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Surface modification of halogenated polymers: 1. Polytetrafluoroethylene

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Solutions of solvated electrons in the presence of magnesium offer many advantages for the surface treatment of PTFE when compared to the classical solutions of solvated electrons in the presence of alkalis: the polymer remains white instead of black, its surface is not destroyed and presents a controlled hydrophilic character. © 1997 Elsevier Science Ltd.

INTRODUCTION

The numerous uses of perfluorinated polymers are well known and generally exploit their good chemical and thermal inertness, their low coefficients of friction and their high electrical resistance[1,2]. However, as a counterpart of these remarkable properties, their bondability is rather low and therefore, surface treatments have to be performed to use them in any applications that required a good bondability to other materials, for example, adhesive bonding, lamination, painting, printing and metallization. The first requirement the treatment has to meet is to modify only the surface but not the bulk of the polymer in order not to change any property of the material. Different types of treatments may be mentioned, among which those proceeding by photochemistry[3], γ irradiation, ion introduction[4] and reduction[5] are the most commonly used. In this paper, we will focus on (i) reductive treatments and (ii) polytetrafluoroethylene (PTFE, $-(CF_2)_n-$) as a perfluorinated polymer.

Reductive carbonization of PTFE may be achieved in liquid[6–8] or solid[9] electrolyte cells during the discharge of a cell consisting of an alkali metal anode and a composite cathode containing the fluoropolymer. Two types of chemical reducing agents may also be used[2]: (i) anion-radicals prepared by the reduction of polyaromatic compounds by alkaline metals in organic solvents (e.g. sodium/naphthalene complexes) and (ii) solvated electrons obtained by dissolution of alkali metals (e.g. lithium, sodium) in liquid ammonia[1,5,10–13] which are the most reductive agents. When used for the

treatment of perfluorinated polymers, these solutions often have the disadvantage of leaving the treated sample porous and blackened. We have developed similar magnesium solutions by electrochemical dissolution although magnesium was thought to be insoluble in liquid ammonia[14,15]. Here, the method is described in the case of PTFE and its potential is investigated by scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (X.p.s.) and the measurement of wettability of the polymer surface.

EXPERIMENTAL

All the reagents were purchased from Aldrich (Fallavier, France) and used without further purification. Teflon plaques were supplied by 3P Ltd (Langres, France). Before treatment, the samples (2–3 cm^2 and 1 mm thick) were pretreated in order to decrease surface contamination. This consisted in washing them for 1 h in refluxing isopropanol and then drying them in an oven (100°C).

Preparation of the solutions of solvated electrons in the presence of magnesium

Liquid ammonia (80 ml) was condensed into an electrochemical cell via an already described set-up[16]. The solvated electron solutions in the presence of magnesium (referred to as the $(e_{s,Mg^{2+}})$ solutions) were obtained via an electrochemical procedure which consisted in the electrolysis of a solution of ammonium tetrafluoroborate (0.3 M) under conditions of controlled current (10^{-1} A cm^{-2}) using a stainless steel cathode (10 cm^2, 156 mesh cm^{-2}) and a magnesium anode. The electrolysis was stopped when 6000 Cb were passed through the circuit.

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Table 1 Concentrations in the solutions of solvated electrons

	$(e_{s,Mg^{2+}})$	(e_{s,Na^+})
$[e^-, NH_3]$	0.15 M	0.15 M
$[Mg(BF_4)_2]$	0.225 M	0.225 M
$[NaBF_4]$	0	0.30 M

*Preparation of the solutions of solvated electrons in the presence of sodium and magnesium*

These solutions were obtained via a similar procedure as for the $(e_{s,Mg^{2+}})$ solutions with the addition of NaBF$_4$ (2.6 g, 24 mmol) after the electrolysis. These solutions were referred to as the (e_{s,Na^+}) solutions.

Treatment by solutions of solvated electrons

The PTFE samples were treated by solutions of solvated electrons as soon as the characteristic blue colour of solvated electrons had been obtained. In general, this involved simply immersing the sample in the solution for 15 min. After treatment, the sample was washed sequentially with aqueous HCl (0.1 M) and distilled water for 30 min, while being agitated in an ultra-sound bath. If the work to be carried out in the solution was to be for a duration of more than 30 min, a constant current density of 3×10^{-2} A cm^{-2} was applied to the cell during the treatment.

Concentrations

The concentrations of the solvated electron solutions were determined after treatment by titration with a strong acid (ammonium bromide):

$$Br^- + NH_4^+ + e_{sol,Mg^{2+}} \rightarrow NH_3 + \tfrac{1}{2}H_2 + \tfrac{1}{2}MgBr_2$$
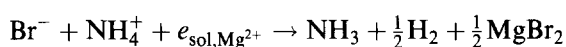
The neutralization was assumed to occur when the blue colour of solvated electrons had disappeared.

The concentrations used are gathered in *Table 1*.

SEM analysis

A JEOL JSM-5200 scanning electron microscope (SEM) operating at an accelerating voltage of 5 kV was used to examine the polymer morphology. For the elemental profile, a Pentafet Link ISIS Oxford analyser was used. The samples were set in epoxy resin and coated with gold using a Polaron SEM coating system.

X.p.s. analysis

The X.p.s. spectra (AlK_α) were recorded with a VG Scientific Ltd (Arcneil, France) ESCALAB. The power rating was 200 W (anode voltage 10 kV, emission current 20 mA). The spectrometer was operated in the constant energy mode (20 eV). The vacuum levels during the acquisition were normally $10^{-7}–10^{-8}$ mb. The spectrometer was interfaced with a microprocessor to facilitate data manipulation. The number of scans per spectrum was generally between 4 and 64 depending on the signal to noise ratio and each 20 eV scan took about 20 s to complete. Most of the measurements were taken at 0° to the normal of the surface, except for during the angle dependant study when the angle was varied between 0 and 70°.

The curve fitting procedure used Gaussian components and relied on least squares minimization. The spectra are all corrected for sample charging, the C 1s peak of adventitious carbon (285.0 eV) being used as the reference.

By comparing the intensities of the specific elemental peaks within a sample and taking into account their relative atomic sensitivity factors, it is possible to calculate the fractional atomic concentration of one element relative to C 1s, using

$$C_{A/B} = \frac{I_A/S_A}{I_C} \qquad (1)$$

where $C_{A/B}$ = fractional atomic concentration of element A relative to carbon; I_A = peak intensity of A; I_C = peak intensity of carbon; S_A = relative atomic sensitivity factor of A. We will focus mainly on the fractional atomic concentrations of fluorine and oxygen relative to carbon (referred to as **F/C** and **O/C** respectively).

I_A is obtained from the peak integral for element A after background removal. This method assumes that the sample is homogeneous throughout the sampling depth and is considered to have an accuracy of $\pm 10\%$. Sensitivity factors depend on the material investigated. In the case of PTFE, the sensitivity factor of fluorine was estimated assuming a ratio $C_{F/C}$ of 2 for an untreated sample ($S_F = 3.7$). For the sensitivity factor of oxygen, we have taken the general value obtained with our spectrometer for polymers since the untreated sample was supposed to contain no oxygen ($S_O = 3.1$).

Wetting measurements

A study of the surface free energy of samples treated by magnesium and sodium solutions was undertaken since this parameter is of fundamental importance when considering surface phenomena such as adsorption, wetting and adhesion. The method used consists of measurement of equilibrium contact angles θ of small sessile drops (2 μl) of probe liquids of various surface tensions, γ_L, and dispersive, γ_L^D, and polar, γ_L^P components ($\gamma_L = \gamma_L^D + \gamma_L^P$) (water: $\gamma_L = 72.6 \times 10^{-3}$ J m^{-2}, $\gamma_L^D = 21.6$ J m^{-2}; di-iodomethane: $\gamma_L = 50.8$ J m^{-2}, $\gamma_L^D = 48.5$ J m^{-2} and 1-bromonaphthalene: $\gamma_L \sim \gamma_L^D = 44.6$ J m^{-2}) deposited on the untreated or treated surfaces of PTFE. Contact angles may be measured experimentally either when the liquid moves forward on the surface of the solid (advancing angles, θ_a), or conversely when it moves backwards on the surface (receding angles, θ_r). Advancing and receding angles were obtained respectively by increasing and decreasing the volume of the drops deposited on the plaque using a microsyringe whose needle was immersed in the drop.

RESULTS AND DISCUSSION

Electrochemical treatment for PTFE surface modification

Magnesium is generally described as insoluble in liquid ammonia. However, the formation of a magnesium solution containing solvated electrons in the presence of the magnesium cation can be achieved by an electrochemical procedure which consists of two steps. In the first one, the electrolysis of an ammonium tetrafluoroborate solution is performed. Ammonium cations are reduced at the cathode according to

$$NH_4^+, BF_4^- + e \rightarrow NH_3 + \tfrac{1}{2}H_2 + BF_4^-$$
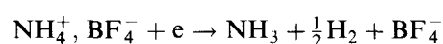
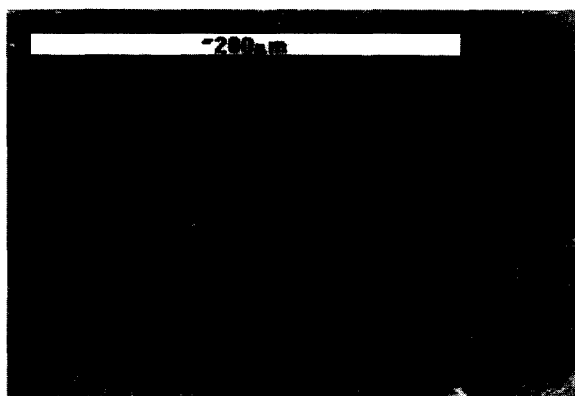The anodic reaction corresponds to the oxidation of

Figure 1 SEM of an untreated PTFE sample (magnification: 350)
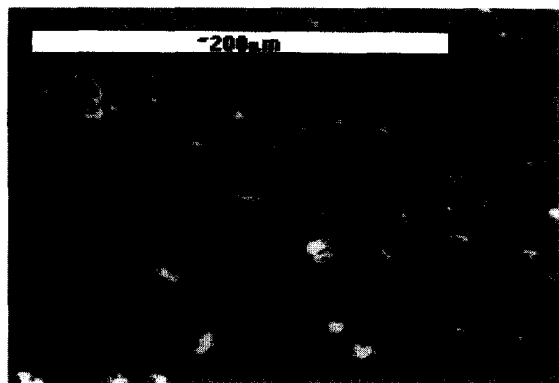

Figure 2 SEM of a PTFE sample treated 15 min in a magnesium solution (magnification: 350)
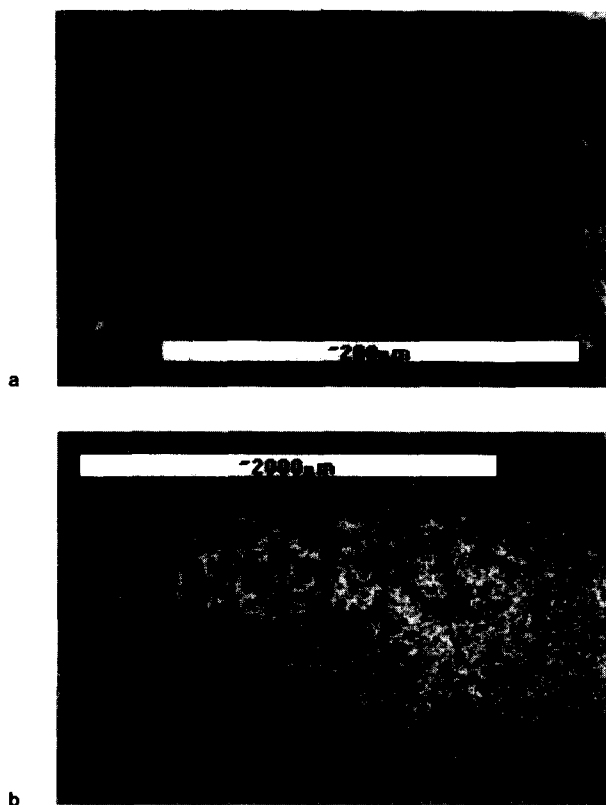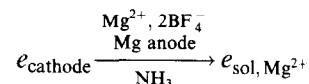

a

b

Figure 3 (a, b) SEM of a PTFE sample treated 15 min in a sodium solution. (a) Magnification: 100. (b) Magnification: 350

the magnesium from the electrode

$$Mg \rightarrow Mg^{2+} + 2e$$

In the second step when there are no more ammonium cations present in the medium, solvated electrons are generated at the cathode

$$e_{cathode} \xrightarrow[NH_3]{\substack{Mg^{2+}, 2BF_4^- \\ Mg \text{ anode}}} e_{sol, Mg^{2+}}$$

PTFE samples were treated in the solutions of solvated electrons in liquid NH_3 for different time durations. The solubility of solvated electrons depended on the amount of tetrafluoroborate salt present in the solution. Most of the experiments were performed with a 0.15 M solution of solvated electrons (concentration of the starting ammonium tetrafluoroborate: 0.3 M). In order to compare such treatments with the classical treatments using sodium, solutions containing both magnesium and sodium were also used. In that case, sodium tetrafluoroborate was added to an already prepared solution of solvated electrons in the presence of magnesium.

Before treatment, the appearance of PTFE was white and after treatment by the magnesium solution there was no visible change. However, when sodium was added to the solution of magnesium, the sample changed dramatically and appeared black and porous.

Scanning electron microscopy

Surface morphology. By analysis of the back-scattered and secondary electron emissions from the sample, images of the surface morphology were obtained. *Figures 1–5* show an untreated surface and surfaces treated by both the magnesium and the sodium solutions for 15 min.

For the untreated sample (*Figure 1*) the image shows the surface to be fairly homogeneous. However, a regular series of parallel lines across the surface can be observed. These are possibly due to machine finishing.

The images of the sample treated by the $(e_{s,Mg^{2+}})$ solution for 15 min (*Figure 2*) show that the lines present on the surface of the non-treated sample have completely disappeared. The surface is also no longer homogeneous and white 'scars', due to accumulations of charge and indicating where surface modification has occurred, can be seen every 30–80 μm. A higher magnification image of one of these surface defects reveals a scar of 10–20 μm in diameter, although it should be noted that such a diameter was difficult to determine as prolonged observation at such a high resolution resulted in the defect area growing. After 19 h of treatment by the magnesium solution, the appearance of the sample did not change.

From the images of the sample treated by the (e_{s,Na^+}) solution for 15 min (*Figures 3a* and *b*) it is immediately apparent that the surface has been attacked to a much greater extent. However, it can be observed that the distance between the defects (taken from one centre to the next) is also $\approx 80 \mu$m, suggesting that the modification begins at similar sites on the surface as during the treatment by the Mg^{2+} solution and is possibly the average distance between the naturally occurring random structural defects of the surface. The diameter of the scars are however much larger than for the Mg^{2+} treatment and practically, the scars cover all the
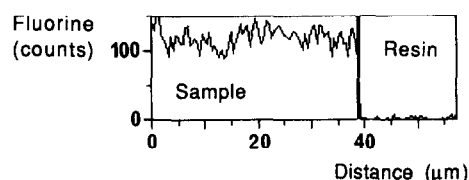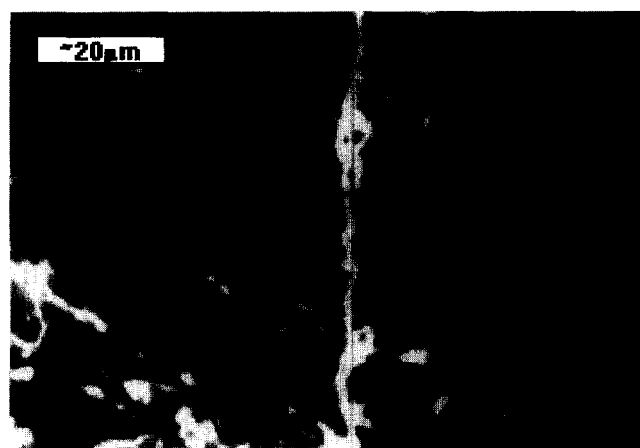
Figure 4 SEM profile image of an untreated sample of PTFE (magnification: 1400). The spectrum below shows the fluorine composition along the line indicated
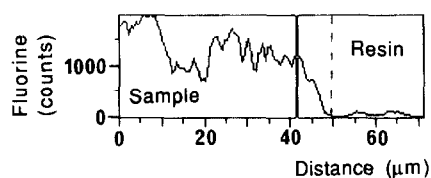

Figure 6 SEM profile image of a sample of PTFE after being treated in a sodium solution for 15 min (magnification: 1400)
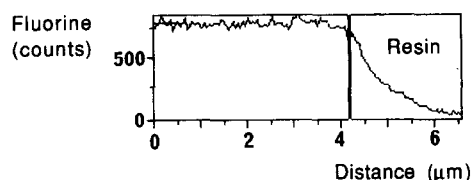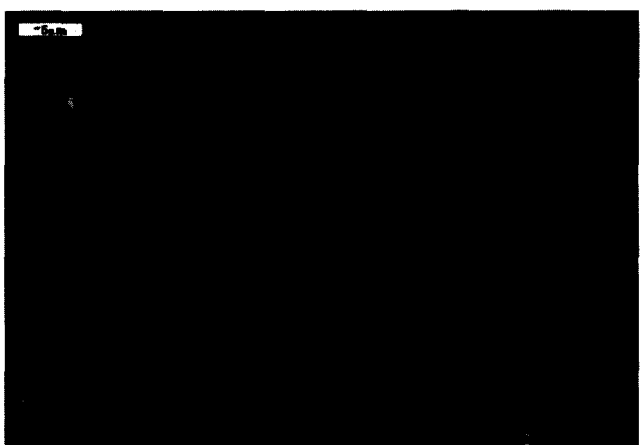

Figure 5 SEM profile image of a sample of PTFE after being treated in a magnesium solution for 19 h (magnification: 2000)

surface. An enlargement of one scar in the early stages of development shows it to have the shape of a 3-pointed star.

Depth profile. By analysing the X-rays emitted from the irradiated sample, it is possible to analyse how the chemical composition of the sample varies with depth. Although the accuracy of this profile was not such that a quantitative microanalysis of the relative amounts of each element could be achieved, as is the case with e.s.c.a., it did provide an estimation of the depth of attack. This was taken as the distance between the

surface and the point where the amount of fluorine detected was the same as in the bulk sample.

Figures 4–6 are relative to the profiles of the different samples. In each figure, the morphology of a slice through the sample is shown, the horizontal line indicates the position from where the profile was taken and the spectrum below shows the fluorine composition along the line indicated.

The profile image of the untreated sample (*Figure 4*) shows a large amount of charge accumulation on the surface (white areas). It can be noted from the accompanying elemental profile that the amount of fluorine in the sample is approximately constant throughout the sampling depth and drops off suddenly as soon as the fluorine free resin starts, as is expected.

However, the profile of the sample which was treated by the Mg solution for 15 min shows an area of gradual decline in the amount of fluorine that was detected. This region can be measured to be about the size of the X-ray probe ($1-2 \mu m$). A similar profile of the sample that was treated by the ($e_{s,Mg^{2+}}$) solution for the 19 h (shown in *Figure 5*) is almost identical and the depth of attack is measured to be of the same order of magnitude. Considering the accuracies of the measurements involved these results are in good agreement.

Figure 6 shows the profile of the sample which has been treated by the e_{s,Na^+} solution. As was the case in *Figure 3*, the Na treated sample is once again seen to be more harshly modified and the porous nature of the surface can be clearly observed. The depth of attack is measured to be $\approx 8 \mu m$.

X-ray photoelectron spectroscopy[17–19]

General aspect of the X.p.s. spectra of PTFE samples. X-ray photoelectron spectra of untreated PTFE plaques consist mainly of two elemental peaks relative to carbon and fluorine atoms (*cf. Figure 7a*). The intensity of the fluorine peak is about eight times higher than that of the carbon peak, in agreement with
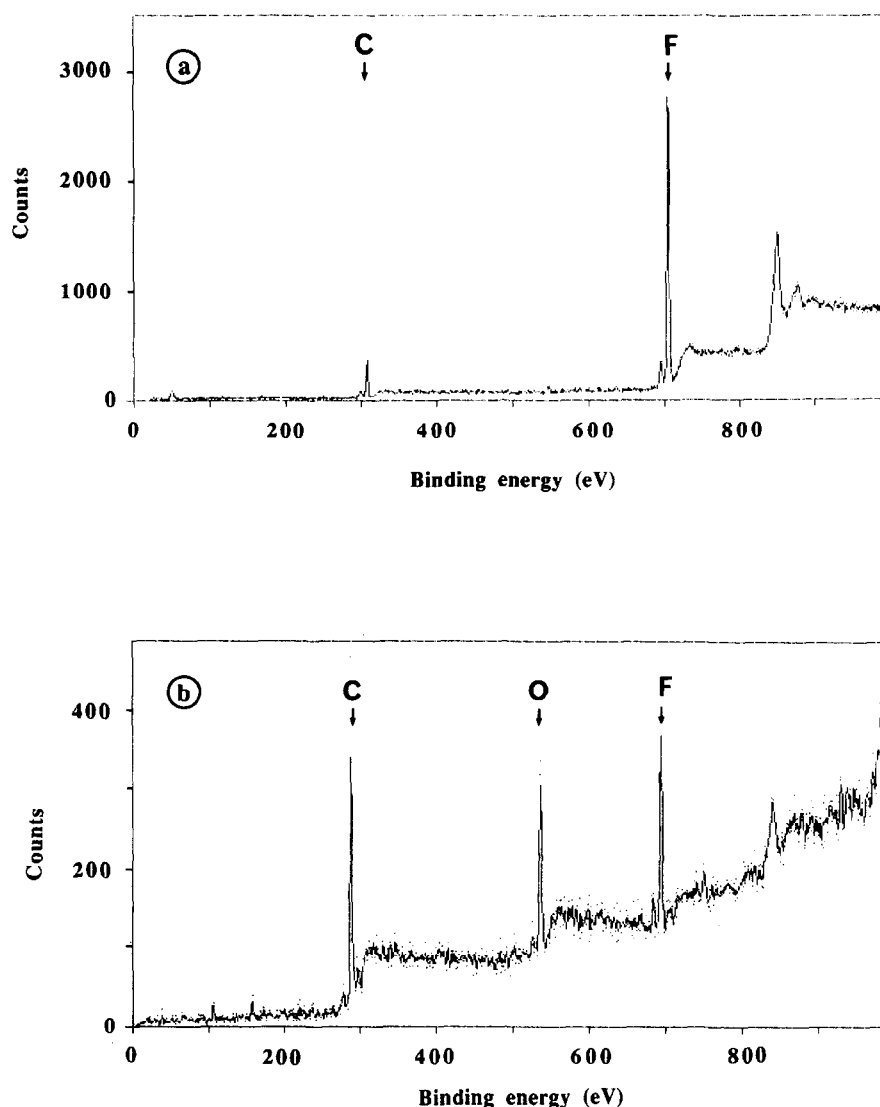
Figure 7 Wide scan X.p.s. spectra of PTFE samples. (a) Untreated. (b) After being treated in a magnesium solution for 30 min

(i) the formula of PTFE $(-(CF_2)_n-)$ and (ii) the sensitivity factor of fluorine relative to carbon $(S_F = 3.7)$. The peak of carbon of an untreated sample corresponds mainly to CF_2 elements (cf. *Figure 8a*). An additional peak relative to oxygen is present on the spectrum of a treated PTFE plaque (cf. Figure 7b). The peak relative to fluorine has considerably decreased and its intensity has become of the same order of magnitude as that of carbon. The peak of carbon of a magnesium treated sample can be decomposed into three elementary peaks which are relative to carbon atoms bound to (i) carbon or hydrogen ($\{C-C, C=C, CH\}$ at $\sim 285\,eV$), (ii) oxygen or one fluorine atom ($\{COH, C=O, CO_2H, CHF\}$ at $\sim 288\,eV$) and (iii) two fluorine atoms (CF_2 at $\sim 293\,eV$) (cf. *Figure 8b*). Deconvolution of the peak at 288 eV into four peaks according to the well-established chemical shifts of each functional group bound to carbon (COH at 286.6 eV, $C=O$ at 288 eV, CO_2H at 289 eV and CHF at 287.9 eV)[19] has not been made since the concentration of the functional groups involved is very small compared to that of the functional groups of the neighbouring peak at 285 eV (C–C, C=C, CH).

No inclusion of magnesium or sodium is observed at the surface of the treated plaques since these elements were not detected by X.p.s.. This is due to the acidic washing of the samples after treatment; when the samples were washed in water only, peaks relative to magnesium or sodium were present and the peak of fluorine became much larger because of the presence of mineral fluorine.

Comparison of the magnesium and sodium treatments. The samples were treated for 1 or 30 min by the magnesium solution or 1 min by the sodium solution.

The results are shown in *Table 2*. The quantity of oxygen in the untreated PTFE is surprisingly large, which should be due to superficial contamination. For the sample treated by the magnesium solution for 1 min the F/C and O/C ratios are very similar to those of the untreated sample. However, after 30 min in the same solution the sample has a relatively high oxygen content and has been defluorinated by 90%. By contrast after just 1 min of treatment in the sodium solution the sample is almost completely defluorinated and has a high $\{C-C, C=C, CH\}$ content, however its oxygen content is still quite low compared to that of the 30 min treatment with just magnesium. The variations of the intensity of the elementary peak of carbon at 288 eV with
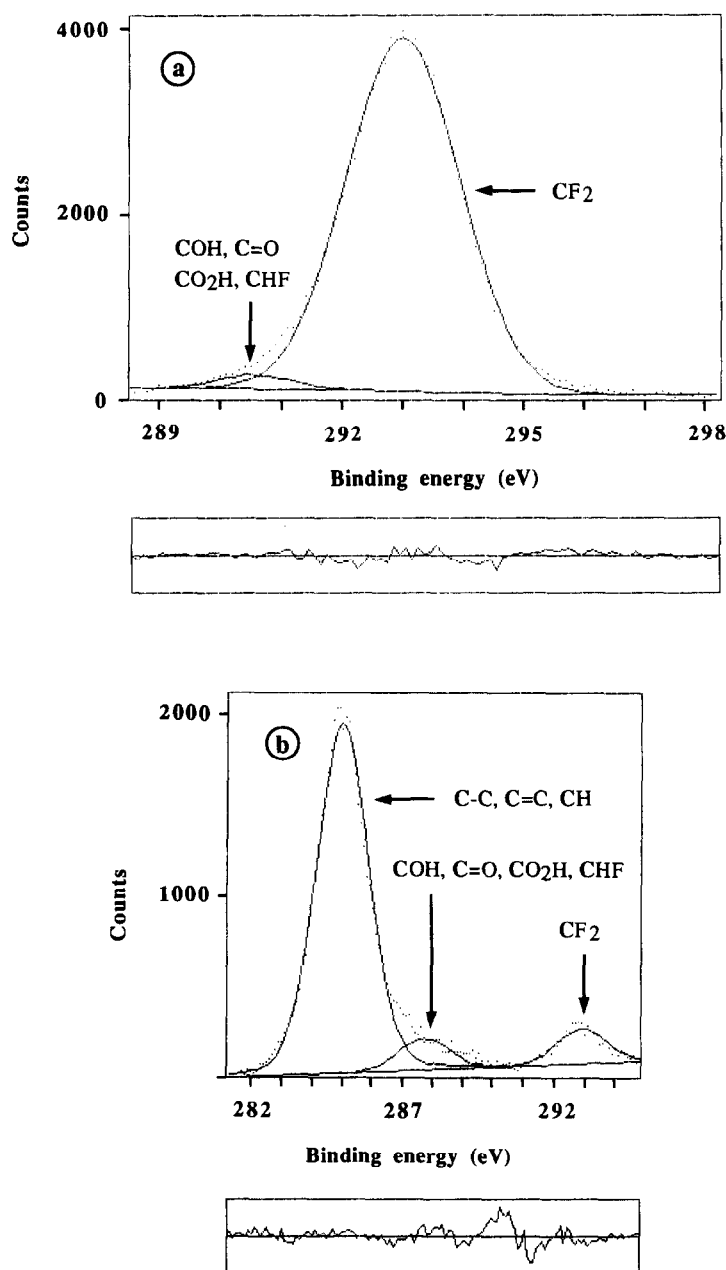
Figure 8 High resolution X.p.s. spectra of PTFE samples, carbon atom peaks. (a) Untreated. (b) After being treated in a magnesium solution for 30 min. The curves below indicate the difference between the experimental (dots) and calculated (solid line) spectra
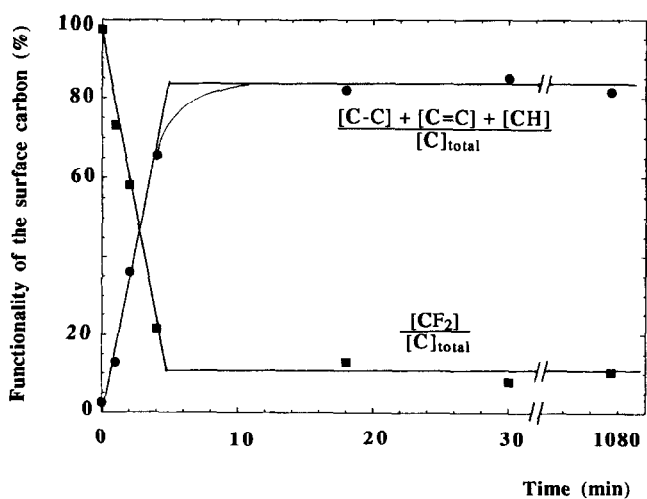

Figure 9 Variation of the functionality of the surface carbon with time (Mg treatment)

the treatment time is not monotone since that peak is relative to both CO and CHF contents whose variations are opposite.

Rate of attack with magnesium solutions. Several samples of PTFE plaque were treated in the 0.3 M $(e_{s,Mg^{2+}})$ solution for various durations of time ranging from 0 min to 18 h. The results of X.p.s. analyses, which are reported in *Figure 9*, clearly show a decrease of fluorine and an increase in the proportions of $\{C-C, C=C, CH\}$ with time of treatment. At the same time, the O/C ratio increases from 0.04 to 0.21 (cf. last line of *Table 2*).

The proportion of $\{C-C, C=C, CH\}$ rises quickly to a maximum of 80–85%, whilst the fluorine content decreases to about 10%. After 30 min of treatment the modifications appear to have ended and no further change is apparent even after 18 h of treatment. For the

Table 2 X.p.s. analysis of samples of PTFE plaque. Influence of the reducing agent (Mg or Na)

$E_b{}^a$ (eV)	Origin of e^-	Peak assignment	Untreated (%)	Mg^b treated$_{1\ min}$ (%)	Mg^b treated$_{30\ min}$ (%)	Na^c treated$_{1\ min}$ (%)
285.0 ± 0.2	C 1s	C–C C=C CH	~ 0	13	85	77
288.3 ± 1.3		COH C=O CO_2H CHF	2.5	14	7	23
292.9 ± 0.3		CF_2	98	73	8	~ 0
532.3 ± 0.2	O 1s	COH C=O CO_2H	100	100	100	100
689.9 ± 0.3	F 1s	CF	100	100	100	100
O/C ratio ($S_O = 3.1$)			0.04	0.05	0.21	0.14
F/C ratio ($S_F = 3.7 \pm 0.3$)			2.0	1.75	0.23	0.01

^{a} Binding energy
^{b} $[NH_4BF_4] = 0.3\,M$; $[e_{s,Mg^{2+}}] = 0.15\,M$
^{c} $[NaBF_4] = 0.3\,M$ added to the latter solution

Table 3 X.p.s. analysis of samples of PTFE plaque. Variation of the functionality of the surface carbon with depth (Mg treatment)

Sample	Angle α (°)	Proportion of C at binding energy, E_b (%)		
		285.0 ± 0.2 C–C, C=C, CH	288.3 ± 1.3 COH, C=O, CO_2H, CHF	292.9 ± 0.3 CF_2
1 min	0 ± 15	13	14	73
1 min	30 ± 15	17	14	70
1 min	45 ± 15	18	14	68
1 min	70 ± 15	50	10	41
2 min	0 ± 15	36	6	58
2 min	30 ± 15	40	13	47
2 min	40 ± 15	46	10	44
2 min	70 ± 15	56	—	44
18 h	0 ± 15	81.5	8.2	10
18 h	30 ± 15	81	9.0	10

Table 4 X.p.s. analysis of samples of PTFE plaque. Variation of the functionality of the surface carbon with the concentrations in the solution

$E_b{}^a$ (eV)	Untreated (%)	$[NH_4BF_4] = 1.5\,mM^b$ (%)	$[NH_4BF_4] = 6\,mM^b$ (%)
285.0 ± 0.2	~ 0	29	67
288.3 ± 1.3	2.5	8.7	13
292.9 ± 0.3	97.5	62	20
532.3 ± 0.2	100	100	100
689.9 ± 0.3	100	100	100
O/C	0.04	0.13	0.26
F/C	2.0	1.5	0.55

^{a} Binding energy
^{b} Saturated solvated electrons solution

first 4 min of treatment the rate of surface modification is linear and the content of {C–C, C=C, CH} increases by about 16% min^{-1} whilst that of CF_2 decreases by about 18% min^{-1}.

Partial defluoration can be observed with such 0.3 M solutions of solvated electrons for times of treatment lower than 5 min.

Depth of attack with magnesium solutions. The sampling depth, d, varies linearly with the cosine of the photoelectron emission angle α as

$$d = d_{max} \cos \alpha$$

When α decreases, bulk emission is increasingly favoured over surface emission. Therefore, analysis at
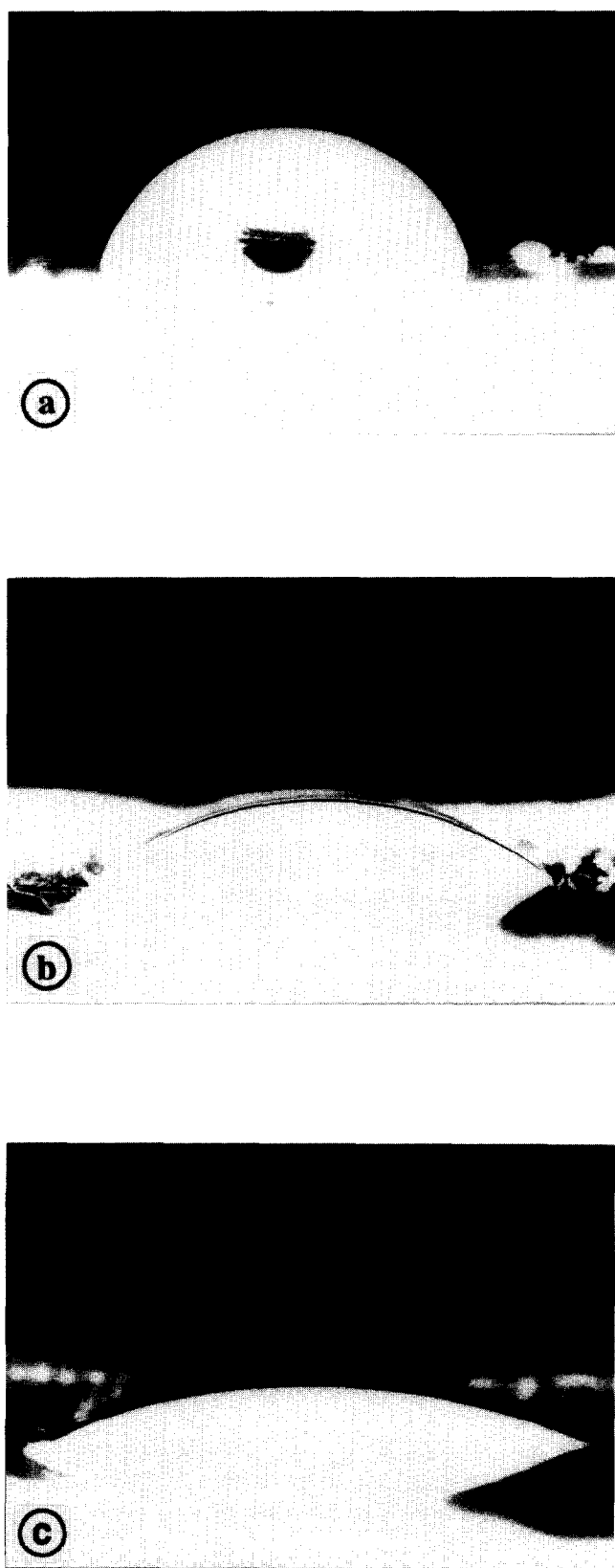
Figure 10 Photographs of drops of 1-bromonaphthalene deposited on the surface of PTFE plaques. (a) Untreated. (b) After being treated in a magnesium solution for 30 min. (c) After being treated in a magnesium solution for 90 min

different emission angles provides a non-destructive depth profile of the sample for a depth of up to 15 nm ($\alpha = 0$). However, because of the low accuracy of angles α ($\pm 15°$), the values of d are not known precisely and therefore only trends can be observed.

Some samples from the previous section were depth profiled by X.p.s.. Angular-dependent X.p.s. analysis was carried out for different times of treatment (cf. *Table 3*). For a treatment of 1 min, the results show that on going from the surface (high angles) towards the bulk (small angles), the amount of $\{C-C, C=C, CH\}$ decreases and levels off at about 10–15%. The C–F percentage content is seen to increase in a similar manner, levelling off at 70–80%. The amount of oxygen appears to be relatively constant with the analysis depth.

The sample that had been treated for 2 min shows a similar trend although the rate of composition change with depth is slower and the values involved are higher than those corresponding to the sample treated for 1 min. This is consistent with the depth of attack increasing with treatment time. After 18 h of treatment the composition is approximately constant at 13 and 15 nm. This suggests an even greater profundity of attack than that explored by X.p.s..

Effect of the concentration of ($e_{s,Mg^{2+}}$). In this experiment the quantity of NH_4BF_4 was varied from 1.5 to 6 mM and the corresponding saturated solutions of solvated electrons in the presence of magnesium were obtained by the electrochemical procedure previously described. The concentrations of solvated electrons were too small to be determined by ammonium titration.

The results are reported in *Table 4*. They show that, for low concentrations the extent of attack depends on the concentration of the electrolyte, both the oxygen and $\{C-C, C=C, CH\}$ contents are observed to increase, and the fluorine content to decrease with an increase in the $e_{s,Mg^{2+}}$ concentration. Partial defluoration of PTFE can therefore be achieved with 15 min treatments when using small amounts of electrolyte.

Effect of the concentration of (e_{s,Na^+}). In a similar manner to the study of the attack at low concentrations of the magnesium cation, an investigation of the effect of low concentrations of sodium was carried out starting from a solution of solvated electrons in the presence of magnesium ($[NH_4BF_4] = 0.3\,M$; $[e_{s,Mg^{2+}}] = 0.15\,M$) and adding to it small amounts of $NaBF_4$. It was observed that even at low concentrations (1 mK < $[e_{s,Na^+}]$ < 5 mM) the reduction by the e_{s,Na^+} solution was almost complete. Visually, the samples showed a quick change from white (untreated) to golden brown then to almost black as the concentration increased.

Effect of the nature of the material. We have applied the magnesium and sodium treatments of PTFE to other forms of the material such as wool and powder. The appearance of all the forms of PTFE before treatment was white and opaque. After treatment in the magnesium solution the plaque remained white, the wool was beige in places and the powder appeared to be a homogeneous medium brown. After being treated with the sodium solution the plaque was black and porous, the wool was black, and the powder was an even dark brown. The X.p.s. spectra were about the same for the three forms.

Wettability

We have studied both advancing and receding contact angles[20] of probe liquids on unmodified and surface

Figure 12 Variation of $\cos\theta_a$ as a function of $\sqrt{\gamma_L^P}/\gamma_L$ (30 min Mg treatment). θ_a, advancing contact angle; γ_L^P, dispersive component of the solid surface free energy; γ_L liquid, surface free energy. The straight line corresponds to the apolar liquids
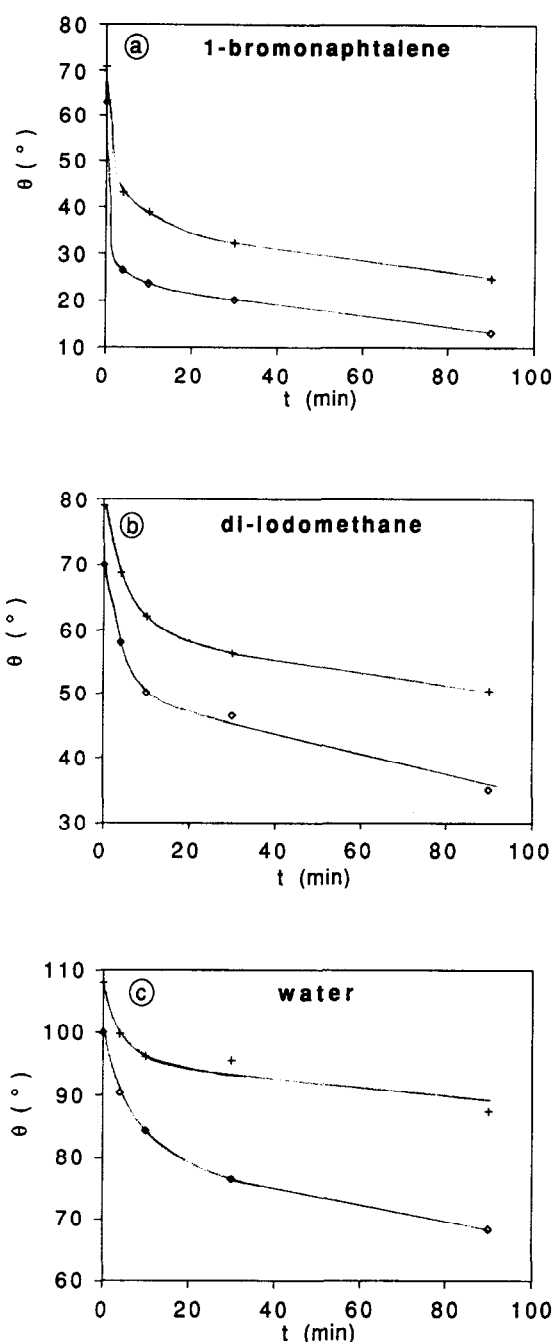
Figure 11 Variations of advancing and receding contact angles of drops of probe liquids deposited on the surface of PTFE plaques with treatment time in the magnesium solution. (a) 1-Bromonaphthalene. (b) Di-iodomethane. (c) Water. +, advancing angles. ◇, receding angles

modified samples of PTFE. Examples of drops of 1-bromonaphthalene deposited on the surface of samples of PTFE (untreated and after being treated in a magnesium solution for 30 and 90 min) are shown in *Figure 10*. The contact angle decreases with treatment time of the sample in the magnesium solution.

The variations of advancing and receding contact angles of drops 1-bromonaphthalene, di-iodomethane and water with treatment time in the magnesium solution are reported in *Figures 11a–c* respectively. For a given time of treatment, the contact angle increases when the polarity of the solvent increases (on going from 1-bromonaphthalene to di-iodomethane and then to water). The decrease of the contact angles with the time of treatment which had already been observed in
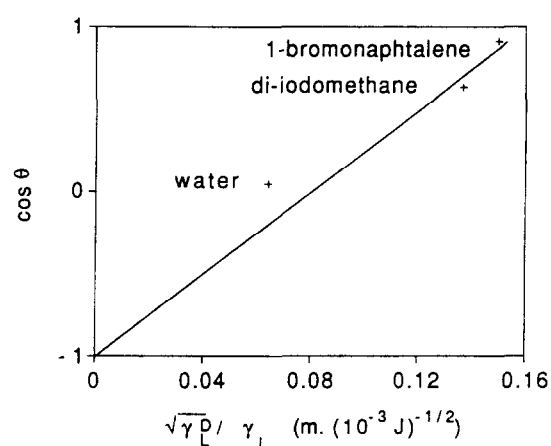
Figure 10 is also clearly evidenced in *Figure 11*. This means that the treatment makes the surface more hydrophilic. The difference between advancing and receding contact angles increases with the solvent polarity (water > di-iodomethane > 1-bromonaphthalene) and the time of treatment. The decrease of contact angles with treatment time is the highest for the least polar solvent: the advancing angle of 1-bromonaphthalene decreases from 71° (untreated) to 25° (90 min treatment) and the receding angle from 63° (untreated) to 13° (90 min treatment) whilst in the same conditions, the advancing angle of water decreases from 108° to 87° and the receding angle from 100° to 68°.

Equilibrium is described by Young's equation[21] relating the three interfacial tensions, γ_{ij}, where i, j represent solid, S, liquid, L and vapour, V, to equilibrium contact angles taken to be θ_a. It is taken that $\gamma_{SV} \sim \gamma_S$ (solid surface free energy), $\gamma_{LV} = \gamma_L$ and γ_{SL} is assumed to be given by Fowkes' relation[22]

$$\gamma_{SL} = \gamma_S + \gamma_L - 2\sqrt{\gamma_S^D \gamma_L^D - I_{SL}^P} \qquad (2)$$

where superfix D refers to the dispersive component of γ and I_{SL}^P is the polar solid/liquid interaction. I_{SL}^P has no generally accepted form but a commonly used (if debatable) form is[23]

$$I_{SL}^P = 2\sqrt{\gamma_S^P \gamma_L^P} \qquad (3)$$

the superfix P again referring to polarity. The combination of Young's and Fowkes' equations leads to

$$\cos\theta_a = 2\sqrt{\gamma_S^D} \frac{\sqrt{\gamma_L^D}}{\gamma_L} - 1 + \frac{I_{SL}^P}{\gamma_L} \qquad (4)$$

and thus by plotting $\cos\theta_a$ vs $\sqrt{\gamma_L^D}/\gamma_L$, γ_S^D may be obtained from the slope given by the essentially apolar liquids (1-bromonaphthalene and di-iodomethane for which $I_{SL}^P \sim 0$). γ_S^P is deduced from the difference between the experimental $\cos\theta_a$ value in water and the calculated value obtained by extrapolation of the preceding straight line for apolar liquids to water (that difference is equal to I_{SL}^P/γ_L). This mathematical treatment led to the following values for a magnesium
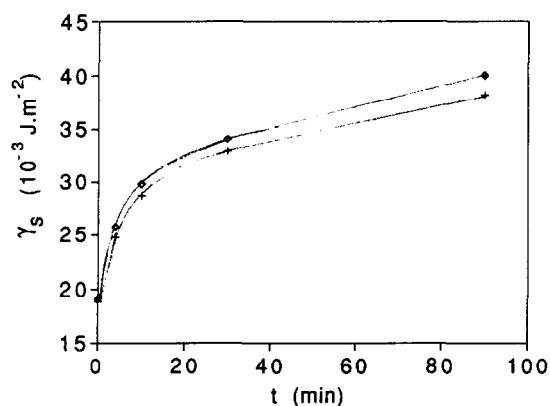
Figure 13 Variation of the solid surface free energy γ_S of PTFE with time of treatment in the magnesium solution. $+$, dispersive component of the solid surface free energy; $\Diamond$, polar component of the solid surface free energy

treatment of 30 min (cf. *Figure 12*)

$$\gamma_S^D = 33.0 \times 10^{-3}\,\mathrm{J\,m^{-2}}, \quad \gamma_S^P = 1.2 \times 10^{-3}\,\mathrm{J\,m^{-2}}$$

$$\text{and} \quad \gamma_S = \gamma_S^D + \gamma_S^P = 34.2 \times 10^{-3}\,\mathrm{J\,m^{-2}}$$

The variation of γ_S as a function of treatment time is represented in *Figure 13*.

The dispersive component of the surface free energy of PTFE increases with treatment time from $18.8 \times 10^{-3}\,\mathrm{J\,m^{-2}}$ for the untreated sample to $33.0 \times 10^{-3}\,\mathrm{J\,m^{-2}}$ and to $38.2 \times 10^{-3}\,\mathrm{J\,m^{-2}}$ for the samples treated respectively for 30 and 90 min in the magnesium solution. At the same time, the polar component increases slightly with treatment time from $0.30 \times 10^{-3}\,\mathrm{J\,m^{-2}}$ (negligible) for the untreated sample to $1.2 \times 10^{-3}\,\mathrm{J\,m^{-2}}$ and to $1.8 \times 10^{-3}\,\mathrm{J\,m^{-2}}$ for the samples treated respectively for 30 and 90 min by the magnesium solution. In all cases, the surface free energy and consequently the hydrophilic character of the surface increase with defluoration.

A similar study run with the samples treated in the sodium solutions was also performed and led to higher values of the solid surface free energy. The results obtained have to be considered with prudence because the increase of the heterogeneous character (rugosity) of the surface may also affect contact angles to some extent.

CONCLUSION

The formation of solvated electrons solutions in liquid ammonia in the presence of the magnesium cation can be achieved by an electrochemical procedure in which solvated electrons are generated in a magnesium tetrafluoroborate solution
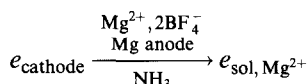
$$e_{\mathrm{cathode}} \xrightarrow[\mathrm{NH_3}]{\substack{\mathrm{Mg^{2+}, 2BF_4^-} \\ \mathrm{Mg\ anode}}} e_{\mathrm{sol, Mg^{2+}}}$$

Solutions of solvated electrons in the presence of magnesium offer many advantages for the surface treatment of PTFE when compared to the classical solutions of solvated electrons in the presence of alkalis.

Before treatment, the appearance of PTFE is white and after treatment by magnesium solutions there is no visible change whilst when treated by sodium solutions, the sample changes dramatically and becomes black and porous.

Scanning electron micrographs of samples treated either by magnesium or sodium solutions also illustrate some major differences of the treatments. The surface, which is fairly homogeneous for untreated samples is no longer homogeneous once treated, but it has been attacked to a much greater extent by the sodium than by the magnesium solutions resulting in a higher heterogeneity and a higher depth of attack ($\approx 8\,\mu\mathrm{m}$ instead of less than $1\,\mu\mathrm{m}$) in the case of sodium solutions.

The results of X-ray photoelectron spectroscopy show that a PTFE sample treated by a magnesium solution for 1 min is very similar to an untreated sample, whilst after 30 min in the same solution the sample has a relatively high oxygen content and has been defluorinated by 90%. By contrast after just 1 min of treatment in a sodium solution the sample is almost completely defluorinated and has a high $\mathrm{C-C/C-H/C=C}$ content. The depth of attack increases with treatment time; for treatment times longer than some minutes, it is larger than the depth explored by X.p.s. (15 nm). Partial defluoration can be observed with 0.3 M solutions of solvated electrons for times of treatment lower than 5 min and also with longer treatments when using smaller amounts of electrolyte ($\mathrm{NH_4BF_4}$).

Therefore the confrontation of SEM and X.p.s. results demonstrates that the depth of attack with the magnesium solution is between 15 nm and $1\,\mu\mathrm{m}$ without any noticeable increase in the porosity of the material. This indicates that, although the reduction is ultimately made by the electrons, the metal cations are in some way associated with the solvated electrons in the solution and hence have an effect on their reactivity and penetration depth. The extent of the reduction is less severe with the magnesium than that of the sodium solution, resulting in a suitably modified surface without the extensive structural damage to a considerable depth observed for the classical sodium solution and which affects the strength of the material.

The determination of the surface free energy of untreated and treated samples of PTFE was obtained by measurement of equilibrium contact angles of drops of probe liquids deposited on the surface of the samples. The surface free energy increases when the samples are treated by solutions of solvated electrons in the presence of magnesium, which means that the hydrophilic character of the surface increases with defluoration.

Adhesion tests of PTFE to other materials are currently being performed since an expected effect of the magnesium treatment is an improvement of the bondability of PTFE. Other surface modification treatments, such as metallization by electroless or chemical vapour deposition (CVD) procedure are currently being studied. Attempts to modulate the surface properties of PTFE by nucleophilic substitution or electrochemical functionalization (chemical bonding of functional groups presenting specific properties) are currently performed. Extension of the treatment to other fluorinated and chlorinated polymers (polyvinyldifluoride, Viton®, Nafion®, polyvinylchloride, polyvinyldichloride, etc.) is also presently being considered.

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