

Selective Etching of Semicrystalline Polymers: CF₄ Gas Plasma Treatment of Poly(ethylene)

M. B. Olde Riekerink, J. G. A. Terlingen, G. H. M. Engbers, and J. Feijen*

Department of Chemical Technology, Section Polymer Chemistry and Biomaterials and Institute for Biomedical Technology (BMTI), University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands

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A series of poly(ethylene) (PE) films with different degrees of crystallinity was treated with a radio-frequency tetrafluoromethane (CF₄) gas plasma (48–49 W, 0.06–0.07 mbar, and continuous vs pulsed treatment). The etching behavior and surface chemical and structural changes of the PE films were studied by weight measurements, X-ray photoelectron spectroscopy (XPS), static and dynamic water contact angle measurements, scanning electron microscopy (SEM), and atomic force microscopy (AFM). With increasing crystallinity (14–59%) of PE, a significant and almost linear decrease of the etching rate was found, ranging from 50 Å/min for linear low-density poly(ethylene) (LLDPE) to 35 Å/min for high-density poly(ethylene) (HDPE). XPS analysis revealed that after CF₄ plasma treatment the PE surfaces were highly fluorinated up to F/C ratios of 1.6. Moreover, CF₄ plasma treatment of PE resulted in extremely hydrophobic surfaces. Advancing water contact angles up to 150° were measured for treated LDPE films. Both SEM and AFM analysis revealed that pronounced surface restructuring took place during prolonged continuous plasma treatment (≥ 15 min). The lamellar surface structure of LDPE changed into a nanoporous-like structure with uniform pores and grains on the order of tens of nanometers. This phenomenon was not observed during plasma treatment of HDPE films. Apart from surface roughening due to selective etching, pulsed plasma treatment did not result in significant surface structural changes either. Therefore, the restructuring of continuously plasma-treated surfaces was attributed to a combined effect of etching and an increase of the surface temperature, resulting in phase separation of PE-like and poly(tetrafluoroethylene)-like material, of which the latter is surface oriented.

Introduction

Gas plasma treatment processes are extensively used for the chemical modification of polymer surfaces.^{1–3} Also, plasma etching treatments have been used to increase surface roughness without aiming for a well-defined surface structure, for instance, to improve properties such as adhesion.^{4,5} However, defined restructuring of a polymer surface on the nanoscale level is of interest for several areas such as biomedical technology, membrane technology, and the microchip industry.

In principle, gas plasma treatment can be used for tailoring the surface structure of phase-separated polymeric systems, i.e., semicrystalline homopolymers, polymer blends, or block copolymers. This application of plasma technology is based on selective etching, i.e., removal of one polymer phase in preference to another. The architecture of the resulting surfaces is determined by the initial phase-separated surface/bulk structure and the difference of etching rate between the two polymer phases. Using this approach, it is envisaged that surfaces can be created which contain tubular or spherical holes, ridges, or tubular

or spherical protuberances. The size of these holes/protuberances will be determined by the domains present in the phase-separated polymer system and can vary between tens of nanometers and a few micrometers.

For semicrystalline polymers, it is known that the amorphous phase is preferentially removed during an etching treatment.^{6–9} Herbert et al. studied the process of ablation of the surface of poly(ethylene) (PE) using ultraviolet radiation in the presence of ozone.⁶ They found that the amorphous regions of PE were preferentially etched during this treatment, resulting in a fine-scale surface topography. Okuno et al. investigated the correlation between crystallinity and plasma susceptibility of poly(ethylene terephthalate) and nylon 66 fibers.⁷ The weight loss after exposure to an air plasma decreased with increasing crystallinity up to a threshold crystallinity, above which appreciable increases in weight loss were observed.

The aim of this study is to develop nanoscale-structured polymer surfaces by selective plasma etching of semicrystalline polymers. Therefore, a series of commercial-grade PE films, varying in crystallinity, is treated with a radio-frequency (RF) tetrafluoromethane (CF₄) plasma. Compared to oxidizing plasmas, a CF₄ plasma is known as a mild etchant. Still, it is much more “aggressive” than an Ar plasma, which is an inert gas resulting in very low etching rates. Moreover, the etching characteristics of a CF₄ plasma are well-known.^{10–15} For example,

* To whom all correspondence should be addressed.

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Table 1. Film Characteristics of the Used Polymers

polymer code/tradename	PE type	additives	film thickness (μm)	density (g/cm^3)
LLDPE1/Stamylex TMX 1000 F	linear low density (C_2/C_8 copolymer)	antioxidant ^a	45	0.902 ^b
LLDPE2/Stamylex 08-026 F	linear low density (C_2/C_8 copolymer)	antioxidant ^a	50	0.910 ^b
LDPE1/Stamylan LD 2100TN00	low density		55	0.921 ^b
LDPE2/Stamylan LD 2600TC00	low density		130	0.926 ^b
LDPE/Stamylan LD type 2300	low density		200	0.93
LMDPE/Stamylex 4026 F	linear medium density (C_2/C_8 copolymer)	antioxidant ^a	55	0.936 ^b
HDPE/Stamylan HD 7751 FC	high density	antioxidant, processing aid ^a	10	0.950 ^b
PTFE/Teflon			500	2.2

^a The amount of additives in the PE films is small and will be neglected. ^b These data were obtained from DSM (test method ISO 1183 (A)).

Meichsner et al. showed that during CF_4 plasma treatment of low-density PE (LDPE) a stationary equilibrium between fluorine incorporation and etching is reached after a short time (<1 min).¹⁵

Furthermore, a comparison is made between continuous and pulsed CF_4 plasma treatment in order to obtain more information about the temperature effects of the different processes that occur simultaneously during plasma etching.

The chemical composition and the wetting properties of the surface of the treated materials are studied by X-ray photoelectron spectroscopy (XPS) and water contact angle measurements using the sessile drop method, respectively. In addition, scanning electron microscopy (SEM) and atomic force microscopy (AFM) are used to investigate the surface structure and topography of the films before and after plasma treatment.

Experimental Section

Materials. Seven types of blown-extruded PE films were kindly supplied by DSM Polyethylenes, Geleen, The Netherlands. Poly(tetrafluoroethylene) (PTFE) film was purchased from Goodfellow, Cambridge, England. The film characteristics of the used polymers are shown in Table 1.

Dichloromethane (purity $\geq 99.5\%$) and acetone (purity $\geq 99.9\%$) were obtained from Merck, Darmstadt, Germany. Tetrafluoromethane (CF_4) gas (Freon-14; purity $\geq 99.95\%$) was purchased from Hoekloos, Amsterdam, The Netherlands. For all experiments except for the water contact angle measurements, ultrapure water obtained from a Milli-Q Plus System (Millipore) was used. For the contact angle measurements, distilled water was used.

Methods. *Cleaning of Polymer Films.* PE and PTFE films were cut into 4×4 cm pieces. These films were cleaned ultrasonically, successively in dichloromethane (10 min, three times), in acetone (10 min, three times), in water (10 min, three times), and again in acetone (10 min), after which the films were dried in vacuo at room temperature (RT) and stored at RT in the dark.

Determination of the PE Crystallinity. The crystallinity of the various (untreated) PE films was determined by differential scanning calorimetry (DSC) according to a standard procedure.¹⁶ The empirical heat of fusion for 100% crystalline PE was set at

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293 J/g.¹⁷ The measurements were performed with a Perkin-Elmer DSC 7 apparatus.

CF_4 Plasma Treatment of Polymer Films. Cleaned films (four) were mounted in a glass holder (exposed surface area per film: 14 cm^2) which was placed in the center region of a gas plasma tubular reactor (length 80 cm, internal diameter 6.5 cm). Three externally placed capacitively coupled copper electrodes were attached to the reactor: a “hot” electrode in the center and a “cold” electrode at both sides of the “hot” electrode at 10 cm distance. The electrodes were connected to a RF (13.56 MHz) generator through a matching network. A detailed description of the plasma apparatus is given elsewhere.¹⁸

The reactor was evacuated to a pressure of 0.01 mbar. Subsequently, a CF_4 gas flow of $10 \text{ cm}^3/\text{min}$ (STP) was established through the reactor for 15 min (pre-delay). The polymer films were then exposed to the plasma (0.06–0.07 mbar and 48–49 W) for either 15 or 180 min while maintaining a constant gas flow ($10 \text{ cm}^3/\text{min}$) through the reactor. Subsequently, the gas flow was maintained for another 2 min (post-delay). Finally, the reactor was brought to atmospheric pressure with air, and the films were removed.

Moreover, pulsed plasma treatment was carried out at the same conditions as mentioned above. This treatment consisted of 900 plasma pulses of 1 s separated by dark periods of 10 s.

To suppress aging effects (i.e., changes of surface chemistry over the course of time because of the mobility of surface functional groups), the treated films were stored at -20°C prior to analysis.²

Determination of Etching Rates. Before plasma treatment, the polymer films were weighed on an analytical balance (Mettler AT261 Deltarange). Directly after a 3 h plasma treatment, the films were weighed again. The weight decrease was converted into an average etching rate, using the formula

$$v_E = \Delta m / tA\rho \quad (1)$$

where v_E is the etching rate [cm/min] of the polymer films, Δm is the weight decrease [g], t is the plasma treatment time [min], A is the exposed surface area [cm^2], and ρ is the density [g/cm^3] of the polymer films.

When the etching rate is calculated with this formula, it is assumed that the weight decrease caused by etching is linear over the course of time.¹⁵ The initial mass increase due to fluorine incorporation is not taken into account here, because it is negligible when compared to the total weight loss after 3 h of plasma etching.

Thermal Posttreatment of Plasma-Treated LDPE Films. Part of the plasma-treated PE films (LDPE type 2300, either treated continuously for 15 min or pulsed for 900×1 s) was subjected to a thermal posttreatment. Untreated LDPE films were thermally posttreated as a reference. The films were exposed to temperatures of 50, 100, or 150°C during a period of 30 s or 30 min at atmospheric pressure. After this treatment, the films were allowed to cool at RT before storage at -20°C .

XPS Analysis. The chemical surface composition of the plasma-treated polymer films was investigated by XPS. The measurements were performed with a Kratos XSAM-800 apparatus

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(Manchester, United Kingdom) using a Mg K α source (15 kV and 15 mA). A spot size of 3 \times 6 mm was analyzed. The pressure during the measurements was 1 \times 10⁻⁷–1 \times 10⁻⁸ mbar. Survey scans (0–1100 eV) were recorded for all samples to qualitatively determine the elements present at the surface. Detailed scans (20–30 eV windows) were recorded to quantify the elemental surface composition. The measured peak areas were converted into atomic percentages by using sensitivity factors known from the literature.¹⁹

Contact Angle Measurements. Plasma-treated films were characterized by static and dynamic water contact angle measurements using the sessile drop method. The measurements were performed with a KRÜSS contact angle measuring system G10/G40 (Hamburg, Germany).

First, static contact angles were measured by placing a water droplet onto the sample with an electronically regulated syringe. Subsequently, a fresh droplet was placed onto the sample and dynamic contact angles were measured by increasing and decreasing the droplet volume with the syringe, resulting in advancing and receding contact angles, respectively. The dynamic contact angle measurement was started directly after the droplet had reached a constant shape and the liquid–solid interface started to move along the polymer surface.

Every contact angle was determined at least 10 times during each measurement, resulting in an average value. For every sample, measurements were carried out in 3-fold.

SEM Analysis. The surface morphology of the polymer films was studied by SEM. Prior to SEM analysis, the samples were sputtered with a 20 Å thick gold–palladium layer. The coated samples were analyzed with a Hitachi S-800 field emission SEM (6 kV and 20° tilt). SEM pictures were taken at 40 000 \times magnification.

AFM Analysis. AFM was used to study the surface topography of the polymer films. The samples were analyzed with a Nanoscope III microscope (Digital Instruments Inc., Santa Barbara, CA). AFM images were recorded in tapping mode at RT in air using silicon cantilevers (Digital Instruments). For each sample, both height and phase images were recorded with the maximum available number of pixels (512). For image analysis the recorded scans were “flattened” using the Nanoscope image processing software. In addition, the mean surface roughness (R_a) was calculated for the scanned area (5 \times 5 μ m) by applying the formula

$$R_a = \sqrt{\frac{\sum_{x,y=1}^N (Z_{x,y} - Z_{\text{average}})^2}{N^2}} \quad (2)$$

Here, the roughness is defined as the normalized standard deviation calculated from the local heights ($Z_{x,y}$) and the average height (Z_{average}) determined over all x, y coordinates (N) measured in the AFM image.

Results

Etching Rate of PE as a Function of Crystallinity.

The crystallinity of the various PE grades increased with density from 14% (LLDPE1) to 59% (HDPE) as was determined by DSC. All films were treated with a CF₄ plasma for 3 h in order to determine the etching rate. The relation between etching rate and crystallinity is shown in Figure 1. For the (L)LDPE grades (crystallinity \leq 36%) the etching rate decreased almost linearly with increasing crystallinity. For PE grades with a higher crystallinity, the further decrease of the etching rate was less pronounced.

The etching rate of PTFE in a CF₄ plasma was also determined. A value of 46 \pm 1 Å/min was found after three measurements, which is in the range of the etching rates shown in Figure 1.

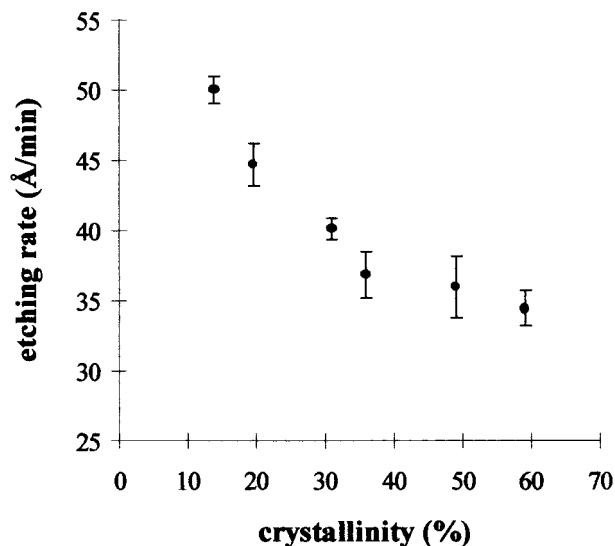


Figure 1. Etching rate as a function of crystallinity of a series of PE grades in a CF₄ plasma ($n = 3$, \pm sd).

Table 2. XPS Data of PE Films Treated with a CF₄ Plasma for 3 h ($n = 3$, \pm sd)^a

sample	C (at. %)	O (at. %)	F (at. %)	F/C ratio
LLDPE1; CF ₄ -180	37.6 \pm 0.8	2.0 \pm 0.2	58.5 \pm 0.5	1.6 \pm 0.1
LLDPE2; CF ₄ -180	38.8 \pm 0.9	1.9 \pm 0.4	57.4 \pm 1.2	1.5 \pm 0.1
LDPE1; CF ₄ -180	38.2 \pm 0.6	2.1 \pm 0.4	57.2 \pm 0.6	1.5 \pm 0.1
LDPE2; CF ₄ -180	38.8 \pm 1.9	2.1 \pm 0.1	56.8 \pm 1.0	1.5 \pm 0.1
LMDPE; CF ₄ -180	39.2 \pm 1.5	2.0 \pm 0.1	55.8 \pm 0.4	1.4 \pm 0.1
HDPE; CF ₄ -180	38.7 \pm 0.6	2.1 \pm 0.5	56.0 \pm 0.6	1.4 \pm 0.1
PTFE; untreated	30.9 \pm 0.6		69.1 \pm 0.6	2.2 \pm 0.1

^a Untreated PE films contain less than 0.5% oxygen and no fluorine at all.

XPS Analysis. The surface of the 3 h plasma-treated PE films (CF₄-180) was characterized by XPS. Untreated PTFE samples were taken as a reference. The results are shown in Table 2.

XPS analysis revealed that during CF₄ plasma treatment the PE surfaces were highly fluorinated. For LLDPE, F/C ratios up to 1.6 were found. Moreover, there seems to be a correlation between the degree of fluorination and the crystallinity. With increasing PE crystallinity, the F/C ratio slightly decreased. Besides fluorination, the PE surfaces were somewhat oxidized during plasma treatment.

To study the difference in treatment between continuous and pulsed CF₄ plasmas, all PE grades were either treated continuously for 15 min (CF₄-15) or treated with 900 plasma pulses of 1 s (CF₄-900 \times 1 s). When the actual plasma discharge time is kept constant (900 s), a reasonable comparison can be made between continuous and pulsed CF₄ plasma treatment. However, it should be noted that dark period effects might occur during pulsed treatment because of the presence of long-living radicals and/or metastables. These effects are not taken into account here. The XPS results of these treatments are shown in Table 3.

Table 3 clearly shows that almost complete fluorination occurred within 15 min of plasma treatment. For all PE grades, a small difference in the degree of fluorination is found between continuous and pulsed treatment, with the latter causing somewhat less fluorination. This difference seems to be most pronounced for the (L)LDPE grade films. Again, fluorination is accompanied by some oxidation during CF₄ plasma treatment.

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Table 3. XPS Data of PE Films Treated with a Continuous (15 min) or a Pulsed (900 × 1 s) CF₄ Plasma (n = 1)

sample	C (at. %)	O (at. %)	F (at. %)	F/C ratio
LLDPE1; CF ₄ -15	41.7	2.6	55.7	1.3
LLDPE1; CF ₄ -900 × 1s	43.9	2.9	53.2	1.2
LLDPE2; CF ₄ -15	41.8	2.5	55.7	1.3
LLDPE2; CF ₄ -900 × 1s	43.4	2.9	53.6	1.2
LDPE1; CF ₄ -15	41.0	2.2	56.8	1.4
LDPE1; CF ₄ -900 × 1s	43.6	2.1	54.2	1.2
LDPE2; CF ₄ -15	42.4	2.2	55.3	1.3
LDPE2; CF ₄ -900 × 1s	43.0	2.6	54.3	1.3
LMDPE; CF ₄ -15	43.2	2.4	54.4	1.3
LMDPE; CF ₄ -900 × 1s	44.6	2.3	53.1	1.2
HDPE; CF ₄ -15	43.5	2.8	53.7	1.2
HDPE; CF ₄ -900 × 1s	43.9	2.6	53.4	1.2

Contact Angle Measurements. Water contact angle measurements were carried out using the sessile drop method. Static and dynamic contact angle data of all treated and untreated PE samples are presented in Figures 2 and 3, respectively. For comparison, the value of the water contact angles of PTFE are represented by dotted lines.

Figures 2 and 3 clearly show that CF₄ plasma treatment of PE resulted in a significant decrease of wettability by water. Advancing angles up to 150° were measured for plasma-treated LDPE (crystallinity ≤ 36%), which is significantly higher than the corresponding value for PTFE (129°). For most PE films no significant difference was found between 15 min and 3 h of treatment. However, a striking difference was observed between continuously treated and pulsed treated (L)LDPE films, with the latter being less hydrophobic. Another remarkable result shown in Figure 3 is the high contact angle hysteresis (here defined as $\theta_{\text{advancing}} - \theta_{\text{receding}}$) found for plasma-treated PE. The largest effect is observed for LDPE films for which hysteresis increased from 17° for untreated films to values of 77° for continuously plasma-treated films.

SEM Analysis. SEM pictures were made of the surfaces of untreated and plasma-treated PE films. Figures 4 and 5 show the surface morphology of two different PE grades (LDPE1 and HDPE, respectively) before and after CF₄ plasma treatment.

The SEM pictures in Figure 4 clearly show that the morphology of the LDPE surface changed significantly during prolonged, continuous CF₄ plasma treatment. Very similar pictures were obtained for the other (L)LDPE films (crystallinity ≤ 36%).

The untreated LDPE surface consists of randomly oriented lamellae. The crystalline lamellae are surrounded by amorphous PE, the major phase of the material. During plasma treatment this lamellar surface structure changed into a nanoporous-like surface structure (Figure 4B,C). The pores/grains that appeared at the surface have a quite uniform size, on the order of tens of nanometers.

This pronounced change of surface structure (i.e., surface restructuring) was not found for pulsed plasma-treated LDPE films (Figure 4D). Although the surface morphology was affected to some extent, the lamellar structure is still present at the PE surface after pulsed plasma treatment.

In the case of plasma-treated HDPE films, a completely different effect of plasma treatment on the surface structure was found, as can be seen in Figure 5. The untreated surface is characterized by organized lamellae. The lamellae are oriented perpendicular to the microscopic film texture, which is possibly induced by the film blow procedure. During prolonged plasma treatment, this oriented lamellar surface structure largely disappeared

(Figure 5B). For shorter plasma treatment times, the surface restructuring was less significant and oriented lamellae are still visible (Figure 5C). Pulsed plasma treatment hardly seemed to affect the surface structure (Figure 5D) of HDPE.

Similar effects were found for plasma-treated LMDPE films, although in this case the surface lamellae are not oriented in one direction.

Thermal Posttreatment of Plasma-Treated LDPE Films. To examine the effect of temperature on the surface structure of the PE films during plasma etching, one type of LDPE film (type 2300) was subjected to a thermal treatment after exposure to a CF₄ plasma (either continuously for 15 min or pulsed for 900 × 1 s). The LDPE films were exposed to a temperature of 50, 100, or 150 °C for either 30 s or 30 min.

SEM analysis (pictures not shown here) clearly pointed out that at temperatures of 50 and 100 °C for 30 s and 30 min no change of surface structure was found after (pulsed) plasma treatment. Moreover, the untreated reference material did not show any change during thermal post-treatment at these temperatures. However, after thermal treatment above the melting temperature (150 °C), the (un)treated LDPE films recrystallized from the melt and the macroscale structure was changed drastically.

AFM Analysis. Tapping-mode AFM analysis was also used to study the surface topography of untreated and plasma-treated PE films. Height and phase images were recorded simultaneously, and the results of LDPE1 and HDPE films are shown in Figures 6 and 7. The values of the mean surface roughness (R_a) of these films are shown in Table 4.

Although the untreated LDPE surface is quite rough (Figure 6A), the surface roughness further increased upon plasma treatment (Table 4). When Figure 6A is compared with Figure 6B,C, a pronounced surface restructuring is visible similar to that observed in Figure 4. The surface lamellae disappeared and were replaced by a granular structure. Figure 6D shows that the LDPE surface structure remained quite intact during pulsed plasma treatment, although the lamellae are not as clearly visible as those in Figure 6A.

Figure 7A clearly illustrates the microscale texture of untreated HDPE induced by film processing (height image) in combination with a nanoscale lamellar morphology (phase image) perpendicularly oriented to the microscale texture. During the 3 h plasma treatment, the lamellae were severely damaged and a rough, undefined structure is obtained (Figure 7B). After shorter treatment times (Figure 7C) and after pulsed treatment (Figure 7D), the microscale texture with its perpendicular lamellar morphology is retained, although substantial surface roughening has occurred (Table 4).

Generally, the observed surface structural changes in Figures 6 and 7 are in good agreement with the results found by SEM analysis (Figures 4 and 5).

Discussion

Etching Behavior of PE in a CF₄ Plasma. The decrease of the etching rate with increasing crystallinity of PE (Figure 1) indicates that in a CF₄ plasma the amorphous phase of PE is etched faster than the crystalline phase. At low crystallinity (≤36%) the PE etching rate showed a linear dependence resulting in the relation

$$v_E = c v_{E,C} + (1 - c) v_{E,A} = (v_{E,C} - v_{E,A})c + v_{E,A} \quad (3)$$

in which v_E refers to the total etching rate, $v_{E,C}$ and $v_{E,A}$ refer to the etching rates of the crystalline phase and the

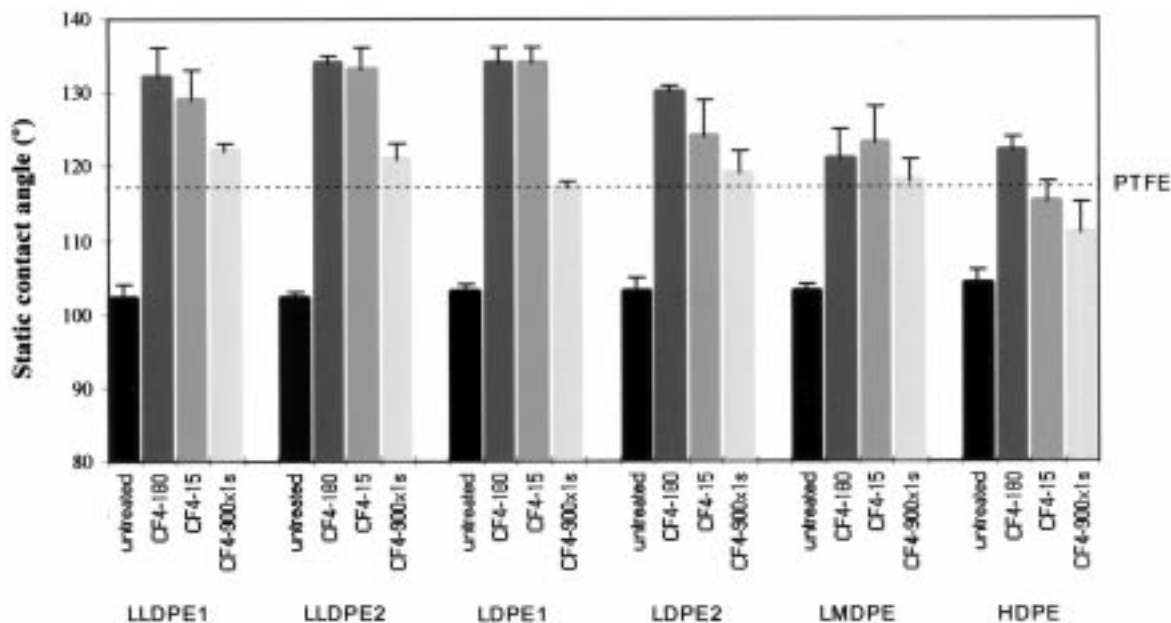


Figure 2. Static water contact angles of untreated and CF₄ plasma-treated PE. The series of PE films were all treated either for 3 h (CF₄-180), for 15 min (CF₄-15), or with 900 pulses of 1 s (CF₄-900 × 1 s). The dotted line represents the static water contact angle of untreated PTFE ($n = 3, \pm \text{sd}$).

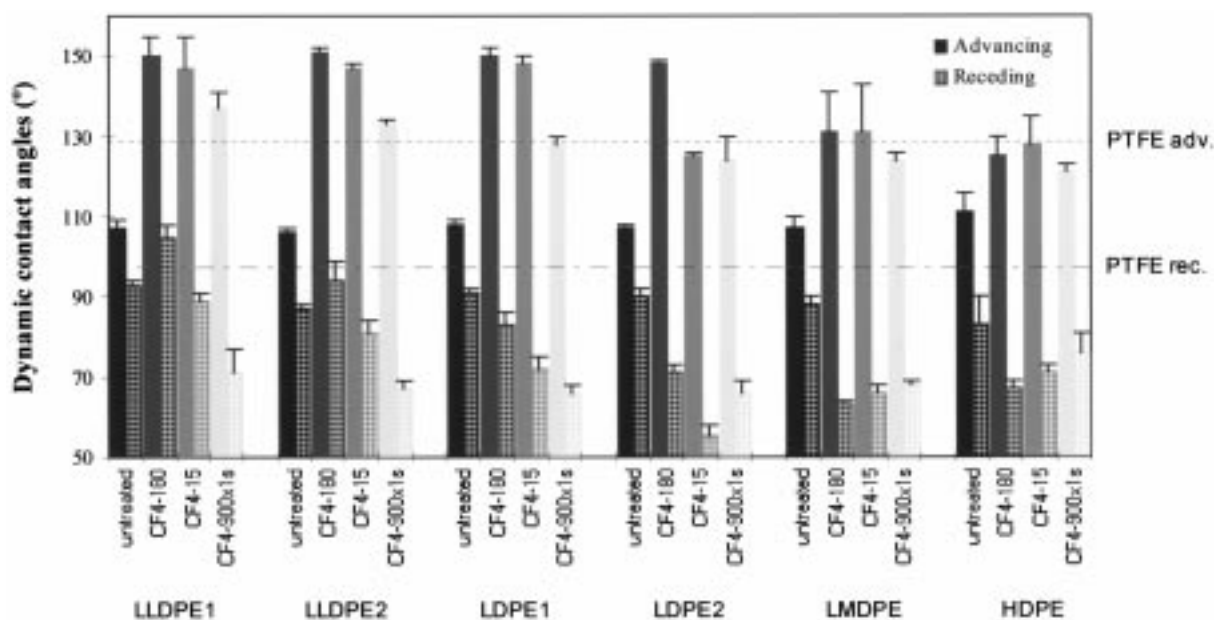


Figure 3. Dynamic water contact angles of untreated and CF₄ plasma-treated PE. The series of PE films were all treated either for 3 h (CF₄-180), for 15 min (CF₄-15), or with 900 pulses of 1 s (CF₄-900 × 1 s). The dotted lines represent the dynamic water contact angles of untreated PTFE ($n = 3, \pm \text{sd}$).

amorphous phase, respectively, and c refers to the crystalline fraction ($C/100$).

This simple model of etching of a two-phase material was also applied by Herbert et al. to explain the linear dependence of the etching rate of PE on crystallinity when using an ultraviolet-ozone treatment.⁶ In this model it is assumed that the etching rates of the crystalline and the amorphous phases have a constant value during the etching process. The difference between these values determines the selectivity of the etching process. When this linear relation is applied to the (L)LDPE grades, it can be calculated that $v_{E,C} = 1 \text{ \AA}/\text{min}$ and $v_{E,A} = 57 \text{ \AA}/\text{min}$. Although this calculation is somewhat speculative and many important aspects involved in the etching process (e.g., temperature effects, surface fluorination, surface roughness, surface vs bulk composition, and

surface restructuring) are not taken into account, it indicates a preferential etching behavior of PE in a CF₄ plasma.

A significant deviation from the linear etching behavior is found for LMDPE and HDPE films. This illustrates that indeed other factors must play an important role during the etching process. A reasonable explanation for the deviating behavior could be found when realizing that the surface characteristics (e.g., morphology, roughness, and chemistry) of the (L)LDPE films differ from those of higher density PE. Table 4 shows that the HDPE surface is rougher than a LDPE surface, resulting in a larger exposed surface area during plasma treatment. Therefore, a higher etching rate than that derived from relation (3) (extrapolating the (L)LDPE linear decrease would result in a HDPE etching rate of $24 \text{ \AA}/\text{min}$) can be expected. The

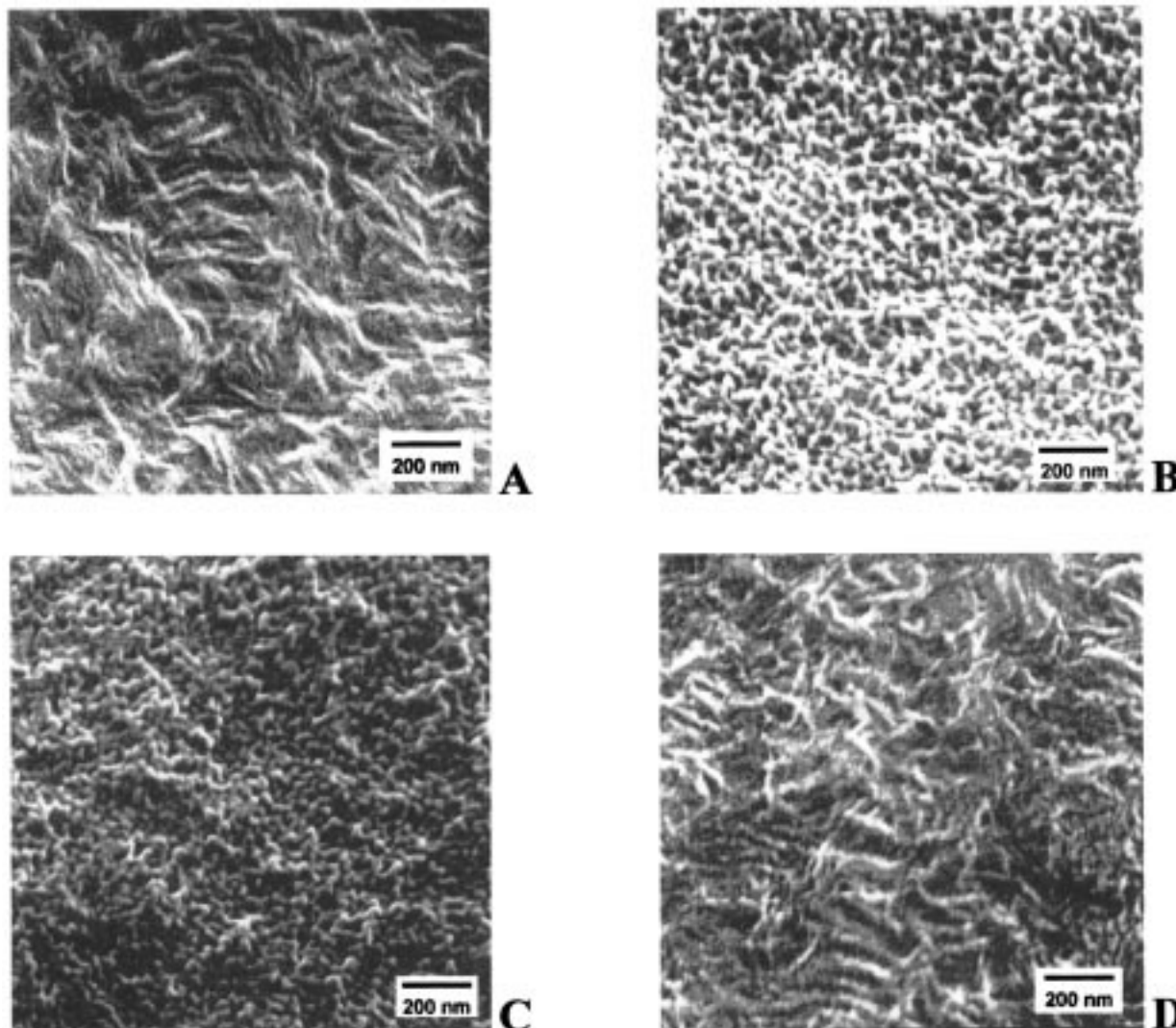


Figure 4. SEM pictures of untreated and CF_4 plasma-treated LDPE1 surfaces: (A) untreated, (B) treated for 3 h, (C) treated for 15 min, (D) treated with 900 pulses (1 s).

impact of the surface structure on the plasma etching process will be discussed further on.

Surface Chemical Changes of PE during CF_4 Plasma Treatment. During CF_4 plasma treatment a high degree of surface fluorination occurred (Table 2). This is not surprising because it is well-known that fluorine radicals are the most reactive species in a CF_4 plasma, yielding high F/C ratios at the polymer surface.^{20–23}

An interesting feature is the slight decrease of the F/C ratio with increasing crystallinity. One reason for the varying F/C ratios might be a difference in the depth of modification. However, this cannot be shown by XPS because of the relatively high roughness of PE surfaces. Another explanation would be that during CF_4 plasma treatment the crystalline phase of PE is somewhat less fluorinated than the amorphous phase. When considering that the crystalline phase is less susceptible to chemical or physical changes and therefore better resistant to etching (Figure 1), this result could indeed be expected.

Another interesting feature shown in Table 3 is the small difference of fluorination between continuously and pulsed treated films. However, from previous experiments (data not shown) it is known that for longer plasma treatment times (30 min) this difference disappears. Comparing the data in Table 2 with those in Table 3 shows that fluorination has practically reached its equilibrium value after 15 min of treatment. If the hydrogen atoms in the PE backbone were completely substituted by fluorine, a theoretically maximal F/C ratio of 2 would be found. However, this maximal value is not reached probably because of the presence of a fluorine gradient at the surface and/or because of the equilibrium between etching (F^\downarrow) and fluorination (F^\uparrow). Furthermore, the occurrence of cross-linking during plasma treatment will limit the F/C ratio.

According to Figures 2 and 3, fluorination of PE is accompanied by some oxidation. During plasma treatment some oxygen-containing species are present in the plasma phase because of reaction of fluorine radicals with the inner glass wall of the reactor (Si_xO_y), yielding Si_xF_y fragments and atomic oxygen.²⁴ However, the small amount of surface oxidation can also be explained by

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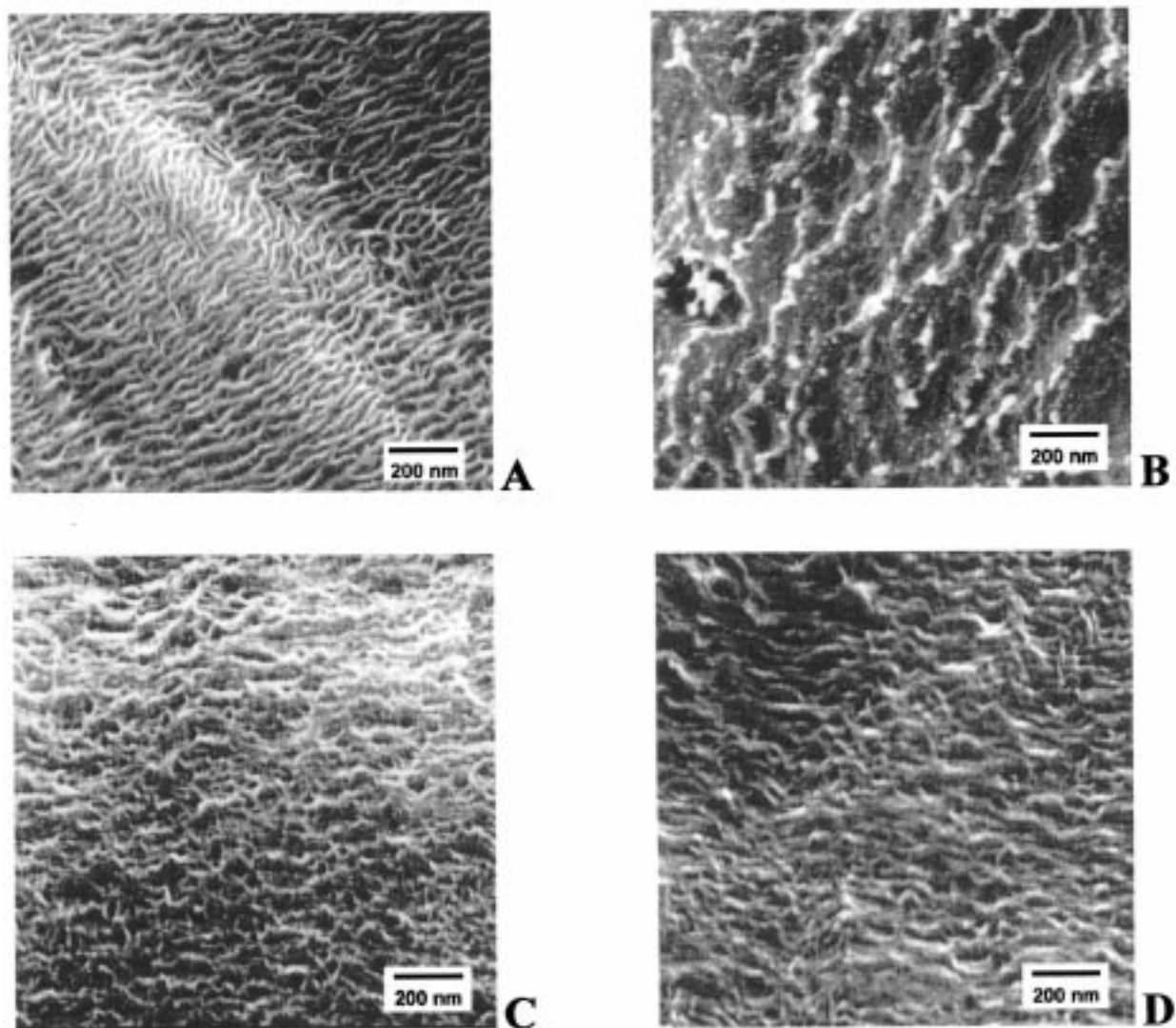


Figure 5. SEM pictures of untreated and CF_4 plasma-treated HDPE surfaces: (A) untreated, (B) treated for 3 h, (C) treated for 15 min, (D) treated with 900 pulses (1 s).

postreactions of surface free radicals, which are still present after plasma treatment, with oxygen in air.

Wettability of CF_4 Plasma-Treated PE Films. Prolonged CF_4 plasma treatment of PE resulted in extremely hydrophobic surfaces (Figures 2 and 3). Similar superhydrophobic surfaces were prepared by Busscher et al. by argon ion etching of FEP-Teflon followed by an oxygen plasma treatment.²⁵ These surfaces have water contact angles higher than 140° .

The high hydrophobicity of the plasma-treated PE surfaces is at least partly due to the large amount of surface fluorination. The occurrence of an equilibrium state for fluorine incorporation is indicated by the fact that no large differences of wettability were found between surfaces treated for 15 and 180 min. This is in good agreement with the corresponding amounts of fluorination discussed above. However, surface fluorination is only part of the explanation for superhydrophobicity because the water contact angles of an untreated PTFE surface are much lower. Therefore, other factors must have a significant influence on the hydrophobicity of these films. In principle, the equilibrium contact angle at a solid-liquid-air interface is dependent not only on the surface chemistry

of the solid but also on its surface structure (e.g., roughness, heterogeneity, and porosity).²⁶⁻³¹ An explanation for the extremely high contact angles is found in the porous character of the plasma-treated LDPE surfaces. Cassie and Baxter derived an equation for the apparent contact angle (θ_A) of a uniform porous surface, based on thermodynamics:²⁶

$$\cos \theta_A = f_1 \cos \theta_1 - f_2 \quad (4)$$

In this equation, f_1 and f_2 are the area fractions of solid-liquid and liquid-air interfaces on the solid, respectively. θ_1 represents the contact angle (advancing or receding) for the solid-liquid interface.

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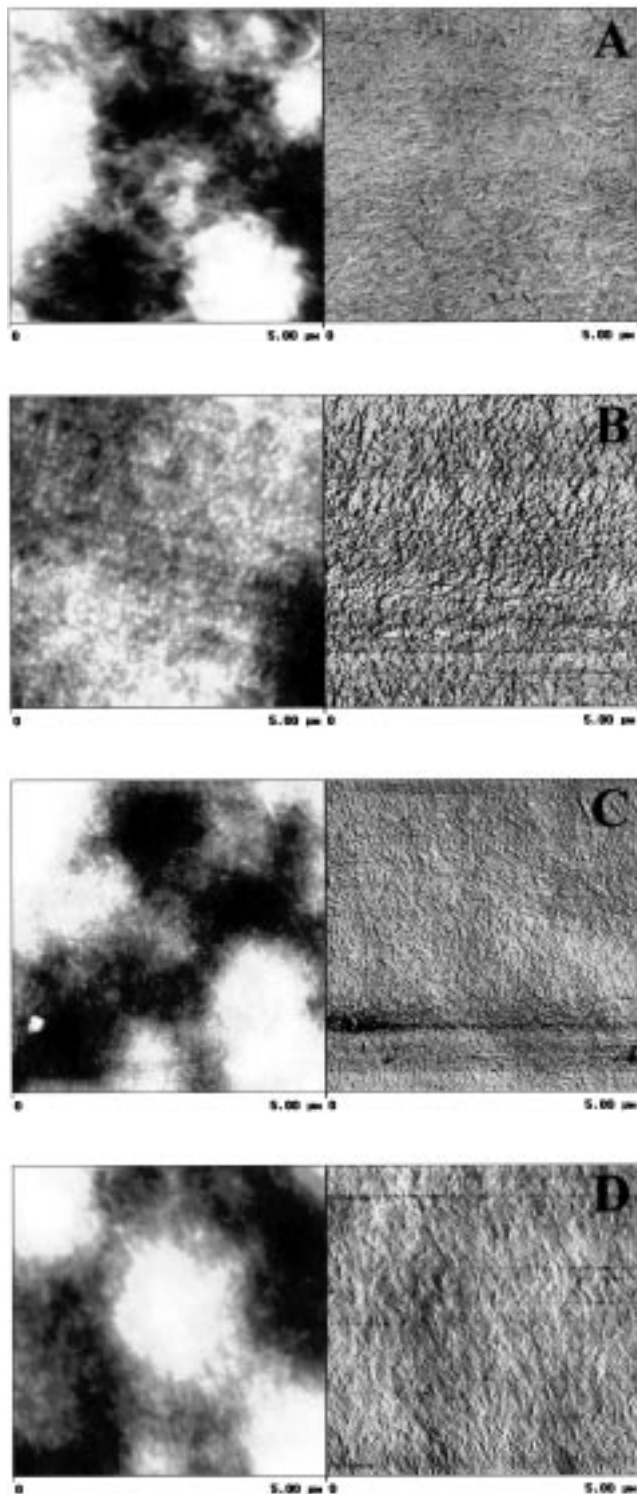


Figure 6. Tapping-mode AFM images (height (left) and phase (right) imaging) of untreated and CF_4 plasma-treated LDPE1 surfaces: (A) untreated, (B) treated for 3 h, (C) treated for 15 min, (D) treated with 900 pulses (1 s).

On the basis of this theory, a rough estimation can be made of the area fractions f_1 and f_2 for PE surfaces after CF_4 plasma treatment. For plasma-treated LDPE1 surfaces, an apparent advancing water contact angle of 150° (θ_A) was found (Figure 2). The advancing contact angle for the solid–liquid interface (θ_1) is set at 129° , which is the advancing contact angle of “solid” PTFE (Figure 2). From these values it can be calculated that $f_1 = 0.36$ and $f_2 = 0.64$. Although this calculation is merely qualitative, it indicates that a surface structural change has indeed

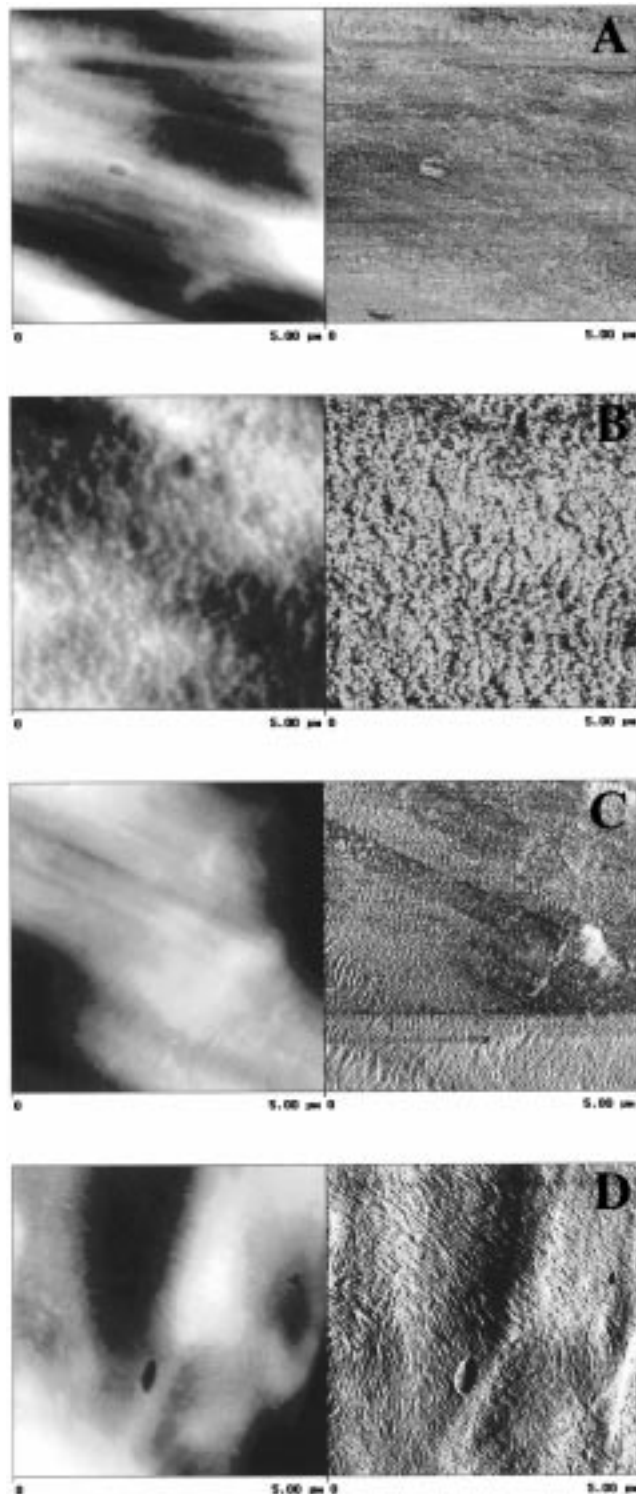


Figure 7. Tapping-mode AFM images (height (left) and phase (right) imaging) of untreated and CF_4 plasma-treated HDPE surfaces: (A) untreated, (B) treated for 3 h, (C) treated for 15 min, (D) treated with 900 pulses (1 s).

taken place during plasma treatment of LDPE surfaces, as was clearly shown by the SEM and AFM results (Figures 4 and 6). These surface structural changes will be further discussed below.

For plasma-treated HDPE surfaces, θ_A is similar or even lower than the assumed value for θ_1 (Figure 3). This suggests that θ_1 probably has a lower value, which seems reasonable when it is realized that the surface chemistry of “solid” fluorinated PE is not exactly equal to that of “solid” PTFE ($\theta_1 = \theta_A = 129^\circ$).

Table 4. Mean Surface Roughness (R_a) of Untreated and CF_4 Plasma Treated PE Films as Calculated from AFM Results (Films Treated Either for 3 h (CF_4 -180), 15 min (CF_4 -15) or with 900 pulses of 1 s (CF_4 -900 \times 1 s))

sample	R_a (nm) ^a
LDPE1; untreated	23
LDPE1; CF_4 -180	30
LDPE1; CF_4 -15	45
LDPE1; CF_4 -900 \times 1 s	49
HDPE; untreated	38
HDPE; CF_4 -180	60
HDPE; CF_4 -15	87
HDPE; CF_4 -900 \times 1 s	91

^a Scanned surface area = $5 \times 5 \mu\text{m}$ ($n = 1$).

Another interesting result shown in Figures 2 and 3 is the significant difference between continuously treated and pulsed treated (L)LDPE films. It is not expected that this difference was only caused by the small difference of surface fluorination (Table 3), but it must also be attributed to changes of surface structure.

Surface Structural Changes of PE during CF_4 Plasma Treatment. The SEM pictures in Figure 4 and the AFM images in Figure 6 clearly show that the LDPE surface is structurally changed during continuous plasma treatment. It should be noted that the nanopores seen in Figure 4B,C cannot be directly imaged as such by AFM because the radius of the AFM tip (~ 30 nm) is on the same order of magnitude as the size of the pores. Thus, the tip cannot penetrate into the pores, resulting in a type of granular structure as shown in Figure 6B.

On the contrary, the surface lamellar structure of pulsed treated films was hardly affected although significant surface roughening took place. This is clearly shown by the hysteresis data in Figure 3 and the surface roughness data obtained from AFM analysis in Table 4. The increase of surface roughness and the preservation of the lamellar surface structure nicely show that CF_4 pulsed plasma treatment is a selective etching process.

Still, the question remains how the striking difference of surface structure between continuously treated and pulsed treated films can be explained. Two possible causes can be responsible for this structural difference.

First, a continuous bombardment by reactive species (e.g., electrons, ions, and fluorine radicals) can cause more surface damage than pulsed bombardment. During the dark periods used in the pulsed plasma treatment, the polymer surface is able to recover, for example, by recombination of dissociated chain bonds and by termination of surface radicals. Although the actual time of discharge (900 s) is equal for continuous and pulsed plasma treatment, the treatment conditions in the latter case seem to be milder.

Second, temperature effects probably play an important role during the etching process.³² During continuous plasma treatment an increase of surface temperature is expected because of heat development caused by fluorination, which is an exothermic reaction. Moreover, a continuous bombardment of reactive species onto the substrate raises the surface temperature significantly.^{33,34} The overall temperature increase might be such that during plasma treatment the melting temperature of PE

is reached at the surface. Together with surface fluorination and preferential etching, this could very well lead to restructuring of the surface. In the case of pulsed plasma treatment, the heat developed at the surface will flow away during the dark periods, thereby preventing a major temperature increase and a subsequent surface restructuring.

To investigate whether temperature effects indeed play a key role in explaining the difference between continuously and pulsed treated PE films, thermal posttreatments were carried out with LDPE. After plasma treatment the surface structures seemed to be quite stable and did not reorganize at temperatures just below the melting temperature of LDPE (110–115 °C). During the thermal posttreatment at 150°, the LDPE films did not retain their film characteristics because the bulk of the films was also affected. This dramatic macroscale change of surface and bulk structures can be easily explained when it is realized that during PE film processing (blown extrusion) a specific morphology is created which simply cannot be recovered after melting and recrystallization of the films. With respect to this extreme thermal posttreatment, it should be noted that during plasma treatment these macroscale changes were not observed. This implies that, although a surface temperature increase is inevitable, the melting temperature will not be reached in the bulk during plasma treatment. A similar conclusion was drawn earlier from experiments with UHMWPE membranes that were treated with a CO_2 plasma.³⁴ Currently, the actual surface temperature increase of PE during CF_4 plasma treatment is being investigated.

So, the question remains whether and how temperature effects influence the surface structure of PE films during plasma treatment. Based on the results obtained so far, the most reasonable explanation for the pronounced surface structural change is a combined effect of preferential etching, fluorination, and an increase of surface temperature. While the amorphous regions are preferentially removed from the surface, fluorination and heat development may induce phase separation at the PE surface, segregating fluorine-rich domains from fluorine-poor domains. The outside of the granular structures seen in Figures 4B,C and 6B,C probably consists of fluorine-rich domains, thus realizing a minimal surface energy. In the case of pulsed treatment, the temperature increase is not sufficient and therefore no phase separation will occur.

Figures 5 and 7 show that the etching process has a completely different effect on HDPE surfaces. Hardly any difference can be seen between the surface structure of continuously and pulsed treated films (Figures 5C,D and 7C,D), which is in agreement with the contact angle data shown in Figures 2 and 3. Apparently, the surface lamellar structure of HDPE is less affected by a temperature increase during plasma treatment which would lead to phase separation (see above). Still, preferential etching of the amorphous phase induced a major increase of surface roughness for all HDPE surfaces (Table 4).

Clearly, the crystallinity of PE does have a major influence on the surface structural changes during plasma treatment. The (L)LDPE grades all show very similar changes, while the etching behavior of LMDPE and HDPE films leads to deviating and undefined structures. This also explains the deviating results for wettability and etching rates of plasma-treated LMDPE and HDPE as compared to (L)LDPE seen in Figures 1–3. Obviously, changes of surface structure during CF_4 plasma treatment have a large influence on the wettability and the etching rate of PE films.

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Conclusions

This study showed that selective plasma etching can be a versatile tool for creating nanostructured polymer surfaces. Both continuous and pulsed CF_4 plasma treatment of PE resulted in a preferential etching process, with the original amorphous phase being etched faster than the crystalline phase.

Moreover, the PE films were highly fluorinated during treatment (F/C ratios up to 1.6), and extremely hydrophobic surfaces were formed with advancing water contact angles of up to 150° .

Besides fluorination, a pronounced surface restructuring took place during continuous plasma treatment of (L)-LDPE films as was revealed by SEM and AFM analysis. The lamellar surface structure was converted into a nanoporous-like structure with uniform domains on the order of tens of nanometers. The change of surface structure was attributed to a combined effect of etching and an increase of surface temperature inducing phase separation of PE-like and PTFE-like material, of which the latter is surface oriented. These surface structural changes were not observed after plasma treatment of

LMDPE and HDPE films, which can most likely be attributed to differences in surface etching behavior. In all cases, the surface roughness increased substantially during plasma treatment, resulting in a large hysteresis.

During pulsed CF_4 plasma treatment of PE films, the initial lamellar morphology remained intact but the surface roughness increased considerably. Therefore, selective etching by pulsed plasma treatment is most suitable when preservation of surface morphology is desired.

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