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X-ray photoelectron spectroscopic investigation of conducting polymer blends

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Abstract Electrochemically prepared films of conducting polymers of polypyrrole and polythiophene and their blends with polyamide have been investigated by X-ray photoelectron spectroscopy. In the N1s region of the spectra of films containing polypyrrole the peak corresponding to N^+ at 402.0 eV is separated from that of neutral N. The intensity of the N^+ peak can be correlated with the electrical conductivity of the films and the spectroscopically derived ratio of F/N^+ is close to 4 indicating that one BF_4^- dopant ion is incorporated for every oxidized nitrogen center. In the spectra of films of polythiophene and its blends peaks corresponding to S and S^+ can not be resolved but again the F/C ratio correlates with the electrical conductivity.

Introduction

The preparation of electroactive polymers with improved chemical and/or mechanical properties is still a scientifically and technologically important issue. Blending is one of the ways to achieve this goal. Blends of polypyrrole and polythiophene with polyamide has proved to be quite successful for some applications [1–3]. Photoelectron spectroscopic investigation of these materials in their unblended forms have been extensively carried out [4–6]. In a previous study we reported on an X-ray photoelectron spectroscopic investigation of polypyrrole and its blends with polyam-

ide [7], here we extend this study to polythiophene and its blends with polyamide.

Experimental

Blends were prepared by electrochemical polymerization of pyrrole or thiophene onto a polyamide coated electrode at a constant predetermined potential. The polyamide films were dipcoated from chloroform solutions of a concentrated polyamide resin (Aldrich Co. 19, 101-9). Electrochemical deposition of polypyrrole was carried out in a three compartment cell equipped with Pt foils (1.0 cm² each) as working electrode at (+1.1 V) and counter electrodes. A capillary (Ag/Ag⁺)-electrode was used as reference electrode and the solvent/electrolyte couple was acetonitrile/tetrabutylammonium tetrafluoroborate. For polythiophene the working electrode was operated at +2.0 V. Electrochemical reduction was achieved by reversing the polarity and discharging the prepared films. X-ray photoelectron spectra of the various films were recorded after thorough washing with the solvent and drying the films being intact on the platinum electrodes. Conductivities were measured using the 4-probe technique [1–3]. The spectrometer used is a KRATOS ES300 with AlK α source. Quantitative data from the XPS data are obtained using the standard procedures [8].

Results and discussion

Part of the photoelectron spectra of pure polyamide (PA), polyamide/polypyrrole (PA/PPY) and polyamide/polythiophene blends (PA/PTh) are shown in Figs. 1, 2 and 3, respectively. In Fig. 1 spectra of polyamide after electrochemical oxidation (PA(oxidized)) and further reduction (PA(ox.+red.)) are also included to ensure that the electrochemical treatment does not introduce additional features. In Figs. 2 and 3 included are the spectra of unblended films of polypyrrole and polythiophene in their conducting forms and after electrochemical reduction. The strong features are due to F1s, O1s, N1s and C1s and S2s and 2p. Since our X-ray source is not monochromatized the F1s, C1s, S2s and S2p peaks are observed as single peaks at around 686, 285, 228 and 164 eV, respectively. The O1s peak

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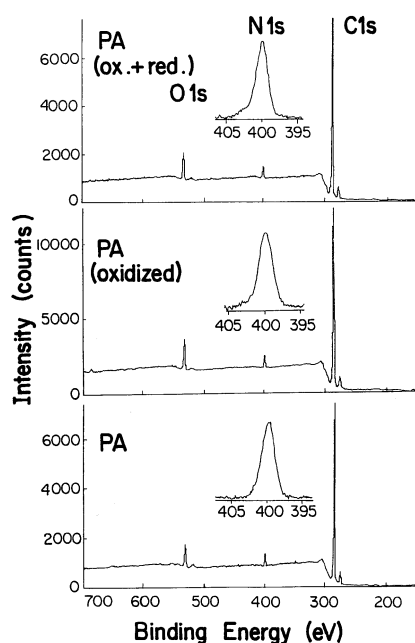


Fig. 1 AlK α photoelectron spectra of polyamide films coated on platinum electrodes. *Bottom* as coated, *middle* after electrochemical oxidation and *top* after further electrochemical reduction. Expanded N1s regions are also shown

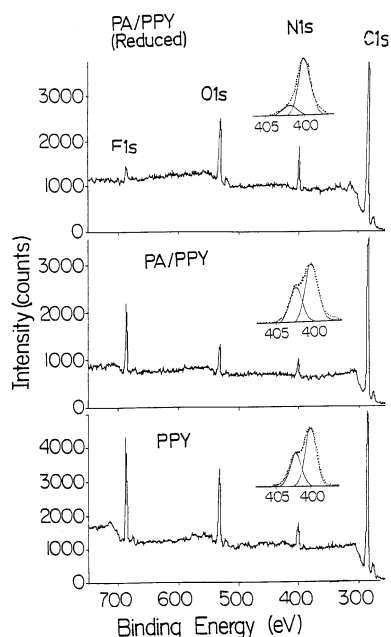


Fig. 2 Photoelectron spectra of electrochemically prepared films of pure polypyrrole (*bottom*), the polyamide/polypyrrole blend as prepared (*middle*) and after electrochemical reduction (*top*). Expanded N1s regions composed of two peaks are also shown

around 532 is broad and can be deconvoluted into 2 or 3 components. The N1s peak in films containing polypyrrole has two components at 399.7 and 402.0 eV which can be assigned to the neutral ($-N-$) and the quaternized nitrogens ($-N^+-$), respectively. The relevant data are collected in Table 1. Examination of

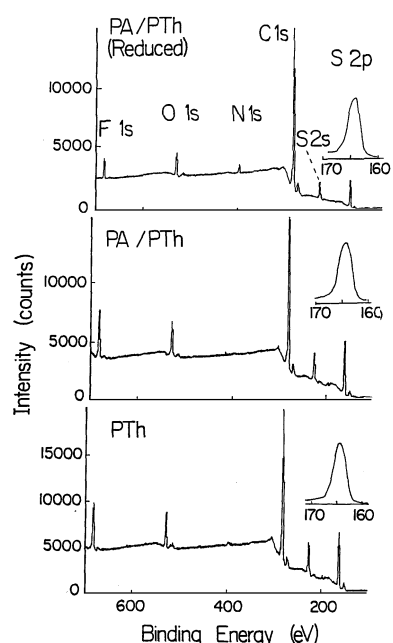


Fig. 3 Photoelectron spectra of electrochemically prepared films of pure polythiophene (*bottom*), the polyamide/polythiophene blend as prepared (*middle*) and after electrochemical reduction (*top*). Expanded S2p regions are also shown

Fig. 1 reveals that no additional features are introduced during electrochemical oxidation and/or reduction of the pure polyamide film. The N/C ratio determined from our result is not far from the stoichiometric ratio given by the supplier (0.05).

The peaks in the XPS of the polyamide/polypyrrole films, as reproduced in Fig. 2, were already discussed in our previous publication [7]. Basically, in the N1s region the intensity of the high binding energy component, assigned to N^+ moieties, correlates with the electrical conductivity of the films. The atomic ratio of F to N^+ derived from our XPS data is close to 4 for these films, indicating that one BF_4^- dopant ion is introduced for every N^+ center. Both the N^+ and the F1s intensities decrease considerably after electrochemical reduction. The polyamide/polypyrrole films exhibit a similar electrical conductivity compared to the films of pure polypyrrole and they are mechanically stronger [2].

Figure 3 displays the spectra of the films of polythiophene, polyamide/polythiophene as prepared and after electrochemical reduction. Unfortunately our resolution does not permit to distinguish between the neutral S and its oxidized form S^+ . Information about electrical conductivities of the films can, however, be derived from the atomic ratios of F/C. As is evident from Fig. 3 and Table 1, the F/C ratio in films of polythiophene and its blend with polyamide are very close to each other and this ratio is smaller in the less conducting electrochemically reduced blend. Similarly, electrical conductivity of the mechanically and chemically stronger polyamide/polythiophene film is comparable to that of the pure polythiophene film [3].

Table 1 XPS data of electrochemically prepared polypyrrole and polythiophene together with their blends with polyamide

	Binding energy (eV) (Atomic percentage)						Atomic ratio		Conductivity (Siemens/cm)
	C1s	N1s		O1s	F1s	S2p	F/N ⁺	F/C	
		-N-	-N ⁺ -						
PA	285.0 (91)	399.8 (2.9)	- -	532.4 (6.1)	-	-	-	-	-
PPy	285.0 (64.7)	399.7 (5.4)	402.0 (3.0)	532.3 (13.6)	686.3 (13.2)	-	4.4	-	2
PA/PPy	285.0 (74.1)	399.7 (5.0)	401.8 (3.1)	532.3 (6.6)	686.3 (11.2)	-	3.6	-	2
PA/PPy (Red)	285.0 (70.7)	399.7 (9.7)	401.8 (1.5)	532.3 (14.7)	686.3 (3.4)	-	2.2	-	0.004
PTh	285.0 (68)		400.5 (1.8)	532.8 (9.7)	686.5 (6.9)	164.5 (14.1)	-	0.10	4
PA/PTh	285.0 (69)		400.6 (1.0)	532.9 (9.1)	686.7 (6.7)	164.6 (14.2)	-	0.10	3
PA/PTh (Red)	285.0 (74)		400.8 (3.1)	532.8 (8.8)	686.8 (3.8)	164.7 (10.3)	-	0.05	0.008

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