Surface Modification of Poly(Ethylene) in an *rf* Downstream Remote Plasma Reactor

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SYNOPSIS

Polyethylene (PE) was treated in a remote downstream reactor with oxygen, nitrogen, hydrogen, and mixed gas plasma. The effects of these treatments were investigated by contact angle goniometry and x-ray photoelectron spectroscopy (XPS). The oxygen plasma treatment allowed a rapid and efficient hydrophilation of the PE, although the samples were placed far outside the main discharge region. In hydrogen plasma treatment, only a small amount of polar functional groups are formed, while the nitrogen plasma results in a surface similar to that in an oxygen plasma treatment. Thirteen percent of oxygen was found by XPS in these samples, while only 3% of nitrogen was present. The mixed oxygen/ hydrogen plasma treatment revealed that 0.1% oxygen in the process gas produced a detectable degree of oxidation. By experiments with quenched atomic oxygen, the singlet molecular oxygen ($O_2^1 \Delta$) was found to be the major reactive species in the surface reaction in our system. The role and the source of radiation in this reaction is discussed. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

For many applications of polymer materials, their surface properties have to satisfy specific demands, which can often hardly be realized by the bulk material. A suitable method to alter the surface properties is to expose the polymer to a low temperature plasma.[1] In this way, functional groups can be introduced into the surface efficiently. However, the chemical reactions occurring during such a process are usually complex.[1-4] The poor selectivity of the plasmachemical functionalization is the main disadvantage of this method.

Most applications of plasma techniques, applied to polymer surface modification, are based on the direct action of the plasma, that is, the material is positioned in the discharge region. Few publications[5-7] dealt with the influence of a remote plasma on polymers. In such an arrangement, the direct action of energetic species (electrons and ions), the hard UV radiation, and the variety of excited species interacting with the polymer are more

or less reduced and the polymer surface is mainly exposed to longer lived species present in the plasma afterglow region. It can be expected that the processes at the solid gas interface are less complex as compared with the direct exposure. Possibly, a certain control of the surface functionalization can be achieved.

In order to prove these facts, we studied the modification of poly(ethylene) in a remote plasma reactor with oxygen, nitrogen, and hydrogen *rf* plasma under relatively mild conditions.

EXPERIMENTAL

Materials

Polyethylene (PE) films (Lupolen) were supplied by BASF. Before treatment, the films had been cleaned with 96% ethanol in an ultrasound cleaner for 5 min and had been dried in a dynamic vacuum at 0.1 Pa for 10 min. The surface of the cleaned PE was characterized by XPS and contact angle goniometry. By XPS, a content of less than 1% oxygen was determined. The advancing (a) and receding (r) contact angles were evaluated in the procedure described below:

Water: $\theta_a = 106°$, $\theta_r = 87°$

Formamide: $\theta_a = 84°$, $\theta_r = 66°$

Tricresylphosphate: $\theta_a = 47°$, $\theta_r = 24°$

The process gasses for the plasma treatment, oxygen, nitrogen (5.0), and hydrogen (5.0) (Linde AG, Berlin) were used as received.

Test liquids for the contact angle measurements were: deionized water with a surface tension of γ_{lv} = 72.8 mJ/m^2, formamide (Fluka, puriss. p.a.) with γ_{lv} = 57.7 mJ/m^2, and tricresylphosphate (Fluka, pract., mixture of isomers) with γ_{lv} = 41.4 mJ/m^2.

Plasma Treatment

Plasma treatment was carried out in an homemade vertical pyrex tube reactor. The tube had a diameter of 10 cm and was about 80 cm long. On the upper part, the reactor was supplied with *rf* power (13.56 MHz, Advanced Energy RTX 600) via ring electrodes outside the tube. The process gas inlets were incorporated axially on the upper end of the tube and radially about 20 cm above the lower end. The sample was placed about 50 cm downstream of the main discharge region. On the lower end, the tube was connected to a rotary pump (Alcatel 2020A). The pressure in the tube was measured with an absolute pressure gauge (MKS Baratron 122A).

Before operation, the reactor was pumped down to a base pressure of 0.1 Pa. The working pressure was in the range between 1 Pa and 50 Pa, depending on the flow rate of the process gases. The gases were dosed by MKS mass flow controllers (type 1259C) in the range between 0.2 and 100 standard cubic centimeters per minute (SCCM).

In a special experimental arrangement, a grid made of tungsten wire or a small vessel filled with mercury were located between the discharge region and the sample plane.

XPS

The XPS spectra were obtained on a SSI Model X/100 spectrometer, using a monochromatic AIK$_\alpha$ photon source. After the samples were removed from the plasma reactor, they were immediately kept under vacuum again in a special container and were carried to the XPS spectrometer.

Contact Angle Goniometry

The advancing and receding contact angles of the test liquids were determined by putting a drop, 3–8 mm in diameter, on the polymer film. The angles

were measured at 295 K, using a goniometer video system G 40 (Krüss GmbH, Hamburg). The advancing and the receding contact angles were measured, enlarging or reducing the drop volume, respectively. Each measurement was repeated 20 times in intervals of 2 sec. This procedure was repeated three times for the advancing angle and once for the receding angle.

The surface tension of the test liquids was controlled by the Wilhelmi plate method, using a tensiometer K12 (Krüss GmbH, Hamburg) and an annealed platinum plate.

The contact angle measurements of the plasma treated samples were performed immediately after removing from the reactor or after derivatization. Repeated measurements after 3 and 8 h, carried out on selected samples, resulted in the same data, though with decreased reproducibility.

RESULTS AND DISCUSSION
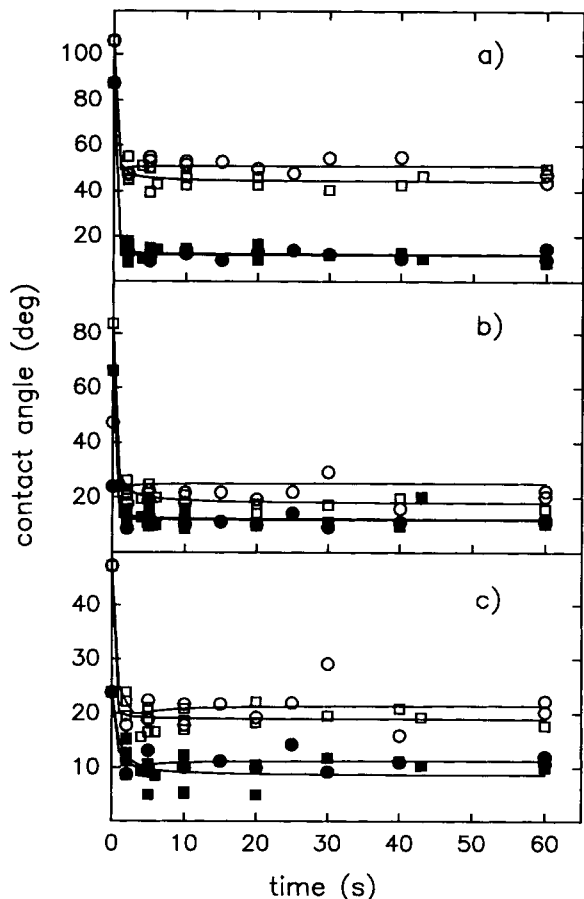
Oxygen Plasma Treatment

The effect of oxygen plasma on PE is strong under the downstream remote conditions reported in this article (Fig. 1). It takes less than one second until a level of modification is reached, which is not changed further in the following minute. This level is achieved at a flow rate of 20 sccm as well as at 100 sccm.

The modification in this stage is characterized by advancing contact angles of 40°, 21°, and 19° for water, formamide, and tricresylphosphate, respectively. Therefore, a hydrophilic surface can be obtained, although the sample is located relatively far away from the main plasma region.

These contact angle values remain constant over a relatively long range of treatment time and they are not decreased further. The receding contact angles are small for all test liquids. It must be concluded that a certain amount of hydrophobic, apolar groups remain after the plasma treatment, possibly due to an equilibrium between the oxidation and sputtering.

The influence of the power input into the plasma is shown in Figure 2. Below 10 W, stable discharge cannot be generated by our equipment. As can be seen under the studied conditions, the power input only slightly influences the amount of surface modification.

In order to study the reactivity of the oxygen plasma, hydrogen was used as a process gas and oxygen was added to it in different amounts. In Figure
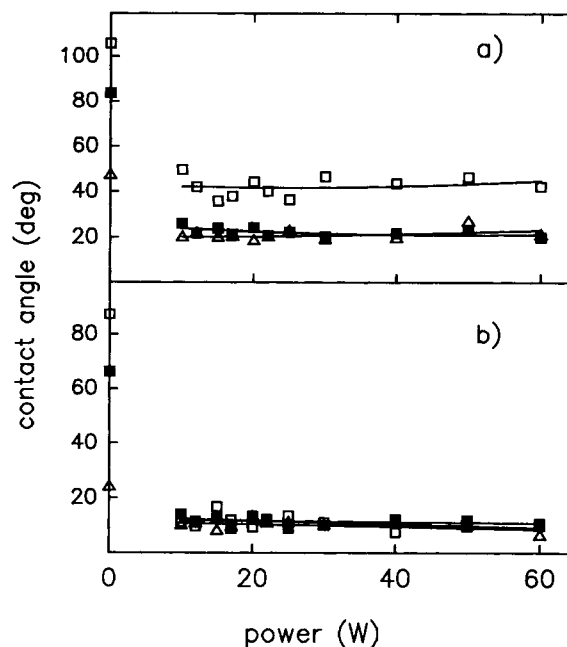
Figure 1 Dependence of contact angles of water (a), formamide (b), and tricresylphosphate (c) on the treatment time in oxygen plasma. (Hollow symbols: advancing contact angle, filled symbols: receding contact angle; □, ■ 20 W, 20 sccm; ○, ● 20 W, 100 sccm).
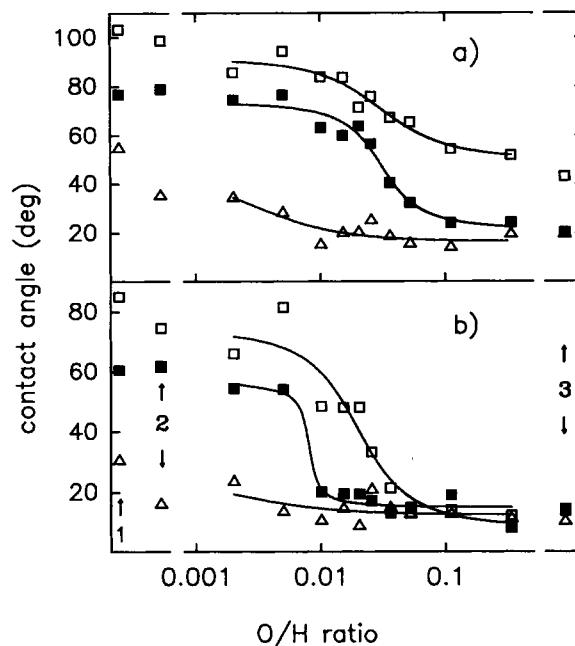
3, the dependence of the contact angles on the oxygen concentration in the process gas, expressed as the O/H-ratio, is depicted. For comparison, the appropriate contact angles of PE, hydrogen plasma-treated PE, and oxygen plasma-treated PE are added.

The receding contact angles with water and formamide are affected if only 0.1% oxygen is present in the process gas. At a concentration of about 5%, the receding contact angles drop down to the level of the oxygen plasma-treated surface. The advancing contact angles show a similar behavior, but shifted somewhat to higher oxygen concentrations.

Remarkably, the FA contact angles drop down more precipitously to the level of the oxygen plasma-treated surface than the water contact angle. Discussing this effect in terms of an acid base model for the interaction of the test liquid with the solid,[8,9] and taking into consideration the pronounced donor

Figure 2 Dependence of advancing (a) and receding (b) contact angles of water (□), formamide (■), and tricresylphosphate (△) on the power input into oxygen plasma. (20 W; 20 sccm, 10 sec).

Figure 3 Dependence of advancing (a) and receding (b) contact angles of water (□), formamide (■), and tricresylphosphate (△) on the O/H ratio in an oxygen/hydrogen plasma. For comparison, the appropriate values of pure PE (1), hydrogen plasma- (2), and oxygen plasma-treated PE (3) are added. (20 W; 20 sccm, 10 sec).

properties of the FA, it is obvious that the O/H-plasma-treated surface exhibits relatively large acceptor properties in the range of the O/H-ratio between 0.02 and 0.2. The results of other studies in our laboratory[10] show that these acceptor properties can be related to hydroxyl groups formed on the surface. Therefore, it can be concluded that hydrogen reduces higher oxygen functionalities to hydroxyl groups and/or hydroxy radicals are formed already in the gas phase and react with the polymer forming hydroxyls.
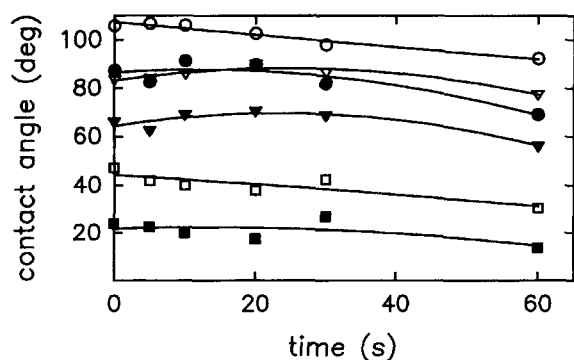
Hydrogen Plasma Treatment

Under the conditions studied, hydrogen plasma has little effect on the wetting behavior of PE. All the test liquids expose a weak trend to smaller contact angles with a longer treatment time (Fig. 4). Remarkably, FA behave different from water and TCP. The interaction of FA with the surface remains small (with a weak decreasing trend) in the first 30 sec of the treatment. Otherwise, the TCP and water contact angle decrease smoothly in the first seconds. In this way, the difference between the water and the FA contact angles becomes smaller with the treatment time.

The contact angle hysteresis remains constant over the studied period, indicating that no change in the sample roughness and chemical heterogeneity occurs.
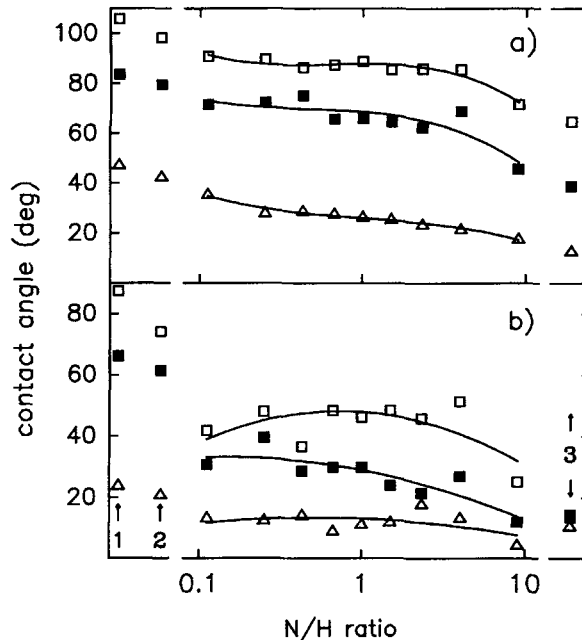
Nitrogen Plasma Treatment

Nitrogen plasma treatment results in a more moderate hydrophilation of PE (Fig. 5), as compared

Figure 4 Dependence of advancing (a) and receding (b) contact angles of water (O, ●; hollow symbol: advancing, filled symbol: receding angles), formamide (△, ▲), and tricresylphosphate (□, ■) on the treatment time in hydrogen plasma. (20 W; 20 sccm).
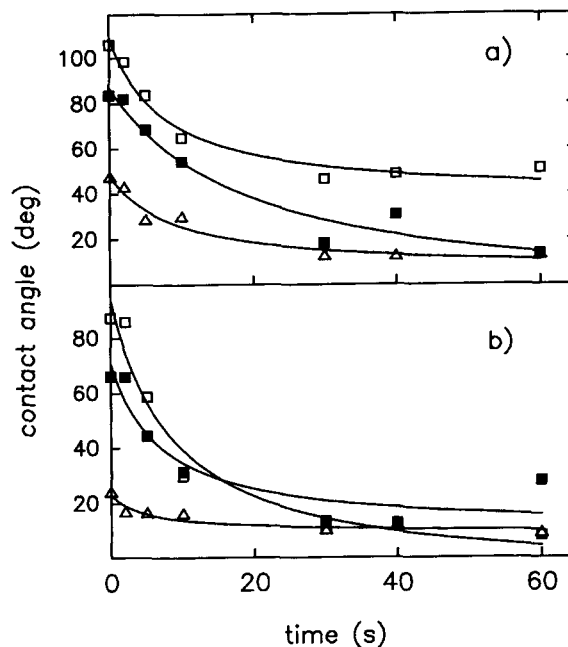
Figure 5 Dependence of advancing (a) and receding (b) contact angles of water (□), formamide (■), and tricresylphosphate (△) on the treatment time in nitrogen plasma. (20 W; 20 sccm).

Figure 6 Dependence of advancing (a) and receding (b) contact angles of water (□), formamide (■), and tricresylphosphate (△) on the N/H-ratio in nitrogen/hydrogen plasma. For comparison, the appropriate values of pure PE (1), hydrogen plasma- (2) and nitrogen plasma-treated PE (3) are added. (20 W; 20 sccm, 30 sec).
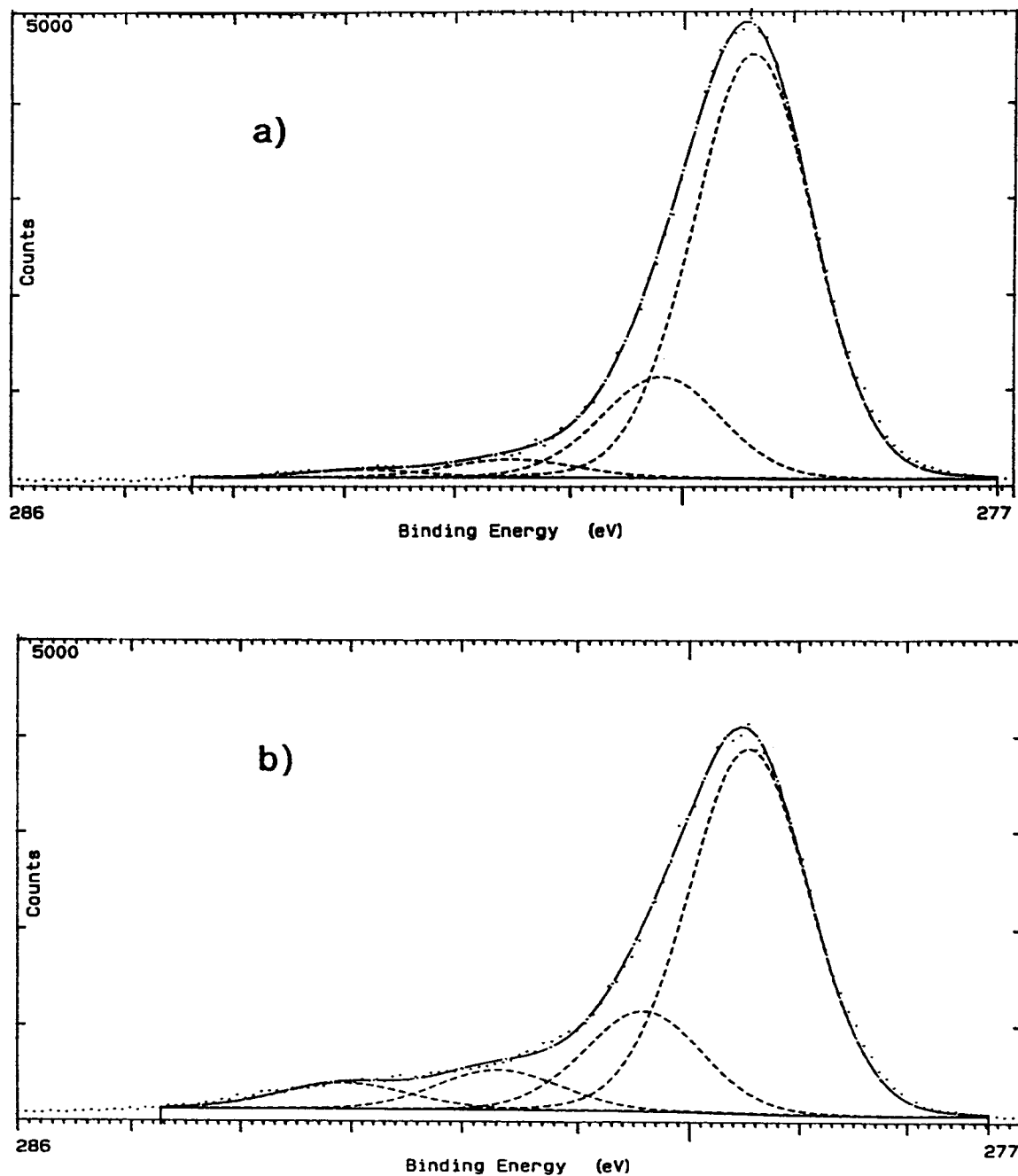
Figure 7   XPS (C1s) spectra of (a) hydrogen/nitrogen and (b) nitrogen plasma-treated PE.

with the oxygen plasma treatment. However, a constant level of the contact angles is reached after 30 sec under similar conditions as in Figure 1 for the oxygen plasma treatment. The advancing contact angles were 46°, 16°, and 12° for water, FA, and TCP, respectively. Remarkably, these values are close to those of the constant level of the oxygen plasma-treated surface.

Determining the surface elemental composition of such a sample by XPS, an oxygen content of 13% was found, while only 3% of nitrogen was present. Consequently, the surface properties of nitrogen plasma treated PE is ruled by oxygen containing functionalities. However, this possibly unexpected result is consistent with data reported in the literature.[6,11]

In principle, the functionalities can rise from two sources: (i) the direct reaction of trace oxygen in the plasma with the surface during treatment and (ii) the saturation of radicals by air or the hydrolysis by humidity after treatment on the exposure to the ambient atmosphere. Although the samples were exposed to air under our treatment conditions, especially the relatively high reactor base pressure, the first source of oxygen seems to be the main one (for a detailed discussion see Ref. 10).

Contemplating that the used nitrogen contains less than 3 ppm oxygen and less than 5 ppm water (obviously having a similar effect as oxygen) a high reactivity of oxygen species has to be assumed.

Comparing the conditions in an O/H- and in an O/N-plasma, large differences are evident. While hydrogen reduces and hydrogenates the oxygen-containing species in the gas phase and on the solid surface, nitrogen exhibits only a "diluting" effect, or at least a much smaller reducing effect. Although only a few ppm of oxygen are present in the process gas, a high amount of oxygen is incorporated into the surface.

It should be possible to suppress the action of the highly reactive trace oxygen by adding hydrogen to the process gas. The influence of the N/H-ratio on the contact angle of the treated surface is shown in Figure 6.

The higher the hydrogen concentration, the higher the contact angle, especially with water and FA. Indeed, the XPS measurement of an H/N-plasma-treated sample reveals a reduction of the oxygen content to 6.2%. However, the nitrogen concentration drops down disproportionately below 1% at the same time. The shape of the C1s signals is a little different from those of the pure nitrogen plasma-treated samples (Fig. 7). By deconvolution of the signals, it can be seen that the content of the species with the smallest binding energy shift is higher in the case of the H/N-plasma-treated samples (Table I). Because this signal can be attributed to C—O functionalities, a higher content of less
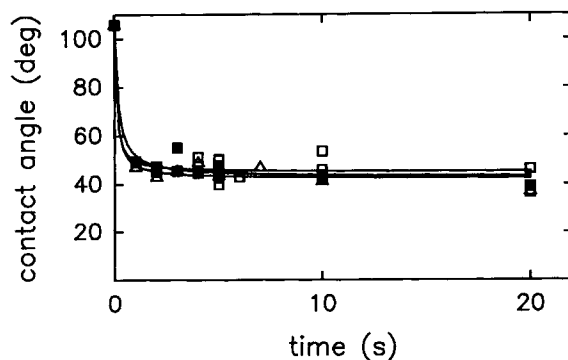
Figure 8 Dependence of advancing water contact angles on the treatment time in an oxygen plasma. [20 W, 20 sccm; (□) normal treatment, (■) with a tungsten wire, (△) with mercury vapor].

oxidized functionalities, for example, hydroxyl groups, can be assumed.

Role of Atomic Oxygen and Molecular Singlet Oxygen

Granier et al.[12] reported that, outside the main discharge region, atomic (O) and molecular singlet ($O_2^1\Delta$) oxygen are the only reactive particles. In order to illustrate which of the species is the most reactive to PE, experiments were performed to quench the atomic oxygen either with a tungsten wire or with mercury vapor. Both experiments are reported to yield a high recombination rate of atomic oxygen.[7,13]

Assuming a high reactivity of the oxygen atoms, the increased recombination rate should affect the dependence of the surface modification on the treatment time as well as on the O/H ratio. However, significant differences were not observed between the normal treatment and that with tungsten or mercury (Figs. 8 and 9). Consequently, oxygen atoms do not play any major role under the studied reaction conditions, probably because they are not present in a substantial amount near the sample.

Table I Concentration of Different Functionalized Carbon Structures of Hydrogen/Nitrogen and Nitrogen Plasma-Treated PE, Determined by XPS

Energy Shift to C—C Signal (eV)	H/N-Plasma		N-Plasma	
	Area-Fraction (%)	Rel. Concentration	Area-Fraction (%)	Rel. Concentration
1	13.9	1	16.8	1
2.5	2.6	0.19	7	0.42
3.8	1	0.07	4.6	0.29
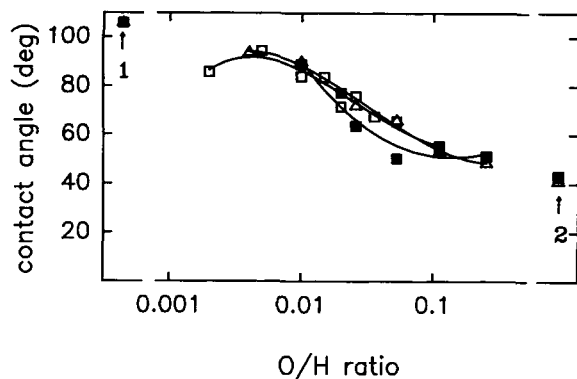
Figure 9 Dependence of advancing water contact angles on the O/H ratio in an oxygen/hydrogen plasma. For comparison, the appropriate values of pure PE (1) and oxygen plasma-treated PE (2) are added. (20 W, 20 sccm, 10 sec; (□) normal treatment, (■) with a tungsten wire, (△) with mercury vapor].

Therefore, the observed oxidation is caused by the molecular singlet oxygen. $O_2^1\Delta$ does not react with alifatic hydrocarbons.[13] It must be concluded that, at first, the PE surface has to be activated before it can be oxidized. In oxygen plasma, the plasma radiation is the only source of such activation forms, for example, excitations, free radicals, double bond, that is, structures that are able to react with $O_2^1\Delta$. In our experimental arrangement this is reasonable. However, Normand et al.[7] stated that radiation has no influence on the treatment of polypropylene. This conclusion was drawn from the comparison of the treatment results in an angular and a straight tube arrangement of the plasma source and the sample compartment. Of course, in the angular tube, the direct irradiation of the sample by the main discharge region is not possible. However, also relatively far away from the main discharge region, atomic oxygen and excited singlet oxygen were found. Consequently, recombination and de-excitation take place far downstream, too. The recombination of the atoms produces radiation of an energy especially able to activate aliphatic hydrocarbons. Possibly, the intensity of this secondary radiation is sufficient to produce activated sites for the reaction with $O_2^1\Delta$.

CONCLUSIONS

Polyethylene can be surface modified in an oxygen plasma in a downstream remote reactor, efficiently yielding a hydrophilic material. During nitrogen plasma treatment, trace oxygen results in the incorporation of a relatively high amount of oxygen into the surface. In contrast, in an hydrogen plasma treatment, under similar conditions, the PE remains hydrophobic, although the oxygen concentration should be comparable. It has been pointed out that singlet molecular oxygen, which cannot be quenched by hydrogen, seems to be the major reactive species in the remote oxygen plasma in our reactor. Therefore, in hydrogen plasma, the oxygen functions formed by the trace oxygen are readily reduced. This reaction can take place only in hydrogen plasma. In nitrogen plasma, the oxygen functionalities remain and it is extremely difficult to exclude the incorporation of oxygen in a nonreducing plasma.

REFERENCES

1. D. T. Clark, A. Dilk, and D. Shuttleworth in *Polymer Surfaces*, D. T. Clark and W. J. Feast, Eds., Wiley, 1978.
2. D. T. Clark, W. J. Feast, W. K. R. Masgrave, and I. Ritchie, *J. Polym. Sci. Polym. Chem. Ed.*, **13**, 857 (1975).
3. H. Yasuda, H. C. Marsh, E. S. Brandt, and C. N. Reilley, *J. Polym. Sci. Polym. Chem. Ed.*, **15**, 991 (1977).
4. D. S. Everhart and C. N. Reilley, *Anal. Chem.*, **53**, 665 (1981).
5. R. Foerch and D. H. Hunter, *J. Polym. Sci. Polym. Chem. Ed.*, **30**, 279 (1992).
6. R. Foerch, N. S. McIntyre, R. N. S. Sodhi, and D. H. Hunter, *J. Appl. Polym. Sci.*, **40**, 1903 (1990).
7. F. Normand, J. Marec, Ph. Leprince, and A. Granier, *Mater. Sci. Eng.*, **A139**, 103 (1991).
8. C. J. van Oss, R. J. Good, and M. K. Chaudhury, *Langmuir*, **4**, 884 (1988).
9. F. M. Fowkes, D. O. Tischler, J. A. Wolfe, L. A. Lannigan, C. M. Ademu-John, and M. J. Halliwell, *J. Polym. Sci. Polym. Chem. Ed.*, **22**, 547 (1984).
10. J. Behnisch, A. Holländer, and H. Zimmermann, *J. Appl. Polym. Sci.*, to appear.
11. D. T. Clark and A. Dilks, *J. Polym. Sci. Polym. Chem. Ed.*, **17**, 957 (1979).
12. A. Granier, S. Pasquiers, C. Boisse-Laporte, R. Darchicourt, P. Leprince, and J. Marec, *J. Phys. D. Appl. Phys.*, **22**, 1487 (1989).
13. B. Ranby and J. F. Rabek, *Photo-oxidation and Photodegradation of Polymers*, Wiley, London, 1975.