

# Introduction of Functional Groups on Polyethylene Surfaces in a Low Pressure Carbon Dioxide Glow Discharge; a Mechanistic Study.

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## Abstract

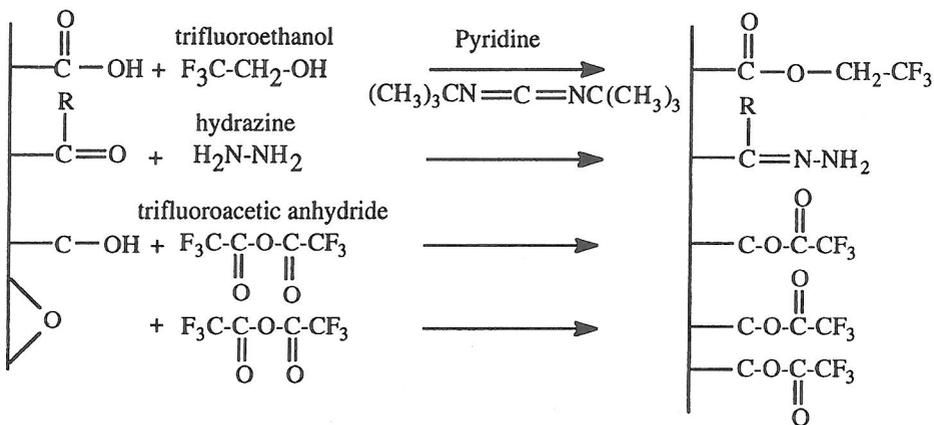
Low density polyethylene (LDPE) films were plasma treated either in the glow or in the afterglow of a carbon dioxide (CO<sub>2</sub>) plasma. The chemical composition of the surface, etching rate and crosslinking after both treatments were compared. Although the surface oxidation in the afterglow was 30 times slower than in the glow, the changes in the surface composition of the surface under both conditions took place in a similar way. The chemical composition of the surface was primarily affected by radical species (likely atomic oxygen) from the plasma phase. Furthermore substantial crosslinking of the film surface was found in the glow, presumably induced by UV radiation.

## Introduction

Introduction of functional groups onto polymeric surfaces in order to alter the surface properties while maintaining the bulk properties has become of large interest during the last decades especially for adhesion improvement and biomedical applications. Gas plasma treatments applying a low pressure plasma have frequently been used to specifically alter the surface properties of polymers. A plasma is a very reactive environment consisting of molecules, atoms, ions, electrons, radicals and metastable species. In a plasma also high energetic UV radiation is generated. All plasma species as well as UV radiation interact with the surface. In an oxidizing plasma these interactions lead to the introduction of various oxygen containing groups. Furthermore short wave UV radiation results in crosslinking of polymer surfaces. High rates of crosslinking of PE were reported when argon or helium plasmas were used [1]. Interaction of plasma species or UV radiation with polymer chains can also result in chain scission.

In this study a low pressure carbon dioxide (CO<sub>2</sub>) plasma is used. The CO<sub>2</sub> plasma treatment of LDPE results in the introduction of a wide spectrum of oxygen containing functional groups, like peroxide, hydroxyl, ketone, aldehyde, carboxylic acid, epoxide, ether and ester groups [2]. A fundamental question in polymer plasma modification is to which extent different plasma species and UV radiation contribute to the final surface composition of the material. Knowledge of the mechanisms of introduction of functional groups, crosslinking and etching is important in order to be able to adjust the surface chemistry and surface stability after plasma treatment in a well defined way. Therefore the influence of various plasma species and UV radiation in a CO<sub>2</sub> plasma on the surface chemistry of LDPE has been investigated. CO<sub>2</sub> plasma treatments of LDPE have been carried out in the glow and in the afterglow region of the

plasma. In case of glow treatment all surface modifying species are present, while in the afterglow region the only active species present are long living radicals generated in the plasma zone. X-ray photoelectron spectroscopy (XPS) combined with gas phase derivatization techniques were applied for analysis of the modified surfaces. The derivatization technique consisted of a reaction of certain functional groups with a reagent containing a tag element (for example fluorine). This element can be detected and quantified by XPS. Derivatization of the surface hydroxyl/epoxide groups, surface ketone and aldehyde groups and surface carboxylic acid groups has been carried out as depicted in fig. 1.



**Figure 1.** Derivatization reactions for the detection of surface carboxylic acid groups, surface ketone/aldehyde groups and surface hydroxyl (and epoxide) groups.

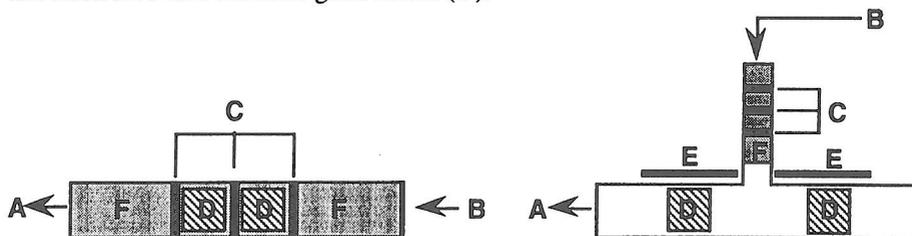
### Materials and methods.

LDPE film: low density polyethylene, thickness 0.2 mm, type 2300, DSM Geleen, The Netherlands. The film did not contain additives. Dichloromethane, acetone, pyridine (all analytical grade), 2,2,2-trifluoroacetic anhydride (TFAA), 2,2,2-trifluoroethanol (TFE), aqueous sodium hydroxide (NaOH 1.00 M) and aqueous hydrochloric acid solution (HCl 1.00 M), Merck Darmstadt, Germany. Hydrazine monohydrate (N<sub>2</sub>H<sub>4</sub>, purity 99%), Janssen Chimica, Tilburg, The Netherlands. Carbon dioxide (CO<sub>2</sub> purity >99.995 %), Hoekloos Schiedam, The Netherlands. Water used in all experiments was doubly deionized.

The LDPE films were washed 4 times for 10 min. in an ultrasonic bath with dichloromethane. The solvent was replaced between each cycle. The procedure was repeated with acetone (4 times), and subsequently with water (4 times). The films were dried overnight at reduced pressure at room temperature.

Plasma treatments (described previously [3]) in the plasma zone (F) were performed in a linear plasma reactor (fig. 2) consisting of a glass tube with an internal diameter of 6.5 cm and a length of 80 cm, equipped with 3 externally placed, capacitatively coupled electrodes (C). The hot electrode was placed in the middle of the reactor tube. The grounded electrodes were placed at a distance of 10 cm from the hot electrode. One side of the reactor was connected to a gas inlet system with flow control (B). The reactor was evacuated by a two stage rotary vane pump or a turbo molecular pump (A). The electrodes were powered through a matching network by a 13.56 MHz radio frequency generator. Control of the plasma treatment was carried out using a computer with a time

control program. 24 LDPE films (20x13 mm) were placed between the two cold and the hot electrodes on a substrate glass holder (D).



**Figure 2.** Schematic representation of plasma treatment in the glow (left) and in the afterglow (right).

The treatments of LDPE outside the plasma zone (afterglow, fig. 2) were performed in a specially designed reactor. The reactor consisted of a main glass tube (80 cm long, internal diameter of 6.5 cm). Perpendicular on this tube a smaller side tube of 30 cm length, and an internal diameter of 4.5 cm was mounted. The plasma was restricted to this side tube (F). The absence of charged particles and excited species in the afterglow was checked with Langmuir probe measurements and Optical Emission Spectrometry (OES). The gas inlet was connected to this side tube (B), while the pumping section was connected to the main tube (A). A screen was mounted around the main tube to prevent any UV generated in the plasma zone to reach the samples. Three electrodes were placed on the outside of the small side tube (C). The hot electrode was placed in the middle of the side tube. The grounded electrodes were placed at a distance of 6.5 cm from the hot electrode. The pumping, plasma generation, and gas distribution system were the same as mentioned before. For afterglow modification 24 samples (D) were placed on glass sample holders in the main tube at a minimal distance of 5 cm from the opening of the side tube.

The general treatment procedure was as follows. The reactor was evacuated until a pressure of 0.01 mbar was reached before a gas flow of 10 cm<sup>3</sup>/min (standard temperature and pressure) was established through the reactor. The pressure was raised to 0.15 mbar. The plasma treatment started after 5 minutes at a power of 35 Watt. The plasma was established through the complete tube. After the plasma treatment the gas flow was maintained for 2 minutes. Subsequently the reactor was brought to atmospheric pressure with air. The films were turned and the other side was treated following the same procedure. After treatment the films were stored at a temperature of -18 °C until characterization in order to prevent reorganization of the surfaces [4].

Gas phase derivatization was carried out by exposing the modified PE surface to TFE, TFAA or hydrazine. In this way a (semi) quantitative indication of the concentration of carboxylic acid groups, hydroxyl/epoxide groups or ketone/aldehyde groups can be obtained [5]. The derivatization procedure has been described extensively elsewhere [2]. After gas phase reaction, the samples were loaded immediately for XPS analysis.

XPS analysis was performed with a Kratos XSAM-800 apparatus (Manchester, United Kingdom). A Mg K<sub>α</sub> source was used (15 kV, 10 mA). The analyser was placed perpendicular to the surface of the sample. The spectra were recorded in the low resolution mode (pass energy 40 eV, FWHM Ag 3d<sup>5/2</sup>: 1.2 eV). Standard sensitivity factors delivered by Kratos were used to convert measured peak areas to atomic concentrations. Only for fluorine empirical sensitivity factors, determined by scanning polytetrafluoroethylene, were used.

## Results and Discussion.

LDPE films were treated in the glow or in the afterglow zone of a CO<sub>2</sub> plasma (fig. 2). The treatment times ranged from 0.1-500 sec. In fig.3 the surface oxygen concentration is given as a function of treatment time for both treatment procedures. The final level of oxygen is independent from the modification procedure. The modification in the glow, however, is about 30 times faster than the modification in the afterglow. The shape of the curves is similar.

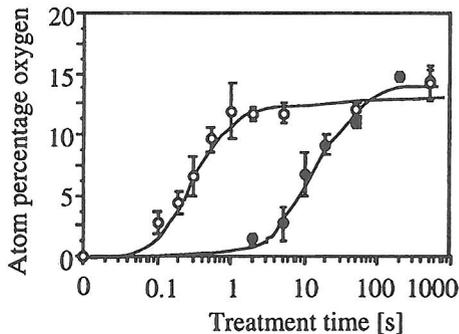


Figure 3. Surface oxygen concentration as a function of treatment time in the glow (○) and in the afterglow (●).

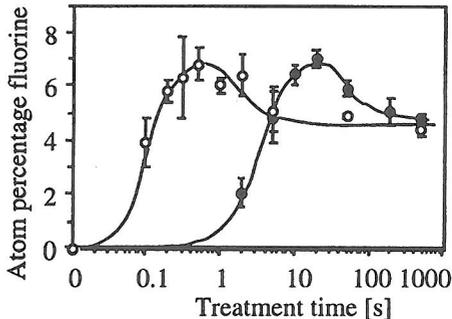


Figure 4. Surface fluorine concentration as a function of treatment time in the glow (○) and in the afterglow (●), after derivatization of the hydroxyl/epoxide groups with TFAA.

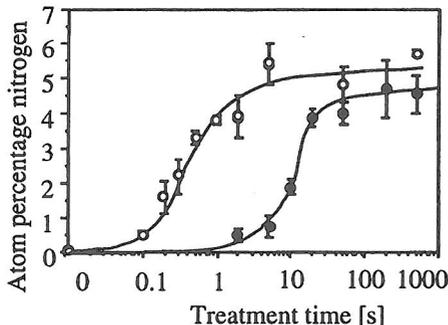


Figure 5. Surface nitrogen concentration as a function of treatment time in the glow (○) and in the afterglow (●), after derivatization of the ketone and aldehyde groups with hydrazine.

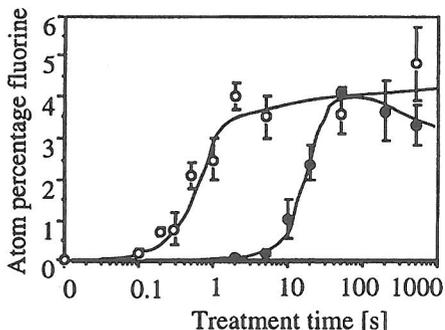


Figure 6. Surface fluorine concentration as a function of treatment time in the glow (○) and in the afterglow (●), after derivatization of the carboxylic acid groups with TFE.

The similarity between the evolution of the surface chemistry during glow and afterglow modification becomes more obvious after derivatization of the different functional groups. In fig. 4 the surface composition as a function of treatment time is given after derivatization of the hydroxyl/epoxide groups using TFAA. After reaching a maximum value of 7 % of fluorine a plateau value of about 4.5 % fluorine is obtained for both treatments. The surface composition after hydrazine derivatization of the

ketone/aldehyde groups is given in fig. 5. The surface concentration of nitrogen levels off at about 5 %. TFE derivatization of the carboxylic acid groups results in a plateau value of about 4 % fluorine on the surface (fig. 6). As was found for the introduction of oxygen in the afterglow also a retardation of about 30 times was found for introduction of the different functional groups. In the afterglow the only active species present are radicals. Therefore the introduction of oxygen containing groups on the surface can only be assigned to these radical species (likely atomic oxygen). Despite the presence of UV, ions and electrons in the plasma zone (as detected by OES and Langmuir probe analysis) the surface oxidation in the glow evolves in a similar, but faster, way. It can be concluded that also in the glow the surface oxidation is completely determined by radicals. The retardation is caused by a difference in radical density between the plasma phase and the afterglow region. The decrease in radical density in the afterglow zone is caused by recombination of formed radicals to CO<sub>2</sub> and oxygen after leaving the plasma zone.

In table 1 the overall etching rate of PE in a CO<sub>2</sub> plasma is given for the glow and the afterglow treatment. This etching is due to abstraction of hydrogen, formation of volatile low molecular weight material as a result of chain scission and release of CO<sub>2</sub>. The etching rate in the afterglow was approximately 30-35 times lower than in the glow. The decrease of the etching rate in the afterglow is comparable with the retardation of the chemical changes (30 times). This resemblance indicates that the etching rate of LDPE in a CO<sub>2</sub> plasma is also determined by radicals. Sputtering of the surface by ions or electrons in the glow has negligible effect. The sputter rate of LDPE in an argon plasma has previously been determined [3]. The overall etching rate in an argon plasma is about 6 Å/min while the rate in a CO<sub>2</sub> plasma is 357 Å/min (table 1). This large difference can only be explained by additional chemical etching of LDPE in a CO<sub>2</sub> plasma.

**Table 1.** Determination of the etching rate and the thickness of the insoluble surface layer of plasma treated LDPE films.

procedure	time	etching rate <sup>a</sup> (Å/min)	D <sup>b</sup> (Å)
Glow	500 s	357	5000
Afterglow	3.5 hr	<10 <sup>c</sup>	100

a Etching rate determined gravimetrically (e.g., weight loss determination).

b Thickness of the crosslinked layer measured by extraction of LDPE films in boiling toluene

c The weight loss was too low to determine the etching rate very accurately.

Comparing the rate of formation of the different functional groups found, after derivatization, it can be seen that the first groups which are introduced, are hydroxyl/epoxide groups. In a later stage ketone and aldehyde groups are formed, while in the last stage carboxylic acid groups are generated. Abstraction of hydrogen from the polymer backbone by an oxygen radical is assumed to be the first, rate determining step in the modification process. The generated radical site can react quickly to hydroxyl or hydroperoxide groups. After reaction of a radical site on the LDPE chain with an oxygen radical, subsequent abstraction of a hydrogen atom next to the formed oxygen containing radical chain can result in fast formation of an epoxide groups by recombination of these two radical chain parts. Chain scission leads directly to the formation of aldehyde groups. In a subsequent reaction with another oxygen radical carboxylic acid groups are formed. The last stage in the progressive oxidation is the release of CO<sub>2</sub>. Especially in latter stages of the oxidation process recombination of radical chain parts results in the formation of ether and ester groups.

Recently our group has presented a model for the observed kinetics of CO<sub>2</sub> plasma treatment of PE in the glow [2]. This model consisted of a (pseudo) zero order oxygen incorporation (starting with hydrogen abstraction) and a first order etching component. The simple kinetic model fits the observed kinetics well except for the incorporation of hydroxyl/epoxide groups. The observed maximum (fig. 4) could not be explained by this model. From fig. 4 and 6 it can be seen that the occurrence of the maximum in the fluorine concentration coincides to the formation of carboxylic acid groups. Since epoxide groups are expected on the surface a reaction of these groups with carboxylic acid groups may occur. The reaction between these two groups becomes significant when sufficient carboxylic acid groups are formed. Because the formation of carboxylic acid groups is slower than the formation of epoxide groups a maximum in the epoxide concentration is expected. This results in a maximum in the fluorine concentration after TFAA derivatization.

Although the introduction of functional groups in the glow is completely determined by radicals, UV causes already after 500 s of treatment crosslinking of a 5000 Å thick surface layer of the LDPE films (Table 1). In the afterglow even after a 25 times longer treatment time only a small amount of insoluble material was found which can either be oxidized material, or a shallow chemically crosslinked layer. Crosslinking of LDPE chains starts just as well as the oxidation of LDPE with the abstraction of hydrogen from the polymer backbone. The fact that the plateau values of the incorporated oxygen and functional groups are exactly the same in both treatment procedures means that the zero order incorporation and the first order etching component in the mathematical model must have the same ratio in both treatment procedures. Significant contribution of UV in initial hydrogen abstraction and the following oxygen incorporation would lead to a change of these ratios and therefore to a higher oxidation level. UV radiation (and also ion or electron bombardment) has only a minor contribution in the rate determining reaction step (abstraction of hydrogen) of the oxidation process

### Conclusions.

CO<sub>2</sub> plasma treatment of LDPE results in a surface containing hydroxyl/epoxide groups, ketone/aldehyde groups, and carboxylic acid groups. Most likely also ether and ester groups are formed on the surface. The oxidation during CO<sub>2</sub> plasma treatment is completely determined by radical species. U.V radiation in the glow region causes a crosslinking of a rather thick surface layer (5000 Å).

### References

- [1]. D.T. Clark, and A. Dilks, *J. Pol. Sci.*, 16, 911-936 (1978).
- [2]. J.G.A. Terlingen, H.F.C. Gerritsen, A.S. Hoffman, and J. Feijen, *J. Appl. Polym. Sci.*, in Press (1995).
- [3]. J.G.A. Terlingen, A.S. Hoffman, and J. Feijen, *J. Appl. Pol.Sci*, 50, 1529-1539 (1993).
- [4]. G.A.J. Takens, J. Terlingen, and J. Feijen, 11th International Symposium on Plasma Chemistry, 3, 1236-1241, (1993).
- [5]. A. Chilcoti, B.D. Ratner, and D. Briggs, *Chem. Mat.*, 3, 51-61 (1991).