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COMPARISON OF PLASMA MODIFICATIONS (AR/O_2, HE/O_2, N_2/H_2, AND NH_3/H_2) OF POLYSTYRENE CONTROLLED BY XPS ANALYSIS

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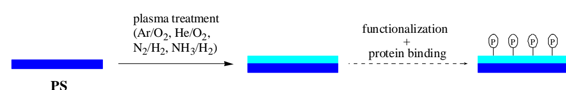
INTRODUCTION: Polystyrene (PS) is a popular substrate for disposable ware in medical diagnostic, primarily due to its optical transparency, durability, low cost, and good mouldability.[1] As polystyrene lacks reactive functional groups, it is customarily modified by various techniques, such as plasma, gamma-radiation grafting or photochemical reactions. Plasma surface treatments are potentially very useful for the covalent incorporation into polymer surfaces of extraneous reactive groups suitable for participation in further, conventional chemical reactions at the surface.[2] It changes the chemical composition and properties such as wettability, metal adhesion, dryability, lubricity and biocompatibility of materials surfaces.[3]

The purpose of this work is to prepare chemically reactive yet specific PS surfaces for high-density bio-immobilization such as protein molecules. These modified PS surfaces are expected to by applied in medical diagnostic tools for use in a proprietary ADS fluorescence reader.[4]



METHODS: PS chip modification was carried out in a capacitively coupled rf reactor operating at 13.6 MHz. The gas admixture was introduced into the chamber at a flow rate of 60 sccm which maintains the chamber pressure at 0.4 mbar. The plasma was generated at a power of 60 W for 3 minutes. A Scientific System ion flux probe (IFT) has been applied to measure the ion flux on the grounded electrode.

XPS analysis was performed using an imaging Kratos Axis Ultra X-ray photoelectron spectrometer equipped with a conventional hemispherical analyser. The X-ray source employed was a monochromatized Al Kα (1486.6 eV) source operated at 150 W. Data acquisition was performed under UHV (10^{-9} mbar) conditions. Analysis area was 0.21 mm^2 (300 µm × 700 µm) using a take-off angle of 70° relative to the surface normal. Charge compensation was performed with a self-compensating device (Kratos patent) using field emitted low energy electrons (0.1 eV) to adjust the main C-C component to 285 eV.[5] The data reduction (atomic concentration, shifting, curve fitting, etc) was performed with CasaXPS Version 2.1.9 software.

RESULTS/DISCUSSION: PS chips are treated with Ar/O_2, He/O_2, N_2/H_2, and NH_3/H_2 plasmas. Ar/O_2 and He/O_2 plasmas are supposed to produce oxygen-containing functional groups while N_2/H_2 and NH_3/H_2 plasmas can produce nitrogen-containing functional groups at PS surfaces.

Table 1 shows the influence of gas mixtures on ion flux and ion doses. A monolayer of PS contains approximately 10^{15} molecules/cm^2. Compared to the doses values given in Table 1 this means that 10^4-10^5 ions/molecule are needed for oxygen- or nitrogen-activation on the PS surface.

Table 1. Parameters for plasma activations[a]

Prim. Gas / Sec. Gas (% / %)	Ion Flux (mA/cm^2)	Ion dose ($Ions/cm^2$)
95 Ar / 5 O_2	9	1.0E+19
95 He / 5 O_2	23	2.6E+19
100 NH_3 / --	26	2.9E+19
92 NH_3 / 8 H_2	26	3.0E+19
95 N_2 / 5 H_2	87	9.8E+19
90 N_2 / 10 H_2	95	1.1E+20
70 N_2 / 30 H_2	101	1.1E+20

[a] Activation conditions: 60 W, 0.4 mbar, exposure of 3 minutes.

In the untreated PS there is no oxygen found. After Ar/O_2 (95/5) plasma treatment, 25 at% O was observed from the survey spectrum, which indicates the introduction of polar O-containing functional groups. Inspecting the C narrow scan spectra reveals functional oxygen containing groups (C-O, C=O, O=C-O, etc) after the plasma treatment (Figure 1). The presence of these O-containing functional groups is also confirmed by static water contact-angle measurements: Untreated PS has a contact-angle of 83 degrees while after Ar/O_2 plasma treatment, it decreased to 47 degrees, showing an increased hydrophilic surface. He/O_2 plasma treated PS gives similar XPS analysis results as Ar/O_2 plasma treated PS (data not shown).

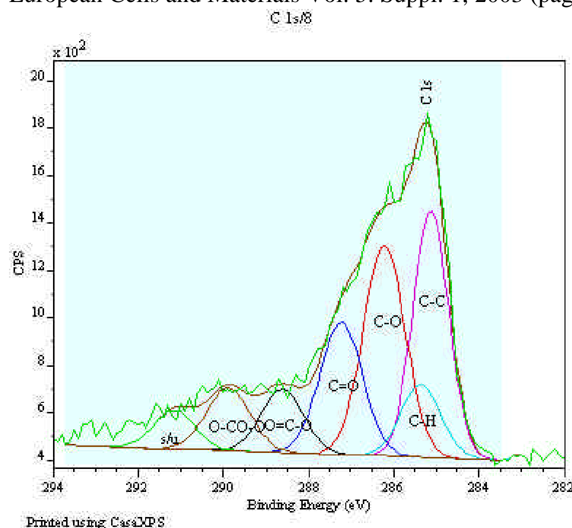


Figure 1. XPS narrow scan spectrum of of PS treated with Ar/O_2 (95/5) plasma.

The efficiency of the plasma activation with N_2 and NH_3 with an admixture of H_2 on PS is checked by nitrogen concentration (at % N) by XPS analysis (Table 2). XPS analysis showed that in the three cases of N_2/H_2 95/5, 90/10, and 70/30 dilution ratio, similar surface modification efficiencies are observed: they give 11±3 at % N. Under the present activation conditions, NH_3 or NH_3/H_2 plasmas are more efficient than N_2/H_2 plasma in providing a nitrogen-amino surface: both NH_3 and NH_3/H_2 (92/8) plasmas give 19 at % N. C1s narrow scan spectrum of PS treated with a NH_3 plasma is shown in Figure 2. It shows the presence of similar CO_x-groups with additional C-N component. Presence of oxygen-containing groups is explained by reaction of the plasma activated surface when transferring the sample for XPS analysis.

Table 2. Nitrogen concentrations of plasma activated PS[a]

Prim. Gas / Sec. Gas (% / %)	at % N
95 N_2 / 5 H_2	11
90 N_2 / 10 H_2	14
70 N_2 / 30 H_2	11
100 NH_3 / --	19
92 NH_3 / 8 H_2	19

[a] Activation conditions: 60 W, 0.4 mbar, exposure of 3 minutes. error: ± 3 at %

Although the ion dose of N_2/H_2 plasmas is high (Table 1), its efficiency to produce nitrogen-containing functional groups at the surface is lower than NH_3 plasma (Table 2), i.e. that the NH_3 plasma is more effective.

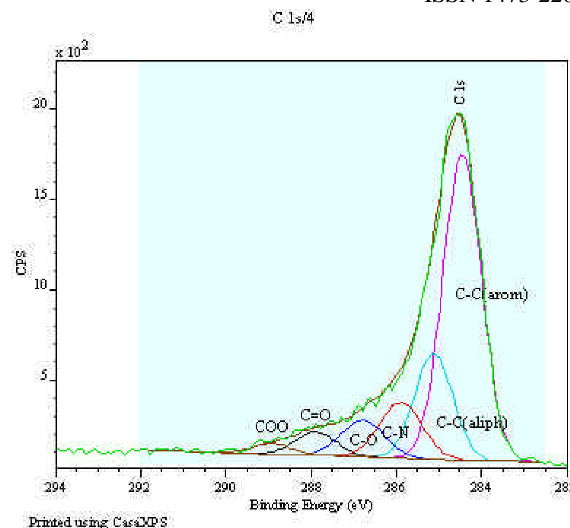


Figure 2. XPS narrow scan spectrum of PS treated with NH_3 plasma.

Conclusions The necessary ion density for PS surface activation is 10^4-10^5 ions/molecule per cm^2. Ar/O_2 and He/O_2 plasmas have similar activation efficiency to give oxygen-containing groups. Admixture of H_2 does not affect nitrogen presence at the PS surface. The NH_3 plasma is almost two times more efficient than the N_2/H_2 plasmas to create active nitrogen-containing sites.[6]

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Reference

[1] S. B. Idage, S. Badrinarayanan. Langmuir **14** (1998) 2780-2785.

[2] T. R. Gengenbach, X. M. Xie, R. C. Chatelier, H. J. Griesser. J. Adhesion Sci. Technol **8** (1994) 305-328.

[3] P. K. Chu, J. Y. Chen, L. P. Wang, N. Huang. Materials Science and Engineering R **36** (2002) 143-206.

[4] patent no. WO 01/14859 A1, EP 1 079 226 A1.

[5] G. Beamson, D. Briggs. *High Resolution XPS of Organic Polymers. The Scienta ESCA300 Database*. John Wiley & Sons Ltd, England, 1992.

[6] X. Gao, Ch. Hollenstein, M. Schawaller, H. J. Mathieu, in preparation.