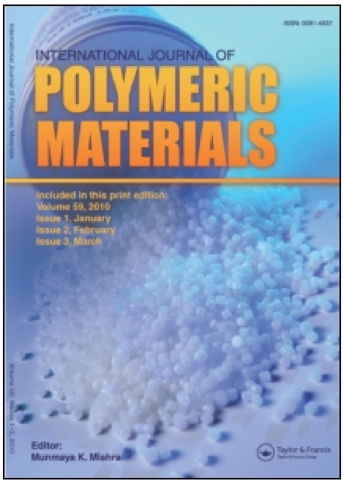

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Controlled Functionalization of Polymer Surfaces by Low Pressure Plasma Treatment

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The effect of low pressure plasma treatment on surface characteristics of polyethylene films is investigated.

KEY WORDS Plasma, low pressure, polyethylene, surface

INTRODUCTION

Low pressure plasma treatment of polymers is a powerful tool to modify their surface properties by the introduction of different functional groups. However, its application in controlled surface engineering of advanced polymer materials is limited due to the chemical heterogeneity of the functionalized surfaces caused by the different reactive plasma species, such as free electrons, electronically excitated atoms and molecules, radicals, ions, and irradiation.

Most applications of plasma techniques to polymer surface modification are based on the direct action of the plasma, i.e., the material is positioned in the discharge region. Only a few publications[1] dealt with the influence of a remote plasma on polymers. In such an arrangement the variety and the energy of species interacting with the polymer are more or less reduced. It can be expected, that the processes at the solid/gas interface are less complex compared with the direct exposure. Posssibly, a certain control of the process can be achieved.

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

EXPERIMENTAL

Materials

Poly(ethylene) (PE) films (Lupolen) were supplied by BASF. Before treatment the film had been cleaned with 96% ethanol in an ultrasound cleaner for 5 min and dried in vacuum.

Plasma Treatment

Two different plasma reactors were used.

First, a special kind of a remote plasma reactor, where the sample is located downstream behind the cathode of a dc glow discharge. The discharge voltage was 750 V and the resulting discharge current was 1.4 mA. After the sample was supplied the reactor was evaluated for 10 minutes to a base pressure of about 2 Pa using a rotary pump (Alcatel 2020A). Then, the gas flow controller (MKS 1959C) was turned on to its maximum (200 sccm) for 5 minutes before the process flow rate of 15 sccm was realized. The resulting pressure during the plasma treatment was 40 Pa.

Second, a homemade pyrex tube reactor. The tube has a diameter of 10 cm and is about 80 cm long. On the lower end the sample compartment is located and the tube is connected to a rotary pump (Alcatel 2020A). On the upper end of the tube and 20 cm above the sample plane, process gas inlets are incorporated axially and radially, respectively. The pressure in the tube is measured with an absolute pressure gauche (MKS Baratron 122A). On the upper part the reactor is provided with rf power (13.56 Mhz, Advanced Energy RTX 600) via ring electrodes outside the tube.

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. Usually, the sample is placed about 50 cm downstream of the discharge region.

Oxygen, nitrogen (5.0), and hydrogen (5.0) (Linde AG, Berlin) were used as received. The gases were dosed by MKS mass flow controllers (type 1259C) in the range between 0.2 and 100 sccm.

Contact Angle Measurements

The advancing and receding contact angles of a test liquid drop on the polymer film were measured using a goniometer video system G 40 (Krüss GmbH, Hamburg). The surface tension of the test liquids was controlled by a Wilhelmi tensiomer K1 (Krüss GmbH, Hamburg) using an annealed platinum plate. As test liquids were utilized: deionized water, formamide (Fluka, puriss, p.a.) and tricresylphosphate (Fluka, pract., mixture of isomers). The advancing (a) and receding (r) contact angles of the untreated PE are:

water: $\theta_a = 107°$ $\theta_r = 89°$
formamide (FA): $\theta_a = 86°$ $\theta_r = 66°$
tricresylphosphate (TCP): $\theta_a = 42°$ $\theta_r = 22°$.

The measurements of the plasma treated samples were performed immediately after removing from the reactor. The presented contact angles are averaged from at least two independent experimental runs and the deviation from the average is not greater than ±3°. Repeated measurements after 3 and 8 h carried out on selected samples resulted in the same data, though, with a decreased reproducibility.

RESULTS

Oxygen Plasma Treatment

The effect of oxygen rf plasma on PE is very strong under the downstream remote conditions studied in this paper. It takes less than one second until a level of modification is reached which is not changed further in the following minute. The modification in this stage is characterized by advancing contact angles of 46°, 21°, and 19° for water, formamide, and tricresylphosphate, respectively. Therefore, a very hydrophilic surface can be obtained, although, the sample is located relatively far away from the main plasma region.

Nearly the same final state was obtained in the case of the remote oxygen dc plasma, however, due to the extremely "weak" plasma conditions, a considerably longer time (about 120s) was necessary to reach it. This time scale allows to investigate the main stages of the modification process by the convenient characterization methods of polymer surfaces, e.g. by contact angle measurements (Figure 1).

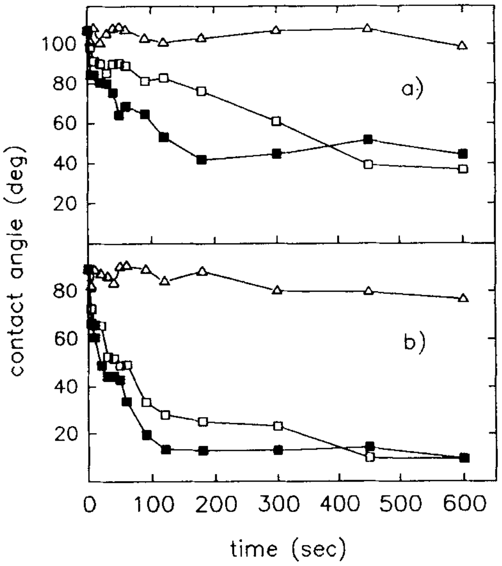

FIGURE 1 Advancing (a) and receding (b) contact angle of water on poly(ethylene) surfaces treated with nitrogen (□), oxygen (■), and hydrogen (△) plasmas in dependence on treatment time (sample position $x = 2$ cm).

Hydrogen Plasma Treatment

Under the studied conditions hydrogen plasma has only a 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 (Figure 1).

Nitrogen Plasma Treatment

Nitrogen plasma treatment results in a more moderate hydrophilation of PE (Figure 1) compared with the oxygen plasma treatment. A constant level of the contact angles is reached only after 30 s and 450 s in the case of the rf and the dc plasma, respectively. Remarkably, the contact angles of the final stage are very 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 are present. Consequently, the surface properties of nitrogen plasma treated PE is ruled by oxygen containing functionalities.

DISCUSSION

More detailed information about the plasma chemical reactions at the polymer surface could be drawn from contact angle data, relating them to the surface free energy of the solid γ_s^{tot} and the test liquid γ_l^{tot} using Young's equation and one of the models assuming an additivity of different molecular interactions that determine the surface energy.[2] The interpretation of the experimental data is, however, complicated by the right choice of the model to be used. According to our experiences meaningful values for the surface free energy of the polymer solid were only got considering the Lifshitz-van der Waals (LW) and the acid-base (AB) interactions as it was proposed by van Oss *et al.*[3]

$$\gamma_i^{\text{tot}} = \gamma_i^{\text{LW}} + \gamma_i^{\text{AB}} \tag{1}$$

$$\gamma_i^{\text{AB}} = 2\sqrt{\gamma_i^{+}\gamma_i^{-}} \tag{2}$$

where γ_i stands for the electron acceptor (Lewis acid) part of the surface free energy of the compound i, and γ_i for its electron donor (Lewis base) part ($i = s, l$). Young's equation in terms of the LW-AB model can now be established

$$(1 + \cos\theta)\gamma_l^{\text{tot}} = 2\left(\sqrt{\gamma_s^{\text{LW}}\gamma_l^{\text{LW}}} + \sqrt{\gamma_s^{+}\gamma_l^{-}} + \sqrt{\gamma_s^{-}\gamma_l^{+}}\right) \tag{3}$$

Measuring the contact angle of three test liquids with known parameters γ_l^{LW}, γ_l^{+}, and γ_l^{-} (see Table I), we were able to calculate the three unknown parameters γ_s^{LW}, γ_s^{+}, and γ_s^{-}. Some results are shown in Figure 2.

The acid and the base components of the surface free energy (Figure 2) underline the similarities in the behavior of the nitrogen and the oxygen plasma. The most pronounced difference is the rapid increase of the contents of functionalized groups

TABLE I

Surface free energy and its components in terms of Equations (1) and (2) of the three test liquids

test liquid	γ_l^{tot}, mJ/m^2	γ_l^{LW}, mJ/m^2	γ_l^{+} mJ/m^2	γ_l^{-} mJ/m^2
water	72.8	21.7	25.5	25.5
formamide	57.4	32.0	3.0	52.9
TCP	40.9	39.2		

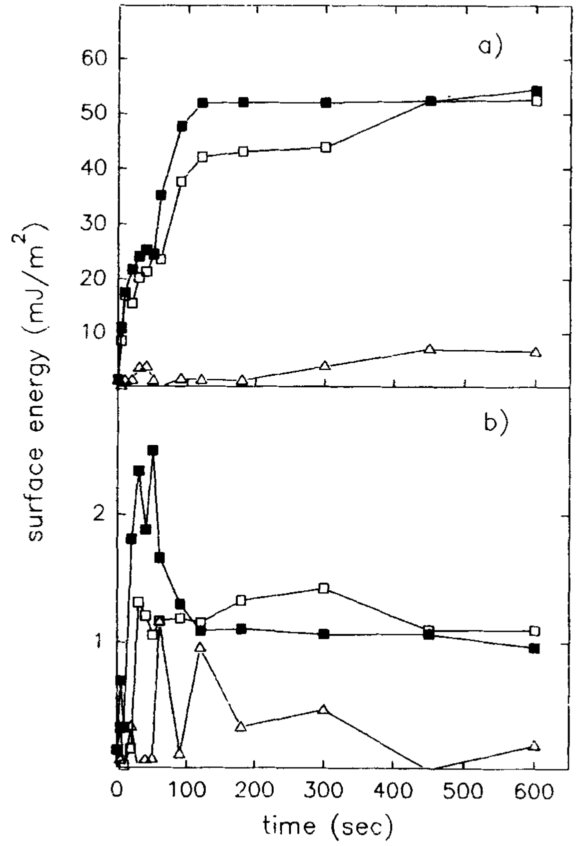

FIGURE 2 Acid (a) and base (b) components of the surface free energy of poly(ethylene) films treated with nitrogen (□), oxygen (■), and hydrogen (△) plasmas in dependence on treatment time (sample position $x = 2$ cm).

acting as electron acceptors during the first 30 seconds of the oxygen plasma treatment. Due to Gutmann's donor-acceptor approach[4] good electron acceptors are hydroxyl and carbon acid groups.

After 60 seconds this first main stage of the plasma/polymer interaction is achieved.

However, it does not mean a complete functionalization of the polymer surface at all, as the high advancing contact angles and the great hysteresis indicate.

The state of complete modification is reached only at a treatment time of about 450 seconds and it is characterized by a total surface free energy of the polymer of about 58 mJ/m^2 as calculated from both the advancing as well as the receding contact angles (Table II). The increase of the total surface free energy from 31 mJ/m^2 for the untreated sample is mainly caused by an increase of the acid-base interactions and only to a minor extent by an increase of the Lifshitz-van der Waals interactions. It is worth noting, that the polymer surface acts as an electron donor as well as an electron acceptor.

From Figures 1 and 2 it must be concluded, that even in the case of the nitrogen plasma the functionalization of the polymer surface is mainly determined by oxygen traces in the plasma deriving from impurities of the nitrogen gas, from oxygen adsorbed by the sample and at the reactor walls, and from leakages in the vacuum system.

The influence of oxygen residues during plasma treatment with inert gases is documented in the literature.[1] However, the fact, that the nitrogen plasma under the specific experimental conditions used in the present work behaves rather like an oxygen plasma contaminated by nitrogen, was unexpected, but may be understood in terms of the classical kinetic theory of gas. According to this theory the number of gas molecules z striking a unit area per second is given by[5]

$$Z = \frac{N_A}{\sqrt{2\pi R 10^{-3}}} \frac{p}{\sqrt{TM}} \tag{4}$$

where N_A is Avogadro's number, R the gas constant, p the pressure, T the absolute temperature, and M the molecular weight of the gas.

Using Equation (4) the collision rate of oxygen molecules deriving from air leakages at a basic pressure of 2 Pa, as it was realized in our dc plasma reactor,

TABLE II

Surface free energy and its components in terms of Equations (1) and (2) of plasma treated PE (calculated from advancing contact angle values)

treatment	γ_l^{tot}, mJ/m^2	γ_l^{LW}, mJ/m^2	γ_l^{+} mJ/m^2	γ_l^{-} mJ/m^2
untreated	32.5	32.4	0.002	0.03
nitrogen, rf	60.6	41.6	3.26	27.5
nitrogen, dc	57.9	41.3	2.21	31.1
oxygen, rf	55.2	40.4	2.35	23.5
oxygen, dc	53.5	40.3	1.57	27.9
hydrogen, rf	34.9	34.5	0.06	0.9
hydrogen, dc	34.5	34.4	0.01	0.2

at 300 K is about 1×10^{18} cm^{-2} s^{-1} compared to about 1×10^{20} cm^{-2} s^{-1} for the nitrogen molecules at the working pressure of 40 Pa. Thus, the collision rates differ only about two orders of magnitude, a difference which easily may be compensated by a higher cross section for the reactions of oxygen plasma species (mainly atomic oxygen and molecular singlet oxygen)[6,7] with the polymer surface and by the fact, that molecular oxygen is reactive towards polymeric alkyl radicals formed during plasma treatment. Moreover, the collision rate of about 1×10^{18} cm^{-2} s^{-1} must be compared with the number of monomeric units at the polymer surface, which may be roughly estimated to 10^{15} per cm^2. Thus, there should be enough reactive oxygen in the nitrogen plasma to cover the polymer surface in a time scale of seconds or so.

At the background of these estimations it becomes obvious, why extreme care has to be taken to get exclusively nitrogen containing functional groups while treating with a nitrogen plasma. Gerenser[8] got such conditions using the chambers of a XPS instrument. In this case the basic pressure was 6.7×10^{-7} Pa (5×10^{-9} Torr) and the collision rate of oxygen molecules with the sample surface is about 4×10^{11} cm^{-2} s^{-1}, e.g. several orders of magnitude lower than the number of monomeric units at the polymer surface.

Similar effects of oxygen residues (though they are present) are not observed for the hydrogen plasma. 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 3 the dependence of the contact angles with the test liquids on the oxygen

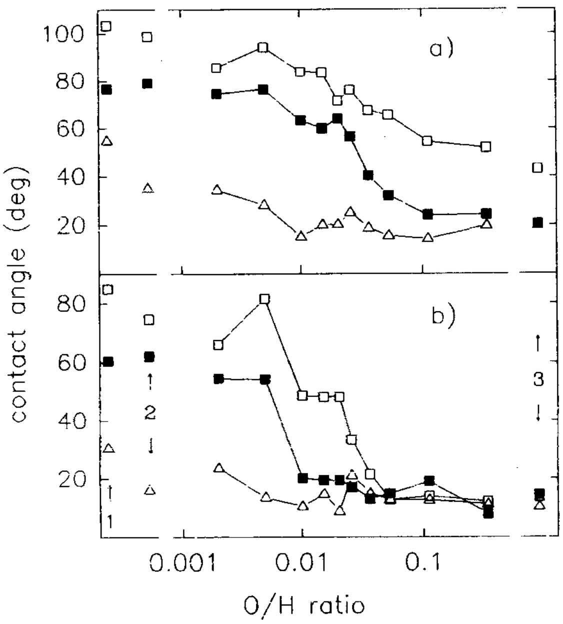

FIGURE 3 Dependence of advancing (a) and receding (b) contact angles of water (□), formamide (■), and tricresylphosphate (△) on the O/H ratio in an oxygen/hydrogen plasma. For comparison the appropriate values of pure PE (1), hydrogen plasma (2) and oxygen plasma (3) treated PE are added. (20 W; 20 sccm,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

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 effected 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 somewhat shifted to higher oxygen concentrations.

Remarkably, FA behave different from water and TCP. The interaction of FA with the surface remains small (with a very weak trend to decrease) in the first 30 s of the treatment. Otherwise, the TCP and water contact angle decrease smoothly already in the first seconds. Discussing this effect in terms of the LW-AB model and taking into consideration the pronounced donor properties of the FA, it is obvious that the surface of O/H-plasma treated surface exhibits relatively large acceptor properties in the range of the O/H-ratio between 0.02 and 0.2. Regarding the results of other studies in our laboratory 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 or hydroxy radicals are formed already in the gas phase and reacting with the polymer to hydroxyls.

What is the background of the high reactivity of oxygen plasma species? A. Granier *et al.*[6] 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 elucidate which of the species is the most reactive to PE, experiments were performed to quench the atomic oxygen either with a tungsten wire[7] or with mercury vapor.[9] Both are reported to yield a high recombination rate of atomic oxygen.

Assuming a high reactivity of the oxygen atoms, the increased recombination rate in the presence of tungsten or mercury should effect the dependence of the surface modification on the treatment time as well as the dependence on the O/H ratio. However, no significant differences were observed between these experiments and that without tungsten or mercury (Figure 4). Consequently, oxygen

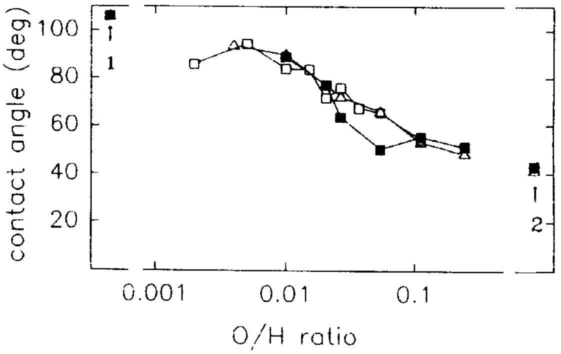

FIGURE 4 Dependence of advancing water contact angles on the O/H ratio in an oxygen/hydrogen plasma. For comparison the appropriate values of pure PE (1) and oxygen plasma (2) treated PE are added. (20 W, 20 sccm, 10 s; □ normal treatment; ■ with a tungsten wire; △ with mercury vapor).

atoms do not play a major role under the studied reaction conditions, probably, due to recombination they are not present in a substantial amount near the sample. Therefore, the observed oxidation is caused by the molecular singlet oxygen. Though, $O_2{}^1\Delta$ do not react with aliphatic hydrocarbons[9] the PE surface first have to be activated before it can be oxidized. In the case of an oxygen plasma the plasma radiation seems to be the only source of such an activation forming free radicals and double bonds, i.e., structures which are able to react with $O_2{}^1\Delta$. However, Normand *et al.*[7] stated that radiation has no influence on the treatment of poly(propylene). 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 excluded. 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 down stream, too. Especially, the recombination of the atoms produces radiation of an energy able to activate aliphatic hydrocarbons. Obviously, the intensity of this secondary radiation is sufficient to produce activated sites for the reaction with $O_2{}^1\Delta$.

CONCLUSIONS

Poly(ethylene) can be surface modified in an oxygen plasma in a downstream remote reactor yielding efficiently a very hydrophilic material. During a nitrogen plasma treatment trace oxygen results in the incorporation of a relatively high amount of oxygen into the surface. In contrast, in a hydrogen plasma treatment under similar conditions the poly(ethylene) remains hydrophobic although the concentration of oxygen residues should be comparable.

It has been pointed out that singlet molecular oxygen seems to be the major reactive species in a remote oxygen plasma. The oxygen containing functional groups formed by the trace oxygen are readily reduced in a hydrogen plasma, but remain in a nitrogen plasma. Thus, it is extremely difficult to exclude the incorporation of oxygen into the polymer surface during treatment in a non-reducing plasma.

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