 / 0.1 M LiClO_4 ; scanning rate $50 \text{ mV}\cdot\text{s}^{-1}$

The voltammogram shows two well-defined reversible redox processes characteristic of polyaniline. These are assigned to oxidation and protonation of the polymer chain (Macdiarmid et al., 1987). At -0.20 V we have only amine ($\text{sp}^3\text{-N}$), indicating the presence of the leucoemeraldine form. As the potential increases, the imine ($\text{N}=\text{sp}^2$) concentration increases gradually and the first oxidation peak of the voltammogram appears at 0.16 V . In this case, the leucoemeraldine salt form is converted into the conductive emeraldine salt form (partially oxidized). During the second oxidation peak (at $\text{pH} = 1.0$, peak maximum at 0.65 V vs SCE) the conductive emeraldine salt form is transformed into the

non-conductive pernigraniline form (full oxidized). During the cathodic sweep, the compounds are formed in the reverse sequence.

The intermediate redox processes are assigned to *ortho*-coupling or to cross-linking (Geniès et al., 1998). The absence of this intermediate redox couple in the cyclic voltammogram of intercalated PAni is a strong evidence that the spatial restraint induces the formation of regular linear chains.

Similar evidences are obtained with the cyclic voltammogram of PAni/sol-gel silica composite. The scanning electron micrographs of the host matrix and respective composite are shown in Figure 3.

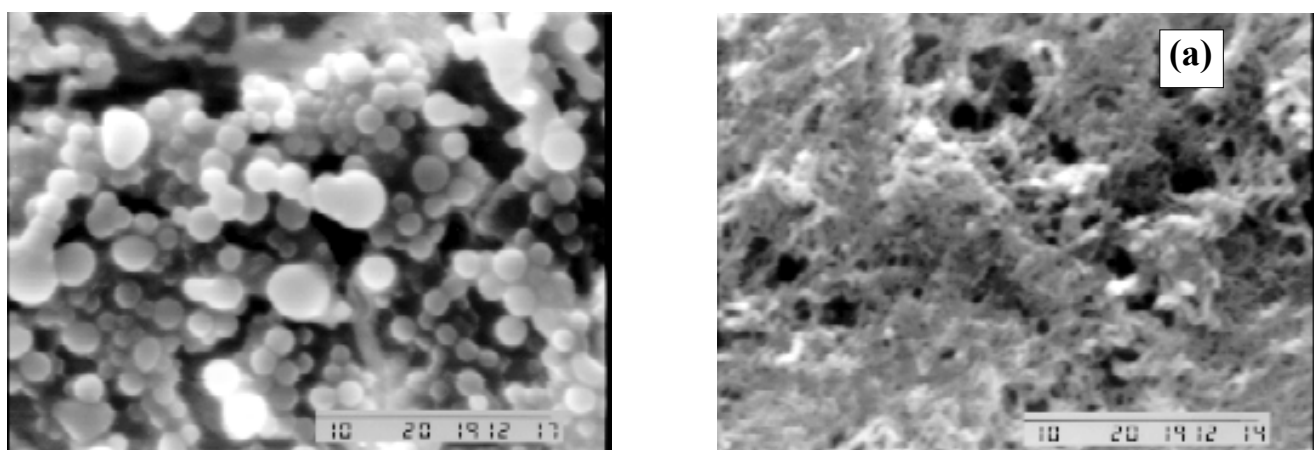


Figure 3 – SEM micrographs of sol-gel silica matrix (a) and PANi/sol-gel silica composite

A globular morphology of the silica particles in the film is determined by the presence of the cross-linking agent (TMDES). The oxidative polymerization process of aniline was conducted in an acid liquid medium which penetrates over the entire length of the interconnected pores of silica sol-gel film. When an electric potential scan is submitted the polyaniline grows from the pore bottoms, in contact with the substrate, through the silica film. By comparing the micrographs we observe the formation of polyaniline in the empty spaces of the silica matrix.

The distribution of the polyaniline inside the porous structure of PVG was studied by transmission electron microscopy. The porous structure of PVG is

quite different from that observed in the silica sol-gel matrix. In PVG the average pore diameter is 80 Å. This is sufficient to accommodate the polymer chains. Figure 4-a shows the TEM image for PVG/PAni nanocomposite, obtained with a $2.5 \cdot 10^5$ magnification. The presence of polyaniline filaments distributed with high organization in the glassy matrix is observed. These filaments have an average diameter of approximately 25 Å. The lower values observed in the diameter of the polyaniline filaments in PVG/Polyaniline indicates that each polyaniline fibril observed in Figure 4-a is formed by parallel aggregation of few polymer chains, and these high organization, represents an evidence the formation of polymeric wires in the bulk of the glassy substrate.

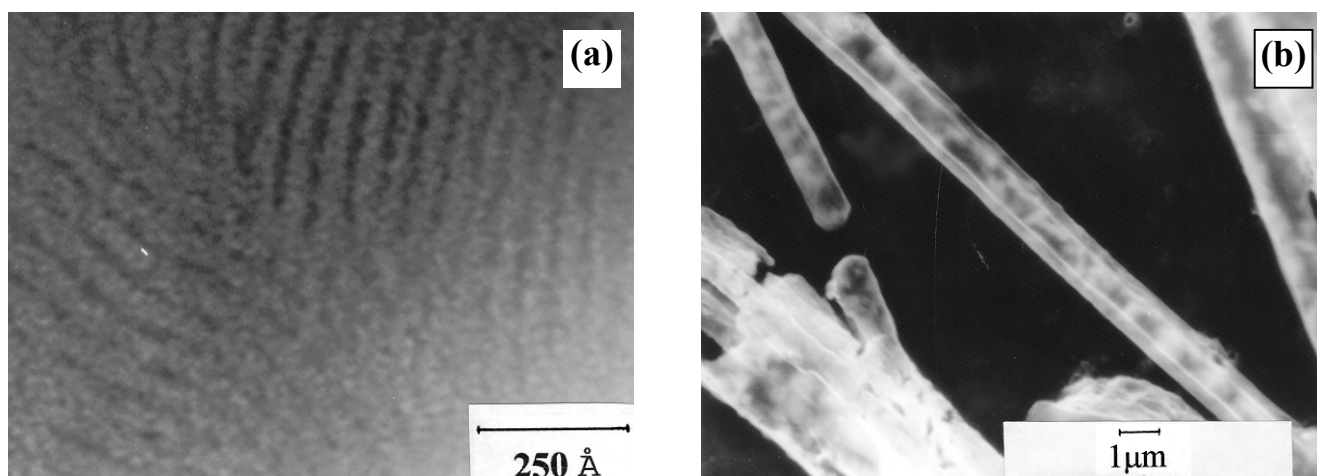


Figure 4 – (a) TEM micrographs of the nanocomposite PVG/polyaniline; (b) SEM micrographs of the polyaniline extracted from PVG nanocomposite with HF

When the PVG/PAni nanocomposite was treated with HF solution, the glassy matrix was dissolved yielding a dark green insoluble polymer, polyaniline emeraldine

salt, confirmed by FTIR and Raman spectra. Figure 4-b shows the image obtained by scanning electron microscopy of the HF extract and indicates that this

material is formed by highly organized polyaniline filaments, that presents a medium diameter of approximately 1 μm . This is much higher than the internal diameter of the PVG pores, indicating that when the PVG/PAni is treated with HF solution (and consequently the vitreous portion of the nanocomposite becomes soluble), the polymer wires begins to aggregate. Similar results were observed by De Vito and Martin (1998) who used an anionic surfactant as the dispersing agent to prevents aggregation process. The aggregation occurs in such a way to maintain the pre-organization conferred by the porous geometry, resulting in a material formed by polyaniline fibrils, with high organization and reduced diameters.

Conclusions

It is observed that the growing of a conductive polymer inside a structurally organized host framework provides a route for controlling the extent of molecular order of their chains. The nanocomposites obtained are proving to be useful materials for exploring the fundamentals of the conduction process in conductive polymers.

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