Hydrophobic recovery of oxygen-plasma-treated polystyrene

E. Occhiello, M. Morra, P. Cinquina and F. Garbassi*
Istituto Guido Donegani SpA, Via G. Fauser 4, 28100 Novara, Italy
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Hydrophobic recovery of oxygen-plasma-treated polystyrene has been studied with regard to its dependence on temperature, molecular weight and plasma parameters, namely radio frequency power. Plasma chemistry has been studied by actinometry, while surface analysis has been performed by X-ray photoelectron spectroscopy (X.p.s.) and contact angle measurements. Molecular weight changes have been investigated by gel permeation chromatography. Plasma-treated surfaces become richer in oxygen and more crosslinked than untreated ones. Two basic mechanisms have been observed: one is based on short range motions within the plasma-modified layer, burying polar groups away from the surface without modifying its X.p.s. composition; the other involves long range motions, i.e. diffusion of non-modified macromolecules or segments from the bulk to the surface, altering its X.p.s. composition. The latter mechanism becomes important upon increasing ageing temperatures, or lowering molecular weight or extent of crosslinking of the surface layer.

(Keywords: polystyrene; hydrophobic; plasma chemistry)

INTRODUCTION

Oxygen plasma treatments have long been known to increase wettability and adhesion of apolar polymers such as polyolefins and polystyrene[1–3]. It is also well known that treated surfaces undergo ageing, leading to hydrophobic recovery and worsening of hydrophilicity-dependent properties with time[4,5]. In this respect polymer surface dynamics has been shown to play an important role[6–9].

Our aim in this work is to provide experimental data and discuss hydrophobic recovery of oxygen-plasma-treated polystyrene (PS) as a function of time, temperature, molecular weight and plasma parameters. PS is a particularly attractive polymer for this purpose, since it is readily available as standards with narrow molecular weight distribution and its molecular dynamics and diffusion[10–12] and surface tension[1,13,14] have been thoroughly studied. Furthermore it is amorphous, so crystallinity effects can be safely neglected.

Kramer and co-workers[15,16] used forward recoil spectroscopy to study the diffusion behaviour of PS treated with reactive ion beam etching, reactive ion etching and plasma etching in barrel and downstream reactors. They worked with high molecular weights, high ageing temperatures and high treatment levels, as shown by alterations in surface morphology. Their focus was on diffusion behaviour.

We focused on the effect of plasma treatment on the surface, mainly on wettability; for this purpose we chose to work at lower treatment levels, to avoid morphology effects hindering the use of contact angle measurements. To alter the extent of surface modification we chose to vary the power of the radio frequency (r.f.) inducing the plasma. Increasing the power means enhancing the energy density of the medium, hence favouring the reaction of plasma species with the polymer surface[17]. The effect on plasma chemistry of increasing r.f. power was checked by actinometry, i.e. monitoring the intensities of spectral lines relative to excited species and comparing them with those of inert species, namely argon atoms[18,19]. This technique has been used in the past to study plasma etching and polymerization[20,21]. To study the effect of molecular weight on hydrophobic recovery, we considered polymers with molecular weights in a wide range (2700–1 020 000). To avoid variations in surface morphology disturbing contact angle measurements, we restricted the range of ageing temperatures to 293–433 K.

The methods used to characterize treated surfaces were X-ray photoelectron spectroscopy (X.p.s.) and water contact angle measurements, a combination which proved particularly effective in the study of hydrophobic recovery of polymers[1,8,9]. Surface crosslinking effects due to plasma treatment were probed by solubility tests and by gel permeation chromatography (g.p.c.). A preliminary account of this work has been presented elsewhere[22].

EXPERIMENTAL

PS standards were purchased from Aldrich and Polymer Laboratories. The following M_w fractions were used: 2700, 4100, 9100, 34 500, 50 000 and 1 020 000, henceforth referred to as PS_{2700}, PS_{4100}, PS_{9100}, $PS_{34\,500}$, $PS_{50\,000}$, $PS_{1\,020\,000}$, respectively. In all cases we found $M_w/M_n < 1.1$, as checked by g.p.c. Polymer portions were dissolved in dichloromethane (10% w/v solutions) and spin-coated on clean glass slides. Solvent removal was completed by annealing the samples under vacuum.

Plasma treatments were performed using a parallel plate reactor, with the samples located on the water-cooled earthed electrode. The plasma parameters adopted

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* To whom correspondence should be addressed

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were as follows: excitation frequency 13.56 MHz; pressure 2 Pa; gas flow 8 cm^3 (STP) min^{-1}; treatment time 20 s. Discharge power was typically 100 W; different values (20, 50, 80 and 150 W) were adopted in order to investigate its effect on surface chemistry. In the case of actinometry, 2% Ar was added. The oxygen and argon used were from lecture bottles supplied by Carlo Erba.

Emission spectra of plasmas were obtained by collection from a quartz window through an optic fibre connected to a monochromator (PAR model 1229) and a microprocessor-controlled multichannel analyser (PAR plasma monitor model 1451A). Emission lines corresponding to oxygen ($3s^5$–$3p^5P$: 777.5 nm) and hydrogen ($2p^2P^0_{3/2}$–$3d^2D_{3/2}$: 656.3 nm) atoms have been calibrated to the $4s^1[1/2]^0$–$4p^1[1/2]$ argon atom line at 750.4 nm. The PS-coated surface within the reactor was kept constant, to ensure reproducibility. Spectra were taken in the last 5 s of the treatment, to avoid time-dependent effects.

To study wettability decay, plasma-treated samples were aged at different temperatures: 293, 353, 373, 393, 413 and 433 K. Contact angle measurements were performed after allowing the sample to reach room temperature in air; the time between extraction from the oven and contact angle measurement never exceeded 8 min, therefore we can safely assume that surfaces probed by contact angles are representative of the ageing temperature. Besides the treated sample, untreated PS subjected to the same thermal treatment was characterized, thus checking that the sample surface had reached room temperature and no thermal oxidation had occurred.

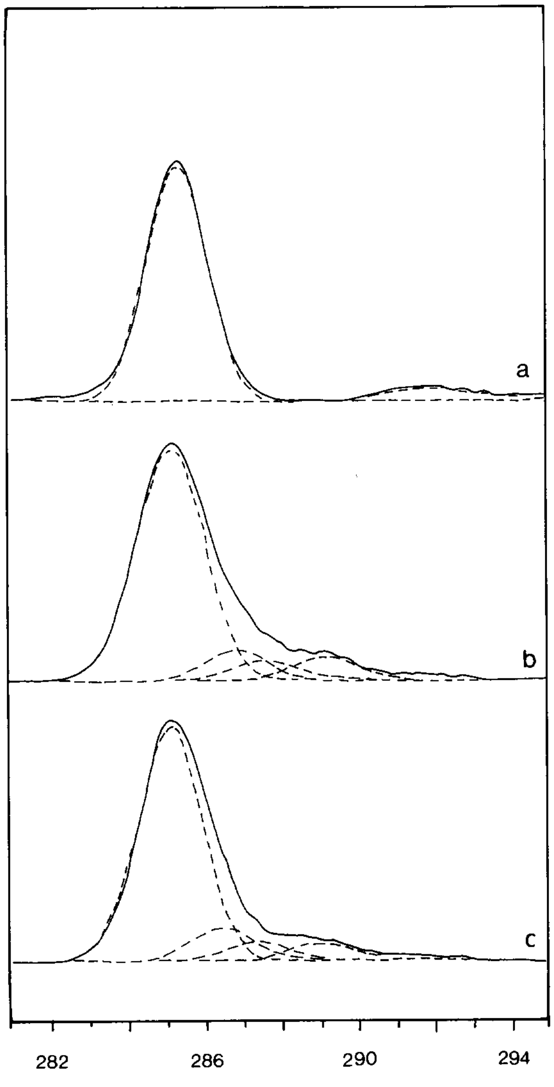

Figure 1 X.p.s. C-1s deconvoluted peaks relative to: (a) untreated PS_{50000}; (b) just-treated PS_{50000}; (c) treated PS_{50000}, aged 1440 h at 293 K

Water advancing (a.a.) and receding (r.a.) contact angles were measured by the sessile drop technique, on a Ramé–Hart contact angle goniometer. Advancing and receding angles were obtained by increasing or decreasing the drop volume while moving the three-phase boundary over the surface. The capillary pipette of the microsyringe was kept immersed in the drop during the entire measurement, as described in ref. 1. Carefully deionized and doubly-distilled water was used, having a surface tension of 72.8 mN m^{-1} (measured using a Cahn DCA 322 contact angle analyser). Contact angle values are the average over at least 10 measurements, performed in different parts of the sample surface. The typical error is ±3°.

X.p.s. spectra were obtained on a PHI model 548 XPS-AES spectrometer, using Mg Kα radiation (1253.6 eV) from a 400 W source. The analysis chamber pressure was maintained near 2×10^{-7} Pa, without baking. The electron take-off angle was 48°.

Signal averaging to improve the signal-to-noise ratio was possible due to the connection of the spectrometer to a PDP 11/50 computer. Further data processing (smoothing, Shirley or linear background subtraction, integration, Gaussian/Lorentzian curve fitting) was carried out using in-house software on a Sperry 1100/72 mainframe computer, details of which are reported elsewhere[23]. The sensitivity factors recommended by the manufacturer and verified by ourselves were used to obtain surface compositions. The reported surface compositions were averaged over three measurements. The error margin was typically below 0.5, expressed in atomic percentage.

G.p.c. was carried out using a Waters 150-C ALC/GPC instrument equipped with a set of four columns PL GEL (10^4–10^3–10^2–10^1 Å) and a differential refractive index detector. The analyses were performed in tetrahydrofuran (THF) at 303 K on plasma-treated powder, to enhance the surface/volume ratio and to improve sensitivity to the surface treated layer. To increase confidence in g.p.c. results, all experiments were repeated five times and the average values are reported.

RESULTS

Effect of plasma treatment

Treating a PS surface with oxygen plasma results in oxidation and extensive damage to aromatic rings. *Figure 1* shows C-1s photoemission peaks relative to untreated (*Figure 1a*) and 100 W oxygen-plasma-treated PS_{50000} (*Figure 1b*). High binding energy components relative to oxygen containing functions (C–OH, C=O, COOH) appear after plasma treatment, while the shake-up feature disappears. At the same time the surface carbon and oxygen atomic percentages averaged over the X.p.s.-observed layer changed from 97.0 to 79.5 and from 3.0 to 20.5, respectively. These results are in agreement with former work by Clark and Dilks on oxygen-plasma-treated PS[24].

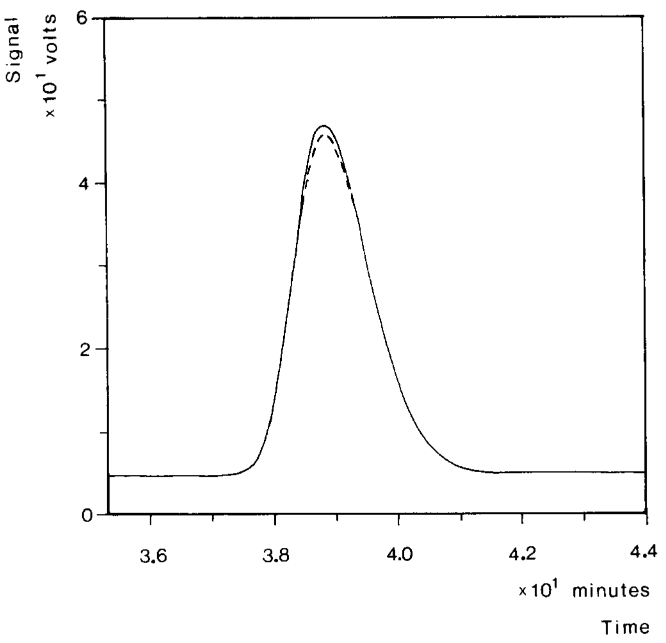

Figure 2 G.p.c. chromatograms relative to untreated (——) and 100 W plasma-treated (---) PS_{9100}

Correspondingly advancing angles, relative to the lowest surface energy component[25], decrease from 90° (untreated PS) to 13° (plasma-treated PS). Receding angles, relative to the highest surface energy component[25], are lowered from 78 to 8°. Scanning electron microscopy (SEM) did not show any alteration of surface morphology, thus changes in wettability can be attributed to chemical effects.

Plasma treatments of polymeric materials may induce the formation at the surface of low molecular weight highly oxidized species. To verify this possibility, aqueous extraction experiments were performed. The water drop used to measure contact angles on treated surfaces was deposited on an untreated surface. No change in contact angle with respect to that measured with 'pure' water was observed, thus excluding extraction of oxidized species from treated surfaces (ref. 6, ch. 2). Furthermore we performed X.p.s. on the water-extracted surface and observed no significant change in surface composition and C-1s peak shape with respect to just-treated samples. Therefore, we can exclude the formation of low molecular weight water-soluble species as a consequence of oxygen plasma treatment of PS surfaces.

We then performed g.p.c. on untreated and plasma-treated samples, to verify possible increases in molecular weight. *Figure 2* shows chromatograms relative to untreated and plasma-treated PS_{9100}. A lower intensity is evident for plasma-treated samples, while no effect on the peak shape is visible. These phenomena can be rationalized assuming some insolubilization after plasma treatment attributed to gelation or infinite network formation of the surface portion of the sample. No concomitant effect was observed on average molecular weight and dispersity; these are dominated by the bulk part of the sample which was unaffected by the treatment.

The results of Kramer and co-workers[15,16] are in agreement with the occurrence of crosslinking events as a consequence of treatment, even if they did not prove it directly.

Effect of ageing time

Plasma-treated PS_{50000} samples were then allowed to age at room temperature (293 K), both in atmosphere and in vacuum. *Figure 3* shows the behaviour of advancing and receding water contact angles as a function of ageing time at room temperature. Advancing angles showed a rapid increase for about 48 h, then stabilized at a limiting value (47°) rather lower than that of the untreated sample (90°). Receding angles did not significantly change with ageing. No significant difference was observed between ageing in air and in vacuum.

Figure 1c shows the C-1s photoemission peak relative to plasma-treated PS_{50000}, having reached limiting contact angles. No difference with respect to just-treated PS_{50000} (*Figure 1b*) was detected; furthermore the corresponding compositions, averaged over the X.p.s.-observed layer, did not show any variation outside experimental error.

The simultaneous variation of advancing contact angles and stability of the X.p.s.-derived composition upon ageing (*Figures 1* and *3*) rules out both contaminant adsorption (which is responsible for decreased wettability of clean high energy surfaces: ref. 1, ch. 6) and the migration of untreated polymer chains from the bulk to the surface. So hydrophobic recovery is attributed to local segmental motions within the plasma-modified layer, burying polar groups away from the surface. The thickness of the layer involved in this process can be considered similar to that observed by X.p.s., i.e. 3–5 nm, using the electron mean free paths reported by Clark *et al.* for polymers and instrumental conditions similar to ours[26]. Hydrophobic recovery by short range motions within the plasma-modified layer is actually typical of a number of polymers, namely polyolefins, polyesters and polycarbonates[8,27,28]. The immobilization of the surface layer by plasma treatment was also observed by Kramer and co-workers[15,16], using forward recoil spectroscopy.

Effect of ageing temperature

The rate and extent of hydrophobic recovery were then studied as a function of ageing temperature. In *Figure 4* the behaviour of advancing and receding water contact angles is plotted as a function of ageing time at 373 K. It is evident that the rate of recovery is higher; 30 min after treatment an advancing angle close to the limiting

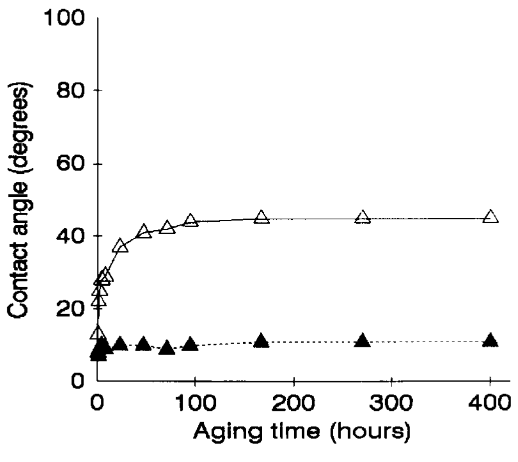

Figure 3 Ageing of oxygen-plasma-treated PS_{50000} at 293 K, as reflected by water advancing (△) and receding (▲) contact angle measurements. (Untreated PS: a.a. = 90°, r.a. = 78°)

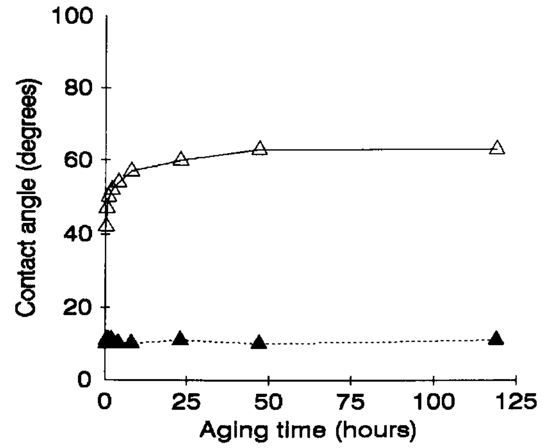

Figure 4 Ageing of oxygen-plasma-treated $\mathrm{PS}_{50\,000}$ at 373 K, as reflected by water advancing (△) and receding (▲) contact angle measurements

value observed at room temperature is reached, and after 23 h recovery is essentially complete.

In *Figure 4* it is already apparent that at 373 K a higher advancing angle is reached, while receding angles are insensitive to ageing, due to the persistence of polar islands at the sample surface. In *Figure 5* limiting advancing and receding angles of treated $\mathrm{PS}_{50\,000}$ are plotted as a function of ageing temperature. Limiting advancing angles show a stepwise increase, without reaching the value corresponding to untreated PS. Receding angles, on the other hand, remain quite stable up to 413 K, then show a slight increase upon ageing at 433 K. Interestingly no significant change in composition of the X.p.s.-observed layer is observed upon increasing ageing temperature, thus reconfirming a recovery mechanism based on short range motions.

Former studies on molecular modelling of hydrophobic recovery of plasma-treated PP showed that the short range mobility of oxidized chains depends on substitution, i.e. on the number and quality of oxygen-containing groups introduced by the treatment[27]. Furthermore it was shown that the temperature dependence of mobility is itself a function of substitution. The change in limiting contact angles reflects the crossover of mobility of differently substituted oligomers with temperature, driven by a compromise between the external (tendency to lower surface energy) and internal (tendency to maximize inter- and intramolecular interactions, mainly hydrogen bonds) driving forces.

Effect of molecular weight

Untreated samples showed no dependence of measured contact angles on molecular weight; in all cases we found a.a. = 90 ± 2° and r.a. = 78 ± 2°, in good agreement with literature data[1]. In *Table 1* contact angles of 100 W plasma-treated PS during ageing are reported as a function of molecular weight, time and ageing temperature.

Below 373 K all samples behave as in *Figures 3* and *4*. The advancing angle very quickly starts to increase, while the receding angle is stable within experimental error. The limiting value of the advancing angle depends on ageing temperature but not on molecular weight.

Above 373 K, low molecular weights exhibit a distinct behaviour. In *Figure 6* limiting advancing and receding angles of treated PS_{2700} are plotted as a function of ageing temperature. Both advancing and receding angles show a dramatic change from the behaviour in *Figure 5*. At 413 K PS_{2700} reaches advancing angles equal to those of untreated PS, while receding angles remain only slightly lower. As shown by the data in *Table 1*, PS_{4100} follows a path similar to that of PS_{2700}, but at higher temperatures. At 413 K, PS_{9100}, in turn, is just starting to deviate from the behaviour of higher molecular weight materials.

Further information is provided by X.p.s.-derived surface compositions (*Table 2*) of samples just treated and having reached limiting contact angles. The behaviour of X.p.s. O/C ratios of PS_{2700} and $\mathrm{PS}_{1\,020\,000}$, having reached limiting contact angles, is further displayed in *Figure 7*. No modification of the surface composition with ageing is observed for $\mathrm{PS}_{1\,020\,000}$ (and $\mathrm{PS}_{50\,000}$) at any ageing temperature. For PS_{2700} (and PS_{4100}) no departure from the above behaviour is visible up to 373 K, then a drastic decrease in O/C ratio occurs, suggesting out-diffusion of non-modified PS. However, out-diffusion is not complete, as shown by a residual O/C ratio higher than that of untreated PS. This is in agreement with the fact that, while advancing angles reach the value of untreated PS, receding ones do not, indicating a residual presence of oxidized functions at the surface. Again (*Table 2*) PS_{9100} shows differences from the behaviour of higher molecular weight species only at 413 K.

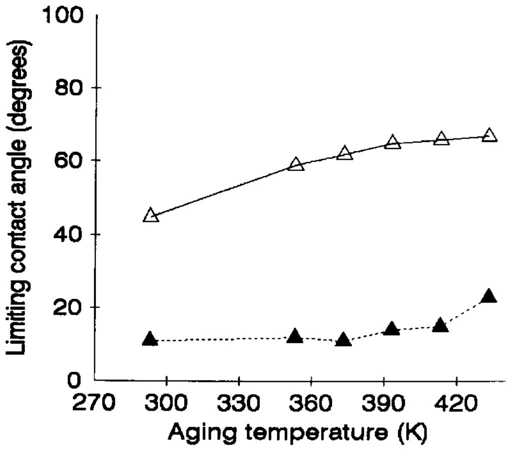

Figure 5 Limiting advancing (△) and receding (▲) contact angles of $\mathrm{PS}_{50\,000}$ as a function of ageing temperature

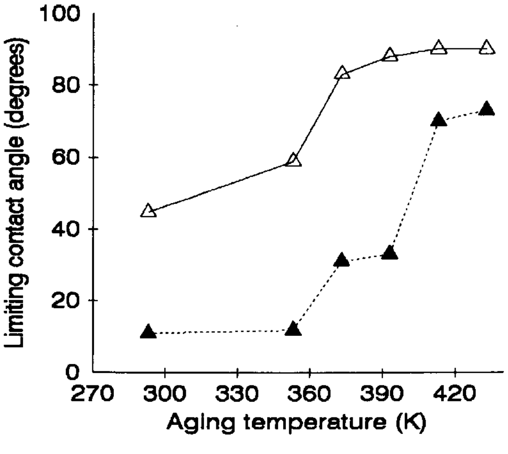

Figure 6 Limiting advancing (△) and receding (▲) contact angles of PS_{2700} as a function of ageing temperature

Table 1 Water advancing (a.a.) and receding (r.a.) contact angles (in degrees) for 100 W oxygen-plasma-treated PS as a function of molecular weight, ageing time and temperature

	2700		4100		9100		50000		1020000	
Time (h)	a.a.	r.a.	a.a.	r.a.	a.a.	r.a.	a.a.	r.a.	a.a.	r.a.
$T = 293$ K										
0.5	15	8	15	8	14	9	13	8	14	7
1.0	22	7	20	8	21	7	21	6	19	7
2.0	25	9	23	8	24	9	23	7	23	9
4.0	28	10	27	8	27	10	27	9	27	9
8.0	29	9	30	10	30	11	28	9	29	9
23.0	37	10	39	10	39	11	37	10	39	10
47.0	41	10	42	10	41	10	40	12	42	11
71.0	42	9	43	11	42	11	42	10	43	11
95.0	44	10	43	10	43	10	42	11	43	10
167.0	45	11	44	9	44	11	43	10	42	10
335.0	45	11	44	10	44	11	43	12	43	11
$T = 353$ K										
0.3	35	10	34	10	33	9	34	9	35	10
0.5	43	10	41	9	44	9	41	9	42	10
1.0	45	10	46	9	46	10	47	10	44	9
2.0	49	11	48	10	51	11	49	10	50	10
4.0	50	11	51	11	53	11	50	9	53	11
8.0	54	10	53	9	55	11	55	11	54	11
23.0	58	12	57	12	59	13	56	12	58	12
47.0	59	13	58	12	59	11	57	11	57	12
119.0	59	12	59	13	59	12	59	10	58	11
$T = 373$ K										
0.3	43	11	42	11	41	11	42	10	42	10
0.5	48	10	48	11	46	10	47	11	46	10
1.0	51	10	52	10	49	11	50	11	50	10
2.0	52	11	54	10	52	10	52	11	51	11
4.0	59	11	56	11	54	10	54	10	55	10
8.0	70	24	58	11	58	11	57	10	56	11
23.0	73	23	61	10	60	11	60	11	62	11
47.0	82	24	62	11	63	11	63	10	63	11
119.0	83	31	62	11	62	11	63	11	63	10
$T = 393$ K										
0.3	51	11	52	10	50	10	53	10	50	9
0.5	54	10	53	12	52	9	54	9	55	10
1.0	72	25	53	10	54	9	54	10	54	10
2.0	84	27	60	10	53	11	54	11	56	10
4.0	83	26	64	13	59	10	59	10	58	11
8.0	86	32	69	19	64	12	62	12	62	11
23.0	88	33	73	24	64	13	63	12	64	13
47.0	87	33	78	28	66	15	65	13	64	13
51.0	88	33	78	27	67	15	65	13	65	13
$T = 413$ K										
0.3	79	30	64	12	62	12	57	12	58	11
0.5	82	32	72	22	54	12	60	11	60	11
1.0	88	35	78	27	67	13	63	12	62	12
2.0	88	36	83	34	68	13	64	12	65	12
4.0	90	54	89	45	73	22	66	13	67	12
8.0	90	70	90	59	76	32	67	16	68	15
23.0	90	70	90	58	75	32	66	12	67	15
$T = 433$ K										
0.3	87	39	78	30	66	14	56	11	57	11
0.5	90	70	86	33	68	14	58	12	58	13
1.0	90	71	89	47	72	28	64	13	64	14
2.0	90	74	90	56	79	32	66	15	66	16
4.0	90	73	90	60	81	33	66	25	67	23
8.0	90	74	90	61	82	33	67	24	67	25
23.0	90	73	90	60	82	33	66	24	66	25

Table 2 X.p.s. compositions for 100 W oxygen-plasma-treated PS as a function of molecular weight and ageing temperature

	2700		4100		9100		50000		1020000	
T (K)	O	C	O	C	O	C	O	C	O	C
Untreated	2.5	97.5					3.0	97.0		
Just treated	20.2	79.8	20.0	80.0	19.9	80.1	20.5	79.5	21.0	79.0
273	20.5	79.5	19.8	80.2	21.3	78.7	19.2	80.8	19.6	80.4
353	19.7	80.3							21.4	78.6
373	15.2	84.8	19.5	80.5	20.2	79.8			21.1	78.9
393	14.0	86.0							20.0	80.0
413	6.2	93.8	11.0	89.0	15.1	84.9	19.5	80.5	19.0	81.0
433	6.4	93.6	9.6	90.4	14.6	85.4	18.9	81.1	19.2	80.8

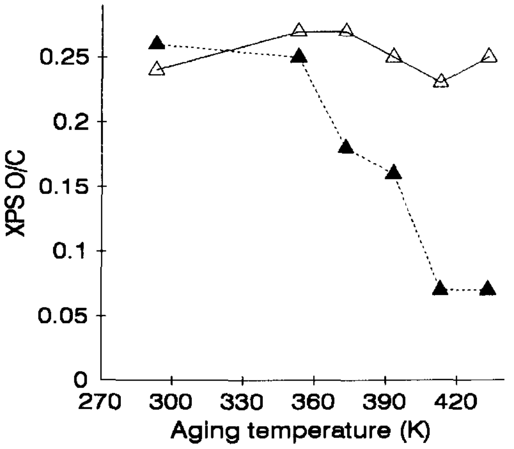

Figure 7 X.p.s. O/C ratios of PS_{2700} (▲) and $PS_{1\,020\,000}$ (△) having reached limiting contact angles, as a function of ageing temperature

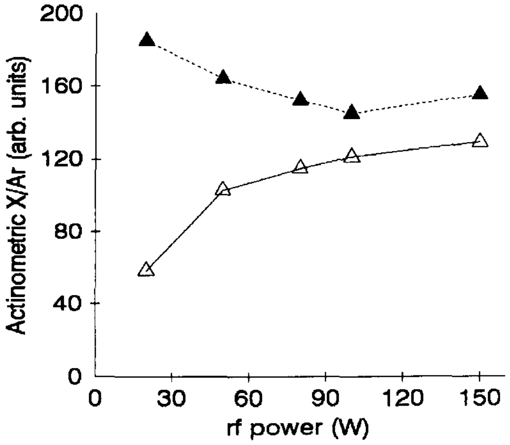

Figure 8 Actinometric O/Ar (▲) and H/Ar (△) ratios, as a function of r.f. power

Table 3 Results of THF solubility and M_w/M_n ratios, both obtained by g.p.c.

PS sample	r.f. power (W)	Insoluble fraction (%)	M_w/M_n
50000	–[a]	0	1.06
50000	100	1.4	1.06
9100	–[a]	0	1.08
9100	20	0	1.09
9100	50	1.8	1.08
9100	100	2.8	1.09
9100	150	2.6	1.08

[a] Untreated

Effect of plasma parameters

Actinometry was used to assess the variation of oxygen and hydrogen atom concentrations in the plasma as a function of r.f. power, consequently assessing electron mean energy and density also, which are dependent upon r.f. power. It must be noted that no general agreement exists on the correct choice of analytical lines in actinometry[29–33]. For this reason, we limited the use of the results arising from actinometric measurements to deductions which can be compared with g.p.c. and contact angle results (as discussed later) which allows (indirect) checking of the correctness of the analytical procedure we used.

O/Ar and H/Ar ratios are plotted *versus* r.f. power in *Figure 8*. Oxygen atoms are the active species in oxygen plasmas, while hydrogen atoms are products of plasma–surface interaction[3,18]. Interestingly O/Ar ratios drop along with an increase of H/Ar ratios, with both levelling at high r.f. powers. This reflects a lower efficiency of the plasma–surface interaction at very low power, resulting in low consumption of oxygen atoms and formation of hydrogen atoms. At higher powers the reaction becomes more efficient and a sort of steady state is quickly reached.

These findings parallel the g.p.c. results reported in *Table 3*. In *Figure 2* the formation of an insoluble fraction due to the crosslinking of the surface layer by the plasma was shown; the results in *Table 3* show that it is power dependent. At 20 W complete solubilization was observed, while at higher powers the insoluble amount increased, with a trend reminiscent of that of the actinometric H/Ar ratio, i.e. with a tendency to saturate at high r.f. powers. No significant difference was observed for M_w and M_w/M_n values, as expected, since they are dominated by the bulk fraction of the sample.

The different extent of surface reaction and crosslinking dramatically influenced hydrophobic behaviours. In *Tables 4* and *5* contact angles of PS treated in oxygen plasma at 20 and 150 W are reported, as a function of molecular weight, time and ageing temperature. In the case of 150 W plasma-treated samples, as suggested by the similarity in plasma chemistry (*Figure 6*) and g.p.c. results (*Table 1*), no important difference with respect to 100 W treatments has been found, even if limiting angles are somewhat lower.

A change is expected in the case of 20 W plasma-treated samples, since the extent of reaction (*Figure 8*) and crosslinking (*Table 3*) are lower. Actually even at low

Table 4 Water advancing (a.a.) and receding (r.a.) contact angles (in degrees) for 20 W oxygen-plasma-treated PS as a function of molecular weight, ageing time and temperature

	2700		4100		9100		50 000		1 020 000	
Time (h)	a.a.	r.a.	a.a.	r.a.	a.a.	r.a.	a.a.	r.a.	a.a.	r.a.
$T = 293$ K										
0.5	13	9	14	8	14	9	15	8	14	9
1.0	24	11	22	9	20	9	19	9	19	8
4.0	28	10	26	12	26	12	25	12	25	10
8.0	52	11	36	12	35	11	35	10	34	11
23.0	60	12	39	10	37	12	39	11	38	11
47.0	61	10	41	11	40	10	38	12	39	12
95.0	61	11	43	12	45	11	44	12	42	10
167.0	60	11	44	11	44	11	43	12	44	10
335.0	60	11	43	11	44	11	45	11	44	12
$T = 353$ K										
0.3	73	18	47	11	38	9	39	9	39	10
0.5	76	30	56	12	49	11	42	11	40	12
2.0	79	34	56	11	56	14	53	11	53	11
4.0	78	32	65	10	61	13	59	13	59	12
8.0	77	32	68	12	64	13	60	11	60	11
23.0	77	34	67	11	63	13	60	12	61	12
119.0	79	34	68	13	64	12	59	10	60	11
$T = 373$ K										
0.3	82	56	78	34	52	11	45	13	41	13
1.0	90	62	81	36	66	14	57	13	56	13
2.5	90	70	87	50	68	16	64	13	64	13
4.0	89	71	88	58	69	13	68	14	68	14
8.0	90	71	87	65	71	14	68	13	68	13
23.0	90	70	88	65	70	12	69	14	67	14
119.0	90	71	88	63	71	14	68	13	68	14
$T = 393$ K										
0.3	90	68	88	63	89	60	80	33	76	28
0.5	90	71	90	60	89	66	82	34	82	30
2.0	90	66	90	64	90	59	90	52	90	50
47.0	90	70	90	63	90	60	90	50	90	51
$T = 413$ K										
0.3	90	68	90	67	90	59	90	60	90	60
47.0	90	78	90	69	90	69	90	60	90	60

temperature PS_{2700} samples already show a departure from the behaviour of 100 W treated samples, with higher limiting angles. Also PS_{4100} and PS_{9100} start to show diffusion-like behaviour at temperatures much lower than for 100 W treatment. Finally PS_{50000} and $PS_{1020000}$ themselves reach very high advancing and receding angles at temperatures above 373 K.

This evidence is further supported by X.p.s. data relative to 20 W just-treated and 393 K aged samples, as presented in *Table 6*. The amount of oxygen introduced by the treatment is lower than for the 100 W treatment, in agreement with actinometric observations. Furthermore, after reaching limiting contact angles at 393 K, a decrease in oxygen concentration parallels the very strong recovery of advancing and receding contact angles, sugggesting that migration of non-modified macromolecules or portions of macromolecules to the surface may be responsible for hydrophobic recovery. The decrease of oxygen concentration is highest for PS_{2700}, in agreement with the very high receding angle (*Table 4*), and lower for the other samples, which actually reach a lower receding angle, suggesting the presence of more oxygen-containing functions close to the surface.

A comparison between the limiting advancing and receding angles reached at 393 K as a function of r.f. power for PS_{50000} and PS_{2700} (*Tables 1*, *4* and *5*) show, for the former, a parallel decline due to a transition of recovery mechanism from migration to short range motions, burying polar groups away from the surface. This behaviour is in good agreement with the increase in reaction efficiency shown by actinometry (*Figure 8*) and in crosslinking of the surface layer (*Table 3*).

In the case of PS_{2700} the mechanism is in any case migration, but at low treatment power, recovery is already complete at 393 K due to the absence of the barrier imposed by the crosslinked layer. For higher powers, crosslinking hinders diffusion, as shown by the decrease in limiting receding angle, while limiting advancing angles are only marginally affected. Actually that is perfectly correct, since receding angles are sensitive to

Table 5 Water advancing (a.a.) and receding (r.a.) contact angles (in degrees) for 150 W oxygen-plasma-treated PS as a function of molecular weight, ageing time and temperature

	2700		4100		9100		50 000		1 020 000	
Time (h)	a.a.	r.a.	a.a.	r.a.	a.a.	r.a.	a.a.	r.a.	a.a.	r.a.
T = 293 K										
0.5	16	9	15	7	16	9	14	7	14	7
1.0	21	8	20	8	21	7	21	6	21	6
4.0	26	8	26	8	28	9	26	7	26	9
8.0	27	9	29	10	30	9	27	9	27	9
23.0	34	9	37	10	37	11	36	9	38	11
47.0	39	9	42	9	39	11	38	9	40	10
71.0	40	9	43	10	42	12	42	10	42	9
95.0	42	10	43	10	42	12	42	10	42	9
167.0	43	11	44	9	43	10	42	11	42	9
335.0	43	11	44	10	43	11	43	11	43	12
T = 353 K										
0.3	33	10	34	10	32	8	34	9	32	9
0.5	43	10	41	9	42	9	41	9	42	10
2.0	48	11	45	9	49	11	49	10	49	9
4.0	50	11	49	11	52	11	50	9	49	11
8.0	52	10	53	9	55	11	55	11	52	11
23.0	56	11	55	10	57	13	55	10	55	9
47.0	56	12	54	12	57	11	56	9	55	11
119.0	59	11	55	11	56	12	56	10	55	11
T = 373 K										
0.3	43	11	42	11	40	9	39	10	42	8
1.0	50	10	52	10	46	9	48	11	50	8
2.0	52	11	54	9	52	9	52	11	51	11
4.0	63	11	56	10	54	9	54	9	55	8
8.0	70	16	60	12	56	11	56	10	56	11
23.0	72	17	61	11	60	11	58	9	58	11
47.0	82	19	61	9	62	10	60	10	59	9
119.0	80	24	60	11	60	10	61	11	59	10
T = 393 K										
0.3	50	11	52	10	48	10	50	10	50	9
0.5	52	9	51	12	49	9	51	9	48	10
2.0	78	27	59	9	56	8	54	13	55	10
4.0	86	32	61	11	60	9	57	11	57	10
8.0	86	34	69	19	63	10	61	12	60	10
23.0	88	33	72	21	60	11	61	11	60	11
119.0	88	33	70	22	60	10	61	11	59	10
T = 413 K										
0.3	70	19	66	14	60	12	50	10	50	9
0.5	76	24	76	12	62	10	56	10	56	11
1.0	83	22	80	19	67	13	58	11	59	10
2.0	88	29	83	29	68	11	59	10	59	10
4.0	90	50	90	32	70	20	63	10	61	12
8.0	90	66	90	49	69	31	64	11	63	12
23.0	90	70	90	51	70	29	65	13	64	12
95.0	90	70	90	60	70	30	64	11	65	10

Table 6 X.p.s. compositions for 20 W oxygen-plasma-treated PS, just treated and aged at 393 K, as a function of molecular weight

	2700		4100		9100		50 000		1 020 000	
T (K)	O	C	O	C	O	C	O	C	O	C
Just treated	17.2	82.8	18.0	82.0	16.9	83.1	17.5	82.5	16.0	84.0
393	5.4	94.6	11.4	88.6	10.0	90.0	9.9	90.1	10.5	89.5

very low amounts of polar groups, in contrast to advancing ones[25].

DISCUSSION

Oxygen plasma treatment of polystyrene surfaces causes introduction of oxygen at the surface along with destruction of aromatic rings (*Table 1*, *Figure 1*) and crosslinking (*Figure 2*, *Table 3*). The extent of the plasma–surface interaction depends on plasma parameters, namely electron energy and density. With increasing r.f. power the onset of a stronger interaction between plasma and PS was observed. This resulted in a larger consumption of atomic oxygen and more formation of atomic hydrogen (*Figure 8*), abstracted from the surface. Conversely higher r.f. power meant a higher amount of oxygen introduced at the surface (*Tables 2* and *6*) and more efficient crosslinking (*Table 3*).

Hydrophobic recovery of oxygen-plasma-treated PS occurs following two different mechanisms, involving short and long range motions, respectively. Hydrophobic recovery by monomeric or segmental motions within the modified layer, leading to burial of polar groups away from the surface, has been observed for other polymers, such as polypropylene, polyethylene, poly(ethylene terephthalate) and polycarbonates[28]. Its temperature dependence can be accounted for by studying the relative mobility of differently substituted segments[27]. As expected, its extent does not depend on molecular weight (*Table 1*), since long range motions are not involved. It is also relatively insensitive to r.f. power (*Table 5*) since the variations in crosslinking and percentage of oxygen at the surface are not sufficient to drastically alter the short range mobility.

The other mechanism, involving long range motions, with diffusion of non-modified macromolecules or portions of macromolecules to the surface, is more efficient but more expensive in terms of activation energy. It can be activated either by providing thermal energy (*Table 1*, *Figures 4* and *5*), i.e. by increasing the temperature or by relaxing constraints, namely lowering molecular weights (*Tables 1*, *4* and *5*), or by limiting the extent of crosslinking of the treated layer (*Table 4*).

Changes in permeability of the treated layer, even if using different techniques on samples which underwent different treatments, were also observed by Kramer and co-workers[15,16]. Comparing different treatments they showed that gentler treatments, such as plasma etching in barrel reactors, allow more permeability of the treated layer than 'hard' treatment, such as reactive ion etching.

The final extent of hydrophobic recovery, when diffusion effects are operating, is a complex function of plasma parameters, molecular weight and temperature (*Tables 1*, *4* and *5*; *Figures 4* and *6*). The factors influencing recovery are the interfacial energy between surface and medium and the chemistry of the surface layer. The latter is difficult to characterize thoroughly, since the plasma–surface interaction involves high energy density chemistry, leading to a number of different reactions and products.

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