Surface modification of polytetrafluoroethylene by microwave plasma downstream treatment

J. P. Badey*†, E. Urbaczewski-Espuche*‡, Y. Jugnet†, D. Sage*, Tran Minh Duc† and B. Chabert*

**Laboratoire d'Etude des Matériaux Plastiques et des Biomatériaux, URA CNRS No. 507, Université 'Claude Bernard', 43 Boulevard du 11 Novembre 1918, 69622 Villeurbanne Cedex, France*

†Centre ESCA de NanoAnalyse et Technologie de Surface (CENATS), Université 'Claude Bernard' 43 Boulevard du 11 Novembre 1918, 69622 Villeurbanne Cedex, France

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The surface modification of polytetrafluoroethylene (PTFE) by microwave plasma treatment was investigated by means of contact angle measurement and e.s.c.a. studies. Various gases (e.g. O_2, O_2/N_2, NH_3) were used. The influence of the various plasma parameters, such as power, gas flow, distance between the sample and the centre of the discharge, treatment time, etc., has been evaluated. No modification was induced by O_2 and O_2/N_2 treatment, whatever the treatment conditions. NH_3 plasma irradiation, however, rendered the PTFE surfaces more hydrophilic, leading to an increase of the polar component of the surface energy from 4.5 to $\sim 57\,\mathrm{mJ\,m^{-2}}$ under optimized treatment conditions. NH_3 treatment led to defluorination, crosslinking, hydrocarbon (CC,CH) bond formation, and incorporation of nitrogen-containing groups, as confirmed by e.s.c.a. Oxygen was also detected at the surface of treated PTFE. Correlations between the contact angle, defluorination rate, and surface nitrogen and oxygen contents, have been established. Optimization of operational NH_3 plasma parameters, leading to the best wettability of the treated samples, is also reported.

(Keywords: polytetrafluoroethylene; microwave plasma; surface modification)

INTRODUCTION

As a result of the high dissociation energy of C–F bonds and the high electronegativity of fluorine atoms, polytetrafluoroethylene (PTFE) displays a high thermal stability, a high chemical resistance, a low friction coefficient, a low index of refraction, and a low surface energy. These properties, which are very important for certain specific applications, and particularly 'rubbing', present considerable disadvantages where adhesion related problems are concerned.

A variety of different treatments have been applied in order to active PTFE surfaces and to enhance adhesion:

(1) Chemical treatments[1–8], e.g. with sodium–liquid ammonia[2] and sodium naphthalide[3], were used at first. However, when such treatment is applied, the difficulty still remains of monitoring the depth profile of the modification, since such treatment can affect not only the surface aspects of the polymer, such as colour and texture[9–11], but also its bulk properties.

(2) Gas plasma techniques, especially radio frequency plasmas, have been widely used to active the surface of numerous polymers[12–15], such as polypropylene (PP), poly(ether ether ketone) (PEEK), poly(ethylene terephthalate) (PET), etc. These appear especially attractive for PTFE because, depending on the gas used in the plasma, they can greatly increase the PTFE wettability. Where gas plasma treatment leads, in the case of hydrocarbon polymers, to the replacement of some of the C–H bonds by polar groups, it has been shown that such treatment of PTFE leads to a partial loss of fluorine[16–19], the production of C=C bonds[20], the incorporation of oxygen by oxygen, air, argon and water vapour gas treatment[16,21–23] and the incorporation of nitrogen with plasmas excited in NH_3, N_2 and N_2/H_2 mixtures[18,22,24–26]. Inert gas plasmas[16,19,27–30] have also been used and lead to a CASING (crosslinking by activated species of inert gases) phenomenon, as shown by Schonhorn and Hansen[27].

Only a few studies have been concerned with PTFE surfaces modified by microwave plasma techniques[23,29]. When compared to the radio frequency technique, the microwave plasma downstream treatment does not involve the participation of ions and electrons in superficial modification process. The role of u.v. irradiation has been found negligible in the case of polypropylene microwave plasma downstream treatment[31]. However, with PTFE[29], it has been shown that u.v. irradiation can modify the surface when using long exposure times, i.e. much larger than those used in this study. Under such conditions, it is possible to realize a superficial physico-chemical modification of the polymer without spoiling its bulk properties. Thus, the aim of this

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‡ To whom correspondence should be addressed

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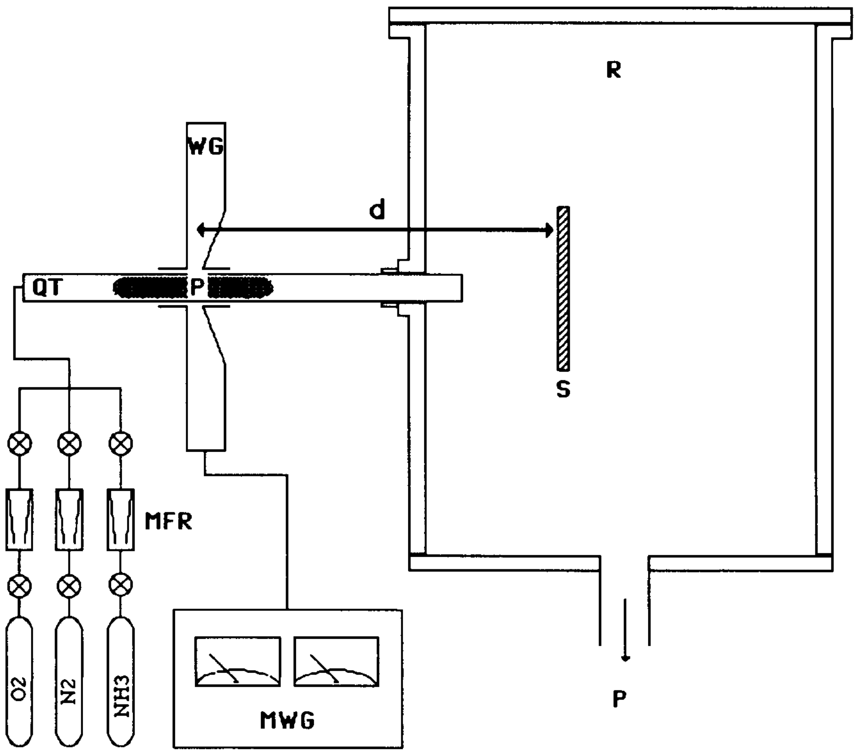

Figure 1 Schematic representation of the microwave plasma apparatus used in this work: R, reactor; S, sample; P, pump; MWG, microwave generator; WG, waveguide; QT, quartz tube; MFR, mass flow regulator; P, plasma and *d*, distance between the centre of the discharge and the sample

work is to study the wetting and the chemical changes in PTFE induced by microwave plasma treatments, using various gases and under different processing conditions.

EXPERIMENTAL

Materials

Polytetrafluoroethylene was obtained in the form of commercially available Teflon sheet (GAFLON (3P), thickness = 0.5 mm). After washing (by Soxhlet extraction with methanol), the samples were then dried at ambient temperature, before the plasma treatment.

Microwave plasma treatment apparatus

The plasma apparatus (*Figure 1*) consists of a 2.45 GHz microwave generator from Rayteck (RK L1200 LRT) which can deliver power levels from 0 to 1200 W. The plasma was created by means of a surface guide in a quartz tube (diameter = 16 mm), with the distance *d* between the sample and the centre of the discharge being fixed at either 30 or 60 cm. In this way, all of the samples were downstream treated. The gas flow was measured by using mass flow controllers (Tylan FC280) over the 0–200 $\mathrm{cm}^3\,\mathrm{min}^{-1}$ range.

Contact angle measurements

The contact angle Θ was evaluated from the height *h* and the base diameter *D* of a sessile drop, by assuming the contour to have a circular shape. Measurements, using water on the samples, carried out immediately after plasma treatment, gave evidence of the efficiency of the modification. Measurements, using water and methylene iodide on treated samples that had been washed for 1 h (by Soxhlet extraction with methanol), allow us to calculate the polar, I_{SW}, and dispersive, $\gamma_{\mathrm{S}}^{\mathrm{D}}$, components of the surface free energy, γ_{S}, by using Fowkes theory[32].

The dispersive and polar components of the surface energy are derived from the following relationship:

$$\cos\Theta = 2\sqrt{\gamma_{\mathrm{S}}^{\mathrm{D}}}\left(\frac{\sqrt{\gamma_{\mathrm{L}}^{\mathrm{D}}}}{\gamma_{\mathrm{L}}}\right) + \frac{I_{\mathrm{SW}}}{\gamma_{\mathrm{L}}} - 1 \qquad (1)$$

where γ_{L} is the surface energy of the wetting liquid (72.8 $\mathrm{mJ\,m^{-2}}$ for water and 50.8 $\mathrm{mJ\,m^{-2}}$ for methylene iodide) and $\gamma_{\mathrm{L}}^{\mathrm{D}}$ its dispersive component (21.8 $\mathrm{mJ\,m^{-2}}$ for water and 48.5 $\mathrm{mJ\,m^{-2}}$ for methylene iodide).

When using a non-polar liquid (such as methylene iodide), $I_{\mathrm{SW}} = 0$ and equation (1) can be rewritten as follows:

$$\cos\Theta = 2\sqrt{\gamma_{\mathrm{S}}^{\mathrm{D}}}\left(\frac{\sqrt{\gamma_{\mathrm{L}}^{\mathrm{D}}}}{\gamma_{\mathrm{L}}}\right) - 1 \qquad (2)$$

$\gamma_{\mathrm{S}}^{\mathrm{D}}$ can therefore be derived from this relationship. From this value, by using a polar liquid (such as water), I_{SW} can be deduced from equation (1). I_{SW} is representative of the polar interaction for a given solid–liquid system.

In order to verify the validity of this method, we have first used two non-polar liquids, namely methylene iodide and α-bromonaphthalene ($\gamma_{\mathrm{L}} = 44.6\,\mathrm{mJ\,m^{-2}}$ and $\gamma_{\mathrm{L}}^{\mathrm{D}} = 44.6\,\mathrm{mJ\,m^{-2}}$ for the latter). For a given treated PTFE sample, the contact angles were equal to $37 \pm 2°$ with α-bromonaphthalene and $50 \pm 2°$ with methylene iodide. These values lead to $\gamma_{\mathrm{S}}^{\mathrm{D}}$ components of 36.1 ± 1.0 and $35.9 \pm 1.0\,\mathrm{mJ\,m^{-2}}$, respectively. Such an experiment was reproduced several times on other samples, and the agreement between the various results was quite satisfactory. Therefore, in the following experiments, we shall only use methylene iodide to estimate $\gamma_{\mathrm{S}}^{\mathrm{D}}$. The standard

Table 1 Influence of various gases/gas mixtures and treatment conditions on the wettability of plasma treated PTFE

Gas	Power (W)	Gas flow ($cm^3 min^{-1}$)	Exposure time (s)	Distance[a] (cm)	Θ_{water} (°)	$\Theta_{methylene\ iodide}$ (°)
Untreated	–	–	–	–	115	84
O_2	100	50	30	60	112	81
	100	50	120	60	110	79
	100	50	600	60	114	82
	100	200	120	60	110	79
	300	200	120	60	111	79
	100	200	120	60	110	80
	500	100	120	30	116	87
O_2/N_2 (80/20)[b]	500	50	120	60	112	80
	500	50	120	30	112	82
O_2/N_2 (20/80)[b]	1000	200	120	60	112	81
NH_3	500	110	120	60	113	83
	500	110	120	30	70	70

[a] Distance between the centre of the discharge and the sample
[b] Volume percentage

deviation (σ) of the angle was better than ±4°. This leads to a σ-value of $\pm 2\,mJ\,m^{-2}$ for the γ_S^D value and $\pm 4\,mJ\,m^{-2}$ for the I_{SW} parameter.

E.s.c.a. measurements

The e.s.c.a. experiments were performed with an ESCASCOPE apparatus (Vacuum Generators) using an unmonochromatized Al X-ray source ($h\nu = 1486.6\,eV$). The X-ray source power was set to 300 W in order to prevent degradation of the sample during the measurements. The vacuum used was in the 10^{-9} mbar range. Charge compensation was partially realized by using a flood gun (electron energy = 3 eV). The binding energies have been calibrated against a value of the C_{1s} hydrocarbon component centred at 285.0 eV. Measurements of the e.s.c.a. spectra were made within 30 min after the plasma treatment and the subsequent exposure to air during the sample transfer.

The atomic ratios were determined from the peak areas and corrected for photoionization cross sections[33], mean free path (estimated as the square root of the kinetic energy) and transmission.

RESULTS AND DISCUSSION

The following points will be examined: first, the choice of gas and the distance *d* between the centre of the discharge and the sample used, in order to improve as much as possible the wettability of the PTFE surface, and secondly, the influence of the treatment time, the gas flow and the power level for a chosen gas. In the following discussion, all of the samples have been microwave plasma downstream treated.

Influence of gas nature on the wettability of microwave plasma treated PTFE

According to the radio-frequency plasma results published in the literature, oxidative gas plasmas[16,21,22] appear to be worth considering since they lead to an incorporation of oxygen-containing functions and thus to an increase in the wettability. A study[34] carried out on polypropylene, which had been treated under the same conditions as ours, showed that an O_2/N_2 gas mixture was more efficient than pure O_2: the presence of nitrogen in the oxygen, even in very small quantities, increased the production of atomic oxygen (the principal active species in the oxygen plasma). The water contact angle, measured on a treated PP surface, had its lowest value for an O_2/N_2 ratio of 80/20.

From the results described above, it seemed worthwhile to compare the influence of both O_2 and O_2/N_2 microwave plasma downstream treatment on PTFE samples. Ammonia gas also appeared to be a useful candidate, since it could lead to the incorporation of nitrogen-containing groups, whose polarity and reactivity could increase the wettability, and thus promote adhesion[18,22,24,25]. Some wettability results which are characteristic of O_2, O_2/N_2 and NH_3 microwave plasma treated PTFE are reported in *Table 1*.

Unlike the radio-frequency results[16], no significant modification of the contact angles is induced by the O_2 plasma, as a function of either power, gas flow, exposure time or distance *d*. The same conclusion is reached concerning the O_2/N_2 mixtures, whatever the proportions of O_2 and N_2, or the processing conditions. Therefore, it seems that due to the high dissociation energy of C–F bonds (~5.35 eV), the PTFE surface is very difficult to modify by either O_2 or O_2/N_2 microwave plasma downstream treatment.

At large distances ($d = 60$ cm) no change of the contact angle is observed when NH_3 is used. However, this is no longer true when small distances i.e. $d = 30$ cm are used. In this case, the contact angle is reduced to 70° (cf. 113° when the distance $d = 60$ cm). We shall now focus on the NH_3 plasma treatment for a distance *d* of 30 cm, and look at the influence of treatment time, power and gas flow on the efficiency of the plasma treatment, as measured by contact angles and chemical modification at the surface of PTFE.

Influence of treatment time, power and gas flow on the wettability and chemical modification of ammonia plasma treated PTFE

Figure 2 shows the water contact angle at the PTFE

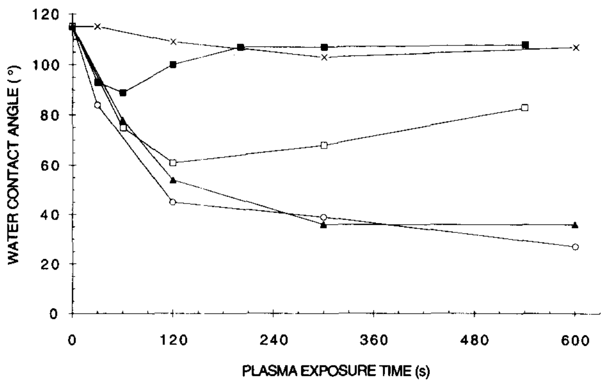

Figure 2 Water contact angles at the PTFE surface as a function of NH_3 plasma exposure time for the following treatment conditions: (■) 500 W–200 cm^3 min^{-1}; (□) 500 W–110 cm^3 min^{-1}; (○) 500 W–27 cm^3 min^{-1}; (×) 200 W– 110 cm^3 min^{-1} and (▲) 200 W–27 cm^3 min^{-1}

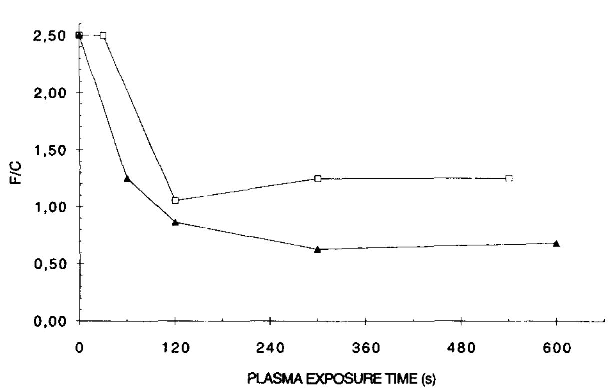

Figure 3 F/C atomic ratios, determined from e.s.c.a. of the PTFE surface, as a function of NH_3 plasma exposure time: (□) 500 W–110 cm^3 min^{-1} and (▲) 200 W–27 cm^3 min^{-1}

surface, after being modified by the NH_3 plasma, as a function of treatment time under various conditions of power and gas flow. For high power levels and a high gas flow (see, for example, the 500 W–200 cm^3 min^{-1} and 200 W–110 cm^3 min^{-1} curves) the treatment time has little influence on the wettability. The contact angle remains high ($\Theta > 90°$) and is not really dependent on the exposure time.

However, under the following conditions, i.e. 500 W–10 cm^3 min^{-1}, 200 W–27 cm^3 min^{-1} and 500 W–27 cm^3 min^{-1}, rapid decrease of the water contact angle from 115 to ~60° is noticed when the samples are exposed to NH_3 plasma for 120 s. The evolution for longer treatment times is less pronounced. At 500 W and 110 cm^3 min^{-1}, for exposure times larger than 120 s, an increase of the contact angle is observed which can be related to the e.s.c.a. results.

PTFE surfaces modified by the NH_3 plasma (500 W–110 cm^3 min^{-1} and 200 W–27 cm^3 min^{-1}) were investigated by e.s.c.a. The evolution of the F/C atomic ratio is displayed in *Figure 3* as a function of the plasma exposure time. A rapid decrease of the F/C ratio is observed for exposure times less than 120 s, after which the ratio for the 500 W–110 cm^3 min^{-1} curve increases slightly, with that of the 200 W–27 cm^3 min^{-1} curve keeping a constant value. The defluorination is more important for the 200 W–27 cm^3 min^{-1} treatment conditions. At the same time, the incorporation of oxygen and nitrogen is clearly observed.

The evolution of the N/C and O/C atomic ratios as a function of the exposure time, for a power of 500 W and a gas flow of 110 cm^3 min^{-1} is reported in *Figure 4*. Both of the N/C and O/C ratios increase rapidly for exposure times less than 120 s. For exposure times larger than this, both ratios decrease slightly; the (N + O)/C ratio value is ~0.18. For a power of 200 W and a gas flow of 27 cm^3 min^{-1}, both the N/C and O/C atomic ratio curves (see *Figure 5*) are different from the previous ones. Indeed, for a treatment time less than 120 s, the N/C ratio increases with treatment time, while the O/C ratio first increases, after which it slightly decreases, with the (N + O)/C ratio keeping a constant value of 0.3 for treatment times larger than 120 s. These observations allow us to conclude that a low gas flow leads to an enhanced incorporation of nitrogen species.

In any case, a good correlation is obtained between the quantitative e.s.c.a. results and the wettability measurements. For treatment times less than 120 s, the defluorination rate increases rapidly. In the meantime, N and O species are incorporated, rendering the surface of the PTFE more hydrophilic, thus leading to a decrease of the water contact angle. For exposure times larger than 120 s, both the F/C and (N + O)/C ratios evolve slightly, with the same trend being observed for the wettability. The slight decrease in both the C/F and (N + O)/C ratios, which is related to the increase of the water contact angle (observed for the 500 W–110 cm^3 min^{-1} treatment) could be tentatively explained by a competition between the modification process and a degradation phenomenon.

Since the water contact angle has a minimum value and the defluorination is at a maximum for the 120 s treatment time, probably corresponding to a minimum

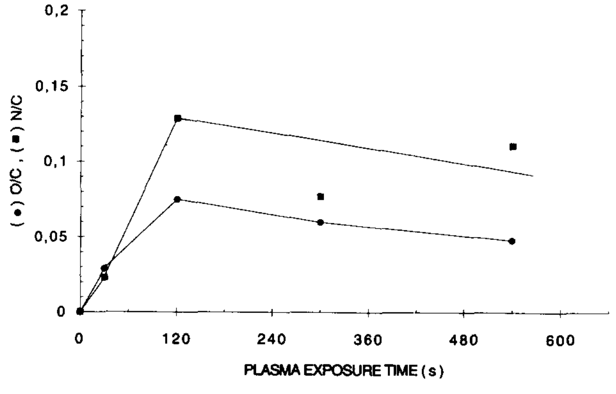

Figure 4 Evolution of N/C (■) and O/C (●) atomic ratios, determined from e.s.c.a. of the PTFE surface, as a function of NH_3 plasma exposure time for a power of 500 W and a gas flow of 110 cm^3 min^{-1}

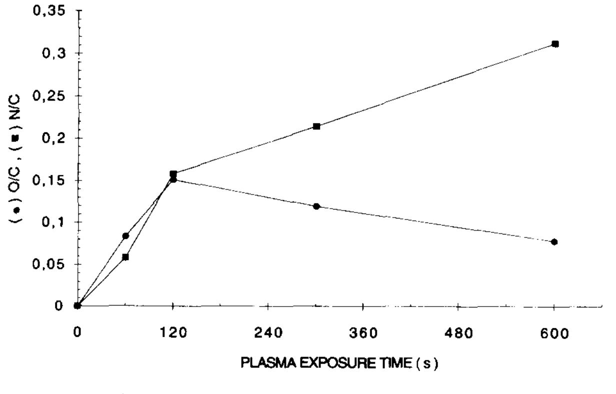

Figure 5 Evolution of N/C (■) and O/C (●) atomic ratios, determined from e.s.c.a. of the PTFE surface, as a function of NH_3 plasma exposure time for a power of 200 W and a gas flow of 27 cm^3 min^{-1}

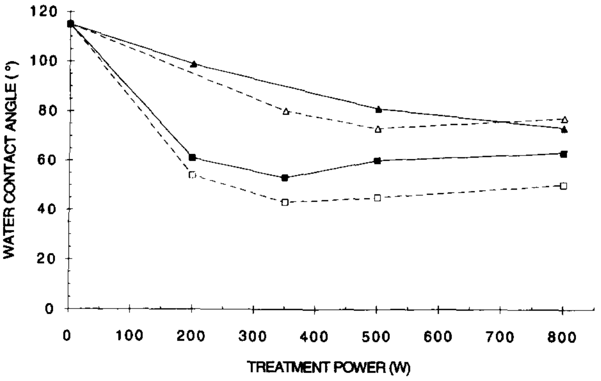

Figure 6 Water contact angle at the PTFE surface, after NH_3 plasma treatment, *versus* power at various gas flows: (□) 27 cm^3 min^{-1} and (△) 110 cm^3 min^{-1}, immediately after treatment (----), and on samples treated then washed by Soxhlet extraction in methanol (—)

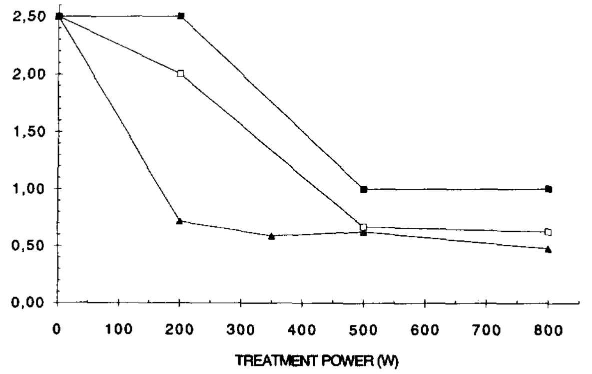

Figure 7 F/C atomic ratios, determined from e.s.c.a. of the PTFE surface, after NH_3 plasma treatment, *versus* power for different gas flows: (▲) 27 cm^3 min^{-1}; (□) 110 cm^3 min^{-1} and (■) 200 cm^3 min^{-1}

degradation of the PTFE surface, a 120 s plasma exposure time will be fixed now in order to study more precisely the effect of power and gas flow on the wettability and chemical changes induced by the NH_3 microwave plasma treatment.

Figure 6 shows the evolution of the water contact angle as a function of the power for various gas flows. The dotted-line curve shows the results obtained on samples immediately after treatment, while the continuous-line curve shows the results obtained on PTFE treated surfaces that have been washed by Soxhlet extraction in methanol. The 'washing after treatment' procedure has more influence on the wettability for the 27 cm^3 min^{-1} treatment, and leads in this case to an increase of the water contact angles by a value of ~5–10°. However, these values still remain largely inferior to that of the untreated sample. E.s.c.a. analysis shows that washing leads principally to a decrease of the N/C ratio, which can be explained by removal of a part of the modified layer during the washing process.

E.s.c.a. measurements performed on all of the treated and washed samples reveal the evolution of the F/C, O/C and N/C ratios as a function of power (see *Figures 7* and *8*). For a flow of 110 cm^3 min^{-1}, in the 0–200 W power range, the power has little influence on defluorination and no nitrogen species are detected at the surface of treated samples, while oxygen moieties are already present in small quantities. In the 200–500 W range, the F/C ratio decreases rapidly, while the N/C and O/C ratios increase at the same rate. For powers larger than 500 W, the F/C, N/C and O/C ratios maintain a constant value (0.7, 0.08, and 0.15, respectively). The same evolution is observed at a flow of 200 cm^3 min^{-1}, with powers larger than 500 W; i.e. F/C ~1.1, N/C ~0.07 and O/C ~0.14. For a 27 cm^3 min^{-1} gas flow, there is a rapid decrease of the F/C ratio and in parallel with this a significant increase of the N/C and O/C ratios in the 0–200 W power range. Each ratio then reaches a constant value; i.e. F/C ~0.7 (this result is essentially the same as the one obtained with a flow of 110 cm^3 min^{-1} for powers larger than 500 W), and N/C ~O/C ~0.13.

If for a gas flow of 27 cm^3 min^{-1}, oxygen and nitrogen moieties are introduced in the same proportion, then for larger gas flows, i.e. 110 and 200 cm^3 min^{-1}, the oxygen quantity detected is greater than the nitrogen quantity introduced by the NH_3 plasma treatment. Thus, depending on the treatment conditions, our results are in agreement with those of Inagaki *et al.*[18], who also ascertained that the O/C atomic ratio was superior to the N/C ratio for NH_3 treated PTFE samples, and those of Hollahan *et al.*[12] who reported the introduction of numerous amino groups onto PTFE surfaces that had been treated by a NH_3 plasma. Concerning the presence of oxygen on the treated surface, Inagaki *et al.*[18] proposed that the detachment of fluorine atoms and oxidation of the PTFE occur simultaneously upon NH_3 plasma irradiation. Other studies[16,19,28] impute the presence of oxygen moieties to the reaction of active sites with atmospheric oxygen.

Chemical modifications induced by the plasma have been identified from the C1s core level spectra, as shown in *Figures 9* and *10*, which were obtained for gas flows of 110 and 27 cm^3 min^{-1}, respectively. For comparison, an untreated PTFE C1s spectrum is included in *Figure 9*. It can be resolved into four components (assuming a 50% Gaussian/Lorentzian shape and a full width at half maximum of 1.9 eV), with the CF_3, CF_2, CF and hydrocarbon (CC,CH) groups at 293.9, 292.4, 290.6 and 285.0 eV, respectively. We notice that even with 'soft' X-ray power, the PTFE is slightly beam damaged, as observed by the presence of the hydrocarbon, CF and CF_3 components. The quantitative results are reported in *Table 2*.

The spectra of the treated PTFE have been resolved into their different components. Four components can be clearly assigned, namely CF_3, CF_2, CF, and hydrocarbon

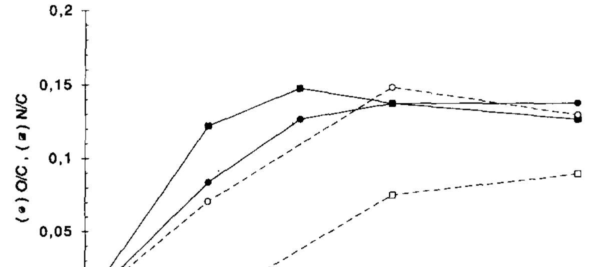

Figure 8 O/C and N/C atomic ratios, determined from e.s.c.a. of the PTFE surface, after NH_3 plasma treatment *versus* power for different flow rates: (—●—) O/C, 27 cm^3 min^{-1}; (--○--) O/C, 110 cm^3 min^{-1}; (—■—) N/C, 27 cm^3 min^{-1} and (--□--) N/C, 110 cm^3 min^{-1}

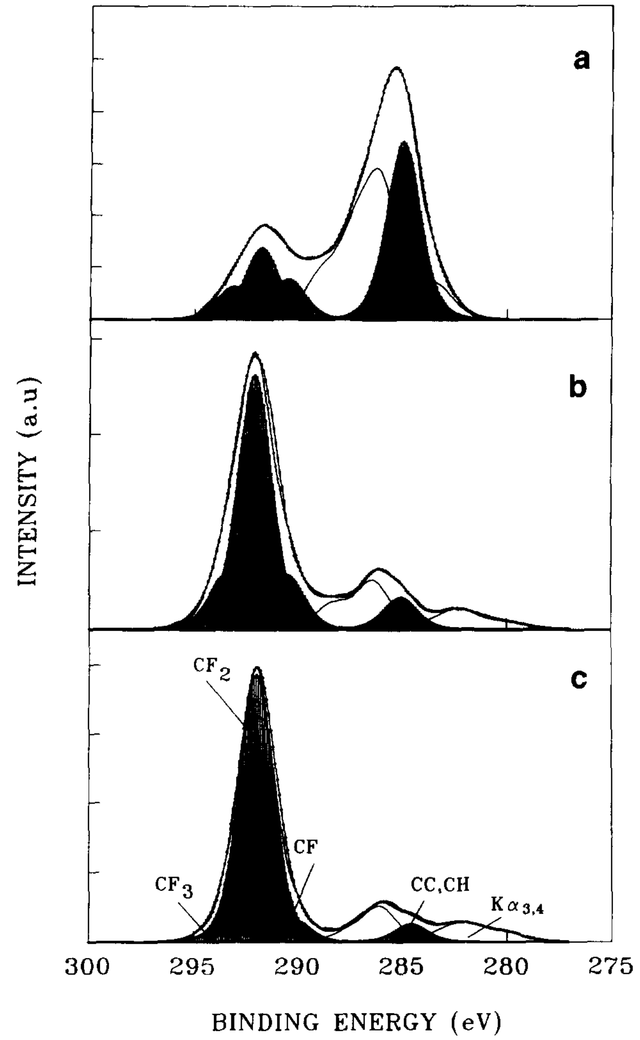

Figure 9 C1s core level spectra of PTFE modified by NH_3 plasma treatment for 120 s under different processing conditions: (a) treated at 500 W and 110 cm^3 min^{-1}; (b) treated at 200 W and 110 cm^3 min^{-1} and (c) unmodified PTFE

(CC,CH), by direct comparison with the untreated PTFE. The remainder, which consists of a superposition of a large number of possible contributions (O–C=O, N–C=O, C–CF_3, C=O, C–CF_2, C–O, C–CF and C–N, in order of decreasing binding energy, plus the Kα3,4 X-ray excited spectrum) have not been voluntarily resolved. Let us just remind ourselves that the sample has been transferred through air before the e.s.c.a. measurements were made, which explains the presence of the oxygenated components.

For a gas flow of 110 cm^3 min^{-1} (*Figure 9* and *Table 2*), an increase in the power from 200 to 500 W is accompanied by an increase in the CC, CH component and a decrease in the fluorinated C1s components. From the atomic percentages of the various carbon species, and by comparison with the untreated PTFE sample, it can be seen that the 200 W treatment is not really efficient, when compared with the high value of the water contact angle. An increase of the power increases the efficiency of the treatment, which leads to a large decrease of the CF_2 component and a large increase of the CC, CH component.

Figure 10 displays the influence of the power on the C1s shape for a 27 cm^3 min^{-1} gas flow. Whatever the power, the contribution of the fluorinated carbon components is low (see *Table 2*). As the power increases, we notice an increase in the CC, CH groups, as well as an increase in the unassigned oxygen-plus-nitrogen-based components. Contrary to the previous 100 cm^3 min^{-1} results, a power of 200 W is already very efficient, as observed from the atomic percentages of the various C1s components. A plateau is reached for each component for powers larger than 350 W.

Therefore, for a given gas flow treatment, the C1s(CF_2)/C1s(CC,CH) ratio decreases as the treatment power

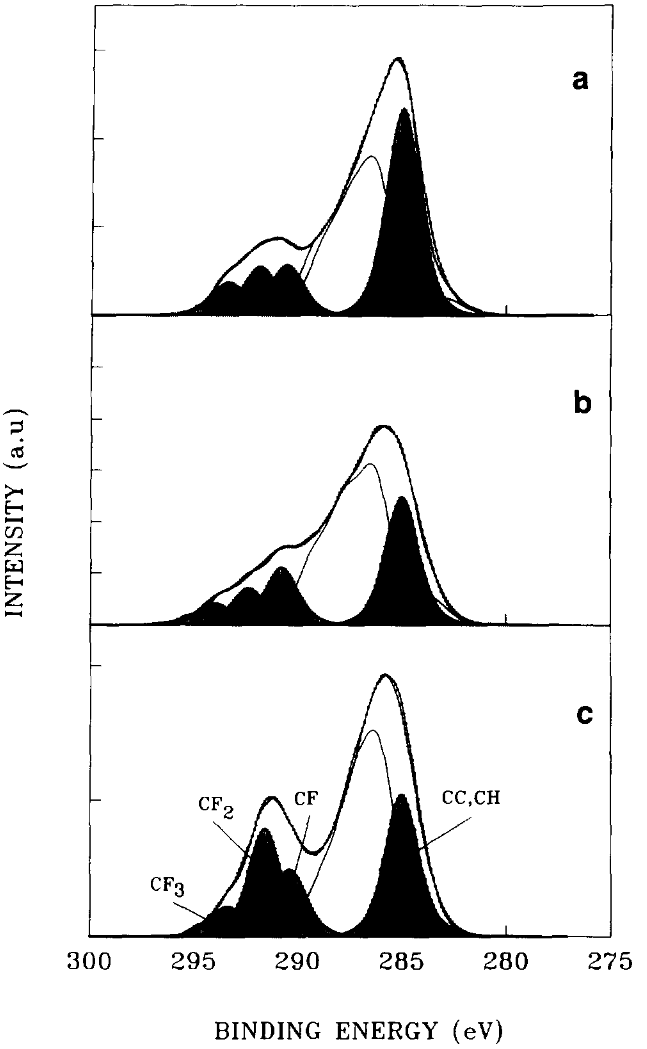

Figure 10 C1s core level spectra of PTFE modified by NH_3 plasma treatment for 120 s under different processing conditions: (a) treated at 500 W and 27 cm^3 min^{-1}; (b) treated at 350 W and 27 cm^3 min^{-1} and (c) treated at 200 W and 27 cm^3 min^{-1}

Table 2 Data obtained from the e.s.c.a. C1s core level spectra of NH_3 plasma treated PTFE, and the corresponding water contact angles, for different treatment conditions

Gas flow (cm^3 min^{-1})	Power (W)	CC^a (%)	CF (%)	CF_2 (%)	CF_3 (%)	CF_2/CC^a	Θ_{water}^{b} (°)
27	200	24.4	9.7	15.5	4.3	0.63	61
	350	23.1	10.3	6.5	3.9	0.28	53
	500	33.8	8.3	7.9	5.4	0.23	60
110	200	6.25	10.75	51.6	10.8	8.26	99
	500	30.2	6.8	12.1	5.6	0.4	81

[a] CC represents the CC and CH hydrocarbon components
[b] Standard deviation (σ) is better than ±4°

Table 3 Water and methylene iodide contact angles measured at PTFE surfaces after sample exposure to a NH_3 plasma for 120 s, followed by washing with methanol (Soxhlet extraction)

Treatment conditions			
Power (W)	Gas flow ($cm^3 min^{-1}$)	Θ_{water} (°)	$\Theta_{methyleneiodide}$ (°)
0	0	115	84
200	200	109	81
500	200	89	71
800	200	78	60
200	110	99	74
500	110	81	62
800	110	73	52
200	27	61	51
350	27	53	41
500	27	60	41
800	27	63	46

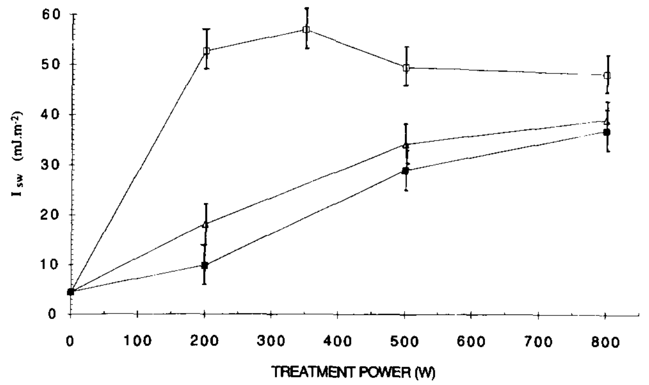

Figure 11 Polar component I_{SW} of the surface free energy *versus* power for NH_3 plasma treatment of PTFE at different gas flows (treatment time = 120 s): (□) 27; (△) 110 and (■) 200 $cm^3 min^{-1}$

increases and the lowest value of this ratio is obtained for the lowest gas flow. The NH_3 plasma treatment initiates defluorination and the species present at the surface of the modified PTFE are mainly hydrocarbon (CC,CH) groups, in addition to nitrogen-based carbon groups created by the plasma and oxygenated carbon species induced by contact with air during the transfer. Some of the CC groups certainly contribute to the surface crosslinking but the formation of crosslinks cannot be detected by e.s.c.a. This detailed e.s.c.a. investigation provides further information on the modification mechanisms involved in microwave plasma downstream treatment and the results obtained can be related to the wetting characteristics.

The water and methylene iodide contact angles (*Table 3*) allow us to calculate both the polar I_{SW} and the dispersive γ_S^D components of the surface free energy of treated PTFE. *Figure 11* shows the evolution of I_{SW} for different treatment conditions. For a gas flow of 27 $cm^3 min^{-1}$, I_{SW} increases rapidly, reaching a maximum value of 57 $mJ m^{-2}$ at ~350 W, and then slightly decreases to ~48 $mJ m^{-2}$. The same trends are observed for γ_S^D (see *Figure 12*). For flows of 200 and 110 $cm^3 min^{-1}$, both I_{SW} and γ_S^D increase slightly as a function of power. Thus, for the same exposure time (120 s), the treatment realized with a high gas flow induces an increase in the wettability only for high treatment power levels, with the modifications to I_{SW} and γ_S^D remaining minimal.

For a low gas flow (27 $cm^3 min^{-1}$), the wettability is vastly improved as soon as the treatment power level reaches 350 W. It can also be noticed that for this gas flow condition, the plasma treatment leads to a significant increase in the dispersive component of the surface energy.

In any case, the evolution of the polar component (I_{SW}) can be related to the defluorination rate and the variation of the N/C and O/C ratios. Only a very few studies[18,19] have been concerned with the dispersive component (γ_S^D). Youxian *et al.*[19], from the results of various radiofrequency plasma treatments, proposed that the superficial modifications consist principally of crosslinking and C=C bond formation. They noticed a decrease in both the water and methylene iodide contact angles, whatever the treatment conditions. The largest decrease was observed with Ar treatment ($\Delta\Theta_{CH_2I_2} = 18°$ and $\Delta\Theta_{H_2O} = 33°$). This variation is quite similar to the one that we observed in this study with 110 and 200 $cm^3 min^{-1}$ gas flows. A methylene iodide contact angle of less than 50° is observed when using a 27 $cm^3 min^{-1}$ gas flow. To explain this variation, we shall now briefly summarize the results that were obtained with a H_2 microwave plasma treatment: these results will be described in more detail in a forthcoming paper. Indeed, similar reactive species are expected for both H_2 and NH_3 plasmas. Under a H_2 plasma treatment, a slight amount of oxygen is incorporated (O/C ~0.06), explaining the slight decrease in the water contact angle from 115 to 83°. The F/C ratio decreases to 0.86 and a large amount of the C1s(CC,CH) component is observed (CF_2/(CC,CH) ~0.6). The principal chemical modification induced by the H_2 treatment is the formation of hydrocarbon (CC,CH) groups and crosslinking, which could explain the decrease in the methylene iodide contact angle from 84 to 55°. Returning to the NH_3 results, defluorination (F/C ~0.6 for 27 $cm^3 min^{-1}$) and the appearance of an enhanced C1s(CC,CH) component (CF_2/(CC,CH) <0.3) can be related to the decrease in the methylene iodide contact angle, as was the case with the H_2 treatment.

To summarize, the NH_3 plasma treatment leads to defluorination, crosslinking, hydrocarbon (CC,CH) bond formation and the introduction of oxygen and nitrogen moieties, whose quantities depend on the processing conditions. The maximum (N + O)/C ratio is obtained with the lowest gas flow (i.e. 27 $cm^3 min^{-1}$), as soon as the

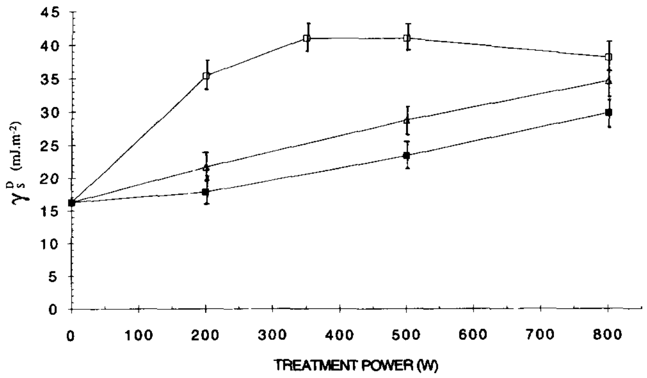

Figure 12 Dispersion component γ_S^D of the surface free energy *versus* power for NH_3 plasma treatment of PTFE at different gas flows (treatment time = 120 s): (□) 27; (△) 110 and (■) 200 $cm^3 min^{-1}$

treatment power reaches 350 W, and these processing conditions lead to maximum values of the polar and dispersive components of the surface energy ($I_{SW} = 57$ mJ m^{-2} and $\gamma_S^D = 41$ mJ m^{-2}).

CONCLUSIONS

The surface modification of PTFE by microwave plasma downstream treatment was studied for various gases, and it has been shown that the nature of the gas is an important parameter. Indeed, no modification of the treated surface was observed with O_2 and O_2/N_2 gases, whatever the chosen treatment conditions, whereas NH_3 plasma treatment was effective for a distance of 30 cm between the centre of the discharge and the sample. The influence of the plasma parameters (exposure time, power, gas flow) on the wettability and the chemical modification of the NH_3 treated surface was evaluated by both contact angle measurement and e.s.c.a. studies.

NH_3 microwave plasma treatment initiates defluorination, leading to an increase in the number of hydrocarbon (CC,CH) groups, plus probably crosslinking, and also to incorporation of nitrogen-and oxygen-containing groups. Relationships between the polar component of the surface free energy of treated samples, defluorination and concentration of oxygen and nitrogen at the surface have been clearly established. Modification of the PTFE is seen to evolve slightly for treatment times greater than 120 s. From a practical point of view, the best wettability is obtained from treatment conducted with a low gas flow, with the polar component of the surface energy reaching 57 mJ m^{-2} under the following conditions: exposure time = 120 s, power = 350 W and gas flow = 27 cm^3 min^{-1}.

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