

Introduction of Functional Groups on Polyethylene Surfaces by a Carbon Dioxide Plasma Treatment

JOHANNES G. A. TERLINGEN,¹ HERMINA F. C. GERRITSEN,¹ ALLAN S. HOFFMAN,² and JAN FEIJEN^{1,*}

¹Department of Chemical Technology and Institute for Biomedical Technology, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands; ²Center for Bioengineering FI-20, University of Washington, Seattle, Washington 98195

SYNOPSIS

Poly(ethylene) (PE) films were treated with a carbon dioxide (CO₂) plasma to study the formation of oxygen-containing functional groups at the surface. Modified and nonmodified films were characterized by X-ray photoelectron spectroscopy (XPS) and water contact angle measurements. During the CO₂ plasma treatment, the PE surface is etched and oxidized, yielding films with a very hydrophilic surface. The oxygen incorporation at the surface is fast and can be described by a combination of a zero-order incorporation and a first-order etching process. Several oxygen functionalities such as carboxylic acid (approximately 14% of the oxygen present), ketone/aldehyde (25%), and hydroxyl/epoxide (5–9%) groups were introduced at the surface by the plasma treatment. This was shown by using derivatization reactions for specific functional groups followed by XPS analysis. The wettability of the plasma-treated surfaces decreased when the films were stored for prolonged periods of time in air. This aging process could not be completely reversed by immersion of the films in water. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Because only the outermost surface layers of a substrate are modified by a plasma treatment, these techniques are applied more and more for surface-modification purposes. Plasma-treatment processes using an oxidizing gas have been frequently used for the introduction of functional groups at polymer surfaces.^{1–5} These groups can be used for the covalent attachment of, e.g., bioactive molecules for biomedical or biosensor applications and for the improvement of the adhesion properties of the surface.

The chemical composition of plasma-treated surfaces depends on the gas used and the experimental conditions applied. When an oxygen or argon plasma is used, a spectrum of oxygen-containing groups including peroxide, hydroxyl, ketone/aldehyde, carboxylic acid, and ester groups are introduced at the surface.^{4,6,7} Recently, we developed a novel method to introduce functional groups at inert polymer sur-

faces. By applying a plasma of an inert gas to a layer of a surface-active compound preadsorbed on a hydrophobic polymer surface, it is possible to couple this layer covalently to the surface. When a surface-active compound with the required functionality is used, it is possible to specifically introduce these groups at the surface. This method has been applied to introduce sulfate groups at polypropylene⁸ and amine groups at PE surfaces.⁹ However, the immobilization of a preadsorbed layer of polyacrylic acid (PAAc) was not successful,¹⁰ due to the fact that PAAc readily decarboxylates during an argon or tetrafluoromethane (CF₄) plasma treatment.¹¹ Therefore, we investigated the possible use of a CO₂ plasma treatment to introduce carboxylic acid groups at inert polymer surfaces, which can be subsequently used for the coupling of bioactive molecules by well-known coupling chemistry.¹²

The use of CO₂ plasmas to modify polymer surfaces has been reported by several authors. Wrobel et al. used a CO₂ plasma to improve the wettability of poly(ethylene terephthalate) fibers.¹³ Stewart and Urban reported that the CO₂ plasma treatment of silicon-rubber resulted in the introduction of

* To whom correspondence should be addressed.

carbonyl¹⁴ and unsaturated aliphatic bonds.¹⁵ Poncin-Epaillard showed that during a microwave CO₂ plasma treatment of poly(propylene), ketone, acid, or ester functionalities are introduced at the surface.^{16,17} Inagaki et al.¹⁸ reported that treatment of PE with an audiofrequency CO₂ plasma resulted in a very hydrophilic surface. The hydrophilic properties were related to the presence of oxygen-containing functional groups (hydroxyl, ketone, and acid) at the surface. Finally, Shard and Badyal¹⁹ reported that polystyrene films are photooxidized by UV radiation in a low-pressure CO₂ environment.

In this study, the surface properties of PE films and the presence of specific functional groups at the surface after treatment of PE with a radiofrequency CO₂ plasma were investigated using water contact angle measurements, X-ray photoelectron spectroscopy (XPS), and derivatization XPS. Derivatization XPS, in which functional groups are tagged with a unique element by a chemical reaction prior to the XPS analysis,²⁰⁻²³ is used to identify hydroxyl/epoxide, ketone/aldehyde, and carboxylic acid groups. The reactions used are given in Scheme 1. In contrast to the studies mentioned previously, the kinetics of the plasma treatment have also been studied. The effect of the plasma treatment time on the wettability, as well as on the surface concentration of different functional groups introduced at the surface, has been investigated. Furthermore, Fourier transform infrared spectroscopy in the attenuated total reflection [ATR] mode (FT-IR-ATR) has been used to obtain additional information on the chemical composition of the plasma-treated surface. Finally, the stability of the plasma-modified surfaces in contact with water or other solvents was studied and the effect of storing the surfaces for prolonged times at different temperatures in air was investigated.

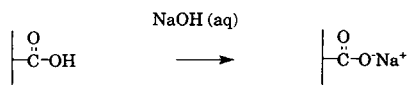
EXPERIMENTAL

Materials

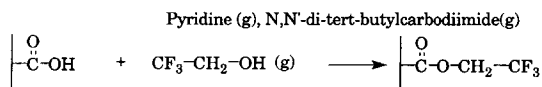
PE film: low-density polyethylene (PE): type 2300, thickness 0.2 mm, DSM, Geleen, The Netherlands. This PE does not contain additives. Polytetrafluoroethylene (PTFE): thickness 0.5 mm, Good Fellow, Cambridge, England. Dichloromethane (GR), acetone (GR), pyridine (GR), *n*-hexane (GR), aqueous sodium hydroxide solution (NaOH, 1.00 M), aqueous hydrochloric acid solution (HCl, 1.00 M), 2,2,2-trifluoroethanol (TFE, purity > 99%), 2,2,2-trifluoroacetic acid anhydride (TFAA, purity

Detection of carboxylic acid groups:

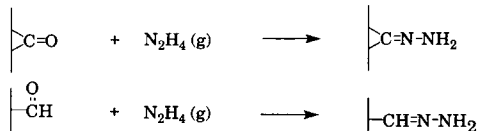
Ion exchange



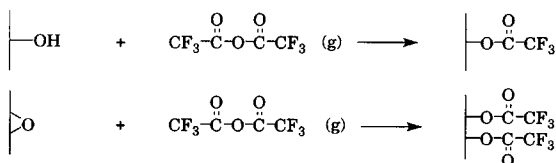
Reaction with 2,2,2-trifluoroethanol (TFE)



Detection of ketone/aldehyde groups:



Detection of hydroxyl/epoxide groups:



Scheme 1 Derivatization reactions used to identify surface-bound carboxylic acid, ketone/aldehyde, and hydroxyl/epoxide groups. The surface analysis was performed with XPS.

> 99%), paraffin (solidification point 52–54 °C): Merck, Darmstadt, Germany. The GR-grade chemicals have a purity of at least 99.5%. Hydrazine monohydrate (N₂H₄, purity 99%): Janssen Chimica, Tilburg, The Netherlands. *N,N'*-di-*tert*-butylcarbodiimide (purity 99%), Aldrich Chemie, Brussels, Belgium. Carbon dioxide (CO₂, purity ≥ 99.995%): Hoekloos, Schiedam, The Netherlands. For all experiments, doubly deionized water was used.

Methods

All films were stored at room temperature (RT) in glass vials in the dark.

Cleaning of PE and PTFE Films

PE or PTFE films (13 × 25 mm) immersed in dichloromethane were placed in an ultrasonic bath for 10 min. The dichloromethane was refreshed and the whole procedure was repeated. The total cleaning procedure consisted of treatment four times with dichloromethane, four times with acetone, and four times with water. Subsequently, the films were dried *in vacuo* at RT and stored.

Plasma Treatment

An extensive description of the plasma-treatment system was given previously.¹⁰ In brief, the plasma system consists of a tubular reactor (internal diameter 6.5 cm) with three externally placed capacitively coupled electrodes spaced at 10 cm distances. One side of the tubular reactor was connected to a turbomolecular pump and to a two-stage rotary vane pump. The other side was attached to a gas inlet controlled by mass flow controllers. The electrodes were powered through a matching network by a 13.56 MHz radio-frequency generator, which was controlled by a timer (Apple IIe computer with a time control program). This system enables an optimal control of the plasma-treatment time. The rise time of the plasma in this configuration is less than 1 ms.

The following plasma-treatment procedure was used: Twelve PE films were placed in the center region of the reactor on a glass substrate holder and the reactor was evacuated to a pressure of 0.01 mbar. Subsequently, a CO₂ flow of 10 cm³/min (standard temperature and pressure) was established through the reactor. After 10–15 min, the films were plasma-treated (50 W, 0.07 mbar). The films were evacuated for 2 additional min under CO₂ flow and the reactor was then brought to atmospheric pressure with air. The films were taken out and turned and, subsequently, the other side of the films was treated according to the same procedure.

Washing of Plasma-treated Films (Ion Exchange)

The hydronium ions of surface-bound carboxylic acid groups were exchanged for sodium ions by washing with a NaOH solution. XPS analysis of these films allows a quantitative determination of the concentration of sodium ions at the surface.^{10,24,25} An optimized procedure described previously was used.¹⁰ In brief, the plasma-treated films were immersed in an aqueous NaOH solution (1.00 M) for 1 h. After removal of the solution, the films were washed twice with methanol and dried *in vacuo* at RT. Films used for water contact angle measurements were washed twice with water instead of methanol.

Aging of Plasma-treated Films

Plasma-treated films (500 s) were stored at different temperatures (50°C, RT, 4°C, or -25°C). Films were first used for contact angle measurements and then immersed in water for 24 h at 50°C. The films were taken out, dried *in vacuo* at RT for 2 h, and used again for contact angle measurements.

Reaction of Surface Carboxylic Acid Groups with TFE

By reacting surface carboxylic acid groups with TFE followed by XPS analysis, it is possible to get a (semi)quantitative indication of the surface concentration of carboxylic acid groups.²⁶ A slight modification¹⁰ of the method described by Chilkoti et al. was used.²⁶ A film was placed vertically in a glass vial on glass beads. Subsequently, TFE (0.45 mL), pyridine (0.2 mL), and *N,N'*-di-*tert*-butylcarbodiimide (0.15 mL) were injected under the film at 15 min intervals. The vial was closed and the reaction was allowed to proceed for 24 h at RT. The film was then immediately loaded for XPS analysis.

Reaction of Surface Ketone/Aldehyde Groups with N₂H₄

To (semi)quantitatively determine the amount of ketone/aldehyde groups on the surface, films were first reacted with N₂H₄ and then analyzed with XPS.^{26,27} A polymer film was placed vertically in a glass vial on glass beads. Subsequently, 0.5 mL of N₂H₄ was injected into the glass beads. The vial was closed and the reaction was allowed to proceed for 30 min at RT. The film was immediately loaded for XPS analysis.

Reaction of Surface Hydroxyl/epoxide Groups with TFAA

The surface concentration of hydroxyl/epoxide groups can be (semi)quantitatively determined by reaction with TFAA followed by XPS analysis.^{24,26,28–30} The procedure used is similar to that described for the N₂H₄ reaction, except that 0.5 mL TFAA was injected into the beads instead of N₂H₄.

Characterization

Contact Angle Measurements

Wilhelmy plate water contact angle measurements^{31–33} were performed with all modified and control films. Furthermore, for plasma-treated films also, aqueous HCl solutions (0.1 M, pH 1) or aqueous NaOH solutions (0.1 M, pH 13) were used for contact angle determinations. The surface tension of these solutions was measured at RT with a Krüss tensiometer (Hamburg, Germany). The measured surface tensions were water 72.7 ± 0.1 mN/m, 0.1 M HCl 72.6 ± 0.1 mN/m, and 0.1 M NaOH 74.5 ± 0.2 mN/m.

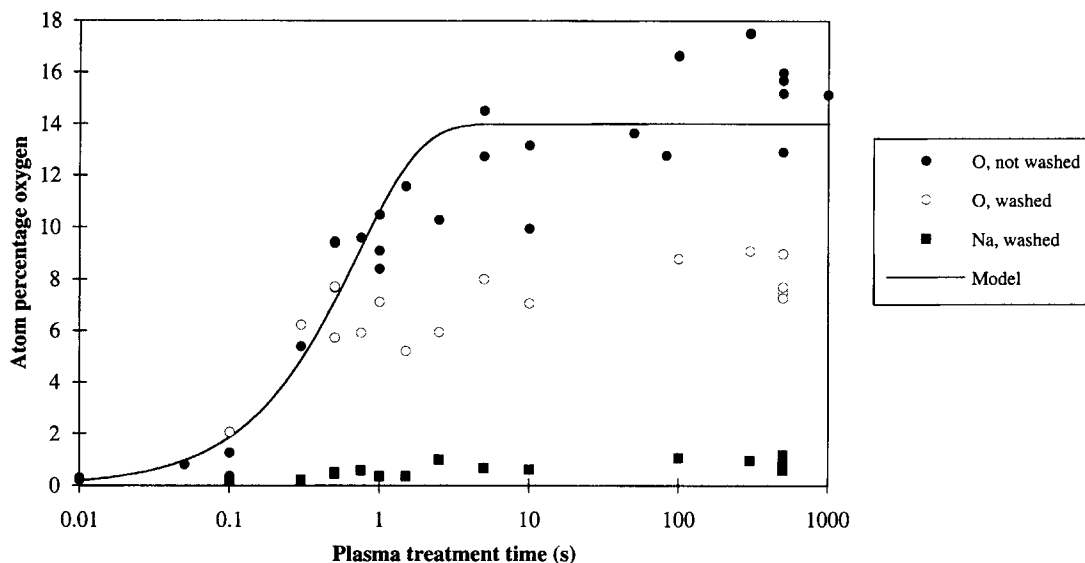


Figure 1 XPS analysis of CO₂ plasma-treated PE films. The amount of oxygen before and after washing with an aqueous NaOH solution (1 h, rinsed twice with methanol afterward) is given as a function of the CO₂ plasma-treatment time. Additionally, for the washed surfaces, the amount of sodium is shown. The best fit for the kinetic model [eq. (2)] for plasma-treated films which were not washed afterward is given by the solid line.

X-ray Photoelectron Spectroscopy (XPS)

XPS measurements were performed with a Kratos XSAM-800 (Manchester, U.K.) apparatus using a MgK α source (15 kV, 15 mA). The samples were analyzed with the analyzer placed perpendicular to the sample surface. A spot size with a diameter of 3 mm was analyzed. The pressure during measurements was typically 1.10^{-8} mbar. The spectra were recorded in the low-resolution mode (pass energy 40 eV, fwhm Ag3d^{5/2}:1.2 eV). Survey scans (0–1100 eV binding energy) were used to qualitatively determine the elements present at the surface. Quantification of the surface elemental composition was performed by recording detail scans (20 eV windows). Standard sensitivity factors delivered by Kratos were used to convert the measured peak areas into atom percentages. To determine a correct empirical sensitivity factor for the F1s peak, a clean polytetrafluoroethylene film was analyzed whenever fluorine-containing films were measured.

FTIR-ATR Measurements

To obtain the required surface sensitivity for the detection of the plasma-induced surface modification, a very thin paraffin layer coated on a KRS-5 crystal was plasma-treated. FTIR spectra were recorded with a Biorad FTS-60 spectrometer (angle 45°, 256 scans). The KRS-5 crystal was coated with paraffin by dipping the crystal for 1 min in a solution

of paraffin in *n*-hexane (0.25 g in 100 mL). The crystal was air-dried and an FTIR spectrum was recorded. The coated crystal was then treated with a CO₂ plasma for 10 s (at both sides) and again a spectrum was recorded.

Scanning Electron Microscopy (SEM)

PE films, plasma-treated films, and plasma-treated and subsequently washed PE films were characterized by SEM, using a JEOL-type JSM-35CF apparatus. The films were sputtered with gold using a Balzers Union Sputter apparatus and analyzed under an angle of 60° at different magnifications (magnifications of 1000 and 5400 were used).

RESULTS

The results of the XPS analysis of CO₂ plasma-treated PE films are given in Figure 1. It can be seen that with increasing plasma-treatment time an increasing amount of oxygen is incorporated at the surface. After approximately 10 s, the amount of oxygen on the surface levels off. If the CO₂ plasma-treated surfaces are washed with an aqueous NaOH solution, the amount of oxygen at the surface decreases, especially at longer plasma treatment times ($t > 1$ s). Moreover, small amounts of sodium are found on these washed surfaces. The etching rate of

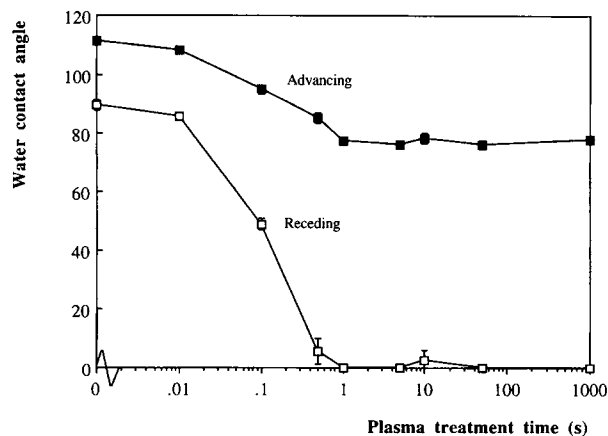


Figure 2 Results of the Wilhelmy plate contact angle measurements of CO_2 plasma-treated films. The films were not washed after the plasma treatment. The averages and standard deviations for three films within one batch are shown. The films were stored for 46 days in air before measurement.

PE films during a CO_2 plasma treatment is gravimetrically determined and is $700 \text{ \AA}/\text{min}$.

By varying the angle between the sample and the analyzer, the depth probed during the XPS measurements can be varied. This method was used to check the homogeneity of the plasma-treated surfaces. The take-off angle was varied from 0° to 75° , which corresponds to a sampling depth of approximately $110\text{--}30 \text{ \AA}$. No dependence of the amount of oxygen on the take-off angle is observed (data not shown).

Water contact angle measurements of CO_2 plasma-treated surfaces are presented in Figure 2. Both the advancing and receding angles decrease

with increasing plasma-treatment time. After a plasma treatment time of 1 s, the advancing contact angles reach a plateau level, whereas the receding angles become zero. It should be noted that the hysteresis, the difference between the advancing and receding contact angle, increases with increasing plasma treatment time (for $t \leq 1 \text{ s}$). Furthermore, no significant differences in contact angles between the first and second dip in refreshed water are observed. Also, for CO_2 plasma-treated films which were washed afterward with an aqueous NaOH solution, water contact angles were measured. The observed contact angles were similar to the contact angles of unwashed films, which were plasma-treated for the same time period (data not shown).

The surface morphology of plasma-treated and untreated PE films was studied with SEM (no pictures shown). The original PE surface is rather smooth and no increase in surface roughness due to the plasma treatment is observed for plasma-treatment times up to 1000 s. At extremely long treatment times (3 h), surface defects are observed. A spongy structure with pores with a typical diameter of $0.1 \text{ }\mu\text{m}$ is obtained.

The amount of fluorine incorporated on the surface of plasma-treated films after derivatization with TFE is given as a function of the plasma-treatment time in Figure 3. The amount of fluorine, which is a relative indication of the surface concentration of carboxylic acid groups, increases with increasing plasma-treatment time and levels off after a treatment time of 1 s. The amount of nitrogen on CO_2 plasma-treated surfaces, due to a reaction of N_2H_4 with ketone/aldehyde groups, is given in Figure 4. The incorporated amount of nitrogen increases with

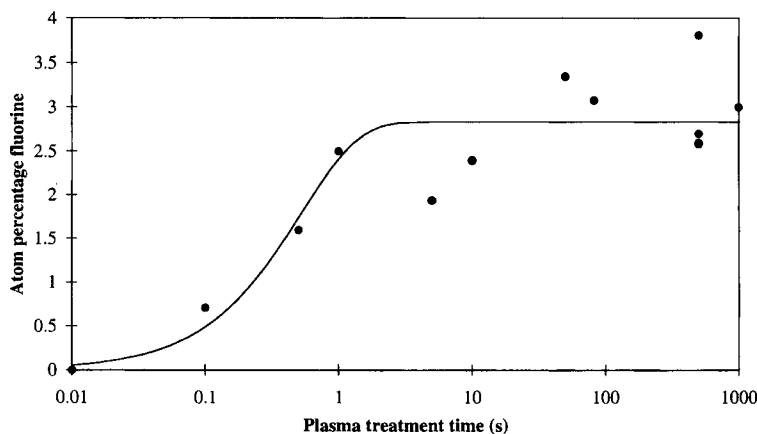


Figure 3 XPS analysis of CO_2 plasma-treated films which were derivatized with 2,2,2-trifluoroethanol (TFE) to tag carboxylic acid groups on the surface. The amount of fluorine on the surface, quantified by XPS analysis, is given as a function of the plasma-treatment time. The best fit for the kinetic model [eq. (2)] is given by the solid line.

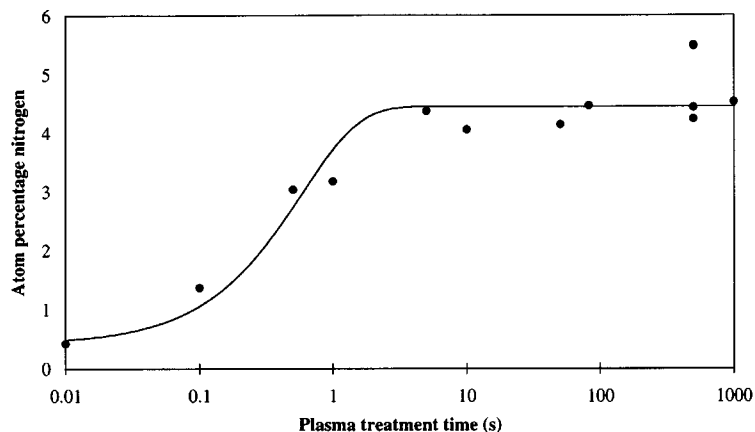


Figure 4 XPS analysis of CO₂ plasma-treated films which were derivatized with hydrazine to tag ketone/aldehyde groups on the surface. The amount of nitrogen on the surface, quantified by XPS analysis, is given as a function of the plasma-treatment time. The best fit for the kinetic model [eq. (2)] is given by the solid line.

increasing plasma-treatment time, and after 1 s, a constant nitrogen level is found on the surface. The surface concentration of hydroxyl/epoxide groups is probed via a reaction with TFAA. The results in Figure 5 show that after approximately 0.5 s the amount of fluorine on the surface reaches a plateau. The surface compositions of plasma-treated films ($t = 500$ s) and of films which underwent ion-exchange or gas-phase derivatization reactions are given in Table I.

To determine whether acid or basic groups are present on the surface of CO₂ plasma-treated films, contact angle measurements using aqueous HCl (0.1M) or aqueous NaOH (0.1M) were per-

formed.^{34,35} The results given in Figure 6 show that the advancing and receding angles at pH 13 are lower than at pH 1. At longer plasma-treatment times ($t \geq 50$ s), no differences between the receding angles at pH 1 and 13 are found.

Paraffin is used as a model compound for the FT-IR-ATR study of the effects of a CO₂ plasma treatment on PE. Paraffin is from a chemical point of view a low molecular weight analog of PE. A KRS-5 crystal was coated with a thin layer of paraffin and then plasma-treated. The spectra before and after plasma treatment are given in Figure 7. For the CO₂ plasma-treated paraffin, new absorption bands at 3400, 1715, 1605, and 1170 cm⁻¹ are found.

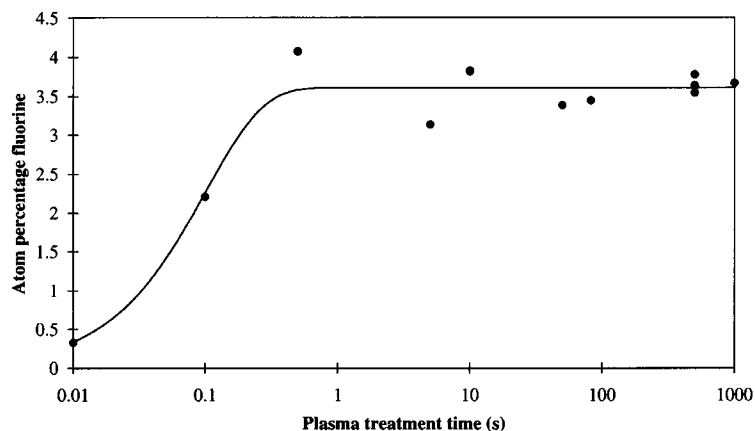


Figure 5 XPS analysis of CO₂ plasma-treated films which were derivatized with 2,2,2-trifluoroacetic acid anhydride (TFAA) to tag hydroxyl and epoxide groups on the surface. The amount of fluorine on the surface, quantified by XPS analysis, is given as a function of the plasma-treatment time. The best fit for the kinetic model [eq. (2)] is given by the solid line.

CO₂ plasma-treated films ($t = 500$ s) stored in air for time periods up to approximately 100 days at different temperatures have been analyzed with XPS and water contact angle measurements. The results for films stored at RT are given in Figure 8. It can be seen that initially very low advancing angles are found and that with increasing age of the film the advancing angle increases. The receding angle remains zero, independent of the aging time. The amount of oxygen on the surface is also not dependent on the aging time. When the films are aged at different temperatures, a temperature dependence of the aging process is also observed (Fig. 9). At higher temperatures, the advancing angle increases more rapidly than at low temperatures. For the lowest temperature used (-25°C), only a slight increase in the advancing angle could be observed. An attempt was made to reverse the aging process by immersing the films for 24 h at 50°C in water. From Table II, it can be seen that this did not reduce the advancing angles for all the films. For some films, especially those stored at -25°C , the films are becoming even more hydrophobic.

DISCUSSION

Chemical Effects of a CO₂ Plasma on PE Surfaces

From the results given in Figure 1 and the gravimetrically determined etching rate, it can be concluded that a CO₂ plasma is a highly etching and surface-oxidizing environment for PE films. A large variety of oxygen-containing groups are introduced at the PE surface. These include carboxylic acid, ketone/aldehyde, and hydroxyl/epoxide groups (see Figs. 3–6). The introduction of these groups on a low molecular weight analog of PE, paraffin, is con-

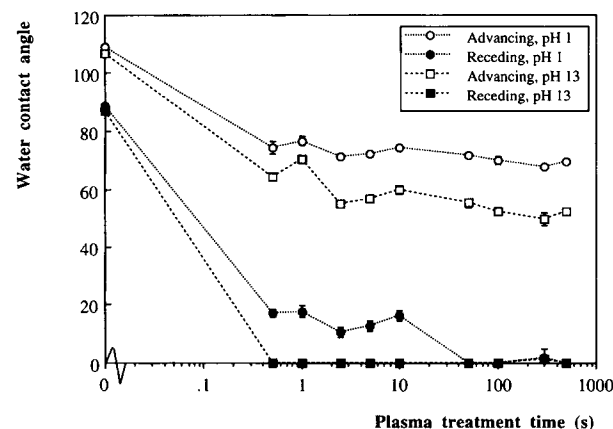


Figure 6 Wilhelmy plate contact angle measurements using 0.1M HCl(aq) or 0.1M NaOH(aq) of CO₂ plasma-treated PE films. The advancing and receding contact angles are given as a function of the treatment time. The averages and standard deviations for three films within one batch are shown. Age of the films: 63 days.

firmed by FT-IR-ATR spectroscopy (see Fig. 7). An increase in absorption in the 3400 cm^{-1} (OH stretch) and 1170 cm^{-1} (C—O stretch) range is observed, indicating the presence of hydroxyl and possibly ether functionalities. Furthermore, an increase in absorption at 1715 cm^{-1} (C=O stretch) has been found, which can be caused by aldehyde, ketone, ester, or carboxylic acid groups. The increase in absorption at 1605 cm^{-1} (C=C stretch) indicates that also unsaturated bonds are introduced at the surface by the plasma treatment.

The presence of carboxylic acid groups on CO₂ plasma-treated PE films is also confirmed by the contact angle measurements given in Figure 6. Due to the carboxylic acid groups on the surface, the advancing and receding contact angles at pH 13 are

Table I XPS Analysis of CO₂ Plasma-treated PE Films

| Treatment | Oxygen | Sodium | Nitrogen | Fluorine | n^a |
|---|----------------|---------------|---------------|---------------|----------------|
| 500 s CO ₂ , not washed | 13.5 ± 0.7 | 0 | 0 | 0 | 9 ^b |
| 500 s CO ₂ , water-washed | 11.0 ± 1.7 | 0 | 0 | 0 | 3 |
| 500 s CO ₂ , methanol-washed | 10.8 ± 1.3 | 0 | 0 | 0 | 3 |
| 500 s CO ₂ , NaOH(aq)-washed | 7.5 ± 0.2 | 0.7 ± 0.1 | 0 | 0 | 3 |
| 500 s CO ₂ , TFE-reacted | 12.5 ± 1.8 | 0 | 0 | 2.9 ± 0.6 | 4 |
| 500 s CO ₂ , hydrazine-reacted | 12.3 ± 1.3 | 0 | 4.7 ± 0.7 | 0 | 3 |
| 500 s CO ₂ , TFAA-reacted | 16.2 ± 1.7 | 0 | 0 | 3.7 ± 0.1 | 3 |

The films were plasma treated for 500 s and subsequently washed [1 h, and in the case of NaOH (aq), additionally rinsed twice with methanol] or not washed. Furthermore, the XPS results for CO₂ plasma-treated (and not washed) films which were derivatized with different gas-phase reactions are given.

^a Number of films analyzed within one batch, for $n \geq 3$, the standard deviation is also given.

^b Three different batches and from every batch three films were analyzed.

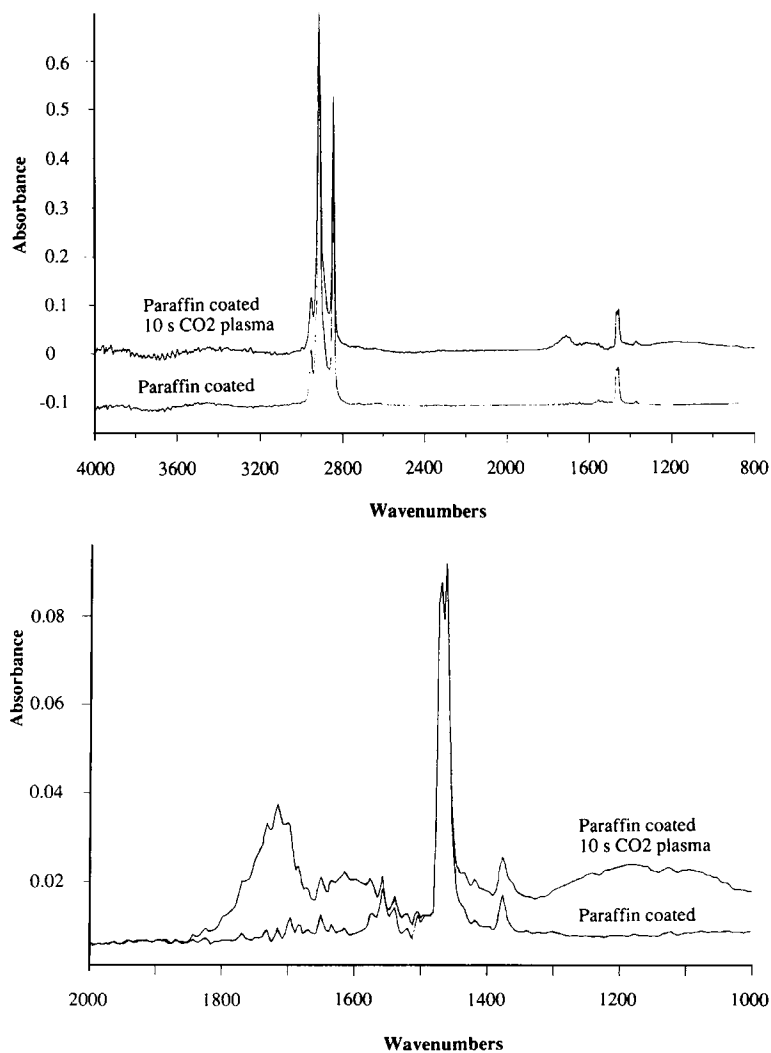


Figure 7 FT-IR-ATR spectra of a paraffin-coated KRS-5 crystal, which was either plasma-treated or not treated. The duration of the CO₂ plasma treatment was 10 s. A survey spectrum is given in (a) and an enlargement of the 1000–2000 cm⁻¹ region is given in (b).

lower than are those measured at pH 1.^{34,35} When the films are plasma-treated for more than 50 s, the surfaces become too hydrophilic (receding angles are 0°) to detect any differences between the receding contact angles measured at pH 1 and 13.

When plasma-treated films are exposed to water, methanol, or an aqueous NaOH solution, the amount of oxygen at the surface decreases (see Table I), indicating that part of the oxidized layer is removed from the surface. Especially during the treatment with NaOH (aq), a substantial amount of oxygen—approximately 45%—is lost. The removal of part of the oxidized layer does not, however, have a detrimental effect on the hydrophilicity of the surface. The surface concentration of carboxylic acid groups can be estimated from the sodium concentration

found on the surface after washing with NaOH. Assuming that the ion exchange of hydronium ions for sodium ions of surface carboxylic acid groups is stoichiometric,¹⁰ it can be calculated that after washing approximately 19% $\{=0.7 \text{ (amount of sodium)} \times 2 \text{ (stoichiometry, 2 oxygen atoms per carboxylic acid groups)} / [1 \text{ (reaction extent)} \times 7.5\% \text{ (amount of oxygen observed)}]\}$ of the oxygen at the surface is present as carboxylic acid groups.

Because solvents drastically change the surface composition of plasma-treated films, gas-phase derivatization reactions have been used to determine (semi)quantitatively the concentration of hydroxyl/epoxide, ketone/aldehyde, and carboxylic acid groups. First of all, some remarks on the yield and specificity of the applied gas-phase reactions should

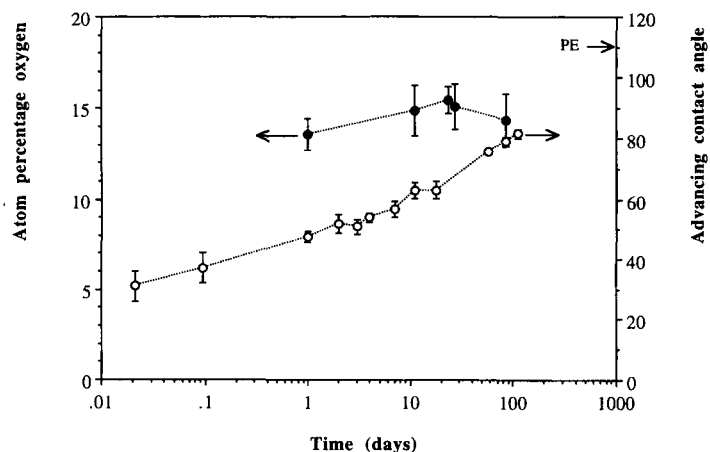


Figure 8 Aging of CO₂ plasma-treated PE films. The films were either used for Wilhelmy plate contact angle measurements or XPS analysis. The advancing water contact angles and the atom percentage oxygen are given as a function of the aging time. The receding water contact angle was 0° for all films. The averages and standard deviations for three films within one batch are shown.

be made. According to Gerenser et al.²⁷ and Chilkoti et al.,²⁶ the reaction of TFAA with hydroxyl groups is stoichiometric. Furthermore, TFAA reacts completely with epoxide groups.^{29,30} Only minor side reactions with ketone and aldehyde groups have been reported.²⁶ The reaction of N₂H₄ with aldehyde/ketone groups is not stoichiometric and is less specific. A reaction yield of 60–70%, which is dependent on the reaction time, was reported by Chilkoti et al.²⁶ Furthermore, these authors reported minor side reactions with carboxylic acid groups and aromatic hydroxyl groups and a significant side reaction with aromatic ester groups. For CO₂ plasma-treated PE surfaces, aromatic ester groups are not expected at the surface. Finally, the reaction of TFE with carboxylic acid groups is nearly stoichiometric (87 ± 15%) after a reaction time of 12 h and, according to Chilkoti et al., quite specific.²⁶ Using these yields, a rough estimation of the concentrations of carboxylic acid groups created on the surface can be made. After reaction of TFE, a fluorine concentration of 2.9% is found on CO₂ plasma-treated films (see Table I). Assuming a reaction yield of 100%, the fraction of oxygen-containing groups present as carboxylic acid groups is 14% $\{=2.9\%$ (amount of fluorine) $\times 2/3$ (stoichiometry) $/[1$ (reaction extent) $\times 13.5\%$ (amount of oxygen present)] $\}$. The fraction present as ketone/aldehyde groups is 25% $[=4.7\% \times 0.5 / (0.7 \times 13.5\%)]$. The fraction present as hydroxyl/epoxide groups cannot be exactly calculated. Based on the assumption that only hydroxyl groups are present, the fraction of oxygen present as hydroxyl groups is 9% $[3.7\% \times (1/3) / (1 \times 13.5\%)]$. When it

is assumed that only epoxide groups are present, this fraction would be 5% $[3.7\% \times (1/6) / (1 \times 13.5\%)]$. In a more detailed study, it was shown that both epoxide and hydroxyl groups are present on CO₂ plasma-modified PE surfaces.³⁶ Approximately half of the oxygen-containing groups present at the surface after a plasma-treatment time of 500 s can be accounted for. Most likely, the rest of the oxygen on the surface is present as other functionalities like peroxide, ethers, and esters.

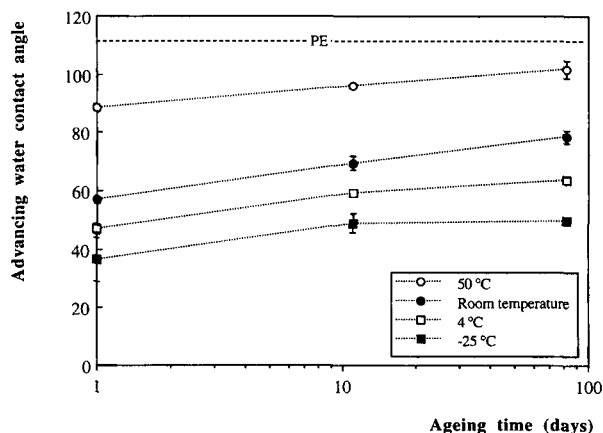


Figure 9 Aging of CO₂ plasma-treated films at different temperatures. The advancing contact angles determined by the Wilhelmy plate method using water are given as a function of the storage time at a certain temperature. The receding water contact angles were 0° for all films. The averages and standard deviations for three films within one batch are shown.

Table II Effect of Aging of CO₂ Plasma-treated PE Films at Different Temperatures on the Wettability

| Aging Time in Days | Aging Temp in °C | θ Advancing | θ Advancing After H ₂ O Treatment |
|--------------------|------------------|-------------|--|
| 11 | 50 | 95.9 ± 0.1 | 71.4 ± 5.8 |
| | RT | 69.4 ± 2.5 | 63.3 ± 3.6 |
| | 4 | 58.9 ± 1.2 | 58.4 ± 11.6 |
| | -25 | 48.8 ± 3.2 | 69.1 ± 1.4 |
| 81 | 50 | 101.5 ± 3.1 | 89.3 ± 2.4 |
| | RT | 78.3 ± 2.3 | 78.1 ± 4.1 |
| | 4 | 63.3 ± 0.9 | 83.4 ± 3.4 |
| | -25 | 49.5 ± 0.5 | 81.2 ± 4.3 |

The advancing water contact angles for aged films and for films aged and subsequently immersed for 1 day in water (at 50°C) are given. The receding angles for all these films are 0°. The averages and standard deviations for three films within one batch are given.

Treating PE films with a CO₂ plasma for more than 1 s results in a wettable surface, as can be seen from the contact angle data in Figure 2. Both advancing and receding angles decrease due to the CO₂ plasma treatment, but the decrease in the receding angle is more pronounced, which results in an increase in hysteresis. From Figure 8, it can be seen that with increasing storage time the advancing angle increases and that the receding angle remains constant (0°). Aging of the films results in an increase in hysteresis. The observed increase in hysteresis in Figure 2 is, thus, at least partially, due to aging of the films before measurement.

It has been reported that crystalline regions of polymers are less rapidly etched than are amorphous regions.^{37,38} It seems likely that the spongelike surface structure observed with SEM at long plasma-treatment times ($t = 3$ h) is a direct consequence of the differences in etching rate between amorphous and crystalline regions at the surface of the semi-crystalline PE films.

Kinetics of a CO₂ Plasma Treatment

Previously, we investigated the chemical modification mechanisms of argon and CF₄ plasma treatment of polyacrylic acid (PAAc) films.¹¹ By covering the PAAc film with materials which differ in their transparency for UV, and by varying the distance between the covering material and the film, it is possible to discriminate between surface modifications induced by reactive species or by UV.¹¹ During the argon plasma treatment of PAAc, a UV-induced decarboxylation has been observed, whereas during the CF₄ plasma-treatment, reactive species from the plasma phase (presumably atomic fluorine) react with the PAAc surface, resulting in a decarboxylated and fluorinated surface. The same method has been

used to study the modification of PE films by CO₂ plasma treatments.³⁹ From this study, it could be concluded that the oxidation and etching of PE films by a CO₂ plasma are induced by reactive species from the plasma phase and that UV radiation itself did not contribute to the surface modification. It is known that atomic oxygen, which is formed during a CO₂ plasma,¹⁸ can etch polymer surfaces.⁴⁰ Therefore, it seems likely that atomic oxygen causes the surface modification during a CO₂ plasma treatment of PE. Combined with the results of Shard and Badyal,¹⁹ it can be deduced that atomic oxygen is most likely photochemically generated in the CO₂ plasma phase.

The modification mechanism of a PE film by a CO₂ plasma treatment seems to consist of at least three processes: First, the surface is sputtered by ions (and/or electrons) from the plasma phase. The second process is the incorporation of oxygen-containing groups. Presumably, this process starts with the abstraction of hydrogen from the polymer backbone by atomic oxygen.^{5,41} The active sites on the backbone can react with oxygen-containing species from the plasma phase to form oxygen-containing groups.⁴¹ The last process is the progressive oxidation of surface-bound oxygen containing groups to more highly oxidized groups on the surface or volatile products (e.g., CO₂).⁵

Because the different reaction steps in the second (oxygen incorporation) and third process (progressive oxidation of containing groups) are unknown, a simplified model is proposed here to describe the observed kinetics. The first process, physical sputtering, is governed by a constant flux of ions (and/or electrons) to the surface. If it is assumed that the sputter rate is independent of the surface composition, the sputter process can be described by a zero-order (etching) process.

The rate-limiting step in the second process, oxidation after hydrogen abstraction, is the abstraction of hydrogen from the backbone by atomic oxygen.⁴¹ It can be assumed that the flux of atomic oxygen to the surface is constant and that the total amount of hydrogen does not significantly change during the reaction. The validity of the last assumption can be derived from the oxidation levels found at the surface at long treatment times. From the XPS data, it can be seen that approximately one out of every six carbon atoms is bound to oxygen. The corresponding decrease in the hydrogen concentration at long treatment times would thus be in the order of 10% or less. The second process can be described by a (pseudo) zero-order reaction. The rate constant of the sputtering process is mathematically incorporated in the (pseudo) zero-order rate constant of the oxidation reaction. The total rate constant of this combination is given by one rate constant (b).

Due to the fact that the progressive oxidation reactions—the third process—are unknown, only one reaction is taken into account here. The final reaction of the third process is the reaction of atomic oxygen with an oxygen-containing group to form CO₂. This will result in a loss of oxygen from the surface. The rate-limiting step of this reaction is assumed to be the activation of oxygen-containing groups by atomic oxygen. The rate of this process is proportional to the flux of atomic oxygen to the surface and the concentration of oxygen-containing groups ($[C]$). The change in concentration of oxygen-containing groups at the surface can be described by

$$\frac{d[C]}{dt} = b - z[C] \quad (1)$$

In this equation, the rate constant of the progressive oxidation of oxygen containing functional groups is given by z . Solving eq. (1) using an initial concentration C_0 at $t = 0$ s yields

$$[C] = ([C]_0 - \frac{b}{z})e^{-zt} + \frac{b}{z} \quad (2)$$

Considering the use of eq. (2) for the description of the oxidation of PE films by a CO₂ plasma, some remarks should be made: At long treatment times, the concentration of a specific oxygen-containing group reaches a plateau level (b/z). Therefore, eq. (2) actually contains only one fitting parameter. Second, instead of absolute concentrations which are required in this equation, only relative concen-

trations are available. The concentrations of different oxygen-containing groups are measured directly or indirectly after reaction with specific reagents with XPS. It is known that XPS is more sensitive to the outermost top-layers than to layers deeper in the surface. To obtain correct relative concentrations, the layer probed with XPS (approximately 110 Å) should be homogeneous. For CO₂ plasma-modified PE films, the homogeneity of this layer was checked with angle-dependent XPS measurements (data not shown).

Equation (2) was fitted to the XPS data of CO₂ plasma-treated films. The best fits for eq. (2) are shown in Figures 1, 3, 4, and 5, respectively, and the fitting constants are given in Table III. It can be seen from these figures that all the lines fit well to the experimental data over the whole range of plasma-treatment times. The kinetic data can thus be described by a simple model containing a zero-order oxygen incorporation process and a first-order etching process of oxygen-containing groups.

The absolute values of the constants in Table III show that hydroxyl/epoxide groups are more rapidly incorporated [incorporation constant $b = 6\text{--}12\% \text{ s}^{-1}$ ($b = 35.6 \times (1/3)/1 = 12\% \text{ s}^{-1}$ (constant $b \times$ stoichiometry/reaction extent) for hydroxyl groups, $b = 35.6 \times (1/6)/1 = 6\% \text{ s}^{-1}$ for epoxide groups)] than for ketone/aldehyde groups [$b = 7.5 \times (1/2)/0.7 = 5\% \text{ s}^{-1}$] and carboxylic acid groups [$b = 5.4 \times (2/3)/1 = 4\% \text{ s}^{-1}$]. This might indicate that initially hydroxyl/epoxide groups are formed, which then react to form ketone/aldehyde or carboxylic acid groups in a second step. This would be in agreement with a progressive oxidation mechanism. It should be noted, however, that the formation of higher oxidized groups like ketone/aldehyde and carboxylic acid groups by the progressive oxidation of oxygen-containing groups is not incorporated in the simplified model presented here.

Aging of CO₂ Plasma-treated PE Surfaces

The effect of storage of plasma-treated surfaces on their surface wettability has been described by several authors.^{18,42–46} Generally, the hydrophilicity of a hydrophobic polymer surface is increased by a treatment with an oxygen or argon plasma. The hydrophilicity of treated surfaces decreases after storage in air. Storage at elevated temperatures leads to a more rapid decrease in the hydrophilicity than does storage at low temperatures.^{43,44} These effects are not unique for plasma-treated films and have also been reported for corona discharge-treated PE films²⁷ and for PE oxidized by chromic acid.^{47,48} Ag-

Table III Kinetics of the CO₂ Plasma Treatment of PE

| CO ₂ Plasma Treatment of PE | | | | | | |
|--|-------------------------------|----------------------|------------------------|---------|-------------|-------------|
| Parameter-fitted | C ₀ (%) | z (s ⁻¹) | b (% s ⁻¹) | b/z (%) | Correlation | |
| [O] | 0 | 1.42 | 19.8 | 14.0 | 0.977 | |
| CO ₂ Plasma-treated PE, Derivatized Afterward | | | | | | |
| Parameter-fitted | Reaction | C ₀ | z | b | b/z | Correlation |
| [F] | TFE | 0 | 1.9 | 5.4 | 2.83 | 0.970 |
| [N] | N ₂ H ₄ | 0.4 ^a | 1.7 | 7.5 | 4.45 | 0.989 |
| [F] | TFAA | 0 | 9.8 | 35.6 | 3.61 | 0.995 |

The elemental compositions obtained from XPS measurements before or after gas-phase derivatization reactions, were fitted with eq. (2). A quasi-Newtonian fitting procedure has been used to obtain the best fit.

^a For clean PE films exposed to hydrazine, a small ($\leq 0.2\%$) amount of nitrogen is also observed with XPS.

ing does not only influence the wettability of a surface, but is also crucial in, e.g., adhesion processes.⁴⁹ The general consensus is that polar groups diffuse away from the surface into the bulk, yielding a lower surface energy.

Figure 8 shows that the advancing contact angle of CO₂ plasma-treated PE films increases with increasing storage time. From the XPS data, it can be seen that the amount of oxygen at the surface remains constant. This indicates that no delayed post-oxidation of the oxidized surface occurs. Furthermore, because no other elements than carbon and oxygen are found at the surface with XPS, and because the amount of oxygen at the surface remains constant, it seems likely that the increase in advancing contact angle is not due to contamination of the surface by hydrophobic compounds. From Figure 9, it can be seen that the rate of increase of the advancing water contact angle is dependent on the storage temperature. At low temperatures (-25°C), no significant aging after 10 days occurs. Storage at this temperature seems to prevent further surface rearrangements. Dielectric loss measurements have shown an increase in mobility of oxidized branched PE chains at a temperature of 20°C .⁵⁰ When it is assumed that surface mobility of oxidized chains governs the observed aging, this increase in mobility would qualitatively explain the observed trend of aging as a function of the temperature.

To explain the kinetics of the surface rearrangements, two types of models, assuming a homogeneous or a heterogeneous surface, have been proposed. Yasuda described the aging of polar groups homogeneously distributed at the surface of plasma-polymerized polymers by a first-order process

[$\log(\cos \Theta) = a - b \cdot t$, in which a and b are constants, Θ is the contact angle, and t is the aging time].⁵¹ This model could not be used to describe the increase in advancing contact angles given in Figure 8. Yasuda proposed an empirical relation to describe the aging process ($\log \Theta = a - \log t$).⁵² This model describes the aging at RT well, but fails to describe the aging at higher and lower temperatures. Also, other kinetic models (zero order, second order) have been explored, but these models cannot satisfactorily describe the observed kinetics.

A good qualitative explanation for the observed kinetics was given by Occhiolo et al.⁴³ This model is based on theoretical calculations for heterogeneous surfaces.^{53,54} According to this model, the advancing water contact angle is very sensitive to a small fraction of low energy (nonpolar) patches on a high-energy (polar) matrix, and the receding angle is very sensitive to a small fraction of high-energy (polar) patches on a low-energy (nonpolar) matrix. Thus, in the case when an increase in the advancing and a constant low receding angle is found, the fraction of low energy (nonpolar) patches on the surface should increase. It seems likely that the highly oxidized amorphous regions on CO₂ plasma-treated PE films reorganize preferentially. By migration of oxidized chains into deeper surface layers or by migration of hydrophobic nonoxidized chains to surface layers, hydrophobic regions can be generated at the surface during the aging process.

Films aged for different periods of time at different temperatures were immersed in water for 24 h at 50°C (and dried afterward for 2 h *in vacuo* before contact angle measurement) in order to reverse the aging process. Some unexpected phenomena have

been found (see Table II). It was expected that upon exposure to water the surface would rearrange to a more hydrophilic state, but according to the contact angle data in Table II this is not generally true. Films aged at 50°C became more hydrophilic and films aged at -20°C became more hydrophobic in water. From Table II it can be seen that after the water treatment at 50°C for 24 h, all the films, regardless of the temperature at which the films are aged previously, have approximately the same advancing contact angle. It seems that this angle depends only on the aging time of the films before they were immersed in water and not on the aging temperature. Based on these observations, it is hypothesized that the aging process consists of (at least) two components: a reversible and an irreversible process.

The general explanation based on adjustment of the surface energy to the environment does not explain all our observations, nor some of the observations made by Holmes-Farley et al.⁴⁸ These authors showed that fluorinated PE films, which were more hydrophobic than were unmodified PE films, age in vacuum at elevated temperatures in such a way that they resemble the "less" hydrophobic, unmodified PE films. These phenomena can be explained by assuming that the total system and not only the surface aims for the lowest possible free-energy state. The free energy of the system is lowered by a surface reorganization over a very shallow surface layer (presumably, the reversible component) and, second, by diffusion of polar groups into the bulk of the polymer under a concentration gradient (irreversible component). Holmes-Farley et al. showed that oxygen- and fluorine-containing groups can indeed migrate to layers deeper than the XPS analysis depth.⁴⁸ This process does not seem to be directly dependent on the surface energy of the system (e.g., water or vacuum) contacting the outside of the films. Presently, the aging process is being investigated in more detail to test this (speculative) model.

CONCLUSIONS

Treatment of PE films with a CO₂ plasma leads to surface oxidation and the formation of hydrophilic surfaces. The CO₂ plasma treatment introduces several oxygen-containing functional groups including carboxylic acid, ketone/aldehyde, and hydroxyl/epoxide groups. The oxygen incorporation at the surface is fast and can be described by a zero-order incorporation and a first-order etching process. The wettability of the plasma-treated surfaces decreases

upon storage in air. This aging process is intensified by storing the films at elevated temperatures in air. Storing the films in water at 50°C could not always reverse this process.

The authors like to thank Dr. G. Engbers for his valuable contributions during discussions and Mr. A. van den Berg for assisting with the XPS measurements. Furthermore, they are grateful to DSM (Geleen, The Netherlands) for financial support for this research.

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Received July 22, 1994

Accepted February 20, 1995