X-ray Photoelectron Spectroscopy Study of Polypyrrole Grown at the Surface of Sulfonated Polyethylene Films

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An X-ray photoelectron study of sulfonated polyethylene films, with different sulfonation degrees (SD) before and after pyrrole polymerization at their surfaces is presented. For SD values of about 2 g/m² the outer surface of polyethylene film becomes fully sulfonated. Sulfonic groups which act as a counterion of the grown polypyrrole (PPy) monitor partially the fixation of PPy at the outer surface. A variation of the pyrrole rings/counterion ratio (7.4–3.9) depending on SD values has been found.

Introduction

X-ray photoelectron spectroscopy (XPS) has been used to characterize unprocessable conducting polymers concerning the nature of dopant species and counterion incorporated to the oxidized conducting polymers.^{1,2} Chemical changes occurring in electrochemical polypyrrole during cycling³ and exposed to different atmospheres⁴ have been successfully investigated by XPS. Analysis of the shape and line width of spectral lines has been used to get information about molecular order and electrical interaction between the oxidized polymer chain and the counterion.⁵ Recently, we have reported data on the preparation, morphology, and electrical conductivity of new conducting materials based on polypyrrole grown at the sulfonated surface of polyethylene films, (PPy-SPE).⁶ In addition, a previous transmission infrared study carried out in our laboratory on sulfonated polyethylene, (SPE) and on PPy-SPE films, with sulfonation degrees up to 2 g/m², revealed the chemical fixation of sulfonic groups exclusively⁷ and allowed us to conclude that polypyrrole develops only at the outer surface of the sulfonated layer of the films.⁸

In this work we report a detailed characterization of sulfonated polyethylene films, with different sulfonation degrees, before and after the pyrrole polymerization on their surfaces. Knowledge of the topological distribution of sulfonic groups, which act as counterions of the PPy chain, is of great importance for a better understanding of the electrical properties shown by these materials.

Experimental Section

Melt crystallized low-density polyethylene films, PE (≈100 μm thick) (PE 040 ρ = 0.92 g/cm³ kindly supplied by Alcudia), were previously sulfonated for different periods of time.⁷ Sul-

fonated polyethylene films, SPE, with different sulfonation degrees, SD (determined as the weight increase per unit area of the PE film after sulfonation), were dipped into a 0.33 M FeCl₃-water solution with a pyrrole/FeCl₃ molar ratio of 0.43⁹ at 0 °C for 1 h, using an ultrasonic bath. Films were repeatedly washed with distilled water until no chloride ions were detected by means of the Ag⁺ test in the washing water.

Polypyrrole (PPy) was chemically prepared using FeCl₃ as oxidant. PPy powder was exhaustively washed and then sintered under a pressure of ≈0.75 MN m⁻² at room temperature.

Photoelectron spectra were acquired with a Leybold LHS 10 spectrometer working in the ΔE = constant mode at a pass energy of 20 eV. The spectrometer was equipped with a Mg anode X-ray source (hν = 1253.6 eV), operated at 12 kV and 10 mA. The samples (1 × 1.5 cm) were attached to the sample-holder whose surface was covered by a gold foil and then placed in an introduction chamber and outgassed at 10⁻⁶ Torr (1 Torr = 133.3 Nm⁻²) before the samples were moved into the turbopumped analysis chamber. The pressure in this chamber was maintained below 4 × 10⁻⁹ Torr during data acquisition. Several 20-eV energy regions of the photoelectrons of interest were scanned at a 20-eV spectrometer pass energy, chosen as a compromise to enable an acceptable energy resolution to be obtained within reasonable data acquisition times. Each spectral region was signal-averaged for a number of scans in order to obtain good signal-to-noise ratios. Although surface charging was observed, particularly for the nonconductive samples, accurate binding energies (BE) could be measured by charge referencing with the Au 4f_{7/2} peak at 83.8 eV. An instrumental resolution of 1.0 eV corresponding to the full width at half maximum (fwhm) of Au 4f_{7/2} was achieved. Quantitative data were obtained by numerical integration of the principal XPS peaks recorded and considering published atomic sensitive factors.¹⁰

Results

PPy-SPE samples prepared under normal stirring of the solution showed both Cl 2p and Fe 2p photopeaks because of trapping of PPy microparticles grown in the reaction solution. However, neither Cl 2p nor Fe 2p peaks were observed in the XP spectra of the samples prepared under ultrasonic bath.

For binding energy (BE) measurements a set of gold-sputtered samples in areas of ca. 0.2 cm² was first used even if a gold foil was present under the investigated sample. The Au 4f_{7/2} line at 83.8 eV was chosen as an internal standard. The binding energies so calculated for

(1) Salaneck, W. R. In *Handbook of Conducting Polymers*; Skotheim, T. A., Ed.; Marcel Dekker: New York, 1986; Vol. 2, p 1337.

(2) Salaneck, W. R.; Erlandsson, R.; Prejza, J.; Lundström, I.; Inganäs, O. *Synth. Met.* 1983, 5, 125.

(3) Pflüger, P.; Krounbi, M.; Street, G. B.; Weiser, G. *J. Chem. Phys.* 1983, 78, (6), 3212.

(4) Erlandsson, R.; Inganäs, O.; Lundström, I.; Salaneck, W. R. *Synth. Met.* 1985, 10, 303.

(5) Pflüger, P.; Street, G. B. *J. Chem. Phys.* 1984, 80 (1), 544.

(6) Rueda, D. R.; Arribas, C.; Baltá-Calleja, F. J.; Fierro, J. L. G.; Palacios, J. M. *Synth. Met.* 1989, 28, C77.

(7) Arribas, C.; Rueda, D. R. *Makromol. Chem.* 1981, 192, 491.

(8) Rueda, D. R.; Arribas, C.; Baltá-Calleja, F. J. Proceedings of the International Conference on Science and Technology of Synthetic Metals, ICSM90, Tübingen, Germany, Sept 1990. *Synth. Met.* 1991, 41, 421.

(9) Armes, S. P. *Synth. Met.* 1987, 20, 365.

(10) Wagner, C. D.; Davies, L. E.; Zeller, M. V.; Taylor, J. A.; Raymond, R. H.; Gale, L. H. *Surf. Interface Anal.* 1981, 3 (5), 211.

Table I. Binding Energies (eV) for PE and SPE Samples

SD, g/m ²	C(1s)	O(1s)	S(2p)
0	283.3		
0.08	284.1	531.3	168.0
0.20	284.1	532.0	168.4
0.86	284.1	532.1	168.5
1.07	284.1	531.9	168.3
2.00	284.1	532.0	168.4
6.57	284.1	531.9	167.9
12.62	284.1	531.8	168.3

Table II. Binding Energies (eV) for PPy-SPE and PPy

SD, g/m ²	C(1s)	O(1s)	S(2p)	N(1s)
0.08	284.5	531.6		399.8
0.20	284.5	532.4	168.1	399.7
0.80	284.5	532.1	168.0	399.6
1.46	284.5	531.8	168.1	399.5
5.78	284.5	532.1	168.1	399.6
PPy	284.4	531.9		399.4

the C 1s lines have been found to be similar and independent of SD for each of the series of samples investigated (284.1 eV for SPE and 284.5 eV for PPy-SPE). An important charging effect was observed for the nonconductive samples (PE and SPE) in relation to the conductive ones (PPy-SPE and PPy) provoking a shifting of 4.4 eV (PE) and 4.9 eV (PES) of the Au 4f_{7/2} line toward lower kinetic energy. However the line profile of the S 2p peak of the sputtered sample (particularly SPE and PPy-SPE) was substantially different from that of its non-sputtered counterpart. In the former case, two well-resolved S 2p lines that must be attributed to sulfonic groups (BE ≈ 168 eV) and to a reduced sulfur (BE ≈ 163 eV) were observed. This latter S 2p peak may likely result from partial reduction of sulfonic groups by Pd metal of the Au-Pd alloy employed in the sputtering process. To avoid this, XP spectra from a new set of nonsputtered samples were recorded in order to carry out the quantitative analysis of the spectra. The BE of the main photopeaks was measured again for the two series of samples with reference to the C(1s) line at the corresponding mean BE value (Tables I and II). Figure 1 shows the C(1s) lines for a representative sulfonated polyethylene sample (SD ≈ 1 g/m²) before (SPE) and after (PPy-SPE) pyrrole polymerization. C(1s) lines for polyethylene (PE) and for polypyrrole (PPy) are also presented for comparison. Note the important apparent shift to lower BE values for the C(1s) peak in PE and to a lesser extent in SPE. This apparent effect is due to the energy referencing in the XP spectra and is particularly important in measuring chemical shifts in materials like conducting polymers as for the nonconductive PE and SPE. Consequently, it becomes extremely difficult, if not impossible, to establish absolute BE values relative to the same internal reference.

S(2p) lines for SPE and for PPy-SPE samples with different sulfonation degrees against BE are shown in parts a and b of Figure 2, respectively. For comparison, all spectra in each figure are normalized to the same number of scans. From an inspection of these spectra, it results that the S(2p) line intensity for PPy-SPE samples is considerably reduced in relation to SPE counterparts. Similarly, Figure 3 represents the XP spectra of the N(1s) level for PPy and PPy-SPE samples.

In order to get an insight into the surface concentration of the different atoms, atomic ratios have been calculated. In this calculation the intensity of the peaks normalized for the number of accumulated scans and published atomic sensitivity factors¹⁰ have been used. As no significant differences in kinetic energy of the photoelectrons of interest exist, the efficiency of the detector was assumed

Figure 1. C(1s) core level spectra for different samples (see text). The intensities (counts per second) are normalized to 10 scans.

to be constant irrespective of the peak scanned. These atomic ratios are summarized in Table III. For SPE samples the S/C and (O/C) ratios increase with increasing SD as could be expected. The O/S ratios are larger than 3 and it would indicate the presence of water (two to three molecules per sulfonic group) tightly bound to the sulfonic groups. In the case of PPy-SPE samples the S/C ratios are 5–3 times lower than for SPE homologues. For the PPy sample the following atomic ratios were found: C/N = 4.5, N/Cl = 5.63, O/N = 0.71.

A better description of the atomic distribution at the outer surface of the samples is gained by plotting the S/C and N/C ratios as a function of SD (Figure 4). For SPE samples the S/C ratio increases rapidly for SD ≤ 1 g/m² and more slowly with increasing SD values. In the case of PPy-SPE samples, the S/C ratios also increase with SD, as they do for SPE counterparts. However, the low S/C values observed for PPy-SPE should be attributed to S(2p) signal shielding by the topmost polypyrrole layer.

The relative proportion of nitrogen (polypyrrole) at the surface of PPy-SPE samples is also shown in Figure 4. The N/C ratio increases in the low SD region (SD ≤ 1.5 g/m²) and remains essentially constant for higher SD values.

Discussion

PPy and PPy-SPE samples show very similar C(1s) BE values (Figure 1 and Table II). These values are in agreement with those reported for conductive PPy with different counterions (BE = 284.2–284.8).⁵ Salaneck et al.² reported a higher value (BE = 285.9 eV) for PPy-BF₄ by adjusting the apparent BE value (284.3 eV) by a Fermi level shift of 1.6 eV. The apparent C(1s) BE values for the nonconductive PE and SPE appear considerably reduced due to charging effect on both preparations. The BE values of N(1s) for PPy-SPE samples (Table II) decrease slowly with increasing SD and are somewhat higher than that found here for PPy. The O(1s) BE values are similar for SPE and PPy-SPE samples and their values (531.3–532.4 eV) are close to that observed for PPy. Furthermore, the O(1s) line shapes observed in SPE and

Figure 2. (a) S(2p) core level spectra of sulfonated polyethylene films with different sulfonation degree values, SD (g/m^2). The intensities (counts per second) are normalized to 10 scans. (b) S(2p) core level spectra of PPy-SPE samples with different SD values (g/m^2). Accumulated spectra are 10 times higher than in part a.

PPy-SPE samples correspond to single peaks, indicating that no appreciable oxidation is present. Then, the intensity of the O(1s) lines would be mainly related to oxygen from hydrated sulfonic groups as the high O/S ratio (Table III) indicates, in agreement with hydration of samples revealed by infrared spectra.^{7,8}

From the results shown in Figure 4 it can be said that below $\text{SD} \approx 2 \text{ g}/\text{m}^2$ the PE surface is not completely sulfonated while above $\text{SD} \approx 2 \text{ g}/\text{m}^2$ the surface becomes fully sulfonated. On the basis of the atomic S/C and O/S ratios (Table III) one can roughly say that SPE samples with $\text{SD} > 2 \text{ g}/\text{m}^2$ possess a population of 8 sulfonic groups per 100 carbon atoms, and each sulfonic group will support two to three water molecules (O/S values in Table III).

Figure 3. N(1s) core level spectra for PPy and PPy-SPE samples with different SD values (g/m^2). The intensities (counts per second) are normalized to 10 scans.

Figure 4. Surface atomic concentration relative to 100 carbon atoms of sulfur (●, ○) and nitrogen (Δ) in SPE and PPy-SPE samples as a function of sulfonation degree.

Table III. Atomic Ratios in the SPE and PPy-SPE Samples with Different Sulfonation Degrees, SD

SD, g/m^2	SPE		PPy-SPE		A_{1560}, cm^{-1}
	S/C	O/S	S/C	N/C	
0.08	0.025	5.07	0.0056	0.086	5.91
0.20	0.034	5.41	0.0067	0.087	6.90
0.80			0.015	0.102	8.48
0.86	0.062	6.01			
1.07	0.065	5.91			
1.46			0.018	0.111	9.10
2.00	0.069	5.20			
5.78			0.029	0.113	
6.57	0.083	5.02			
12.62	0.084	4.92			

The N/S ratio decreases from 15.3 to 3.9 in the explored SD range. This could indicate a large variation of the number of pyrrole units per counterion for the PPy-SPE system depending on SD. This number is 3 or 4 for electrochemical PPy prepared with conventional electrolytes^{11,2} while higher values (6 and 9) have been also reported in the case of polypyrrole supported in polyelectrolytes.¹² The higher values obtained here (15.3 and

Figure 5. Dependence of N/C on S/C atomic ratios for PPy-SPE samples.

Figure 6. Infrared spectral region (2000–400 cm^{-1}) for sulfonated polyethylene films with a similar sulfonation degree ($\text{SD} = 1.1 \text{ g/m}^2$) before (a, SPE) and after (b, PPy-SPE) pyrrole polymerization.

13) for the lowest sulfonated samples seem to be unrealistic and they might be taken with care as S(2p) signal become shielded by the topmost PPy layer. A representation of N/C against S/C found for PPy-SPE samples is given in Figure 5. A linear relationship between N/C and S/C with a slope 1.97 is observed for samples with $\text{SD} \leq 2 \text{ g/m}^2$. Above $\text{SD} = 2 \text{ g/m}^2$ N/C does not increase anymore and becomes independent of S/C. For S/C values tending to zero, i.e. for a minimum surface concentration of sulfonic groups sufficiently apart each other, 7.4 pyrrole units per sulfonic group can be calculated. On the other hand, from a transmission Fourier transform infrared (FTIR) spectroscopy study of PPy-SPE samples ($\text{SD} \leq 2 \text{ g/m}^2$) we derived a number of 4 pyrrole units per sulfonic group, for SD values tending to zero.⁸ Representative transmission FTIR spectra for SPE and PPy-SPE samples are shown in Figure 6 for comparative purposes. The infrared results contrast, in principle, with the results obtained here by XPS. This discrepancy must be related to the different sample information provided by both techniques. In the case of FTIR transmission spectra, the whole thickness of the sulfonated layer is examined. For $\text{SD} \leq 2 \text{ g/m}^2$ the sulfonated layer reaches values up to $5 \mu\text{m}$ as determined from the intensity decrease of the IR doublet at $730\text{--}720 \text{ cm}^{-1}$ observed in SPE films in relation to that

Figure 7. Dependence of the integrated absorbance of the band at 1190 cm^{-1} on the S/C atomic ratio (●) and that of the band at 1560 cm^{-1} on the N/C atomic ratio (Δ) for SPE and for PPy-SPE samples, respectively.

of PE.¹³ This result supports the microstructural modification (crystal destruction) observed for chlorosulfonated¹⁴ and sulfonated¹⁵ PE. Considering the semicrystalline structure of polyethylene¹⁶ and the preferential chemical attack to the amorphous regions during sulfonation,¹⁷ some of the sulfonic groups must be located under the film surface (being not observed by XPS) even for the lowest sulfonated sample. Thus, these inner sulfonic groups will be responsible for the lower value derived by FTIR spectroscopy.

In order to support the above interpretation, the absorbance of the band at 1190 cm^{-1} (associated to the sulfonic group)¹⁸ against the atomic S/C ratio for SPE samples is shown in Figure 7. $A_{1190} = 2 \times K \times \text{SD}$ where $K = 10.25 \times 10^4 \text{ g}^{-1} \text{ cm}$ is the integrated absorption coefficient of the band determined from transmission spectra of SPE films⁷ and the factor 2 takes into account the two sulfonated faces of the film. Furthermore, integrated absorbance of the band at 1560 cm^{-1} (related to PPy)⁸ measured from transmission spectra of PPy-SPE samples (last column of Table III) are also represented against N/C values in Figure 7. A linear relationship between A_{1560} and N/C is observed for PPy-SPE samples and would indicate that the PPy is located essentially at the outer surface of the sulfonated films, in agreement with infrared results.⁸ This representation suggests that A_{1560} seems to be observable above $\text{N/C} = 2\%$, which is roughly the sensitivity for the infrared technique. On the contrary, the variation of A_{1190} with S/C for SPE samples clearly indicates that sulfonation is a volume-process, even for the lowest sulfonated samples. Indeed, having taken into account the absorption coefficients for these two bands ($K_{1190} = 10.25 \times 10^4 \text{ g}^{-1} \text{ cm}$ and $K_{1560} = 6.2 \times 10^4 \text{ g}^{-1} \text{ cm}$)^{7,8} and assuming a similar IR sensitivity for the two bands, a theoretical linear relationship between A_{1190} and S/C can be established (dashed line in Figure 7). Then, the lowest sulfonated SPE samples show higher absorbances at 1190 cm^{-1} than those expected for a strict sulfonation of the outer layer of PE films.

In addition, from infrared data a surface concentration of PPy calculated according to the expression: $A_{1560}/2K_{1560}$

(11) Diaz, A. F.; Kanazawa, K. K.; Gardini, G. P. *J. Chem. Soc., Chem. Commun.* 1979, 635. Pfluger, P.; Street, G. B. *Polym. Prepr.* 1982, 23, 122.

(12) Iyoda, T.; Ohtani, A.; Shimidzu, T.; Honda, K. *Chem. Lett.* 1986, 687.

(13) Arribas, C. Doctoral Thesis, Universidad Complutense, Madrid, 1991.

(14) Martinez-Salazar, J.; López-Cabarcos, Rueda, D. R.; Cagiao, M. E.; Baltá-Calleja, F. J. *Polym. Bull. (Berlin)* 1984, 12, 269.

(15) Fonseca, C.; Pereña, J. M.; Fatou, J. C.; Bello, A. J. *Mater. Sci.* 1985, 20, 3283.

(16) Wunderlich, B. *Macromolecular Physics*; Academic Press: New York, 1974; Vol. 1.

(17) Martinez-Salazar, J.; Keller, A.; Cagiao, M. E.; Rueda, D. R.; Baltá-Calleja, F. J. *Colloid Polym. Sci.* 1983, 261, 412.

(18) Lowry, S. R.; Mauritz, K. A. *J. Am. Chem. Soc.* 1980, 102, 4665.

(g/m²) was previously reported.⁸ Thus, assuming a realistic value of 1.5 g/cm³ for the conducting PPy density,¹⁹ values in the range 0.3–0.5 μ m for the thickness of the PPy layer can be derived.

Conclusions

From the above results we can conclude that for sulfonation degrees of about 2 g/m² the surface of sulfonated polyethylene films becomes completely filled by sulfonic groups. Above this SD value a sulfonated polyethylene layer containing a bit more of 8 sulfonic groups per 100 carbon atoms is present. Sulfonic groups are partially monitoring the fixation of conducting polypyrrole. Thus,

(19) Malhotra, B.; Kumar, N.; Chandra, S. *Prog. Polym. Sci.* **1986**, *12*, 179.

above SD $\approx$ 1.5 g/m² the surface concentration of PPy remains also constant (N/C $\approx$ 0.112). However the PPy concentration is already significant for the lowest SD values investigated (N/C = 0.086). For SD values tending to zero, the number of pyrrole units per sulfonic group is about 7 and it goes down to 3.9 for the highest sulfonated samples.

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