



Constitution of novel polyamic acid/polypyrrole composite films by *in-situ* electropolymerization



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ABSTRACT

The preparation and characterization of polyamic acid-polypyrrole (PAA/PPy) composite films are reported in this paper. The thin films were synthesized by electrochemical method from a solution containing controlled molar ratio of chemically synthesized polyamic acid (PAA) and pyrrole monomer. Homogenous films were obtained by incorporating PAA into electropolymerized polypyrrole (PPy) thin film. The concentration of PAA (1.37×10^{-6} M) was kept fixed throughout the composite ratio analysis, whilst the concentration of PPy was varied from 1.90×10^{-3} M to 9.90×10^{-3} M. The PAA/PPy thin films were electrodeposited at a glassy carbon electrode (GCE) and characterized using Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, Atomic force microscopy (AFM), Scanning electron microscopy (SEM) and voltammetry. The composition that best represented the homogenous incorporation of PAA into PPy matrix was observed at a PAA/PPy ratio of 1: 4.13×10^{-3} . This composite was observed to have two sets of coupled peaks with formal potential 99 mV and 567 mV respectively. The D_e determined from cyclic voltammetry using the anodic peak currents were found to be twice as high (5.82×10^{-4} cm²/s) compared to the D_e calculated using the cathodic peak currents (2.60×10^{-4} cm²/s), indicating that the composite favours anodic electron mobility. Surface morphology and spectroscopy data support the formation of a homogenous polymer blend at the synthesis ratio of 1: 4.13×10^{-3} .

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1. Introduction

The classic conducting polymers polyacetylene, polyaniline, polypyrrole and their derivatives have been studied extensively for the development of conducting or semi-conducting polymer materials for potential application in charge storage devices, electromagnetic screens, sensors, membranes and corrosion protective coatings. Examples of composites containing polypyrrole that have been reported in literature include composites of polyethylene and polypyrrole (PE/PPy), polypropylene and polypyrrole (PP/PPy), and poly (methyl methacrylate) and polypyrrole (PMMA/PPy) and they were prepared by means of a chemical modification method, resulting in a network structure of polypyrrole embedded in the insulating polymer matrix. Composites with excellent thermal stability and conductivity in the range of 10^{-11} to 1 S/cm was obtained, depending on the PPy content. The above mentioned conductive composites were earmarked for the application as antistatic packaging materials [1]. Composites of PPy

with polyimide (PI) as insulating matrix polymer was prepared via electrochemical methods and FTIR confirmed that there was a chemical interaction between the two polymers. Thermal analysis supported this conclusion that the PI/PPy composite film contained copolymers of PI and PPy [2]. Polypyrrole-polyindene composites prepared via electrochemical methods, where PPy was used as a suitable electrode in the polymerization of indene to produce homogeneous polypyrrole/polyindene composites [3]. More recently conducting polymer/polyamic acid composites were synthesized by casting polyamic acid (PAAC) film onto the surface of stainless steel followed by electrochemical deposition of polypyrrole [4]. The polyimide resin was introduced as a matrix to produce composites with improved mechanical properties, high temperature stability and desirable electronic properties [4]. Polypyrrole-polyethylene glycol conducting polymer composites, graphene oxide/polypyrrole composites and poly(methyl methacrylate)-polypyrrole composites have all been previously reported as a means to produce highly conductive semiconducting materials with good mechanical properties [5–7].

In this paper we report the synthesis of novel polyamic acid/polypyrrole composites prepared by one step electrochemical method, *in-situ*. Atomic Force Microscopy (AFM), Scanning Electron Microscopy (SEM), Raman and FTIR spectroscopy data support

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the formation of a unique material with superior electrochemical kinetics observed using cyclic voltammetry (CV) and Square wave voltammetry (SWV).

2. Experimental

2.1. Chemicals

4,4'-oxydianiline (ODA), 1,2,4,5-benzenetetracarboxylic acid (PMDA), tetrahydrofuran (THF), methanol (MeOH), triethylamine (TEA), acetonitrile (ACN), pyrrole (98%) was vacuum distilled and stored frozen under nitrogen, disodium hydrogen phosphate, potassium dihydrogen phosphate, were all obtained from Sigma-Aldrich, South Africa. All chemicals were of analytical reagent grade and were used without further purification.

2.2. Synthesis of materials

2.2.1. Synthesis of Polyamic acid

PAA was prepared according to known procedure [8]. Synthesis of PAA was carried out in organic medium from 4,4'-oxydianiline (ODA) and 1,2,4,5-benzenetetracarboxylic acid (PMDA) precursors. The preparation involved the mixing of 0.01 mol of ODA in 42 mL of THF and the mixture was stirred in a 0.5 L round-bottom flask until all ODA was dissolved. To that mixture 0.01 mol of PMDA powder was added over 1 h. 35 mL of MeOH containing 2.78 mL of TEA was later added. The solution was stirred for 24 h, resulting in a dark yellow viscous solution of PAA. The solid content of the resulting PAA was 9.8%. This viscous PAA was soluble in phosphate buffer solution (PBS) pH 7.

2.2.2. Synthesis of PAA/PPy composites

The PAA/PPy was synthesised via *in-situ* polymerization processes. The concentration of polyamic acid was fixed at 1.37×10^{-6} M throughout the composite ratio evaluation. The concentration of PPy was varied from 1.90×10^{-3} to 9.09×10^{-3} M. The ratios to produce the desired composites were as follows: $1:1.34 \times 10^3$; $1:2.81 \times 10^3$; $1:4.13 \times 10^3$; $1:5.41 \times 10^3$; $1:6.64 \times 10^3$. The solutions were stirred for a minute and degassed before experiments.

2.3. Instrumental techniques

Voltammetric experiments were performed on BASi 100B electrochemical work station (LG Fayette) using the conventional three-electrode system. For the electropolymerization of polyamic acid, polypyrrole and PAA/PPy composites, the working electrode used was glassy carbon electrode (GCE) (diameter 3.00 mm) and Platinum electrode (diameter 1.00 mm, Sigma Aldrich) while a Platinum wire and a Ag/AgCl (3 M NaCl, Bioanalytical Systems Ltd., UK) electrode were used as counter electrode and reference electrode, respectively. Alumina micro-polish (1.00, 0.30 and 0.05 mm alumina slurries) and polishing pads (Buehler, IL, USA) were used for polishing the electrode. Materials were also prepared on screen printed carbon electrode (SPCE) (diameter 3.00 mm), for characterization by scanning electron microscopy (SEM). SEM images were recorded on a Hitachi S3000N scanning electron microscope. An acceleration voltage of 20 kV was employed. Surface morphology of the materials on SPCE was studied with atomic force spectroscopy (AFM) tapping mode (NanoSurf[®], Wirsam, South Africa). The structural changes within composites were studied using Fourier transform spectroscopy (PerkinElmer Spectrum 100, FT-IR spectrometer) as well as Raman measurements (LabRam HR by Jobin-Yvon Horiba scientific Explora, France) with a 1200 lines mm^{-1} grating coupled to a microscope (Model BX41, Olympus). The excitation of Raman scattering was operated with a laser at a

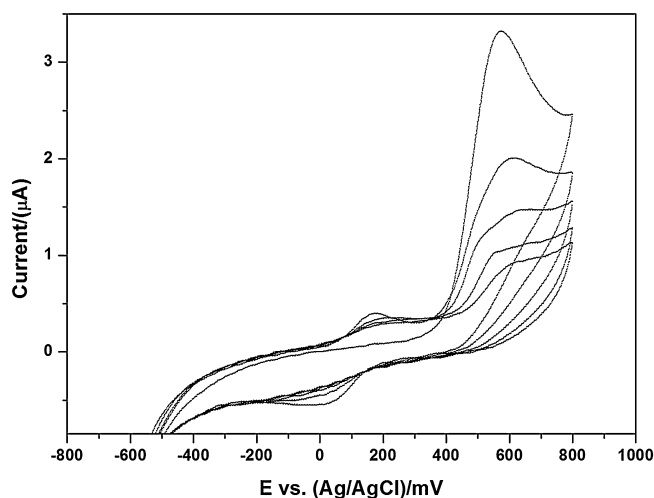


Fig. 1. Electrochemical polymerization of PAA in 0.2 M PBS (pH7).

wavelength of 532 nm. The laser beam was focused on the sample using a x100 microscope objective.

3. Results and Discussion

3.1. Electrochemical synthesis and characterization of PAA

Cyclic voltammetry (CV) is widely used to characterize conducting polymer films, by studying the reversibility of electron transfer, since oxidation and reduction can be monitored in the form of a current-potential diagram. The electrochemical polymerization of PAA film on glassy carbon electrode (GCE) was achieved by cycling the potential repeatedly between -400 and 600 mV at a scan rate of 50 mV/s for 20 cycles. The cyclic voltammogram for the polymerization of PAA film on the glassy carbon electrode (GCE) surface are shown in Fig. 1.

The electrodeposited PAA film was further characterized in 0.2 M PBS (pH 7) at scan rates between 50 mV/s and 100 mV/s (Fig. 2). As the potential was scanned from -1000 mV to 1000 mV, two quasi-reversible redox couples were observed at 190 mV and 516 mV respectively.

From the CV data, PAA film was considered to be a multicomponent system [9]. Multicomponent systems are the

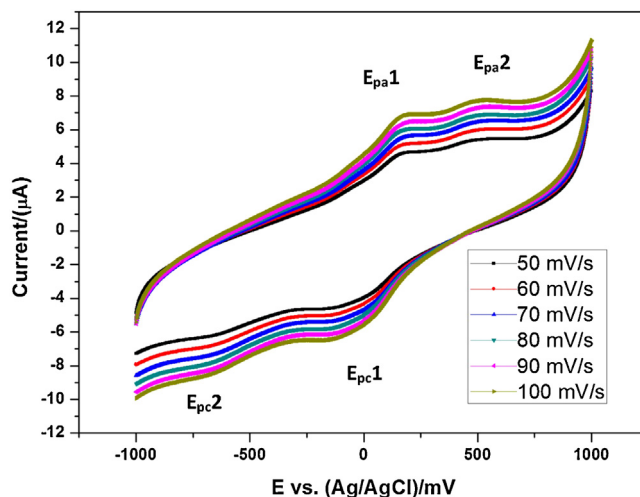


Fig. 2. Cyclic Voltammogram (CV) of PAA film on a GCE in 0.2 M PBS (pH 7) at different scan rates; 50, 60, 70, 80, 90 and 100 mV/s.

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