Functionalization of UHMW poly(ethylene) membranes by a carbon dioxide plasma treatment.

J.G.A. Terlingen, M. ter Beek, J. Feijen

Department of Chemical Technology and Institute of Biomedical Technology, University of Twente, P.O. Box 217, 7500 AE, Enschede, The Netherlands.

Abstract

Ultra high molecular weight (UHMW) poly(ethylene) (PE) membranes were modified with a low pressure (cold) radiofrequent carbon dioxide plasma treatment to introduce functional groups on their surface and to improve their water permeability. To prevent morphological changes on the membranes a pulsatile plasma treatment was necessary. The complete surface of the membrane was modified by the plasma treatment, although the facial (external) surface was modified faster than the internal surface. The water permeability was greatly increased by the plasma treatment.

Introduction

For biomedical and biotechnological applications immobilized enzymes on polymer supports are of increasing interest. In order to have a high density of immobilized enzymes, which is a necessity for some biotechnological applications, the polymer support must have a large specific surface area on which the enzymes can be immobilized. Membranes have inherently a large specific surface area due to their porous structures and thus offer opportunities for this type of enzyme immobilization.

For the immobilization of enzymes several demands concerning the surface chemistry can be formulated. Firstly the surface must contain sufficient functional groups, like e.g. carboxylic acid groups, which can be used for covalent coupling. Covalent coupling of the enzymes is required to prevent enzymes from leaking away from the surface. Furthermore the surface needs to be hydrophilic to prevent denaturation and thus loss of enzymatic activity of the immobilized enzymes. Especially for immobilized enzymes on membranes the surface hydrophilicity has a beneficial secondary effect; the membrane can be easily wetted by aqueous solutions. This enhances the ease of use considerably.

In this article the use of biaxially drawn UHMW PE membranes for enzyme immobilization is investigated. These membranes have good mechanical properties and a large internal surface (typically 18 m^2/g). However these membranes are quite hydrophobic and lack the presence of functional groups on the surface, which can be used for further covalent coupling. Therefore we investigated the use of a plasma treatment to introduce functional groups on the surface. Based on previous work [1] in which a carbon dioxide plasma treatment was used to introduce different oxygen containing functional groups on low density PE, a carbon dioxide plasma treatment was selected for the membrane modification.

Several aspects have been investigated. Firstly whether it is possible to modify a delicate structure like a biaxially drawn microporous membrane with a

plasma without changes in the membrane structure. Furthermore whether the whole membrane surface or only part of the surface is modified. In this study the modification of the membrane is separated in modification of the facial surface, and modification of the internal surface. The modification of the facial surface is probed with XPS and derivatization XPS. In this method prior to the XPS analysis a specific gas phase reaction is applied on one type of functional group. This reaction introduces a tag element e.g. fluorine on the surface which can be detected and quantified by XPS measurements [2,3]. The modification of the internal surface is analyzed by a specific experimental set-up and by water flux measurements.

Experimental

Materials

Biaxially drawn UHMW PE membranes (type B3C2, thickness 20 μm, porosity 80 %) and high density (HD) PE films (type 6751F, thickness 20 μm) were obtained from DSM (Geleen, The Netherlands). Dichloromethane (purity >99.5 %), acetone (purity >99.5 %), 2,2,2-trifluoroethanol (TFE) (purity >99 %), 2,2,2-trifluoro-acetic acid anhydride (TFAA) (purity >99 %) were obtained from Merck (Darmstadt, Germany). N,N-di-tertiar-butylcarbodiimide (purity 99 %) and hydrazine monohydrate (N_2H_4) (purity 99 %) were obtained from Aldrich Chemie (Steinheim, Germany). Carbon dioxide (purity $\geq$99.995 %) was obtained from Hoekloos (Schiedam, The Netherlands). All chemicals were used without further purification. Doubly deionized water was used in all experiments.

Cleaning of UHMW PE membranes and HDPE films.

UHMW PE membranes and HDPE films were ultrasonically cleaned in dichloromethane for 10 min. Fresh dichloromethane was added and the procedure was repeated. The total cleaning procedure consisted of 4 times treatment with dichloromethane, 4 times with acetone and 4 times with water. Subsequently the films were dried in vacuo at room temperature and stored.

Plasma treatment.

An extensive description of the plasma treatment system has been given previously [4]. In brief the plasma treatment 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 treatment procedure is as follows. The samples to be treated were placed in the center region of the reactor and evacuated (to 0.01 mbar). Subsequently a CO_2 flow of 10 cm^3/min. (standard temperature and pressure) was established through the reactor. After 10 min. the samples were plasma treated (90 W, 0.04 mbar, different treatment times). After the plasma treatment the samples were evacuated for 2 min. under flow. The reactor was then brought to atmospheric pressure with air and the samples were taken out.

XPS Analysis.

XPS analysis was performed with a XSAM-800 spectrometer (Kratos, Manchester, Great Britain) using a Mg K_a source (15 kV, 15 mA). The analyzer was placed perpendicular to the sample surface and a spot size of 3 mm was used.

Derivatization XPS

Detection of different functional groups was performed by using derivatization XPS. Detailed description of the followed procedures are given elsewhere [1]. The amount of hydroxyl/epoxy groups was quantified by using a gas phase reaction with TFAA and by determining the amount of fluorine introduced on the surface by XPS [5,6]. By using the appropriate stochiometry factors and reaction yields the amount of hydroxyl/epoxy groups on the surface, expressed as the fraction of oxygen introduced at the surface, can be calculated [1]. The amount of ketone/aldehyde groups was quantified by a reaction with N_2H_4 [5,7] and the amount of carboxylic acid groups by a reaction with TFE (using N,N-di-tertiair-butylcarbodiimide as an activating agent) [4,5].
Water flux measurements.
A membrane with a diameter of 45 mm was weighted and placed in a stirred cel of 80 ml (Spectrum, Houston, Texas, USA). The time in which 10 ml of water permeates through the membrane was measured. The measurements were performed at room temperature with a pressure difference of 1.5 bar over the membrane.

Results and discussion

Plasma treatment of biaxially drawn UHMW PE membranes.

When biaxially drawn UHMW PE membranes were treated with a continuous CO_2 plasma for more than 0.5 s, macroscopic shrinkage of the membrane was observed. This shrinkage was confirmed by electron microscopy (data not shown) and is caused by heating of the polymer surface by the plasma treatment. From DSC (differential scanning calorimetry) measurements it was concluded that the shrinkage was not due to melting of the fibrous structure of the membranes. The temperature of the membrane during the plasma treatment does not reach the melting temperature (144 °C). The shrinkage is probably due to relaxation of stretched amorphous chains, which occurs at a lower temperature.

To prevent the membranes from shrinking, the plasma treatment time was reduced to pulses of 0.1 s plasma with 1 s rest between two pulses. By using this modification procedure the membranes could be plasma treated with retention of the membrane structure as was shown with electron microscopy (data not shown). Furthermore the specific surface area (typically 18 m^2/g) and the maximum pore size (1.6 μm) were not altered by the plasma treatment. Only after longer (accumulate) plasma treatment times (typically 100 s = 1000 pulses) the fibres and the fleeces between the membranes were affected due to the etching character of the plasma treatment. The fibres became 'sponge like' and the fleeces almost completely disappeared. The 'sponge like' character of the fibres is caused by the faster etching of the amorphous phase compared to the crystalline phase [8,9].

Modification of the facial membrane surface.

The modification of the facial (external) surface of the UHMW PE membranes was investigated by XPS analysis. From Fig.1. it can be concluded that the oxidation of the surface increases with increasing plasma treatment time and that it levels out at an accumulative treatment time of 5 s. At this stage the surface chemistry reaches a steady state resulting from the equilibrium between an oxidation and an etching process. The rate limiting step in the oxidation is assumed to be the

(pseudo) zero order process of abstraction of hydrogen from the polymer backbone [1]. This abstraction is probably caused by oxygen radicals. The second process is the first order etching of oxygen containing groups [1]. In this process the final product is carbon dioxide. This process leads to the loss of oxygen from the surface. The mathematical description for the kinetics of a CO_2 plasma treatment is given elsewhere [1]. From Fig. 1 it can be seen that this simple kinetic model fits well over 3 orders of plasma treatment times.

By applying derivatization XPS some insight in the surface chemistry at the plateau level (100 pulses) is obtained. The carboxylic acid groups are reacted with TFE and after reaction 3.5 % fluorine was observed on the surface. Considering the appropriate stochiometry and a reaction yield of 100 %, it can be calculated that approximately 11 % of the oxygen on the surface is present as carboxylic acid groups. Especially carboxylic acid groups are suited for further covalent coupling of bioactive molecules e.g. by well known carbodiimide chemistry. Hydrazine monohydrate was used for the tagging of aldehyde/ketone groups. After tagging 4.5 % nitrogen is observed. This corresponds to an aldehyde/ketone concentration of 15 % of the oxygen present. Also the amount of hydroxyl/epoxide groups was probed by tagging these groups with TFAA. After reaction 5.5 % fluorine was observed on the surface, which corresponds to an hydroxyl/epoxide concentration of 9-5 % of the oxygen present. This uncertainty in the amount introduced is due to the fact that no discrimination between epoxide and hydroxyl groups can be made by this reaction. The range given here is based on the maximum values when only hydroxyl groups are introduced (9 %) or when only epoxide groups are used (5 %). The rest of the oxygen is presumably involved in other oxygen containing functionalities like peroxide, ether and ester groups [10,11].

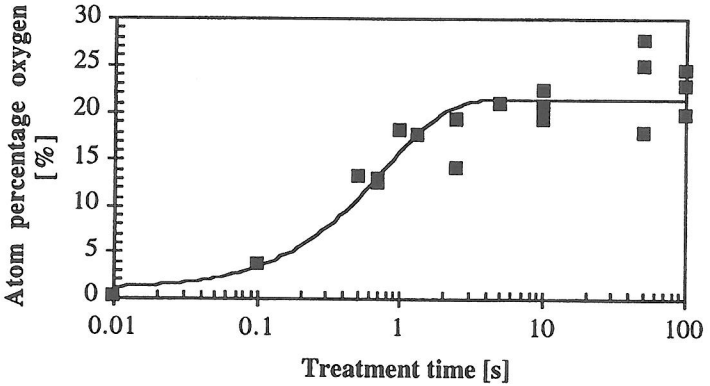

Figure 1: Oxidation of the UHMW PE membrane surfaces with a carbon dioxide plasma treatment. The amount of oxygen measured with XPS is given as a function of the accumulative plasma treatment time. The line is the best fit for the model consisting of two components: a zero order oxygen introduction and a first order oxygen etching process [1].

Modification of the internal membrane surface.

The modification of the internal membrane surface was studied by two indirect methods. In the first method the UHMW PE membrane was sealed on a HDPE

film. This device was plasma treated and subsequently the UHMW PE membrane was removed and the covered side was analyzed with XPS. When this side is oxidized then the total membrane surface must be oxidized. In Fig. 2 the results of the XPS analysis of plasma treated HPDE and of plasma treated covered HDPE films are given. From this figure it can be concluded that the covered HDPE films are indeed oxidized after a treatment time of 100 s (1000 pulses). The oxidation level of the covered HDPE films is lower than of the uncovered films. Furthermore the oxidation of

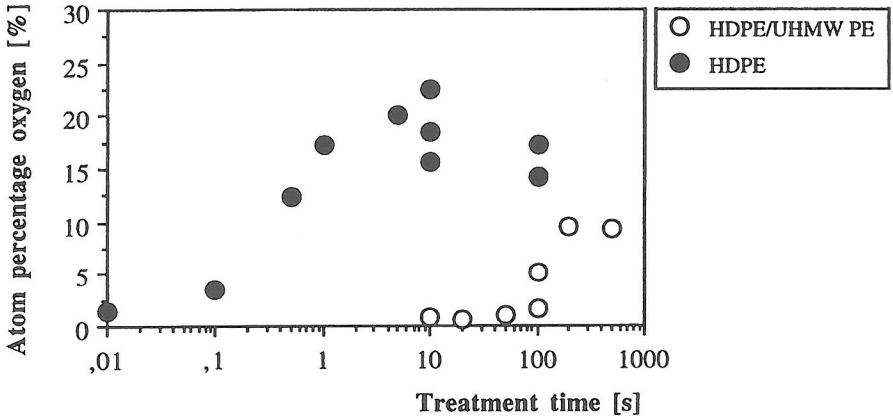

Figure 2: Plasma treatment of HDPE films and of HDPE films which were covered by a UHMW PE membrane during the plasma treatment (HDPE/UHMW PE). The amount of oxygen introduced on the surface, measured with XPS, is given as a function of the accumulative plasma treatment time. The covered side of the HDPE film, after removal of the UHMW PE membrane is analyzed.

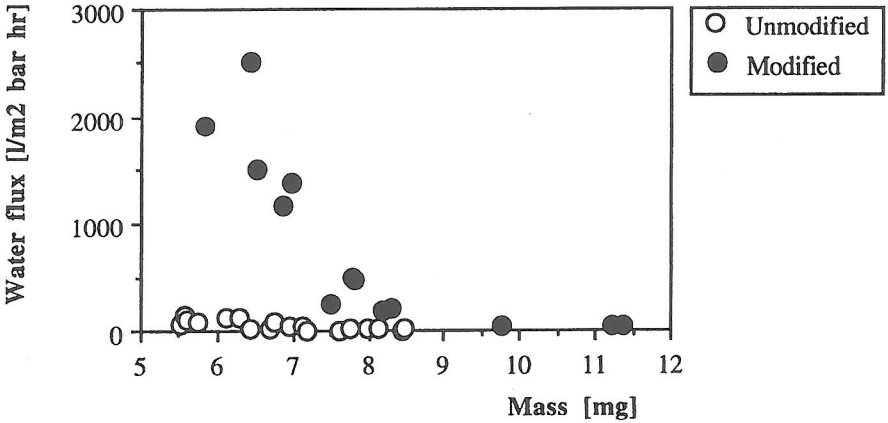

Figure 3: Water flux measurements on plasma treated and untreated UHMW PE membranes. Because the membranes vary in thickness, the water flux is given here as a function of the membrane weight. The membranes were plasma treated for 100 pulses (accumulative treatment time 10 s).

the covered films is retarded (approximately 100 times) compared to the uncovered films. From the fact that the covered films are oxidized it can be concluded that the internal membrane surface is modified. It should however be noted that at a treatment time of 100 s also some morphological changes are observed on the membrane. From the fact that the oxidation level of the covered film is less than that of the uncovered films it can be concluded that most likely a gradient in oxidation exists over the membrane. The facial surface has a higher oxidation level than the internal surface.

The second indirect method for the determination of the modification of the internal membrane surface is water flux measurements. The water flux for unmodified and modified membranes with different thicknesses (and thus weights) are measured. From Fig. 3 it can be seen that the unmodified membranes are hardly permeable for water, but that most of the modified membranes are very permeable. The water flux for these membranes are orders higher. Furthermore it can be seen that the permeability decreases with increasing thickness (weight). Most likely this effect is caused by the oxidation gradient over the membrane for thicker membranes. Although the facial surface and part of the internal surface is modified, the center region of the membrane may still be unaffected by the plasma treatment at relatively short times (10 s). This causes a drastic decrease in the water permeability.

Conclusion

Biaxially drawn UHMW PE membranes can be successfully oxidized by a pulsatile CO_2 plasma treatment. At the facial surface different oxygen containing functional groups were detected; hydroxyl/epoxide, ketone/aldehyde and carboxylic acid groups. These groups can be used as a chemical handle for further covalent coupling of bioactive molecules. Furthermore by the CO_2 plasma treatment also the internal membrane surface is oxidized. This was shown by the oxidation of HDPE films which were covered during the plasma treatment with a UHMW PE membrane. The oxidation of the internal membrane surface drastically increased the water permeability.

Acknowledgements

The authors thank DSM (Geleen, The Netherlands) for financial support for this research.

References

[1] J.G.A. Terlingen, H.F.C. Gerritsen, A.S. Hoffman, J. Feijen, J. Appl. Polym. Sci., in press (1995).
[2] D. Briggs, Chapter 9 in: Practical Surface Analysis, Vol. 1: Auger and X-ray Photoelectron Spectroscopy, eds.: D. Briggs and M.P. Seah, John Wiley & Sons, Chichester (1990).
[3] C.N. Reilley, D.S. Everhart and F F.-L. Ho, Chapter 6 in: Applied Electron Spectroscopy for Chemical Analysis, eds.: H. Windowi and F.Ho, J. Wiley & Sons, New York (1982).
[4] J.G.A. Terlingen, A.S. Hoffman, J. Feijen, J. Appl. Polym. Sci., **50**, 1529 (1993).
[5] A. Chilkoti, B.D. Ratner and D. Briggs, Chem. Mater., **3**, 51 (1991).
[6] A. Chilkoti, B.D. Ratner, Surf. Interface Anal., 17, 567 (1991).
[7] L.J. Gerenser, J.F. Elman, M.G. Mason and J.M. Pochan, Polymer, **26**, 1162 (1985).
[8] J. Friedrich, J. Gähde, H. Frommelt and H. Wittrich, Faserforsch. u. Textiltechnik/Z. Polymere, **27**, 604 (1976).
[9] J. Friedrich and J. Gähde, Acta Polym., **31**, 52 (1980).
[10] F. Poncin-Epaillard, B. Chevet and J-C. Brosse, Eur. Polym. J., **26**, 333 (1990).
[11] F. Poncin-Epaillard, B. Chevet and J-C. Brosse, Makromol. Chem., **192** 1589 (1991).