Electrically Conducting Polyaniline-PBMA Composite Films Obtained by Extrusion

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ABSTRACT: Poly(n-butyl methacrylate) (PBMA)–polyaniline (PANI) composite films were obtained by extrusion by use of two methods: the first method consisted of polymerizing a thin layer of PANI, with Cl^- as dopant, on the extruded film of PBMA; the second method was based on blends of PBMA and PANI produced by the extrusion of the two polymers by using dodecylbenzene sulfonic acid (DBSA) as dopant. The thermal properties, electrical conductivity, and morphology of the composite films obtained were measured. The sensitivity of the composites films as detectors of hydrogen peroxide and ammonia was evaluated. The change in the electrical resistance on exposure to different aqueous solutions of these components shows a linear behavior.© 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 179–183, 2003

Key words: composites; conducting polymers; extrusion; sensors

INTRODUCTION

Electroconductive polymers have been studied extensively over the last few decades, as they show potential use for technological applications, such as batteries, photoelectrochemical devices, chemical and biological sensors, functional membranes, electromechanical actuators.[1–8]

Polyaniline (PANI) and polypyrrole (PPy) are among the best known synthetic polymers that exhibit good chemical, electrical, and optical properties associated with their insulating and conducting forms. The most important properties of PANI and PPy include their controllable electrical conductivity, lower density than metals, good environmental stability, and ease of preparation from common chemicals.[9,10]

A problem for the technological applications of freestanding PANI and PPy films is their hardness and brittleness, which make them difficult to process. To overcome this problem, conventional thermoplastics and conductive polymers are usually processed together, allowing the fabrication of composite films, which exhibit a good balance of electrical conductivity, mechanical properties, and processing characteristics. A number of techniques have been used to achieve this goal, including casting from solutions of thermoplastics with electroconductive polymers using solvents,[1,11] oxidative polymerization of adsorbed pyrrole or aniline monomer onto an insulating matrix,[12,13] electrochemical polymerization of pyrrole or aniline monomers in a solution containing dissolved thermoplastics,[14] electrodeposition of electroconductive polymer films onto an insulating coating,[15] emulsion polymerization,[16] and mechanical mixing.[17,18]

In our previous work, PANI–poly(n-butyl methacrylate) (PBMA) and PPy–poly(vinyl chloride)-carboxylated (PVCc) composite films were fabricated by casting, and their potential use as biosensors was evaluated.[1,9] Although the results were good, the casting method involved solvent evaporation, and the environmental factor should be considered if we want to make the films in a larger scale.

In the present study, the preparation of electroconductive composite films of PANI–PBMA by using hot-melt extrusion is presented. Two methods were tested. In the first method, the composite films were obtained by deposition of polyaniline chloride (PANI-Cl) on the extruded material; in the second method, the films were obtained by blending PANI–dodecylbenzene sulfonic acid (PANI-DBSA) and poly(n-butyl methacrylate) (PBMA) during the extrusion process. The ther-

mal stability of the raw materials was studied by thermogravimetry (TGA). The electrical properties of the composite films, their morphology by scanning electron microscopy (SEM), and their performance as sensors for H_2O_2 and NH_3 in aqueous solutions were evaluated.

EXPERIMENTAL

Preparation of composites samples

Aniline (99%) was supplied by Aldrich (Milwaukee, WI). Ammonium persulfate (APS, 98%) was provided by ChemCorp (NJ) and hydrochloric acid (HCl, 37%) was supplied by Merck (Darmstadt, Germany). All chemicals were used as received.

Method I

Chemical polymerization of aniline on an insulating matrix obtained by extrusion

PBMA films were obtained in a Laboratory Maxwell Extruder, model CS-194 AV. The film was immersed in a swelling solution containing aniline dissolved in water, which was subsequently polymerized in an oxidative solution of $(NH_4)_2S_2O_8$ in 1 mol L^{-1} HCl. The polymerization of aniline on the thermoplastics surface depends on the film exposure time and the concentrations of monomer and oxidant solutions. The parameters for optimal polymerization are as follows: monomer solution concentration, 0.07×10^{-2} mol L^{-1}; exposure time in solvent/monomer solution, 2 min; exposure time in oxidant solution, 5 min. The polymerization was performed at room temperature and under gentle agitation. Finally, the film was rinsed with distilled water and dried at room temperature.

Method II

Preparation of PBMA/PANI-DBSA blends by extrusion

Synthesis of PANI-Cl. Amounts of 0.0631 mol of aniline and 0.0402 mol APS were dissolved in 50 and 125 mL of 1 mol L^{-1} HCl aqueous solution, respectively. The APS solution was slowly added to the aniline solution in nitrogen atmosphere. The reaction mixture was constantly stirred as it was chilled to 5°C in an ice bath during the first 3 h. The total reaction time was 24 h. The final product was filtered and washed several times with 1 and 0.1 mol L^{-1} HCl aqueous solutions, dried in vacuum at room temperature, and ground into powder in a mortar.

Synthesis of dodecylbenzene sulfonic acid doped polyaniline (PANI-DBSA). Aniline (Bann Química, Paulinia, Brazil), APS (Cromato Produtos Quimicos, Paulinia, Brazil) as oxidant, and dodecylbenzene sulfonic acid

(DBSA, Jassen Chimica) as dopant were used as received. Aniline (3.13 mol) and APS (1.5 mol) were separately mixed with 9.75 mol DBSA and 7.5 mol NaCl in 30% ethyl alcohol aqueous solution, with vigorous stirring until homogeneous solutions were obtained. The APS solution was slowly added to the aniline solution and the resulting solution was kept at 5°C for 24 h with continuous mechanical stirring. The precipitate PANI-DBSA obtained was filtered and washed sequentially with ethyl alcohol and distilled water several times, dried in vacuum at room temperature for 12 h, and ground into powder in a mortar.[19,20]

Preparation of PBMA/PANI-DBSA composites. The composites were made by mixing PBMA and the conductive polymer (PANI-DBSA) at different mass ratios in the extruder. The rotational speed was 152 rpm and the temperatures of rotor and head were 100 and 120°C, respectively, for all runs. Both components were fed together to the extruder through the hopper and the composites were obtained as tapes with 1 mm thickness.

Characterization

The thermal properties of powder polyaniline chloride and PANI-DBSA were measured by using a Perkin–Elmer DTA-7 differential thermal analyzer and a Perkin–Elmer TGA-7 thermogravimetric analyzer. The electrical characteristics of the composites films prepared by method I were evaluated by measuring the surface resistance along the longitudinal direction. The measurements were made at two points separated 10 mm of each other. The electrical conductivities of composite films prepared by method II were measured by the standard two-point probe method. The morphology of composite films was observed by using a JEOL 5410LV scanning electron microscope. The performance of the composites as sensors was tested by immersing the PBMA/PANI films prepared by the two methods in H_2O_2 and NH_3 aqueous solution with an exposure time of 10 and l min, respectively. After exposure, the films were dried at room temperature and the changes in electrical resistance were measured.

RESULTS AND DISCUSSION

Thermal properties

Differential thermal analysis (DTA) and TGA runs were conducted to study the thermal behavior of the thermoplastic, PBMA. The values obtained were used to set the extruder operating temperature to prepare the composites by method I. These values were T_{onset} = 185°C and T_g = 39°C.
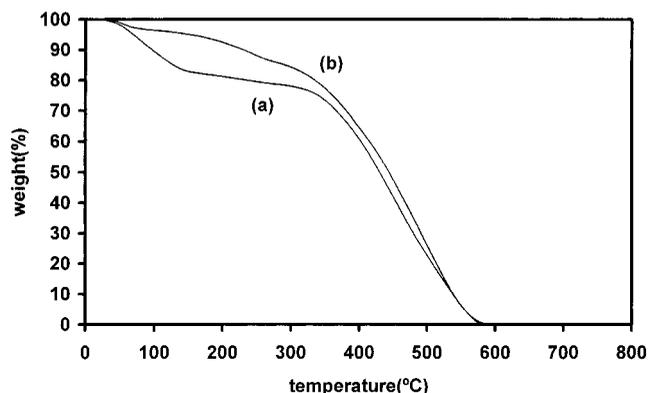
Figure 1 TGA of conducting polymers (a) PANI-Cl and (b) PANI-DBSA.

The thermal properties of PANI-DBSA were measured by thermogravimetric analysis with a heating rate = 10°C min^{-1}, gas flow rate = 20 mL min^{-1}, and nitrogen as purge gas. Figure 1 shows a comparison of the thermal stability of the conducting polymers synthesized by chemical methods. Considering the first weight loss as humidity, the PANI-DBSA has better thermal stability than the chloride-doped polyaniline. The temperature of 200°C is sufficient to process the PANI-DBSA with PBMA. It is also known that DBSA increases the electrostatic interactions,[18] derived from long alkyl chains, which efficiently improves the processibility of the PANI–DBSA complex.

Electric conductivity

The composites elaborated by method I by use of the optimal parameters of polymerization showed resistance values of 2.3 × 10^4 $\Omega_\square$.

In method II, the effect of the initial amount of PANI-DBSA on the melt-mixed composites of electrical conductivity was investigated (Table I). Blends prepared in this work presented conductivity in the 10^{-6} to 10^{-4} S cm^{-1} range. The electrical conductivity of the blend increased with PANI-DBSA concentration.

TABLE I
Conductivity of the PBMA/PANI-DBSA Blends as a Function of PANI-DBSA Content Obtained by Method II

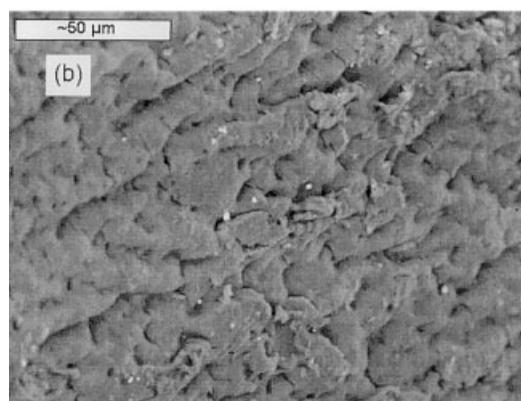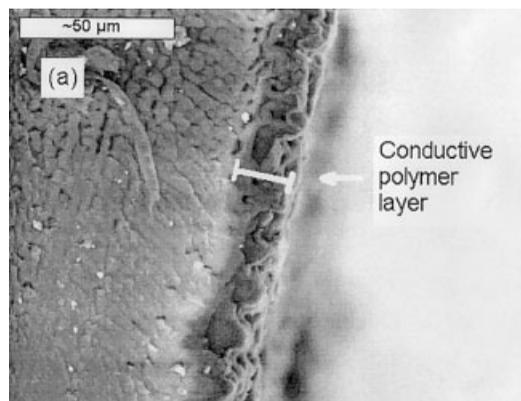| % PANI-DBSA	σ (S cm^{-1})
40	<1 × 10^{-9}
50	6.4 × 10^{-6}
60	4.1 × 10^{-5}
70	2.3 × 10^{-4}
100	2.0 × 10^{-2}

Figure 2 SEM micrographs of composite PBMA/PANI-Cl prepared by method I, (a) cross section, (b) surface morphology.

Morphology

SEMs of the cross sections and the conducting polymer surface of the films prepared by method I are shown in Figure 2(a, b), respectively. Figure 2(a) shows that the conducting polymer layer has a thickness of nearly 20 μm and the interface between both components exhibits good adhesion. The surface of the PANI-Cl is homogeneous [Fig. 2(b)] but not smooth, and it shows some
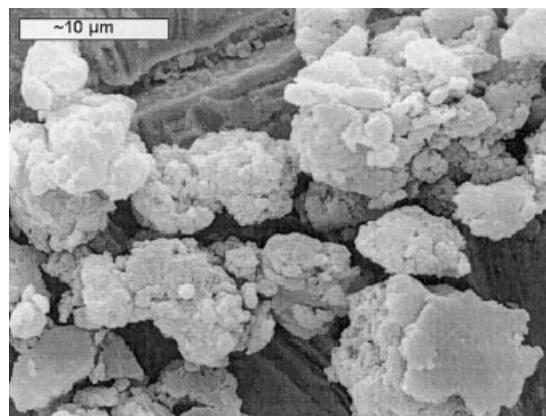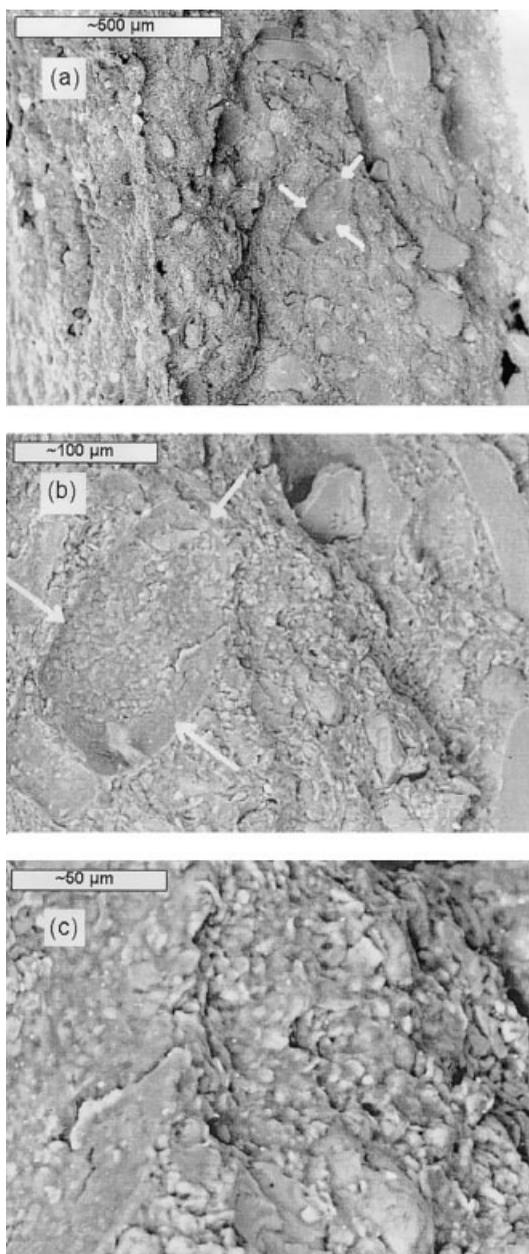

Figure 3 SEM micrographs of powder PANI-DBSA.

Figure 4 SEM micrographs of composite PBMA (30%)/PANI-DBSA (70%) prepared by method II at different magnifications: (a) 100×, (b) 350×, and (c) 750×.

channellike structure that should favor diffusion of chemical species from aqueous solutions to the surface.

SEMs of PANI-DBSA powder used in the preparation of films by method II is shown in Figure 3. SEM images of the films prepared by method II are shown in Figure 4, in which three magnifications show a broad particle size distribution. The largest magnification [Fig. 4(c)] suggests that the thermoplastic acts as an adhesive to the PANI-DBSA particles. Figure 4(a, b) shows holes where large particles of the conducting polymer were placed. The adhesion of these large particles is weak because of its size.
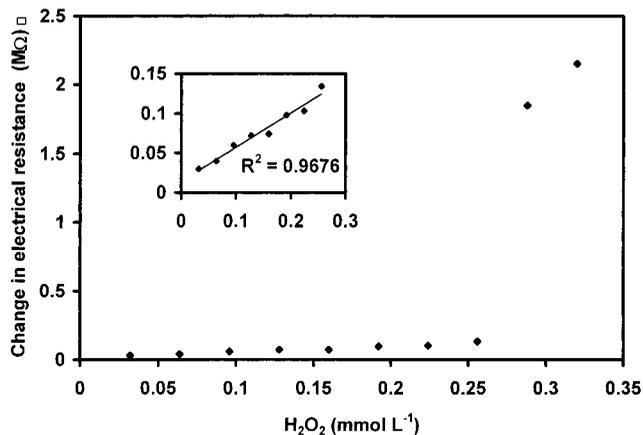
Figure 5 Resistance change behavior of PBMA/PANI-Cl composite film obtained by method I on dipping in H_2O_2 aqueous solution.

Sensitive response

The behavior of the composite PBMA/PANI-Cl prepared in method I is shown in Figure 5. The resistance increases linearly with H_2O_2 concentration in the range of 0.032 to 0.256×10^{-3} mol L^{-1}. The oxidant H_2O_2 causes degradation of PANI in the composite.[9]

Figure 6 shows the behavior of the composite prepared by method I in the presence of NH_4OH. The NH_4OH causes dedoping of polyaniline and the conductivity changes asymptotically with NH_4OH concentration.

The electrical resistance variation for the composite films with 70% in PANI-DBSA content, obtained by method II, was measured as a function of NH_4OH concentration (Fig.7). Despite the low conductivity values, we obtained a linear sensitive response to concentrations between 2.56 and 25.56×10^{-3} mol L^{-1}.

The same composite films, PBMA (30%)/PANI-DBSA (70%), were used to analyze the sensitivity to H_2O_2 solutions. The electrical resistance did not
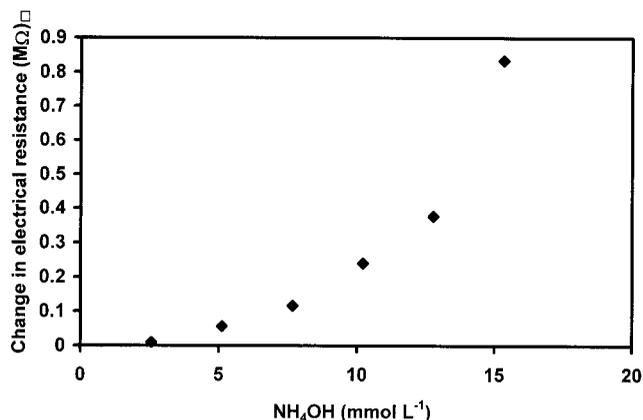
Figure 6 Resistance change behavior of PBMA/PANI-Cl composite film obtained by method I on dipping in NH_3 aqueous solution.
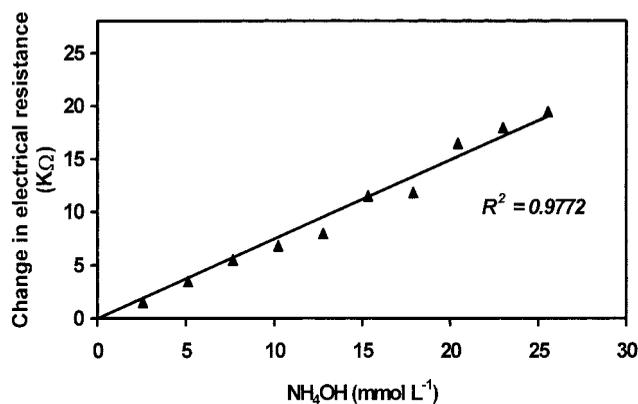
Figure 7 Resistance change behavior of PBMA (30%)/PANI-DBSA (70%) composite film prepared by method II on dipping in NH_3 aqueous solution.

change substantially in the 0.032 to 0.32 $\times$ 10^{-3} mol L^{-1} H_2O_2 concentration range.

The electrical response to H_2O_2 and NH_4OH aqueous solutions suggests that the obtained films have potential applications as chemical sensors. The NH_3 concentrations used are equivalent to urea serum concentrations and the H_2O_2 concentrations correspond to acid uric serum concentrations.

Because H_2O_2 causes degradation of PANI in the composites, it might not be a reusable sensor. However, in the case of ammonia, the sensors can be re-doped by exposure to a 1 mol L^{-1} HCl solution for 1 min and dried for 24 h, recovering the original resistance. The films prepared by method I can be reused at least three times, and the films prepared by method II can be reused at least five times.

CONCLUSION

Two types of composite PANI-PBMA films were obtained by extrusion. Method I is based on the surface polymerization of aniline on the extruded PBMA and it produced a composite film sensitive to H_2O_2 yielding a linear repose in a range where it can be used as biosensor to uric acid. This type of sensor is easy to handle, because it has just a thin layer of conducting polymer (near 20 μm). These films also show good sensitivity to ammonia and showed a reusability of three cycles.

Composites prepared via method II showed no sensitivity to H_2O_2 but good sensitivity for ammonia in the range where they can also be used as biosensors for urea. Because of the dopant (DBSA), this sensor has higher thermal stability. The high content of PANI makes it a stiff material but which may be used as sensor quite easily. They also showed recycling potential, giving five cycles of use.

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