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A comparative study of the effects of ammonia and hydrogen plasma downstream treatment on the surface modification of polytetrafluoroethylene

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Polytetrafluoroethylene (PTFE) was treated with hydrogen and ammonia microwave plasmas and the effects of treatment were evaluated by means of advancing and receding contact angle measurements, X-ray photoelectron spectroscopy, secondary-ion mass spectroscopy and atomic force microscopy analysis. Hydrogen plasma downstream treatment principally leads to defluorination and creation of C–C and C–H groups. This surface modification results in a slight decrease of the water contact angle and a large decrease of the methylene iodide contact angle. No evolution of the surface properties occurs over a period of at least two months following treatment. Ammonia plasma downstream treatment leads to defluorination and creation of C–C and C–H groups, as already observed with the H_2 plasma, but also to the introduction of nitrogen-containing groups. The modification produces a decrease of both water and methylene iodide contact angles. A large hysteresis is found with water contact angles due to the reorientation of the polar groups when the surface is in contact with a polar liquid. The surface modifications that result after a NH_3 plasma treatment are less stable than after a H_2 treatment. Nevertheless, after two days of ageing the water contact angle reaches a constant value, which is largely inferior to that of the untreated PTFE. Copyright © 1996 Elsevier Science Ltd.

(Keywords: polytetrafluoroethylene; microwave plasma; surface modification)

INTRODUCTION

Polytetrafluoroethylene (PTFE), as a result of its chemical stability, is of great interest for a number of applications. Nevertheless the same lack of reactivity is at the origin of numerous problems in creating polymer/polymer composites. Indeed, its inert and hydrophobic surface prevents the establishment of good interfacial bonding.

Thus a variety of treatments have been applied in order to activate the PTFE surface and enhance adhesion. The conventional chemical treatments[1–8] induce chemical changes at the surface of the polymer but they also affect its bulk properties. For this reason, gas plasma techniques and especially remote plasma treatments, as used in this work, are very interesting. The depth of modification is, in this case, lower than 1 μm. By moving the sample outside the main plasma region, first the influence of charged species such as electrons or ions is cancelled and secondly the number of reactive species able to interact with the surface is greatly reduced due to the short lifespan of most species.

From the numerous results found in the literature, especially with radiofrequency (r.f.) plasma[9–20], it seems interesting to use ammonia gas. Indeed, according to Hollahan *et al.*[20] the expected functionalization by NH_3 treatment consists of amine groups whose reactivity could enhance the adhesion properties with respect to an epoxy matrix.

The aim of this work is to compare the effects of an ammonia and a hydrogen microwave plasma downstream treatment on the surface modification of PTFE. We will characterize the plasma-treated surface as a function of the various processing parameters (power, gas flow and treatment time). The wettability, the chemical modifications and the topography will be studied respectively by contact angle measurements, X-ray photoelectron spectroscopy (X.p.s.), secondary-ion mass spectroscopy (s.i.m.s.) and atomic force microscopy (a.f.m.). In addition the ageing of the treated surfaces will be evaluated.

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EXPERIMENTAL

Materials

Polytetrafluoroethylene, in the form of commercially available PTFE sheet (Gaflon, thickness 0.5 mm), was used. After Soxhlet extraction by washing in methanol, the samples were dried at ambient temperature and then plasma-treated.

Microwave plasma treatment apparatus

The plasma apparatus was described in a previous study[21]. Briefly, it consists of a 2.45 GHz microwave generator from Rayteck (RK L1200 LRT) which can deliver a power from 0 to 1200 W. The plasma was created by means of a surface guide in a quartz tube (diameter 16 mm) and the distance between the sample and the centre of the discharge was fixed to 30 cm. All the samples were downstream-treated. Two gases were used: ammonia and hydrogen. The gas flow was measured with mass flow controllers (Tylan FC280) in the 0–200 sccm (standard $\mathrm{cm}^3\ \mathrm{min}^{-1}$) range.

Contact angle measurements

The contact angle was evaluated from the height h and the base diameter D of a sessile drop assuming the contour to have a circular shape. Measurements were performed with water (a polar liquid) and methylene iodide (an apolar liquid) on samples that were washed for one hour through a Soxhlet extraction in methanol directly after treatment. This washing helps to remove soluble low-molecular-weight species that pollute the drop of liquid deposited on the surface. It is then possible to measure both the advancing and receding contact angles and to evaluate the contact angle hysteresis.

X-ray photoelectron spectroscopy

The X.p.s. experiments were performed with the Escascope apparatus from Vacuum Generators using an unmonochromatized Al X-ray source ($h\nu = 1486.6\,\mathrm{eV}$). The X-ray source power was set to 300 W in order to prevent degradation of the sample during measurements. The vacuum was in the 10^{-9} mbar range. Charge compensation was partially realized with a flood gun (electron energy 3 eV). The binding energies have been calibrated against a value of the CC, CH C1s component centred at 285.0 eV. The X.p.s. measurements were made within 30 min following the plasma treatment. Air exposure occurs during the sample transfer.

The atomic ratios were determined from the peak areas corrected for photoionization cross-sections[22], mean free path (estimated as the square root of the kinetic energy) and transmission.

Secondary-ion mass spectroscopy

The s.i.m.s. experiments were performed with the Perkin-Elmer PHI 7200 apparatus using a caesium ion gun (8 KeV), a time-of-flight analyser and a channel plates detector. Charging effects were corrected by a flood gun. This technique is sensitive to the first two layers of the samples.

Atomic force microscopy

The a.f.m. experiments were performed with a Nanoscope III from Digital Instruments operated in 'tapping mode'. The images were obtained in constant-force mode, i.e. the height of the sample is adjusted at each point in the scan through a feedback system to maintain a constant force between the tip and the sample. The images obtained are directly related to the topography of the surface. The used cantilever spring constant was $50\,\mathrm{N\,m^{-1}}$. The arithmetic average height (R_a) was calculated. This is defined as the arithmetic average of the absolute values of the deviations of the profile height from the mean line within the sampling length:

$$R_a = (1/L)\int_1^L |z - \bar{z}|\,\mathrm{d}x$$

Measurements have been carried out on polished samples and absolute R_a values are not significant. Our aim is to compare untreated and treated surfaces and each treated surface image has to be compared to the corresponding untreated one, since the arithmetic average heights have been measured at the same place on the sample.

RESULTS AND DISCUSSION

All through this study, various techniques will be used in order to deliver complementary information about the treated surface.

Table 1 Advancing contact angles with water and methylene iodide, dispersive (γ^D) and non-dispersive (I_{SW}) components of the surface energy, F/C and O/C atomic ratios measured by e.s.c.a. as a function of the processing parameters (gas flow, power, exposure time) for hydrogen downstream plasma treatment

Gas flow (sccm)	Power (W)	Treatment time (s)	$\theta^a_{H_2O}$ (deg)	$\theta^a_{CH_2I_2}$ (deg)	γ^D ($\mathrm{mN\,m^{-1}}$)	I_{SW} ($\mathrm{mN\,m^{-1}}$)	F/C	O/C
0	0	0	115	84	16.2	4.5	2.45	0
30	200	60	95	75	21	24	1.53	0.05
30	350	60	87	55	33	23	0.95	0.07
30	500	60	88	57	32	23	0.85	0.09
30	800	60	86	63	28	28	0.98	0.09
50	350	60	83	55	33	28	0.90	0.08
50	350	120	85	50	36	23	0.76	0.08
100	350	60	85	55	33	25.5	0.86	0.06
100	350	120	92	49	36.5	14	0.86	0.06
200	350	60	88	55	33	22	0.74	0.06
200	350	120	92	47	38	13	0.86	0.04

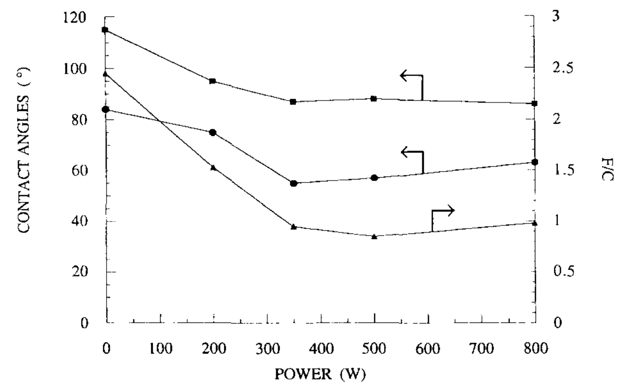

Figure 1 F/C ratio (▲), water contact angle (■) and methylene iodide contact angle (●) as a function of the power for H_2 treated PTFE under the following conditions: 30 sccm, 60 s

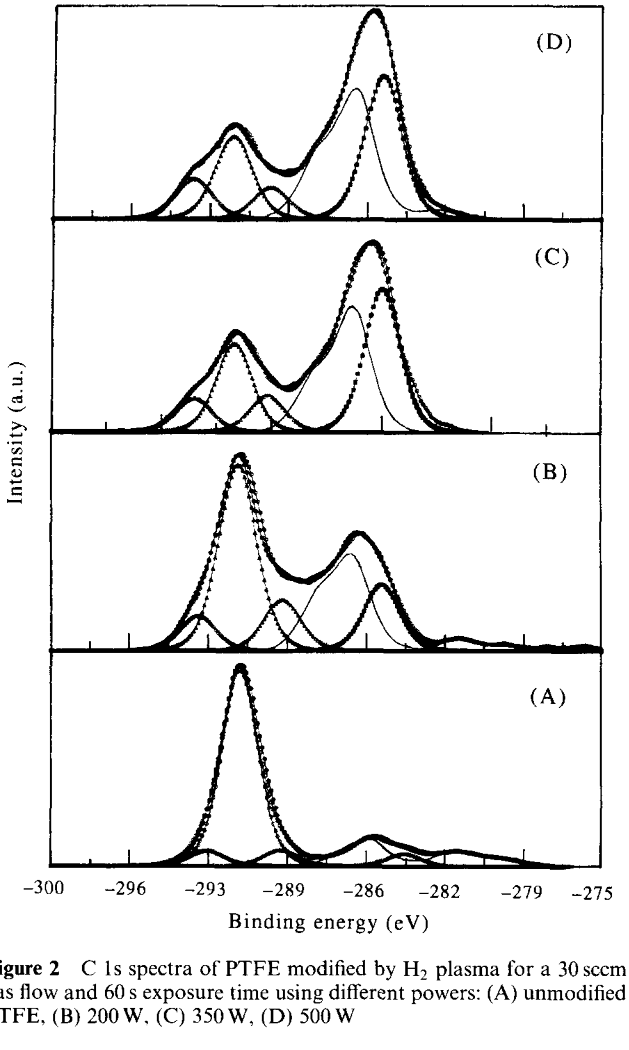

Figure 2 C 1s spectra of PTFE modified by H_2 plasma for a 30 sccm gas flow and 60 s exposure time using different powers: (A) unmodified PTFE, (B) 200 W, (C) 350 W, (D) 500 W

Table 2 CF_2, CF, CF_3 and CC C 1s percentages determined on X.p.s. C 1s spectra for plasma treatments realized at 30 sccm during 60 s with different power conditions

	Percentages				
Power (W)	CF_2	CF	CF_3	CC	CF_2/CC
200	38.3	10.5	6.7	12.8	3
350	18.7	7.7	7.0	30.2	0.62
500	17.0	6.6	8.1	29.3	0.58

Indeed, water and methylene iodide contact angles allow the determination of the dispersive (γ^D), and the non-dispersive (I_{sw}) components of the surface energy (γ_s) following Fowkes' theory. The calculation has been detailed in a previous study[21].

Receding contact angle measurements can provide further information about the extreme surface behaviour as a function of the environmental nature. Very often, the advancing contact angle is greater than the receding contact angle with different reasons being invoked to explain this hysteresis phenomenon, such as the surface topography[23–26], surface heterogeneity[27,28], swelling[29] and superficial reorganization[30–35].

Surface topography[23–26]. Calculations on model surfaces[23,24] showed that, in general, hysteresis increases with roughness. In the case of high roughness, the surface can be considered as 'composite': indeed, the surface under the liquid drop is constituted of either the solid or air. According to de Gennes[25], defects smaller than 0.1 μm do not favour the phenomenon of hysteresis and it seems that hysteresis depends more on the shape than on the size of the defect[26].

Surface heterogeneity[27,28]. A heterogeneous surface can be represented by areas having specific wettabilities. As for rough surfaces, a heterogeneous surface can lead to numerous metastable configurations and finally to hysteresis.

Segmental mobility and superficial reorganization[30–35]. In this case, a reorganization of lateral chains, or chain segments, as a function of the environmental nature occurs in order to minimize the interfacial energy: in contact with air, the low-energy species are located at the surface, whereas in contact with water the polar high-energy species are at the water/solid interface. This phenomenon supposes that chains or segments are mobile enough to reorient in order to minimize the interfacial energy.

Correlations between wetting properties, on the one hand, and chemical and topological modifications induced by the plasma, on the other, will be established through X.p.s., s.i.m.s. and a.f.m. measurements.

Hydrogen plasma treatment

Water and methylene iodide advancing contact angles, $\theta^a_{H_2O}$ and $\theta^a_{CH_2I_2}$ respectively, are reported in *Table 1* for various processing parameters. The water contact angle remains high ($\theta > 85°$), whatever the processing conditions, whereas the methylene iodide contact angle decreases from 84° to about 50°. The treatment time and the gas flow have no significant influence on the contact angle values. For a given set of gas flow and treatment time values, $\theta^a_{H_2O}$ and $\theta^a_{CH_2I_2}$ decrease as the power increases and they reach a constant value for powers higher than 350 W.

Methylene iodide advancing contact angles are rarely mentioned in the literature. The results obtained in our laboratory on other polymers (polypropylene, poly(ether ether ketone)) show that no variation of this angle occurs after plasma treatment, indicating no evolution of the dispersive component of the surface energy. Thus PTFE has a singular wettability behaviour and this has been confirmed by Youxian *et al.*[11], who noticed the same trend on PTFE modified by various r.f. plasma treatments.

The wetting results appear well correlated to the X.p.s. measurements (*Table 1*). We notice a large decrease of the F/C atomic ratio, whose value depends on the used power. Indeed, the same kind of evolution is observed for both the F/C ratio and the water and methylene iodide contact angles, as displayed in *Figure 1*. At the same time, we notice the incorporation of oxygen, whose content is not dependent on the power. This is possibly due to the fact that the samples are exposed to the atmosphere before the X.p.s. analysis. The defluorination is clearly

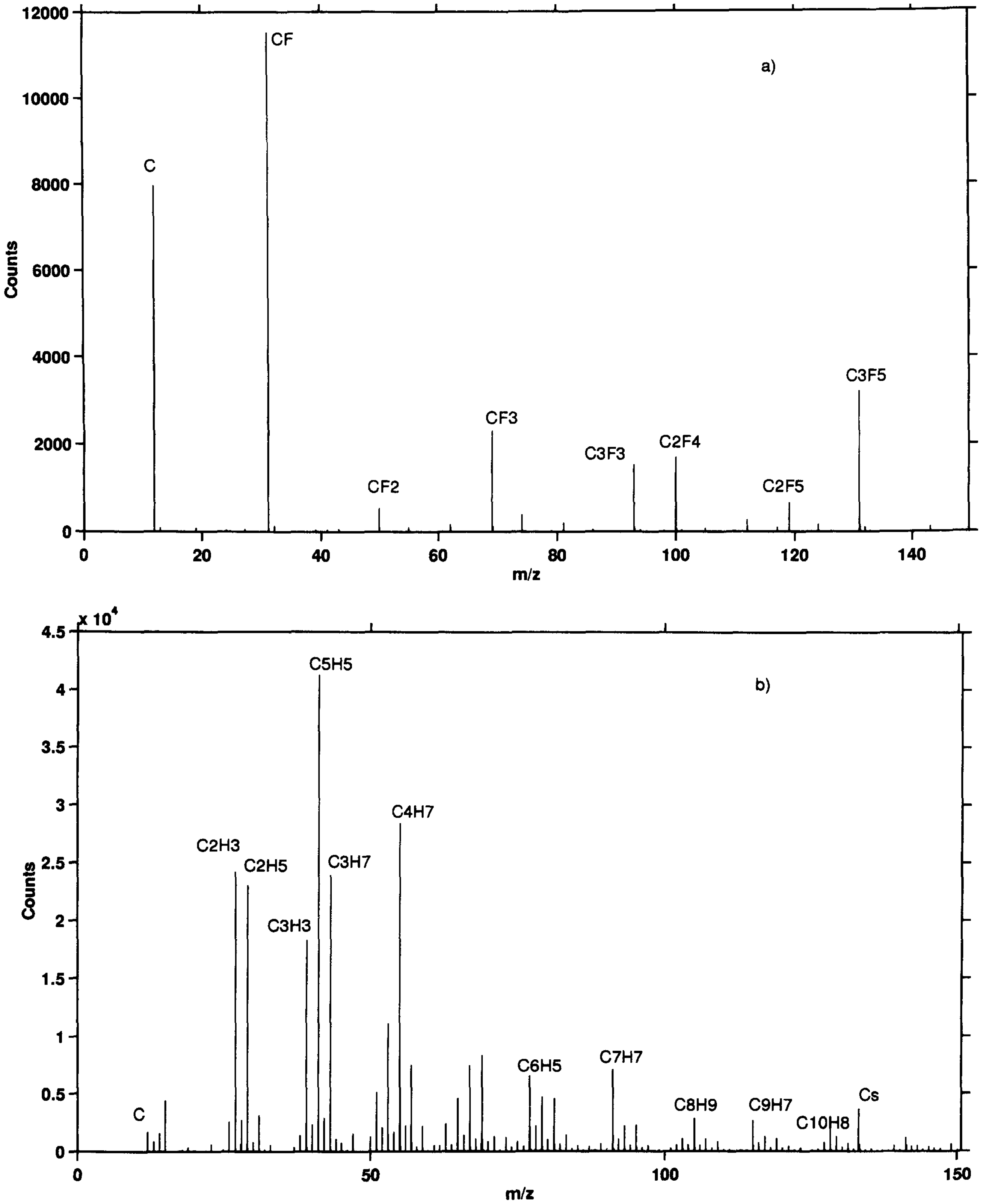

Figure 3 Positive-ion s.i.m.s. spectra for (a) untreated PTFE and (b) H_2 plasma-treated PTFE

Table 3 Advancing (θ^a) and receding (θ^r) contact angles with water and methylene iodide as a function of the processing parameters for H_2 downstream plasma treatment

Gas flow (sccm)	Power (W)	Treatment time (s)	$\theta^a_{H_2O}$ (deg)	$\theta^r_{H_2O}$ (deg)	$\theta^a_{CH_2I_2}$ (deg)	$\theta^r_{CH_2I_2}$ (deg)
0	0	0	115	109	84	79
50	350	60	83	76	55	44
50	350	120	85	79	50	41
100	350	60	86	82	54	42
100	350	120	92	87	49	43
200	350	60	88	82	55	46
200	350	120	92	83	47	41

Table 4 Average roughness R_a (nm) determined on polished untreated PTFE sample and on the same sample after H_2 plasma treatment (H_2 treatment conditions: 350 W, 100 sccm, 120 s). Measurements were carried out on the same position on the sample

Rastered area (μm^2)	100 × 100	30 × 30	5 × 5	1.5 × 1.5
Untreated PTFE	22.2	14.4	9.8	7.5
H_2 Treated PTFE	19.2	14.8	10.5	7

evidenced from the C 1s spectra measured under various power conditions (*Figure 2*). As explained in a previous study[21], the untreated PTFE C 1s spectrum can be resolved into four main components, CF_3, CF_2, CF and CC,CH at 293.9, 292.4, 290.6 and 285.0 eV respectively. The rest of the spectrum is the sum of various possible contributions (O–C=O, C=O, C–O and induced $\underline{C}$–CF_3, $\underline{C}$–CF_2, $\underline{C}$–CF plus the K_α 3.4 X-ray excited spectrum). The areas of the CF_3 and CF components keep almost constant values whatever the treatment conditions. As a function of increasing power, the CF_2 intensity decreases to the profit of the CC,CH component. The CF_2/CC C 1s component ratio is constant for powers larger than 350 W (*Table 2*). However from X.p.s. measurements, we are not able to make a distinction between CC single or double bonds.

S.i.m.s. appears to be a valuable tool for showing the presence of unsaturation. A comparison of the s.i.m.s. spectra for untreated and H_2 plasma-treated PTFE is reported in *Figure 3*. Among these $(C_xH_y)^+$ components, some which appear at *m/e* 77, 91, 105, 115 and 128 are attributed to cyclic ions which are only found for unsaturated hydrocarbon polymers. The fluorinated components $C_aF_b^+$ vanish after plasma treatment, while hydrogenated components $(C_xH_y)^+$ appear[36,37].

To summarize, a H_2 plasma principally leads to defluorination, to the formation of saturated and unsaturated CC bonds and to a small oxygen uptake. These chemical modifications lead to a small increase of the non-dispersive component of the surface energy and a significant increase of the dispersive component of the surface energy (*Table 1*).

We will now discuss the receding contact angle measurements reported in *Table 3*. H_2 plasma treatments do not lead to an increase of water contact angle hysteresis. As previously discussed, the H_2 plasma does not create polar groups at the PTFE surface. Thus no reorientation phenomenon takes place when the surface is in contact with water, which explains why the water advancing and receding contact angles are almost equal.

Concerning the methylene iodide contact angles, the hysteresis is higher for treated PTFE than for untreated PTFE. In order to find out whether a topological change is at the origin of this phenomenon, a.f.m. experiments have been carried out. No drastic change is observed when comparing untreated and H_2 treated samples. The average roughness R_a values measured at different scales and displayed in *Table 4* do not vary significantly. The hysteresis therefore seems to be related more to the chemical modifications than to roughness changes.

Ammonia plasma treatment

The evolution of both wettability and chemical changes are detailed in a previous paper[21]. The plasma treatment has been shown as more efficient at low gas flows. Some water contact angles and methylene iodide contact angles are reported in *Table 5* for different processing parameters. Contrary to a hydrogen plasma, an ammonia plasma treatment shows a dependence on the treatment time. Indeed, for a given gas flow and a given power, both $\theta^a_{H_2O}$ and $\theta^a_{CH_2I_2}$ decrease as the exposure time increases (*Figure 4*). These results are related to the decrease of the F/C ratio and the increase of both the N/C and O/C ratios as determined by X.p.s. (*Table 5* and *Figure 5*).

As previously observed with a hydrogen plasma, wettability increases as the power increases and it tends towards a constant value for high powers (*Figure 6*). Similarly, the CC C 1s component increases as a function of the power[21].

S.i.m.s. results, not displayed here, confirm the X.p.s. results (defluorination, oxygen and nitrogen uptake,...).

Table 5 Advancing contact angles with water and methylene iodide, dispersive (γ^D) and non-dispersive (I_{sw}) components of the surface energy, F/C, O/C nd N/C atomic ratios measured by e.s.c.a. as a function of the processing parameters (gas flow, power, exposure time) for ammonia plasma downstream treatment

Gas flow (sccm)	Power (W)	Treatment time (s)	θ_{H_2O} (deg)	$\theta_{CH_2I_2}$ (deg)	γ^D (mN m^{-1})	I_{sw} (mN m^{-1})	F/C	O/C	N/C
0	0	0	115	84	16	4.5	2.45	0	0
30	200	120	61	51	35	53	0.7	0.12	0.08
30	350	120	53	41	41	57	0.6	0.15	0.13
30	500	120	60	41	41	49.5	0.63	0.14	0.14
30	800	120	63	46	38	48	0.48	0.13	0.14
110	350	120	82	58	31	31	0.72	0.14	0.09
200	350	120	92	71	23	25	1.67	0.04	0.06
30	200	60	79	52	35	32	1.05	0.08	0.06
30	200	300	72	43	40	36	0.75	0.14	0.14

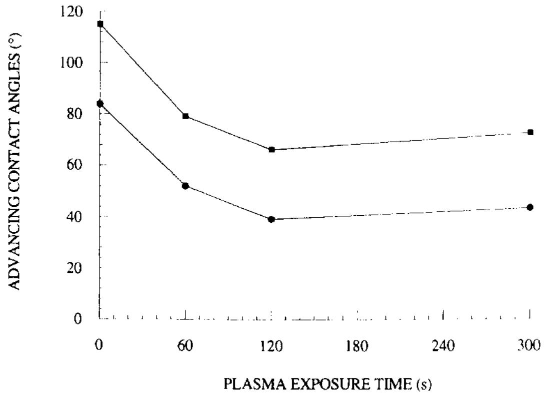

Figure 4 Water (■) and methylene iodide (●) contact angles as a function of treatment time for NH_3 treated PTFE under the following conditions: 30 sccm, 200 W

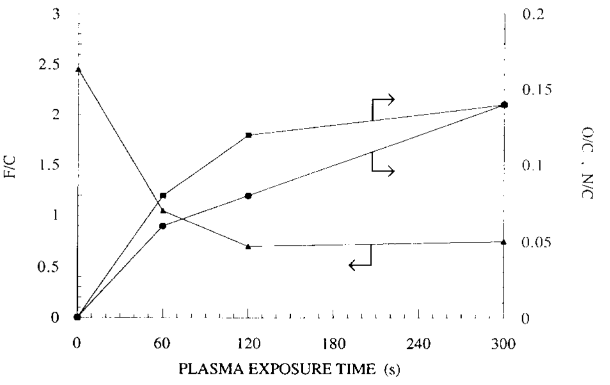

Figure 5 F/C (▲), N/C (●) and O/C (■) ratios as determined by X.p.s. *versus* treatment time for NH_3 treated PTFE under the following conditions: 30 sccm, 200 W

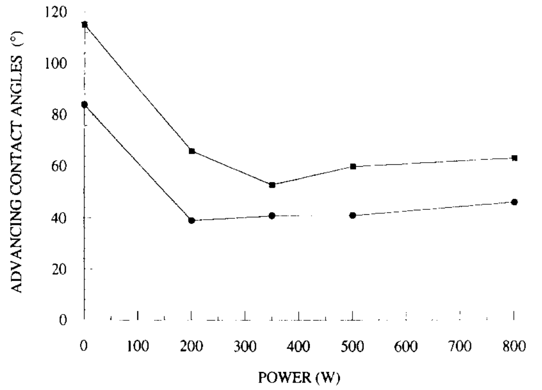

Figure 6 Evolution of the water contact angle (■) and methylene iodide contact angle (●) as a function of the power for NH_3 treated samples at 30 sccm gas flow and 120 s exposure time

As found in the case of a H_2 plasma, the positive-ion spectrum is dominated by the occurrence of a cyclic ion peak indicative of a high degree of unsaturation.

The hysteresis contact angle values are summarized in *Table 6*. Contrary to hydrogen treatment, ammonia plasma treatment leads to an important hysteresis of the water contact angle. In contact with water, nitrogen- and oxygen-containing groups reorient to minimize the interfacial energy and a very low receding water contact angle is then measured. For the methylene iodide, the receding contact angles are very low, leading to a large hysteresis. As mentioned above, roughness may be at the origin of this hysteresis.

A.f.m. results, reported in *Figure 7*, show that, although no major change is observed for short treatment times, large modifications appear for long treatment times. These structural changes correspond to an increase of the R_a values by a factor of 3 (*Table 7*). In our conditions, i.e. for treatment times smaller than 120 s, the topological changes cannot be at the origin of the methylene iodide contact angle hysteresis.

DISCUSSION

From the above results it emerges that the modifications induced by a H_2 plasma are sensitive only to the plasma power. On the contrary, NH_3 treatment efficiency depends on all of the processing parameters studied, i.e. the power but also gas flow and treatment time.

For treatment times less than or equal to 120 s, no significant structural changes have been noticed on either H_2 or NH_3 treated PTFE. Under such conditions, the dispersive and non-dispersive components of the surface energy are accessible from advancing contact angle measurements (see *Tables 1* and *5*).

The γ^D component is identical for H_2 and NH_3 treated samples (almost $35\,\mathrm{mN\,m^{-1}}$). The I_{sw} component depends on the gas nature; it is higher after a NH_3 plasma ($I_{sw} = 50\,\mathrm{mN\,m^{-1}}$) than after a H_2 plasma ($I_{sw} = 28\,\mathrm{mN\,m^{-1}}$). The incorporation of polar functions (nitrogen-containing species) following a NH_3 plasma treatment can explain this difference. It also explains the high value of the water contact angle hysteresis, the hysteresis being negligible after H_2 treatment. The occurrence of nitrogenated polar species appears to be one of the main differences between the NH_3 and H_2 plasmas. We have shown previously that both H_2 and NH_3 plasmas have a similar behaviour with respect to the chemical modifications: defluorination, oxygen incorporation, and C–C, C=C bond formation, leading to comparable γ^D values.

These results underline the prominent role of hydrogen in both H_2 and NH_3 modification processes. This is consistent with results obtained on PTFE surfaces treated either by N_2 or by a mixture of H_2 and N_2 plasmas in our laboratory. Indeed N_2 plasma treatment has no influence on the PTFE wettability while the modifications induced by H_2/N_2 are of the same order as those obtained with ammonia treatment.

Table 6 Advancing (θ^a) and receding (θ^r) contact angles with water and methylene iodide as a function of the processing parameters for NH_3 downstream plasma treatment

Gas flow (sccm)	Power (W)	Treatment time (s)	$\theta^a_{H_2O}$ (deg)	$\theta^r_{H_2O}$ (deg)	$\theta^a_{CH_2I_2}$ (deg)	$\theta^r_{CH_2I_2}$ (deg)
0	0	0	115	109	84	79
30	200	120	61	20	51	23
30	350	120	53	15	41	22
30	500	120	60	21	41	21
30	800	120	63	20	46	17
110	350	120	82	40	58	31
200	350	120	92	71	71	51
30	200	60	79	59	52	47
30	200	300	72	22	43	15

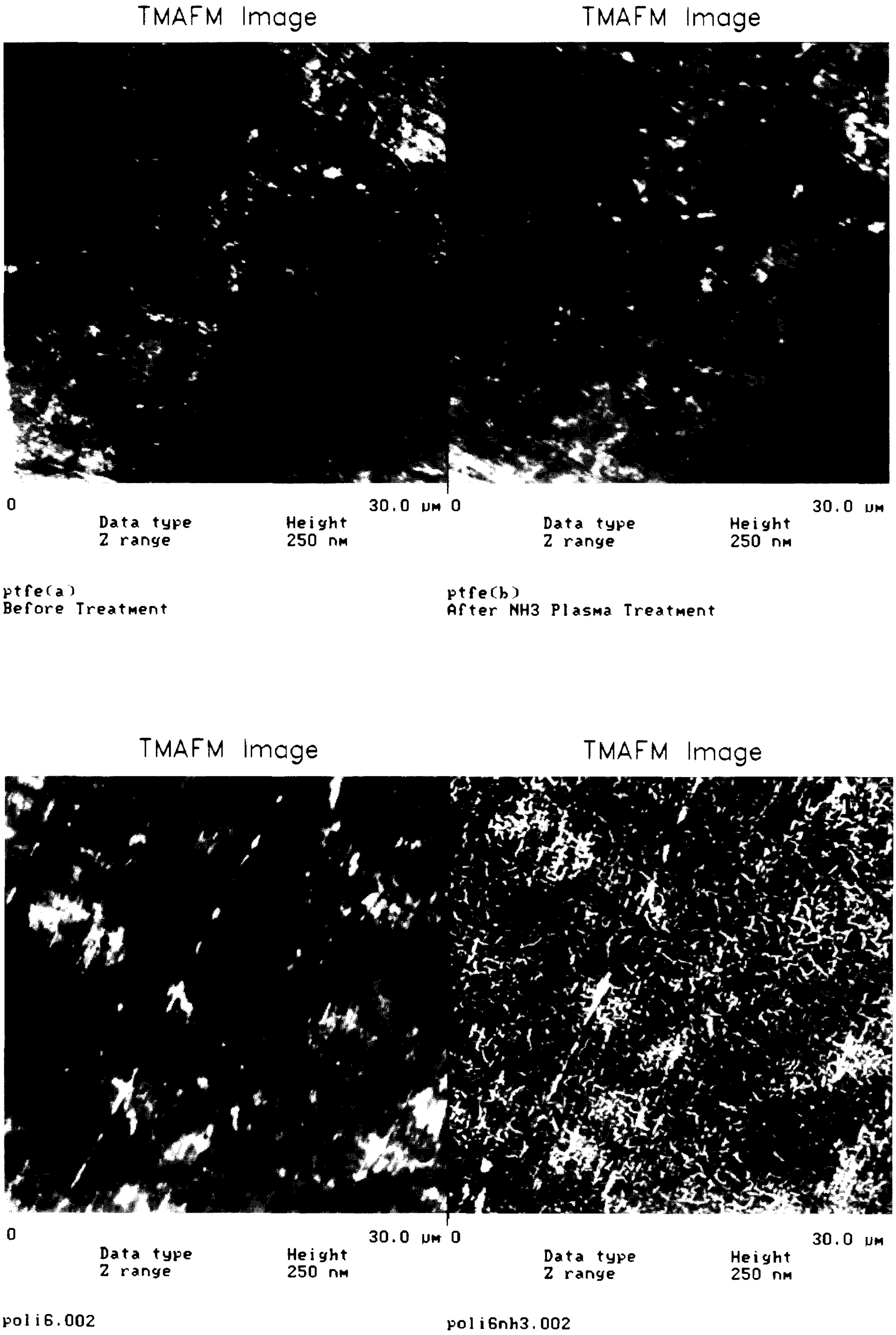

Figure 7 Evolution of the surface topography after NH_3 plasma treatment. The traces on the left-hand side correspond to the untreated PTFE; the traces on the right-hand side correspond to the treated PTFE. Treatment times are (top) 120 s and (bottom) 600 s

Table 7 Average roughness R_a (nm) for polished untreated PTFE samples and the same treated samples under various processing conditions. Measurements were carried out on the same position on the sample

Studied area (μm^2)	100 × 100	10 × 10	5 × 5	1.5 × 1.5
Untreated PTFE	19	8	7	5.5
NH_3 treated PTFE (350 W, 30 sccm, 120 s)	19	8	7	5
Untreated PTFE	30	13	12	7
NH_3 treated PTFE (500 W, 30 sccm, 600 s)	37	34	33	28

D'Agostino *et al.*[38] have shown that the main species created in a NH_3 r.f. plasma are H_2 and N_2. Assuming a similar decomposition process in the case of microwave plasma, we can advocate, as the first step of modification, the breaking of CF bonds by hydrogen atoms, following the mechanism proposed by Clark and Hutton[39].

For both H_2 and NH_3 plasmas, the first steps of modification could be described by equations (1) and (2), where the • and * represent respectively radical and excited species:

$$-[CF_2-CF_2-CF_2-CF_2]- + H^\bullet \rightarrow HF + -[^\bullet CF-CF_2-CF_2-CF_2]- \quad (1)$$

$$-[^\bullet CF-CF_2-CF_2-CF_2]- + H^\bullet \rightarrow -[CHF-CF_2-CF_2-CF_2]^*- \quad (2)$$

In the case of H_2 treated samples the further modifications could proceed following equations (3a) and (3b):

$$-[CHF-CF_2-CF_2-CF_2]^*- \xrightarrow{-HF^*} -[CF{=}CF-CF_2-CF_2]- \quad (3a)$$

$$-[CHF-CF_2-CF_2-CF_2]^*- \rightarrow -[CHF-CF_2-CF_2-CF_2]- \quad (3b)$$

Any unsaturation could then be rapidly saturated by $H^\bullet$ or from radical sites able to disproportionate (chain scission) or abstract atoms from adjacent chains (radical transfer) or recombine to form a crosslink.

In the case of NH_3 treated samples, in addition to these reactions, the $-[^\bullet CF-CF_2-CF_2-CF_2]-$ species can react with N, NH_2 or NH to form C–N bonds. The occurrence of these reactions would depend on the lifespans of the N, NH_2 or NH species.

In both cases, the X.p.s. and s.i.m.s. results are totally in agreement with the proposed modification mechanisms. Indeed, as seen previously, both H_2 and NH_3 plasma treatments lead to defluorination, single and double CC bond formation and hydrogen uptake. For NH_3 treated samples we further observe the appearance of a N 1s peak on the X.p.s. spectra. As previously discussed, the oxygen species observed are due to air exposure when the samples are removed from the microwave reactor.

Thus the only point which remains to be confirmed is the presence of crosslinks at the treated surface. A way to find out whether crosslinks are effectively present is to study the stability of the treated surfaces. Indeed, very often, the hydrophilicity obtained is lost with time[40–43] depending on the polymer nature[44], the temperature and on the storage conditions[42]. Several mechanisms have been proposed to explain the hydrophobic recovery of polymers. Among them, the main one consists of the reorientation of the surface polar groups away from the surface and the other one corresponds to the migration of untreated polymer chains from the bulk to the surface depending, of course, on the presence or not of crosslinks.

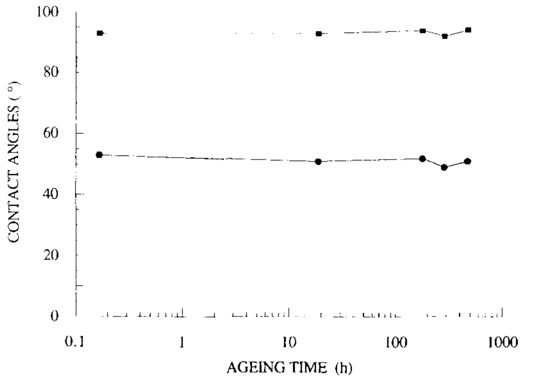

Figure 8 Evolution of the water contact angle (■) and the methylene iodide contact angle (●) as a function of the storage time of a H_2 treated PTFE

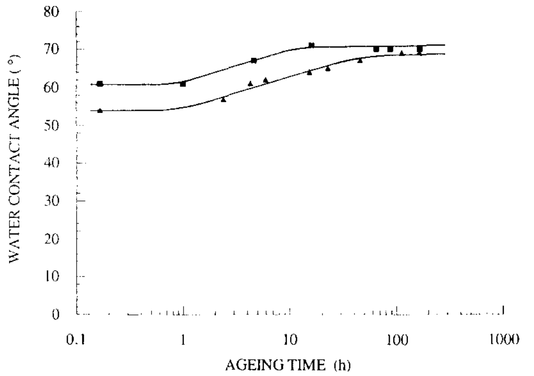

Figure 9 Evolution of the water contact angle as a function of the storage time of a NH_3 PTFE sample treated under the following conditions: (▲) 200 W, 30 sccm, 120 s; (■) 500 W, 100 sccm, 120 s

In this study, contact angle measurements and X.p.s. analysis were performed after various times of storage at ambient temperature and atmospheric conditions on samples treated by H_2 and NH_3 plasma.

Within the accuracy of the contact angle measurements, the surface of H_2 plasma-treated PTFE appears stable during extended periods of storage (see *Figure 8*). No significant evolution is noticed on either the advancing or the receding contact angles. As we have seen already, the H_2 modification process leads principally to a decrease of the F content and an increase of the number of CC,CH groups, very few polar functions being created. Nevertheless, the surface energy is $37\,mN\,m^{-1}$ after plasma exposure whereas it is $16.3\,mN\,m^{-1}$ for untreated PTFE. The extreme surface is very different from the bulk but this state remains stable with time. No migration process occurs.

Figure 9 shows the evolution of the water contact angle measured on NH_3 treated PTFE surfaces as a function of the storage time at ambient temperature. The modification appears quite stable whatever the plasma processing conditions. No significant evolution of the contact angle

Table 8 F/C, O/C and N/C ratios measured by X.p.s. on PTFE samples immediately after plasma treatment and after 64 h ageing time

Power (W)	Gas flow (sccm)	Treatment time (s)	Just after treatment F/C	Just after treatment O/C	Just after treatment N/C	After 64 h ageing time F/C	After 64 h ageing time O/C	After 64 h ageing time N/C
0	0	0	2.5	0	0	–	–	–
200	30	120	0.8	0.15	0.16	0.91	0.09	0.1
500	110	120	1	0.07	0.13	1.25	0.08	0.08
500	110	540	1.25	0.05	0.11	1.25	0.05	0.06

is observed during the first 2 h, after which the contact angle increases before reaching a constant value where it stabilizes for 2 days storage. The magnitude of the increase in the contact angles depends somewhat on the treatment conditions but the variations are of no great significance and the maximum increase is always less than 15°. The constant value reached is in all cases inferior to the water contact angle measured on untreated PTFE. Compared with our results, Xie *et al.*[23] found a more pronounced dependence of the water contact angle on the storage time in air. But they also remark that the advancing contact angle does not return to the untreated PTFE value.

E.s.c.a. (electron spectroscopy for chemical analysis) was performed on samples immediately after treatment and after 64 h storage (thus in the plateau region). The results are presented in *Table 8*. The F/C ratio does not vary with the storage time. The N/C ratio decreases whereas the O/C ratio stays roughly constant in agreement with Xie's results[42]. The very low value of the water contact angle, which does not increase to the untreated surface value, indicates that most of the polar groups stay at the extreme surface, most likely immobilized by adjacent crosslinks.

CONCLUSION

Surface modifications of PTFE by microwave plasma downstream treatments were studied for hydrogen and ammonia gases.

In contrast to a H_2 plasma, a NH_3 plasma irradiation was found to be dependent on the exposure time. It renders the PTFE surfaces hydrophilic, leading to an important decrease of the water contact angle due to a high defluorination rate and to the grafting of nitrogen and oxygen species on the treated surface.

Both H_2 and NH_3 plasma lead to defluorination, to the formation of CC, CH and C=C bonds and to crosslinks. Nevertheless the number of C=C bonds formed was found to be higher for H_2 treated samples.

Concerning the modification mechanisms, it has been concluded that hydrogen atoms play the major role in the modification process during H_2 treatment and also in the first step of the modification by NH_3 plasma.

Contrary to H_2 plasma treatment, NH_3 plasma treatment leads to a high hysteresis of the water contact angle due to the reorientation of the polar groups at the PTFE surface in contact with water.

Hydrogen plasma-treated surfaces are stable during an extended period of storage. The most pronounced ageing process was observed for NH_3 treated samples and, in this case, the maximum increase in the water contact angle was less than 15°. The slight variation of the water contact angle was attributed to the presence of crosslinks at the treated surface.

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