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FIB-SIMS investigation of carbazole-based polymer and copolymers electrocoated onto carbon fibers, and an AFM morphological study

Marina Serantoni[a,*], A. Sezai Sarac[b], David Sutton[c]

[a] *Materials and Surface Science Institute, University of Limerick, Limerick, Ireland*
[b] *Istanbul Technical University, Department of Chemistry, Polymer Science and Technology, Maslak 80626, Istanbul, Turkey*
[c] *Department of Applied Sciences, Limerick Institute of Technology, Limerick, Ireland*

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Abstract

The work presented in this paper reports preliminary results obtained by focused ion beam-secondary ion mass spectroscopy (FIB-SIMS) analysis in the study of micro-sized carbon fiber electrocoated by conjugated-nonconjugated polymers such as poly(*N*-vinylcarbazole-co-methylthiophene), poly(*N*-vinylcarbazole-co-vinylbenzene sulfonic acid) and polycarbazole. The aim of this study was to investigate by FIB-SIMS analysis the presence and concentration gradient of certain elements via depth profiling of the coating on selected carbon fibers. The presence of dopant ions together with their gradient of concentration in the coating layer was elucidated as well as the thickness of the copolymer layer electrocoated onto the carbon surface. AFM analysis performed on the electrocoated fibers yielded information regarding the surface morphology and roughness.

Keywords: FIB-SIMS; Carbon fiber; Conductive polymers

1. Introduction

Electrocoating of conjugated and nonconjugated random copolymers as surface functionalising materials on carbon fiber produces a novel material with interesting properties. The application of these coatings onto the carbon fiber surface enhances the interaction of the carbon fibers as a reinforcement material in polymer matrix [1]. Further application of these novel materials involves the preparation of miniaturized chemical sensors capable of operating outside the laboratory environment. The use of carbon fiber homogeneously coated by conductive polymers with well-defined surface functionalities should be suitable for the miniaturization of electrodes for detection of particular molecules [2]. Several copolymer- and polymer-coated (anodic) electrodes have been shown to be an effective electrode system for the determination of *p*-aminophenol at low detection limits [2]. The nature of copolymeric films, their structure and compositions plays an important role in the final properties of modified carbon surface. The interest for the characterization of these functionalised thin films is increasing [3–8] and recently electropolymerization (anodic coating) techniques, and morphological studies of thiophene oligomers on carbon fiber have been reported [9–11]. Electrocoated poly(*N*-vinylcarbazole-co-methylthiophene) (P[NVCz-co-MeTh], poly[*N*-vinylcarbazole-co-*p*-vinylbenzene sulfonic acid] (P[NVCz-co-VBSA]), polycarbazole and poly[carbazole-co-methylthiophene] onto carbon fiber (CF) micron sized electrodes have previously characterized by atomic force microscopy (AFM), Raman, FTIR-ATR and XPS spectroscopy [12–15]. Results indicate that the coating properties depend mainly on the initial feed ratio and the reactivity of monomers.

Methods for the morphological and elemental characterization of the electrocoated carbon fibers are under development [12–15] and an investigation of these materials via focused ion beam-secondary ion mass spectroscopy (FIB-SIMS) is presented in this paper. The following samples of electrocoated carbon fibers were investigated by FIB-SIMS: carbazole (Cz#12), *N*-vinylcarbazole-vinylbenzenesulfonic acid (NVCz-VBSA#3) and *N*-vinylcarbazole-methylthiophene (NVCz-MeTh#4) (Fig. 1).

* Corresponding author. Tel.: +353-61-234158; fax: +353-61-213529.
E-mail address: marina.serantoni@ul.ie (M. Serantoni).

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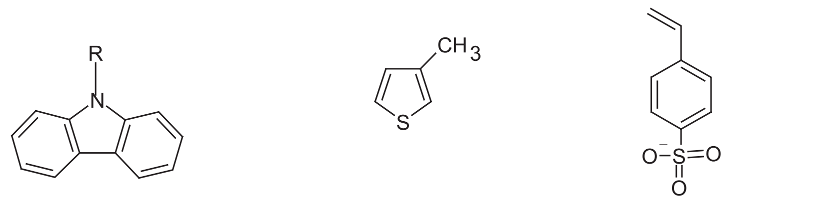

Fig. 1. Formula of electrocoated monomers.

These conductive polymers are mainly derivatives of heterocyclic conductive copolymers and vinyl–vinyl pendant conjugated systems. The elements of most interest to this analysis were: sulphur (32 amu), which indicate the presence of MeTh in the coating; nitrogen (14 amu) due to the carbazole molecule present on all samples, chlorine (35 amu) related to the insertion of support electrolyte into the coating; and oxygen (16 amu), which indicates the oxidation of the copolymer. The results of this novel technique are the subject of this paper together with AFM and FIB images that show the morphology of the surface under study and the cross-sections of the coated fibers.

2. Experimental

2.1. Materials

Polyacrylonitrile (PAN) based carbon fibers were used for this study (Hexcel AS4C, 12K with 12,000 single filaments of diameter from 5 to 6 μm). The monomers, *N*-vinylcarbazole (NVCz), vinylbenzene sulfonic acid (VBSA), methylthiophene (MeTh) and carbazole (Cz) were obtained from Merck (synthesis grade) and tetramethylammonium perchlorate (TMAP, Fluka, >99%)) was employed as the supporting electrolyte into *N*,*N*-dimethylformamide (DMF) (Fluka, puriss. grade), the solvent in the electrochemical cell.

2.2. Conditions for the anodic coatings of polymers

Electrochemical surface functionalisation by electrocoating of CF samples has been previously reported [7]. The area of the each fiber electrodes was 0.01 cm^2 (fibers were covered to a height of 60 mm in the cell). Electrodeposition of polymers on the carbon fiber was performed galvanostatically at 40 °C for constant current density of 10 A/cm^2, using the carbon fibers as the anode. The initial concentrations of monomers used were 0.05 M for NVCz and 0.05 M for VBSA in the case of poly[NVCz-co-VBSA], 0.017 M for NVCz and 0.240 M for MeTh in the case of poly[NVCz-co-MeTh] in solution of DMF containing 0.1 M TMAP. The initial concentration of monomer for polycarbazole electropolymerisation was 0.075 M in solution of DMF containing 0.1 M TMAP.

After electrolysis, the carbon fibers were washed thoroughly with water, acetone and tetrahydrofuran (THF), and dried overnight in a vacuum oven at 1 mbar and 50 °C, to prevent the adsorption of oligomeric species, which may be formed in solution during electrocoating.

2.3. FIB-SIMS measurements

The instrument used for these analysis is a FEI FIB 200 SIMS III (Focused Ion Beam Workstation), gallium (Ga) ion beam 10–30 keV, 1–11,500 pA beam current, 9 nm resolution. Focused Ion Beam (FIB) technology has become an important part of failure device analysis and surface analysis in the semiconductor industry. The FIB in conjunction with secondary ion mass spectroscopy (SIMS) is also versatile in the characterisation of materials, providing information such as site-specific elemental analysis and elemental depth profiling.

For this study, samples were prepared by cutting off a section of the electrocoated fibers and dispersing them on to a conductive adhesive surface glued into the aluminium sample holder, which was then placed into the vacuum chamber of the FIB. In order to carry out the investigation of the four samples, a design for the experiments was established. Initially, a suitable coated fiber was selected. A mass survey spectrum (MSS) of the sample was carried out for a depth of 1 μm by a rectangle measuring approximately 20 μm by 2 μm (Fig. 2). As the FIB mills the selected area the SIMS is continually collecting information of the ion species being evacuated from the sample. This results in an accumulative survey spectrum of the sample to a selected depth in the sample, in our case 0.5 μm. This was performed in both the positive and negative ion collection mode. From the data collected in the survey spectrum, a selection of the elements detected was identified for further analysis via depth profiling. Dept profiling (DP) and end point detection (EPD) were carried out for depths greater than 0.5 μm. An EPD trace is a measure of total stage current (beam current + secondary electron current) as a function of the depth milled while the beam current remains constant, only material-dependent variations in secondary electron yield