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ANEXO

Artículo aceptado para publicación relacionado con la Tesis de Maestría:

"Electrically Conducting Polyaniline-PBMA Composite Films Obtained by Extrusion"

Autores:
M.M. CASTILLO-ORTEGA, T. DEL CASTILLO-CASTRO, J.C. ENCINAS, M. PEREZ-TELLO, MARCO-A. DE PAOLI, R. OLAYO

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Dra. María Mónica Castillo-Ortega
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MÉXICO

Dear Prof. Castillo-Ortega:

Your manuscript on "ELECTRICALLY CONDUCTING POLYANILINE-PBMA COMPOSITE FILMS OBTAINED BY EXTRUSION" (No. P520) has been carefully reviewed and I am pleased to inform you that it will be published in a future edition of the Journal of Applied Polymer Science.

May I take this opportunity to thank you for contributing your work to our journal.

With best regards, I am

Sincerely,

Bill Perkins

William G. Perkins, Associate Editor
Journal of Applied Polymer Science

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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 using 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 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.

KEY WORDS

Composites, Conducting polymers, extrusion, sensors.

INTRODUCTION

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

Polyaniline (PANI) and polypyrrole (PPy) are among the best known synthetic polymers which 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 free-standing polyaniline and polypyrrole 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], electro-deposition of electroconductive polymer films onto an insulating coating [15], emulsion polymerization [16] and mechanical mixing [17, 18].

In a previous work by the authors, polyaniline-PBMA and polypyrrole-poly(vinyl chloride) carboxilated (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 involve solvent evaporation, and the environmental factor should be considered if we want to make the films in larger scale.

In the present study, the preparation of electroconductive composite films of polyaniline-poly(n-butyl methacrylate) 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 polyaniline-dodecylbenzene sulfonic acid (PANI-DBSA) and poly(n-butyl methacrylate) (PBMA) during the extrusion process. The thermal 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, was evaluated.

EXPERIMENTAL

Preparation of composites samples

Aniline (99%) was supplied by Aldrich. Ammonium persulfate (APS, 98%) was provided by ChemCorp (New Jersey, USA) and hydrochloric acid (HCl, 37%) by Merck. All chemicals were used as received.

Method I

Chemical polymerization of aniline on an insulating matrix obtained by extrusion:

Poly (n-butyl methacrylate) (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: monomer solution concentration, 0.07 x 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 chloride doped polyaniline (PANI-Cl):

0.0631 mol of aniline and 0.0402 mol of 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 three hours. 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 dodecylbenzenesulfonic acid doped polyaniline (PANI-DBSA)

Aniline (Bann Quimica, Paulinia, Brazil), ammonium persulfate (APS, Cromato Produtos Quimicos, Paulinia, Brazil) as oxidant and dodecylbenzene sulfonic acid (DBSA, Jassen Chimica) as dopant were used as received. 3.13 mol of aniline and 1.5 mol of APS were separately mixed with 9.75 mol of DBSA and 7.5 mol of 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 for 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 r.p.m. 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 using a Perkin-Elmer DTA-7 differential thermal analyzer and a Perkin-Elmer TGA-7 thermogravimetric analyzer. The electrical characteristic 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 using a JEOL 5410LV Scanning Electron Microscope (SEM). 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 1 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 thermogravimetric analysis (TGA) runs were done 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 Tg = 39 °C.

The thermal properties of PANI-DBSA were measured by thermogravimetric analysis with a heating rate = 10 °C min^{-1}, gas low 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 processability of the PANI-DBSA complex.

Electric conductivity

The composites elaborated by method I using the optimal parameters of polymerization showed resistance values of $2.3 \times 10^4\ \Omega_{\square}$.

In method II, the effect of the initial amount of PANI-DBSA on the melt mixed composites electrical conductivity was investigated (table 1). 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.

Morphology

Scanning electron micrographs of the cross sections and the conducting polymer surface of the films prepared by method I are shown in Figure 2 (a) and (b), respectively. Figure 2a 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 (Figure 2b) but not smooth, and it shows some channel like structure that should favor diffusion of chemical species from aqueous solutions to the surface.

Scanning electron micrographs of PANI-DBSA powder used in the preparation of films by method II is shown in Fig. 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 (Figure 4c) suggests that the thermoplastic acts as an adhesive to the PANI-DBSA particles. Figures 4a and 4b show holes where large particles of the conducting polymer were placed. The adhesion of these large particles is weak because of its size.

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

Fig 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 to 25.56 x 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 change substantially in the 0.032 to 0.32 x 10^{-3} mol L^{-1} H_2O_2 concentration range.

The electrical response to H_2O_2 and NH_4OH aqueous solutions suggest 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 sensors. However, in the case of ammonia, the sensors can be redoped 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.

CONCLUSIONS

Two types of composite polyaniline-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, since it has just a thin layer of conducting polymer (near 20 μm). They 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 sensivity 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 them a stiff material but with no problem to be used as sensor. They also showed recycle potential giving five cycles of use.

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Fig. 1 TGA of conducting polymers (a) PANI-Cl and (b) PANI-DBSA.
Fig. 2 SEM micrographs of composite PBMA/PANI-Cl prepared by method I, (a) cross section, (b) surface morphology.
Fig. 3 SEM micrographs of powder PANI-DBSA.
Fig. 4 SEM micrographs of composite PBMA(30%)/PANI-DBSA(70%) prepared by method II at different magnification (a) 100 X, (b) 350 X and (c) 750 X.
Fig. 5 Resistance change behavior of PBMA/PANI-Cl composite film obtained by method I on dipping in H_2O_2 aqueous solution.
Fig. 6 Resistance change behavior of PBMA/PANI-Cl composite film obtained by method I on dipping in NH_3 aqueous solution.
Fig. 7 Resistance change behavior of PBMA(30%)/PANI-DBSA(70%) composite film prepared by method II on dipping in NH_3 aqueous solution.

TABLE 1
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	$< 1 \times 10^{-9}$
50	6.4×10^{-6}
60	4.1×10^{-5}
70	2.3×10^{-4}
100	2.0×10^{-2}

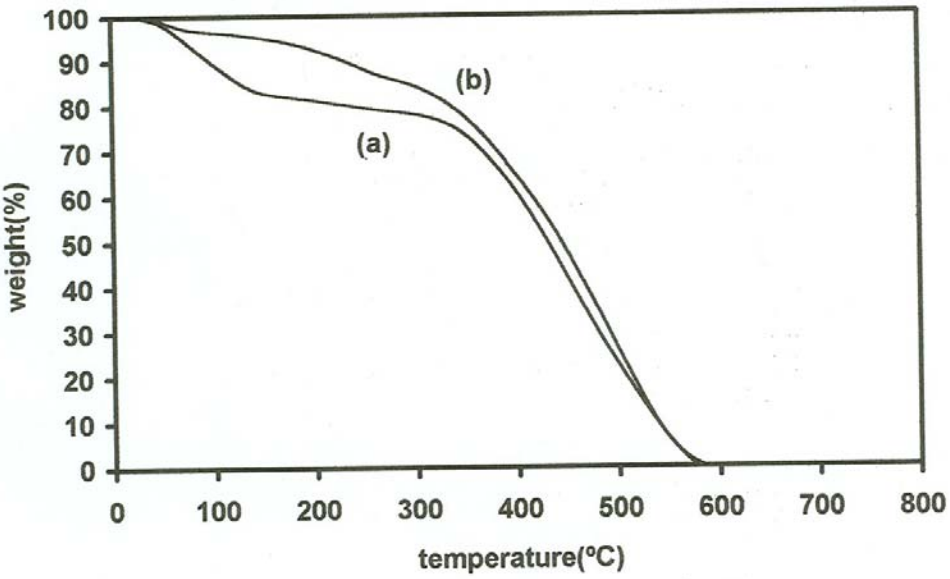
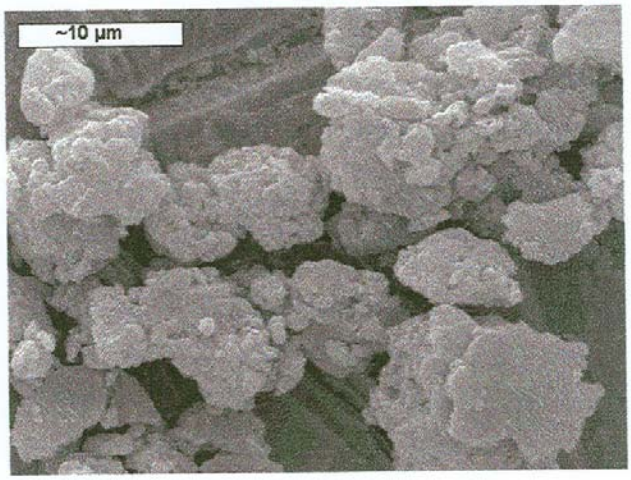


Figure 1



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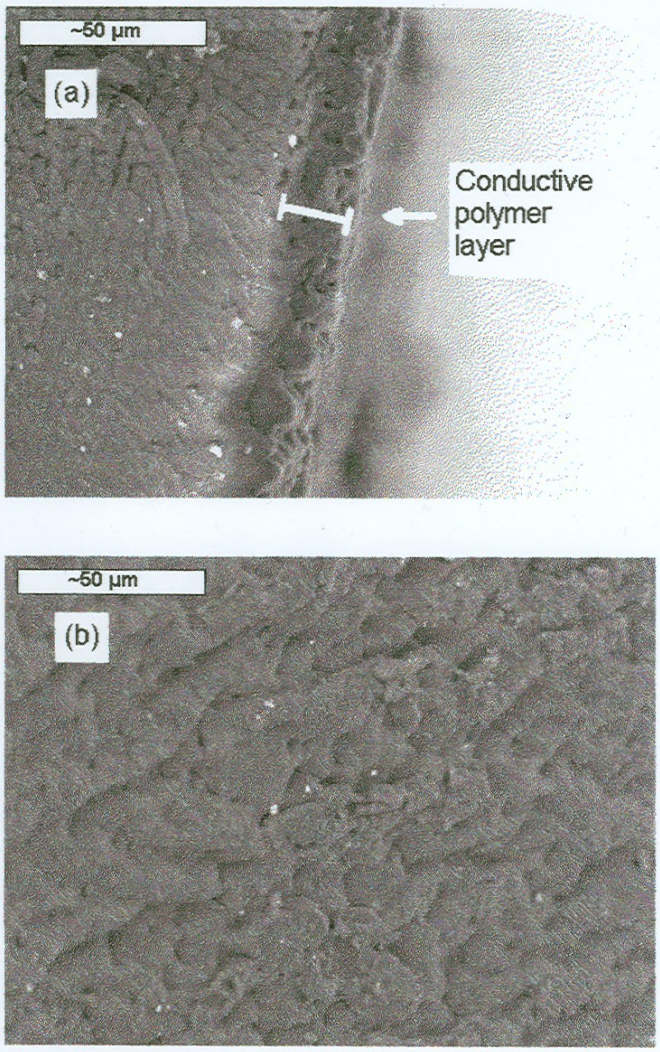

Figure 2

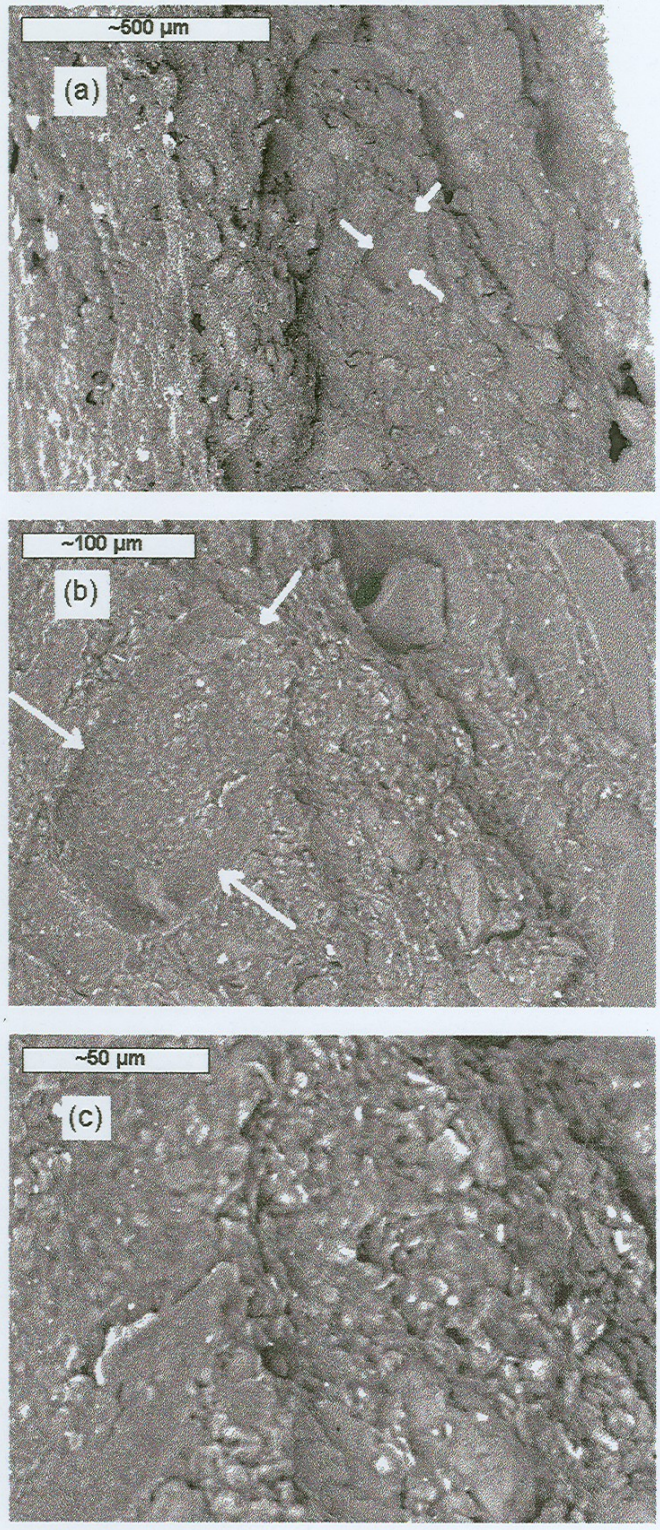

Figure 4

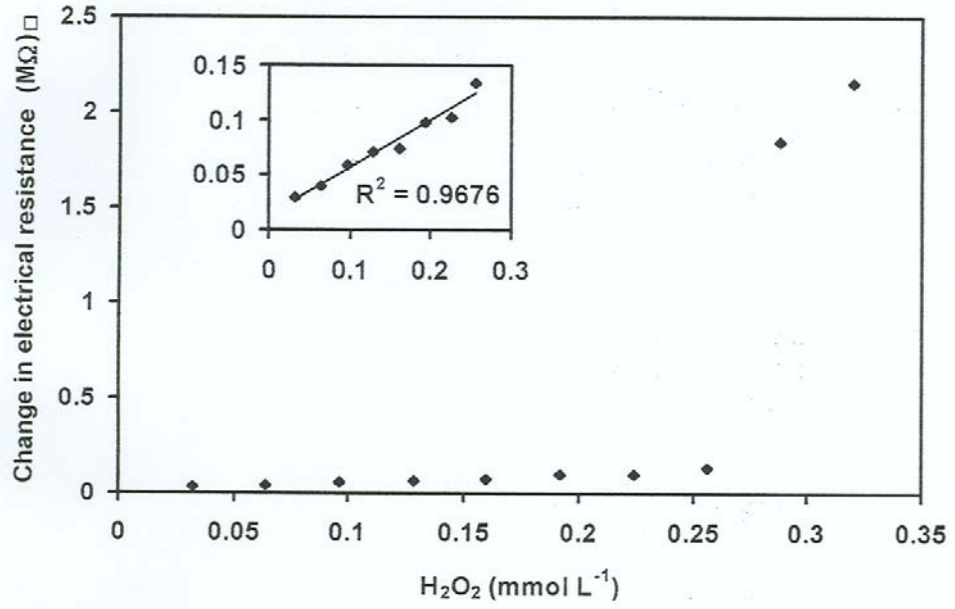

Figure 5

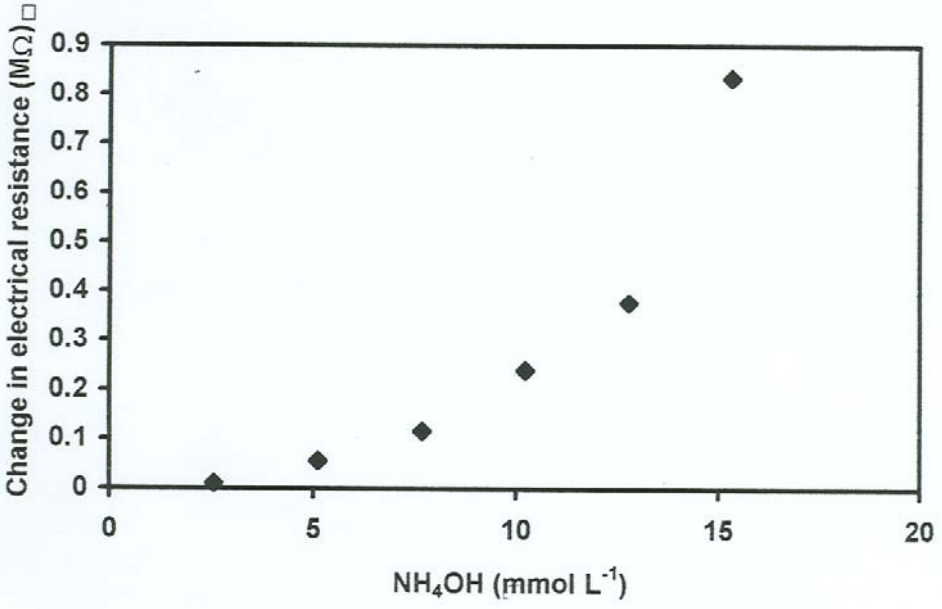

Figure 6

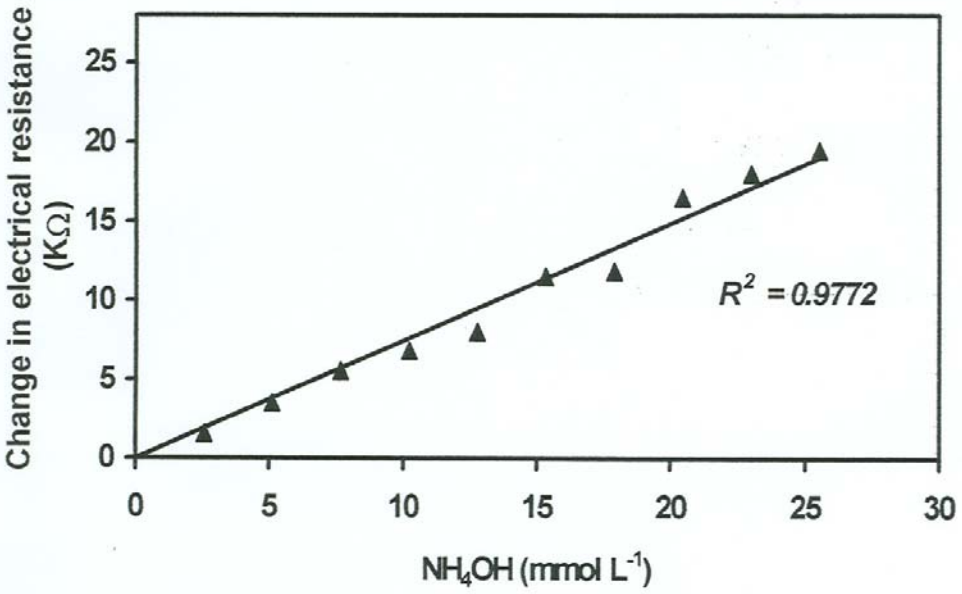
Change in electrical resistance (KΩ)
25
20
15
10
5
0
0
5
10
15
20
25
30
R^2 = 0.9772
NH_4OH (mmol L^{-1})

Figure 7