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Synthesis and measurement of the optical and electrical properties of polyaniline and polypyrrole thin films

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In this work we report experimental results for resistive and optical changes that have intrinsically conducting polyaniline and polypyrrole polymer films, produced by the modification of synthesis parameters, such as the monomer volume and the initiator and dopant molar concentrations.

Keywords: Conducting polymers; specific resistance; electrochromic film.

En este trabajo se reportan los resultados experimentales para cambios resistivos y ópticos que realizan intrínsecamente la polianilina y polipirrol polímero películas, producido por la modificación de los parámetros de síntesis, tales como el volumen de monómero y el iniciador y dopante concentraciones molares.

Descriptores: Polímeros conductores; resistencia específica; películas electrocrómicas.

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1. Introduction

Conduction in materials is achieved from the free movement of electrons within; unlike metals, polymers are macromolecules formed by covalent bonds of small structures (monomers) that are repeated throughout the molecule. The electrons that form the bonds in the polymer are located and associated with a couple of atoms inside the molecule and therefore they cannot move. This is the reason why most polymers are insulators. When the bonds along the polymer chain are alternating single and double bonds, the structure becomes made of conjugated double bonds. Conjugated systems can be present in linear chains and also in aromatic rings. This type of structure is characteristic for conducting polymers.

Two ingredients are essential in order to obtain a conducting polymer: conjugated double bonds and a doped structure. The single and double bonds forming the conjugated structure of these macromolecules may shift between them (they are in resonance), providing the electrons with a considerable degree of free movement, but not so high as to become conductive.

For the polymer to be really conductive, the conjugated electronic structure must be disturbed by removing or adding electrons, through oxidation or reduction reactions, respectively. This process is known as doping [1].

Thus, the first conducting polymer, doped polyacetylene, was obtained by the oxidation of the polyacetylene chain with iodine vapor, increasing its original conductivity by 109 times [2]. Among the known conducting polymers, we have polyacetylene, polyaniline (PANI), polyphenylenevinilidene (PPV) and polypyrrole (PPy) [3,4] that can be doped in order to obtain a significant increase in their conductivity. For this reason in this paper we study the variation in key physical properties, such as optical absorbance and electrical conductivity, due to changes of the synthesis parameters of polyaniline and polypyrrole thin films.

2. Experimental

The synthesis and preparation of polyaniline films in its conductive state (emeraldine salt) and polypyrrole was carried out by the chemical bath method [5]. In the starting synthesis procedure, we added 0.25 ml of the aniline monomer and 15 ml of a 2.0 M HCl aqueous solution, under stirring, at room temperature (25°C). After the monomer drops were completely dissolved in acid solution, we added 30 ml of a 0.1 M ammonium persulfate, (NH₄)₂S₂O₈, aqueous solution.

For the synthesis of polypyrrole, we added 0.20 ml of the pyrrole monomer, to 15 ml of a 1 M HCl aqueous solution and afterwards 30 ml of 0.1 M ammonium persulfate, (NH₄)₂S₂O₈, aqueous solution. For the synthesis of polypyrrole, we added 0.20 ml of the pyrrole monomer, to 15 ml of a 1 M HCl aqueous solution and afterwards 30 ml of 0.1 M (NH₄)₂S₂O₈ to initiate the polymerization of the monomer. Subsequently, the glass substrates, washed with deionized water, were introduced into the previously prepared chemical solution. About a few minutes later, the polymer began to deposit on the glass substrate, forming thin black-color films of polypyrrole and blue-color films of polyaniline (polyaniline films became green at the end of chemical bath deposit time, of about 1 hour). Coated glass substrates (2.5 cm width and 5.0 cm length) were then washed thoroughly with distilled water and dried. These conditions were the basis for carrying out the following changes of the synthesis parameters [6]. For polyaniline, we varied the volume of the monomer: 0.1, 0.15, 0.20, 0.25, 0.30 and 0.35 ml. The concentration of the (NH₄)₂S₂O₈ oxidizing agent aqueous solution was also varied: 0.005, 0.01, 0.05, 0.1, 0.2 and 0.3 M. For polypyrrole, changes were made...
to the monomer volume: 0.15, 0.20, 0.25, 0.30, 0.35 and 0.40 ml and the (NH$_4$)$_2$S$_2$O$_8$ aqueous solution concentration: 0.005, 0.01, 0.03, 0.05, 0.1 and 0.3 M. Finally, for both polymers, we varied the dopant HCl aqueous solution concentration: 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 M.

The optical absorption visible light spectra of the prepared films were taken with an Ocean Optics S-2000 spectrophotometer within a 400 to 750 nm wavelength range. Absorbance variations at different synthesis conditions were recorded at 490 nm wavelength for polyaniline and at 600 nm for polypyrrole.

We measured the specific electrical resistance of the synthesized polymer films by the four probes method, using a Keithley 2001 multimeter and the van der Pauw technique. This technique is widely used to determine the resistivity and the Hall mobility of flat samples; it is based upon a mapping theorem and can be extended to anisotropic media [5,7]. For completing the measurement method, we built the system for determining the specific resistance of the films employing a stable power ac supply [8], shown in Fig. 1.

The XR-2209 voltage controlled oscillator provides a signal, which is applied to the operational amplifier, therefore providing a stable ac current output source, which is then directly connected to the thin film. The film electrical connection settings required by the technique are shown in Fig. 2. By the rotation of the connections of the power supply and voltmeter, we can separately measure $R_{ab,cd} = V_{dc}/I_{ab}$ and $R_{bc,da} = V_{ad}/I_{bc}$. In order to measure the current and voltage, we used the National Instruments USB-6218 data acquisition card with ±0.05 µA and ±0.05 mV accuracy. Each set of measurements was taken averaging three results with a ±2σ uncertainty. According to the van der Pauw technique [7], the specific resistance of a sample with uniform thickness d, can be calculated from:

$$\rho = \pi \frac{R_{ab,cd} + R_{bc,da}}{2} \frac{f}{\ln 2} \left( \frac{R_{ab,cd}}{R_{bc,da}} \right).$$  \hspace{1cm} (1)

Where $f$ is defined as a solution of:

$$\left( \frac{R_{ab,cd} - R_{bc,da}}{R_{ab,cd} + R_{bc,da}} \right) = \frac{f}{\ln 2} \arccos \left( \frac{e^{(\frac{\pi^2}{16})}}{2} \right).$$  \hspace{1cm} (2)

This alternative method can be extended in order to accomplish nonswitching van der Pauw measurements, using two different modulating frequencies [9].

3. Results and discussion

Changes in the physical properties of polyaniline and polypyrrole films shown in Figs. 3 to 8 correspond to the experimental results of the specific resistance, R, and absorbance, A.

Figure 3 shows that the polyaniline film conductivity tends to increase as the monomer synthesis volume increases, from 0.15 to 0.3 ml. Within the same interval, the optical absorbance tends to increase together with the electrical conductivity. The maximum conductivity is attained at a 0.3 ml aniline volume and there is a sharp decrease of conductivity when the aniline volume is further increased (0.35 ml).

In Fig. 3 we observe that the point of highest conductivity of the polyaniline films relates to a high point in absorbance, but at the highest point of absorbance corresponds to a relatively lower absorbance.
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Figure 4. Specific resistance and absorbance of polypyrrole films prepared with different amounts of monomer.

Figure 5. Polyaniline films prepared with different \((\text{NH}_4\text{)}_2\text{S}_2\text{O}_8\) molar concentration.

Figure 6. Polypyrrole films prepared with different \((\text{NH}_4\text{)}_2\text{S}_2\text{O}_8\) molar concentration.

Figure 7. Polyaniline films prepared with different HCl molar concentration.

The conductivity state due to a significant shift in the wavelength of the maximum absorbance. As with polyaniline films, for varying amounts of monomer, the high conductive states of the polypyrrole films in Fig. 4 are related to points of high absorbance, whereas the lower conductive state corresponds to a decrease in absorbance. Also, at the point of highest pyrrole volume there is a shift of the maximum absorbance wavelength. Polyaniline films show a color change (Fig. 9) that ranges from intense light green for the polyaniline film with the least amount of monomer, to dark green, due to the gradual change towards the state of higher conductivity [10], which is evident by the corresponding decrease of the measured resistance. In the case of polypyrrole (Fig. 10), we appreciate a color change from dark brown to intense blue, corresponding to the highest monomer amount, indicating the shift towards a lower state of conduction, as confirmed by the measured resistance.

In Figs. 5 and 6, showing the specific resistance and the absorbance of the polymer films prepared with varying amounts of oxidizing agent, the states of high conductivity are related to points of high absorbance whereas low conductivity states show a reduction in absorbance. For polyaniline, there is a gradual change in color (Fig. 9), ranging from blue and gray at the lowest and at the highest \((\text{NH}_4\text{)}_2\text{S}_2\text{O}_8\) concentration (extreme graph sides), passing through a deep green color along the intermediate points, corresponding to the region where we can obtain a conductive state. The conductivity is gradually lost towards the graph ends, as made evident by the change of color. For polypyrrole (Fig. 10), we can observe a color change from the initial dark brown to the gray-blue, at the point of maximum \((\text{NH}_4\text{)}_2\text{S}_2\text{O}_8\) concentration.

The last synthesis parameter studied was the concentration of the dopant (HCl). In Figs. 7 and 8 we can see a transition from low to high conductivity states and its relationship to a decrease of the absorbance, while varying the HCl dopant concentration, employed during the synthesis procedure. For the polyaniline films, we appreciate a change of color (Fig. 9) ranging from yellow-green for the lower HCl concentration to dark green for the high HCl concentrations. For polypyrrole, we observe the films color change, from yellow, for the lower HCl concentration, to dark brown, for higher HCl concentra-
We have been mentioning the color change of polymer films shown in Figs. 9 y 10. The change in coloration is related to the transition from a conductive to a non-conductive state (and viceversa) produced by chemical oxidation or reduction of the polymer films. This relationship between the electric properties and color is known as electrochromism.

The conductivity of polypyrrole films can be higher than that of polyaniline films; however, they may undergo a transition towards lower non-conductive states at some synthesis conditions.

4. Conclusions

Results obtained show the effect of three fundamental synthesis parameters (amount of monomer, oxidizing agent concentration, and doping agent concentration) on the specific resistance and on the visible light absorption spectra of polyaniline and polypyrrole films. Results also indicate the relationship between the conductive states of the films and their optical absorbance. The films absorbance follows the same trend (the trend to increase or decrease) as the electrical conductivity, at varying amounts of monomer and oxidizing agent employed in the synthesis procedure, whereas the absorbance and the electrical conductivity follow opposite trends when varying the doping agent concentration. Besides the effect of the synthesis parameters on the electrical conductivity and visible light absorbance, we can also relate those changes to the films color [11]. Such electrochromic performance involving multi-color changes is also related to shifts in the wavelength of the absorbance, due to the various protonic and oxidative states observed. The electrochromic behavior exhibited by polyaniline and polypyrrole films and by other conducting polymers is a property that can be used in several optoelectronic applications.

The change from the conductive state (oxidized) to the non-conductive (reduced) state of the polymer is reversible and is associated to the polymer redox (oxidation and reduction) properties. The results obtained can be useful for the optimization of the synthesis parameters of these polymer films, with potential application in chemical sensors and other devices [12,13].

APPENDIX

Abbreviations:

- $\rho$ resistivity ($\Omega \text{ m}$)
- $d$ film thickness (m)
- $f$ function of resistivity (adimensional)
- $R_{ab,cd}$ Resistance of a square ($\Omega$)
- $R_{bc,da}$ Resistance of a square ($\Omega$)
- $\sigma$ Standard deviation