

# Synthesis and Electroactivity of Polystyrene/polyaniline Core-shell Composites

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**Abstract** - Series of polystyrene/polyaniline core-shell composites were synthesized by adding reactive surfactant anilinium dodecylsulfate (DS-AN) as the monomer of polyaniline. DS-AN conversion to polyaniline was calculated by thermogravimetric analysis. Electron microscopy (high-resolution mode) showed that the conductive polymer was deposited over the polystyrene cores in the form of thin coatings. Composites electrical conductivity, determined by the 4-probe method, was in the range  $10^{-6}$ – $10^{-2}$  S cm<sup>-1</sup>. The percolation-tunneling mechanism, according to the curve of conductivity (S cm<sup>-1</sup>) versus polyaniline (wt%), was the electron transfer mechanism. Finally, all the composites were electroactive, as shown by cyclic voltammetry.

**Keywords:** Conducting polymer, Core-shell composite, Inverse surfmer, Polyaniline, Surfmer

## 1. Introduction

Conducting polyaniline (emeraldine base salt) has been commonly mixed with thermoplastic polymers to overcome processability limitations of polyaniline (PAni) derived of its infusibility and poor solubility in common solvents. PAni/thermoplastic composites are quite popular because, depending on the thermoplastic matrix, conducting composites with different attributes can be obtained. Colloidal PAni/thermoplastic core-shell composites are a particular form to produce conducting composites. This kind of arrangement allows controlling composite morphology and composition. Among the wide variety of combinations with thermoplastics, the polystyrene/polyaniline core-shell composites have been widely reported. In these studies, the strategy to deposit the shell of polyaniline has been greatly varied. For instance, Barthet et al. (1998) synthesized PAni-coated polystyrene latexes. Nonuniform PAni coatings were obtained using conventional aniline polymerization conditions (aniline monomer, ammonium persulfate, 1.2 M HCl at 25 °C). In contrast, more homogeneous PAni coatings were obtained when polymerizing aniline hydrochloride at 0 °C in water. Yang and Liao (2009) developed a methodology for fabricating nanostructured PAni films from polystyrene/PAni core-shell particles. Results showed that due to their large surface area and porosity, the films response was fast to different conditions, especially to dry gas flow and ethanol vapor.

In this study, we have used anilinium dodecylsulfate (DS-AN) as a precursor of conducting polyaniline to synthesize series of polystyrene/polyaniline core-shell composites. In particular, the characterization of electroconducting and electroactive properties was of great interest, as an intermediate step towards potential and practical applications; i.e., in chemical sensor design. DS-AN represents as a new concept of reactive surfactant or surfmer, as its functionality lies on the anilinium group and not on the polymerizable carbon-carbon double bond. This feature greatly distinguishes DS-AN from the traditional surfmer concept (Lacroix-Desmazes and Guyot, 1996). However, the intention is similar that DS-AN performs as a surfactant and as a monomer of polyaniline.

## 2. Experimental Section

### 2.1 Core-shell Composites

Polystyrene/polyaniline core-shell composites were synthesized as follows: First, polystyrene core was synthesized by conventional emulsion polymerization using DS-AN ( $20 \text{ mmol dm}^{-3}$ ) as the stabilizer, and 2,2'-azobis(2-methylpropionamide) dihydrochloride ( $0.00184 \text{ mol dm}^{-3}$ ) to launch free radical polymerization. Second, polyaniline shell was obtained via oxidative polymerization. In this stage, extra amount of DS-AN was added as the monomer of polyaniline. Ammonium persulfate (APS) was used as the oxidizing agent at a molar ratio of 1.2:1.0 (APS:DS-AN).

### 2.2 Characterization

#### 2.2.1 Electron Microscopy

Scanning electron microscopy in transmission mode (STEM) was performed in a field emission electron microscope (JSM-7401F; JEOL) at 30KV. To prepare the samples, two drops of latex were dispersed using sonication for 5 min in 30 mL of tridistilled water. Subsequently, a drop of latex was placed and left dry on a holey-carbon-cooper grid.

#### 2.2.2 Composite Thermal Stability

Composites thermal stability was characterized using a thermogravimetric analyzer (SDT Q600, TA Instruments). The evaluations were performed under air atmosphere at a heating rate of  $10 \text{ }^\circ\text{C min}^{-1}$ .

#### 2.2.3 Electroactivity

Cyclic voltammetry (CV) was performed using a potentiostat analyzer (model 1260 plus 1287, Solartron). Electrochemical measurements were performed in a standard three-electrode cell at room temperature, using Pt wire (area= $0.03 \text{ cm}^2$ ) as the counter electrode, and Ag/AgCl/saturated KCl as the reference electrode. The working electrode was a Teflon cylinder packed with carbon paste, with a copper wire inserted through one end of the cylinder. The sample of dried composite was deposited on the opposite end to copper wire. The electrolyte was a sulfuric acid ( $\text{H}_2\text{SO}_4$ ) solution  $0.1 \text{ mol dm}^{-3}$ . All cyclic voltammogram were recorded at a scan rate of  $50 \text{ mV s}^{-1}$  by sweeping the potential between  $-800$  and  $+1400 \text{ mV}$  against Ag/AgCl reference electrode.

## 3. Results and Discussion

Series of composites corresponding to proportions of 6, 10, 15, 20, 30, or 40 wt% DS-AN, with respect to polystyrene content, were synthesized. The final products of this stage were green-stable dispersions. Fig. 1(a-d) portraits micrographs of pure polyaniline, pure polystyrene, and core-shell composites synthesized with 6 and 40 wt% DS-AN. Pictures with the lowest and the highest concentrations of DS-AN were only included since no visual differences among the composites were observed. The polyaniline (PAni) obtained from DS-AN is usually observed in the form of large agglomerations of semispherical and elongated particles with variable dimensions. The polystyrene particles, on the other hand, are well-defined spherical particles with diameters in the range of 80 nm and evident narrow polydispersity. Concerning the core-shell composites, no appreciable change in the particle size, with respect to the control of polystyrene or among themselves, was observed. Progressive surface deformation with the increment of DS-AN was observed.

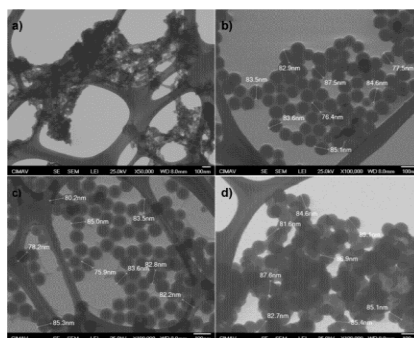


Fig. 1. Micrographs of TEM. a) PANi, b) Polystyrene, c) Polystyrene/PANI 6 wt% DS-AN, and d) Polystyrene/PANI 40wt% DS-AN.

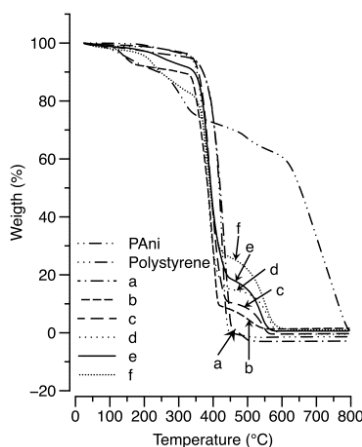


Fig. 2. Particles size distribution of the polystyrene/PANI core-shell composites.

As a complementary technique to characterize core-shell microstructure and composition, thermogravimetric analysis (TGA) was performed. The traces of polystyrene core, pure polyaniline obtained with DS-AN via oxidative polymerization, and the different core-shell composites are shown in Fig. 2. As noted, the core-shell composites presented clear combination of pristine polymers profiles, with more similarity to polystyrene at lower concentrations, and to PANi at higher concentrations. In particular, the transition observed at ca. 350 °C, associated to PANi backbone degradation (Orata and Buttry, 1987), is perfectly observed in all the composites (ca. 450°C), and is associated to the proportion of PANi in the composite.

Cyclic voltammetric (CV) was used to determine PANi electroactivity. Fig. 3 shows voltammograms of core-shell composites recorded at sweep rate of  $50 \text{ mV s}^{-1}$ , in  $0.5 \text{ M H}_2\text{SO}_4$  aqueous solution. In general, the composites exhibited two oxidation peaks and a reduction peak corresponding, respectively, to leucoemeraldine/emeraldine, and emeraldine/permanganiline redox transitions. The first oxidation peak, at 200 mV, was attributed to the oxidation of the fully reduced polyaniline (leucoemeraldine) to the radical cations (emeraldine salt). Whereas the second oxidation peak, at 640 mV, was attributed to the oxidation of the radical cations (emeraldine salt) to permanganiline, accompanied by the exchange of protons, and *vice versa* for their corresponding reduction peaks. In addition, the anodic peak, at 300 mV, represents the formation of benzoquinone (permanganiline).

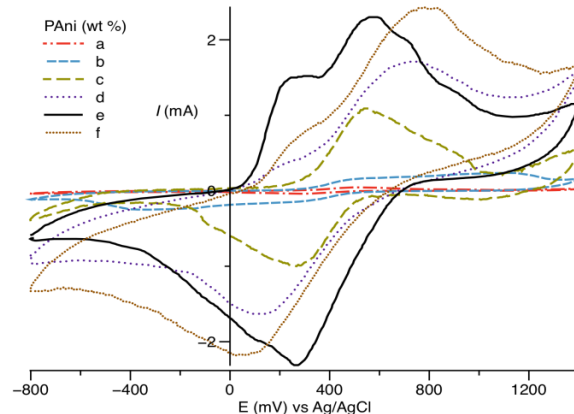


Fig. 3. Voltammograms of polystyrene/PAni composites. a) CPAni 3.3, b) CPAni 8.0, c) CPAni 13.3, d) CPAni 18.7, e) CPAni 26.7, and f) CPAni 37.3.

The voltammetric behavior was similar to those obtained for substituted polyanilines (Lin and Chen, 2000). The anodic and cathodic potential values corresponding to the first and second peaks, obtained from the voltammograms for different composites. Hosseini and Entezami (2001) reported the cyclic voltammograms of PAni/polystyrene blends, which presented two redox couples for oxidation potentials (425 mV, and 770 mV) and reduction (500 mV, and -150 mV).

#### 4. Conclusion

We successfully applied reactive surfactant DS-AN as the monomer of polyaniline to synthesize polystyrene/polyaniline core-shell composites via oxidative polymerization. Several analytical techniques gave evidence of polyaniline presence in the composites. According to electron microscopy, polyaniline was deposited on the polystyrene cores as a thin conducting layer, as shown by the low contribution of the polyaniline shells to the overall core-shell composite diameters, differently from several reports. From electroactive properties we believe that it is possible to develop, based on the composites nature, materials with piezoresistive response for sensor design.

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