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PANI Conductivity: A Dependence of the Chemical Synthesis Temperature

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Summary: This work evaluated the influence of the synthesis temperature on the polyaniline (PANI) properties obtained by *in-situ* polymerization onto a poly (terephthalate) (PET) substrate. The residual mass of these syntheses was dried under vacuum, obtaining PANI powders for each temperature investigated. PANI/PET thin films and PANI powders were characterized by atomic force microscopy (AFM), field emission scanning electron microscopy (FEG-SEM), X-ray diffraction (XRD), ultraviolet-visible spectroscopy (UV-Vis) and four-point probe techniques. The UV-Vis results showed that the synthesized PANI presents the emeraldine oxidation state. By means of XRD technique, it was possible to verify that the PANI powders present crystalline form. The AFM and FEG-SEM techniques showed that the decrease in PANI/PET and PANI powders electrical conductivity with increasing of the synthesis temperature is related to the polymeric aggregates morphology.

Keywords: conductivity; *in-situ* polymerization; morphology; polyaniline; synthesis temperature

Introduction

The conductive polymers have attracted considerable attention due the scientific importance and great potential in technological applications. The polyaniline (PANI) is undoubtedly the conducting polymer that has been more extensively studied, mainly because of its physical-chemical, mechanical and electrical characteristics, which enable the development of innovative electronic devices.[1,2]

The PANI synthesis is usually chosen according to the application, in which this polymer will be used.[3] In this way, the PANI can be synthesized by chemical oxidation[4] or electrochemical[5] of aniline in acid medium, and the conventional chemical synthesis can be conducted using a variety of different oxidizing agents and acids. The synthesis conditions may influence the film properties that are strongly dependent on their microstructure and morphology. These properties are related to the presence of defects, reticulations, among other. There is an increasing in the search to obtain polymers with greater uniformity, stability, better chains organization, reproducibility and higher conductivity.[6–8] Synthesizing temperature is the most important factor influencing the structure of polyaniline. Polyaniline synthesized at a low temperature, usually shows higher conductivity, although the opposite effect has been reported by Lin *et al.* [9] and Adams *et al.* [10] In the present study the influence of chemical synthesis temperatures (0, 10, 20 °C) in the structures, morphology and conductivity of PANI/PET and PANI powders by UV-Vis, AFM, FEG-SEM, XRD and four-point probe techniques were evaluated.

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Experimental Part

Materials

Aniline ($C_6H_5NH_2$, Aldrich) was purified by distillation at 4 °C. Ammonium persulfate ($(NH_4)_2S_2O_8$), sodium hydroxide (NaOH), cloridric acid (HCl, Merck), toluene (C_7H_8, Mallinckrodt) and methyl ethyl ketone ($CH_3COC_2H_5$, Synth) were used without pretreatment. Water was purified to 18 $M\Omega^*$ cm^{-1} resistivity, using the Milli-Q system (Millipore Inc.). The substrate polyethylene terephthalate (PET) (Nashua XF-20,) and the toner (HP LaserJet).

Preparation of PANI/PET and PANI Powders

The experimental procedure used for obtaining HCl-doped PANI thin films is described by Manzoli *et al.*[11] In the present work, the PANI/PET films were deposited on PET substrates by *in-situ* polymerization.

PANI powders were obtained by filtration of the reaction products from *in-situ* chemical synthesis used in the PANI/PET preparation. After filtration, the powders were dried in oven. All PANI powder measurements were performed from pellets with the same physical dimensions, which were obtained using 5 ton. The influence of the synthesis temperatures (0, 10 and 20 °C) in the conductivity, structure and morphology of the PANI films and powders were evaluated.

Characterization

The characterization of the PANI film on PET substrate (PANI/PET) and powders (PANI powder) was performed by Dimension V (Veeco) AFM, using a pyramidal silicon nitride tip attached to a cantilever with a spring constant of 42 $N\,m^{-1}$, in tapping mode at a scan rate of 1 Hz. The images were processed and the thickness of PANI/PET interface was calculated with Gwydion© 2.1 data analysis software (Version 2.18, November 2008). The structural evaluation of the PANI/PET and powders was realized by X-ray diffraction (XRD) with Shimadzu instrument (Lab X XRD-6000 model) at 30 kV and 30 mA, Cu Kα radiation in step-scanning mode, using a step width of $0.01°\,s^{-1}$ and a fixed time of 5 s. The electrical conductivity was obtained by four-point probe technique, using a voltage-current source Keithley model 236 programmable, connected to a device for measuring conductivity of Signatone containing four equidistant points online. The UV-visible spectra were performed in a spectrophotometer Shimadzu (model UV-1601PC) from 400 to 900 nm. The topographical images for PANI powder surfaces were obtained by field emission scanning electron microscopy (FE-SEM) in equipment JEOL, JSM-6701F model.

Results and Discussion

PANI electronic transitions provide important information about HCl-doping effectiveness. In this way, the PANI/PET and PANI powder samples obtained at different synthesis temperatures were analyzed under UV-Vis radiation (Figure 1a–b). In these spectra two characteristic bands of conducting polymers are observed around 420 and 800 nm related to the polaron absorptions and poly (semiquinone) radical cations, respectively.[12,13] According to the literature,[14] the presence of these bands (420 and 800 nm) is characteristic of the HCl-doped PANI, indicating the doping efficacy. No significant alteration was observed in the band wavelengths in the 1a–b, indicating that all HCl concentration used during the synthesis process acted as dopant in the PANI structure, since the polaron bands spectra were maintained in the same wavelength.

PANI structural characterization in a long and medium order in the crystalline lattice was realized by XRD (Figure 2a–c). By analysis of the 2a–b, it was possible to verify the presence only of the PET substrate diffracted peaks according to Nasef,[15] which can be visualized in the region of approximately 8 to 55°. The more intense PET reflection ($2\theta = 5$ to $35°$) correspond to the PANI diffracted peaks

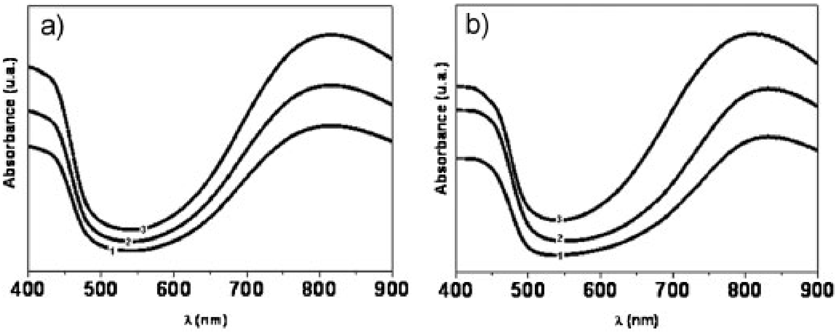

Figure 1.
UV-Vis Spectra (a) PANI/PET and (b) PANI powder at different synthesis temperatures: (1) 0 °C, (2) 10 °C e (3) 20 °C.

region, suggesting an overlap of the PANI peaks by PET peaks.

In Figure 2c are shown the XRD patterns characteristic of the HCl-doped PANI,[16,17] indicating that PANI powders are polycrystalline and present a single PANI-HCl phase. This result is in agreement with the UV-Vis spectrum (Figure 1a–b) that indicates PANI-HCl phase formation.

In order to evaluate the synthesis temperatures influence in the PANI-HCl powders crystallization, it was calculated the crystallinity degree from XRD patterns (Figure 2) based on Teixeira *et al.*[18] The obtained values for crystallinity degree were 66.3, 62.8 and 63.0% at 0, 10 and 20 °C, respectively. This result suggests that the synthesis temperature do not present

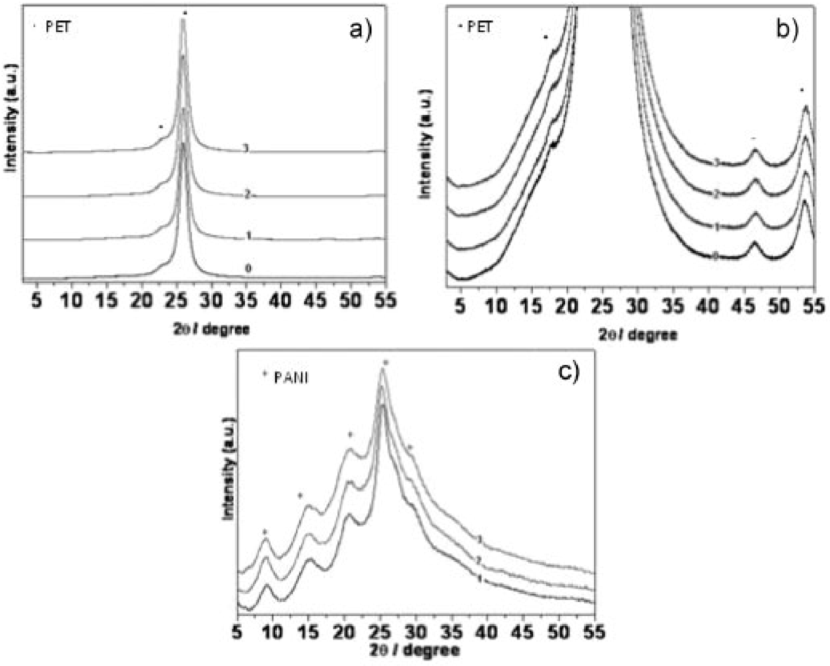

Figure 2.
X-ray diffraction patterns: (a) PANI/PET, (b) PANI/PET high magnification (c) PANI powder. PANI films and PANI powders in different synthesis temperatures: (0) PET substrate without synthesis thermal treatment, (1) 0 °C, (2) 10 °C, (3) 20 °C.

significant influence in the PANI crystallization process.

Roughness values and electrical conductivity for PANI/PET and PANI powders are described in Table 1. In this table, it can be observed that the PANI/PET and PANI powders present a reduction of the electrical conductivity with the synthesis temperature increasing. By analysis of the PANI/PET surface roughness (Table 1) and of the PANI/PET AFM images (Figure 3), it was observed that the roughness values increased with higher synthesis temperatures, suggesting a major homogeneity and ordering of the PANI grains in the PET substrate in lower synthesis

Table 1.
PANI/PET and PANI powders roughness and electrical conductivity at different synthesis temperatures.

Temperature (°C)	PANI/PET roughness (nm)	PANI/PET Conductivity ($S\,m^{-1}$)	PANI Powder Conductivity ($S\,m^{-1}$)
0	71.07 ± 5.01	219.00 ± 0.02	969.82 ± 1.03
10	82.47 ± 2.42	2.81 ± 0.27	285.39 ± 0.94
20	95.42 ± 4.53	0.15 ± 0.01	253.91 ± 0.72

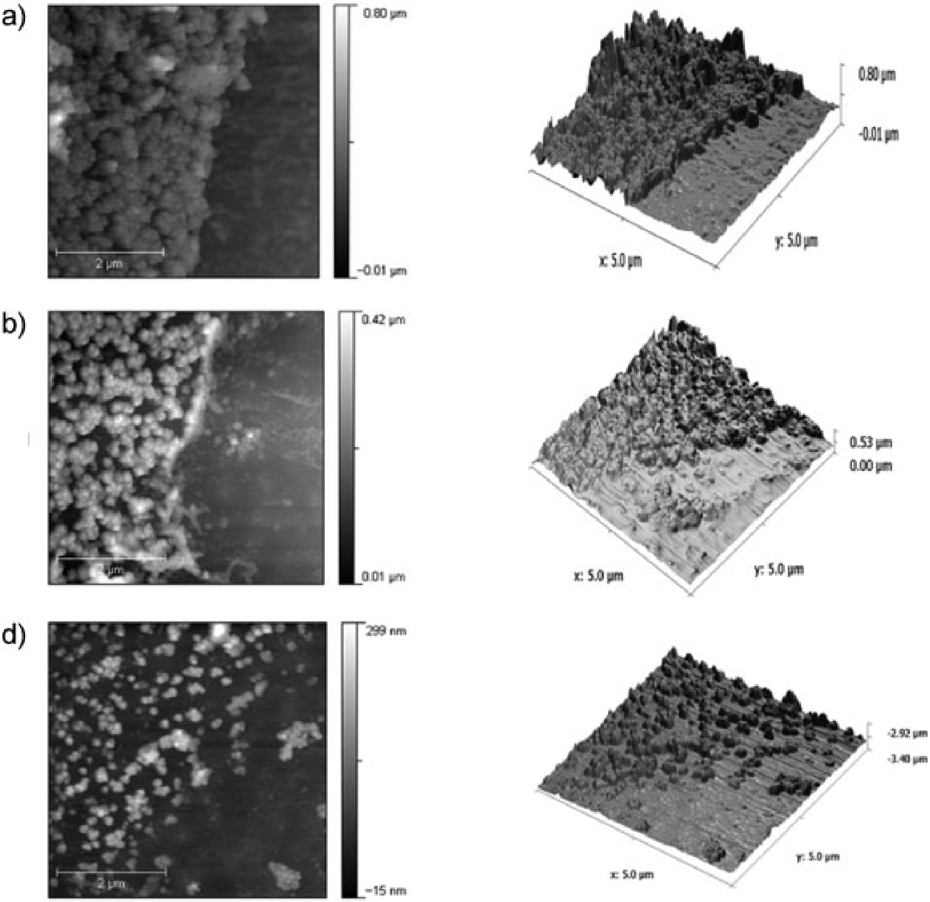

Figure 3.
AFM images in 2D and 3D of the PANI/PET at different syntheses temperature: a) 0 °C, b) 10 °C and c) 20 °C.

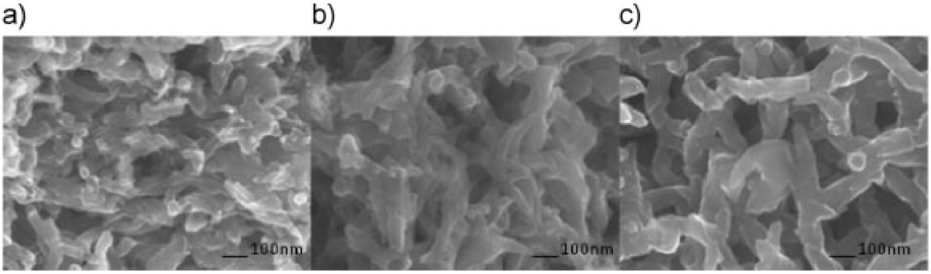

Figure 4.
PANI powders FE-SEM at different synthesis temperatures: a) 0 °C, b) 10 °C and c) 20 °C.

temperatures. It is known in the literature[19] that lower synthesis temperature lead to a slower polymerization, favoring the formation of larger and more ordered polymeric aggregates. According to Mattoso *et al.*[20] more ordered molecularly polymeric aggregates present few defects that disrupt the conjugation of the polymer chain, leading to higher conductivity. It was possible to observe the same behavior of electrical conductivity for the PANI powders. The XRD results showed that the crystallinity degree values remained practically constant with synthesis temperature increasing, indicating that the PANI crystallinity is not the major responsible by the conductivity value variations (Table 1).

Significant differences can be observed for the PANI powders morphology (Figure 4) in the synthesis temperatures. By analysis of these figures, it can be observed an increase of the distance between the polymeric aggregates with synthesis temperature decreasing. In this way, an improvement compaction of the polymeric aggregates occurs, which can be the responsible by the conductivity improvement with the synthesis temperature diminishing.

Conclusion

In this work, it was possible to verify the synthesis temperature effects on the PANI/PET and PANI powders structure, morphology and conductivity. The XRD and UV-Vis results indicated PANI-HCl phase formation. The PANI-HCl powders crystallinity degree values showed that the crystallization process was not significantly influenced by the synthesis temperatures of 0, 10, 20 °C. The PANI/PET and PANI powders electrical conductivities were strongly influenced by films and powders morphology, decreasing electrical conductivity with increase of the synthesis temperatures. The possibility of manipulation of the material size and shape is of great importance for a better use of conductivity property, thus extending its applications.

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