

Chapter 10

Plasma Modification of Polymer Surfaces and Plasma Polymerization

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Abstract An ionized medium consisting of electrons, ions and possibly of neutrals and photons, which meets some additional criteria, is called a plasma. According to this definition, the term plasma covers a wide range of phenomena. Low pressure plasmas, as discussed here, are universal tools for surface treatment. Depending on the process parameters and the process gas material loss or material deposition can predominate. In the intermediate case a shallow surface layer is modified with respect to its chemical and/or physical properties.

In the first part of this chapter low pressure plasma surface modification of polymeric materials is discussed. The second part introduces the deposition of thin polymer films by means of plasma polymerization.

10.1 Plasma Modification of Polymer Surfaces

10.1.1 Why Use Low Pressure Plasma?

Advantages

- Elementary processes with high activation energies of several electron volts are possible in low pressure plasmas without elevated gas (ion, neutral) temperatures. There is almost no thermal load for sensitive polymer materials during low pressure plasma treatment.
- While the chemical structure of a shallow surface layer can be changed significantly, the bulk properties remain unchanged.
- An extremely wide range of surface modifications can be obtained with different low pressure plasmas.
- The amount of toxic byproducts is low compared to other methods.

Disadvantages

- Because of the high vacuum necessary, low pressure plasma applications are quite expensive.
- Due to the multitude of elementary reactions occurring simultaneously, it is impossible in most cases to calculate in detail the physical and chemical behavior of a plasma. This applies especially to plasma–surface interactions.
- It is difficult to restrict the variety of functional groups formed in a plasma treatment to a well defined set of species.
- Scaling up a plasma process from laboratory size to industrial dimensions is far from a straight forward procedure.
- It is difficult to replace batch processes by continuous processes (air to air processes).

10.1.1.1 How to Overcome These Problems

- The high expenses for plasma equipment will decrease when this technique becomes more popular, especially in industry scale applications. On the other hand, the costs for wet chemistry processes will exceed those for plasma processes with higher waste disposal expenses.
- The increasing power of computer systems allows nowadays the creation of complex models to predict real plasma processes. Especially with the use of Monte Carlo codes, an adequate treatment of a wide range of elementary processes in the plasma volume, the plasma sheath and the surface region can be done. Nevertheless, there is a significant lack of necessary input values like rate constants, cross-sections and sticking coefficients.
- With a better knowledge of elementary processes, especially at the polymer surface, the choice of process parameters will become less empirical. This also covers the problem of a poor selectivity of plasma processes with regard to the range of formed species. Another approach to a more uniform surface chemistry is to combine the plasma process with pre or post plasma treatments.
- A solution for problems related to reactor scaling will become available with future progress in simulation techniques. In contrary, the problem of continuous air to air plasma processing of polymers is a more serious one. There is a strong contradiction of the polymer inherent outgasing tendency and the requirement of a clean process. This will possibly restrict the application of more sophisticated plasma treatments to batch processes with limited material throughput.

10.1.2 How to Apply Low Pressure Plasma

10.1.2.1 Plasma Parameters

When a polymer is immersed into a plasma the interaction processes are governed by internal plasma parameters.

- Type of species present in the plasma
- Spatial distributions
- Energy distributions
- Directional distributions

The internal plasma parameters are determined in a complex way by external plasma parameters (process parameters, accessible for the user).

- Reactor geometry
- Type of excitation
- Applied power
- Process gas
- Gas pressure
- Gas flow

Consequently, for a given application, a specific reactor design and an appropriate set of process parameters are necessary.

10.1.2.2 Plasma Generation and Reactor Design

For plasma generation on a laboratory scale electrical gas discharges are used. An AC excitation is necessary for the treatment of insulating materials like polymers. The most popular excitation frequencies are in the radio frequency (RF) and the micro wave (MW) range. In the case of MW excitation an additional magnetic field can be applied to meet the criterion for electron cyclotron resonance (ECR):

- The setup for RF excitation is the most simple one. In the case of a capacitively coupled RF discharge two electrodes are mounted into a vacuum chamber. A process gas with a typical pressure of a few pascal is introduced. When the RF voltage exceeds a certain value the discharge ignites. This value is generally within the range of some hundred volts depending on gas, pressure and reactor geometry.
- In the case of MW excitation no electrodes are necessary. A higher degree of ionization is achieved for MW discharges in general and especially for MW-ECR discharges. The use of the ECR effect is restricted to pressures < 1 Pa. A setup with a MW excitation is more complicated and more expensive compared to one using RF.

For a given type of plasma excitation, the position of the sample in the reactor volume is an important parameter. This applies to the surface modification of polymers and especially to the case of plasma polymerization discussed below:

- When the sample is placed directly in the excitation volume of the discharge, there is a relatively high flux of active particles to the treated surface. Moving the sample away from the discharge (remote plasma position, afterglow) decreases the flux and restricts the variety of active particles to long-living species. Depending on the reactor geometry, the sample can be shielded from the action of vacuum ultraviolet radiation.
- In the case of capacitively coupled RF discharges significant self bias voltages can appear at the treated surface when the sample is placed on the powered electrode. This leads to high ion energies up to several hundred electron volts.

10.1.2.3 The Variety of Effects

During low pressure plasma treatment a shallow surface layer of the polymer of some 10 nm is modified due to the action of energetic particles and vacuum ultraviolet radiation. The surface modification can be understood as a dynamic equilibrium of competing functionalization and degradation processes.

There are effects, common to almost all plasma processes, such as hydrogen loss and overall material ablation. Other effects are characteristic for the specific type of plasma, such as the introduction of functional groups containing foreign atoms. To illustrate the complexity of plasma surface modification, some experimental observations are given here:

- Low pressure plasma treatment usually leads to the simultaneous formation of different functional groups (e. g. carbonyl and hydroxyl groups in an oxygen discharge).
- Functional groups formed in a plasma treatment can migrate to the subsurface. As a result, the number of accessible functional groups may decrease over time.
- Stable radicals formed at the polymer surface can cause post plasma reactions on different time scales.
- A plasma treatment can cause graphitization of a polymer surface, which strongly affects the electrical conductivity.

All these effects and many others depend on the type of plasma and the plasma parameters. A particular effect can be pronounced or suppressed by an appropriate choice of the experimental conditions. For that purpose, a set of diagnostic techniques is necessary.

10.1.2.4 Diagnostic Techniques

Due to the fact, that the modification effects at the polymer surface can not be derived in detail from the knowledge of external process parameters, the following strategy is used:

- Internal plasma parameters are measured. When correlations are found between process parameters and internal plasma parameters, surface effects can be predicted at least qualitatively.
- Specific surface effects expected from the behavior of the plasma have to be proved or to be disproved with adequate surface diagnostic techniques.

Table 10.1 Diagnostic techniques (most popular methods mentioned first)

| Plasma diagnostics | Surface diagnostics |
|-------------------------------------|---|
| Langmuir probe diagnostics | X-Ray photoelectron spectroscopy |
| Optical emission spectroscopy | Fourier transform infrared spectroscopy |
| Mass spectroscopy | Contact angle goniometry |
| Energy dispersive mass spectroscopy | Atomic force microscopy |
| Laser induced fluorescence | Fluorescence labelling |
| Calorimetry at catalytic surfaces | Secondary ion mass spectroscopy |
| | Streaming potential measurement |

10.1.3 Examples

In many cases the main purpose of low pressure plasma polymer modification is a more hydrophilic surface. In the initial phase of the plasma treatment the wettability is improved significantly. When the equilibrium between functionalization and degradation (etching) is reached, the value of the contact angle becomes constant (Fig. 10.1).

Due to different reasons (polymer chain mobility, post plasma reactions with the ambient air) the obtained effect is not stable (hydrophobic recovery). However, on a long time scale, most materials remain more hydrophilic than before the plasma treatment (Fig. 10.2).

To avoid the hydrophobic recovery, the plasma-activated surface can be used to graft or to adsorb other polymers immediately after treatment. Here, the adsorption of a polyelectrolyte is shown. As a result, a more hydrophilic and more stable surface modification is obtained (Fig. 10.3).

Fig. 10.1 Static water contact angle of NH₃ plasma treated FEP. Reprinted with permission from [1]

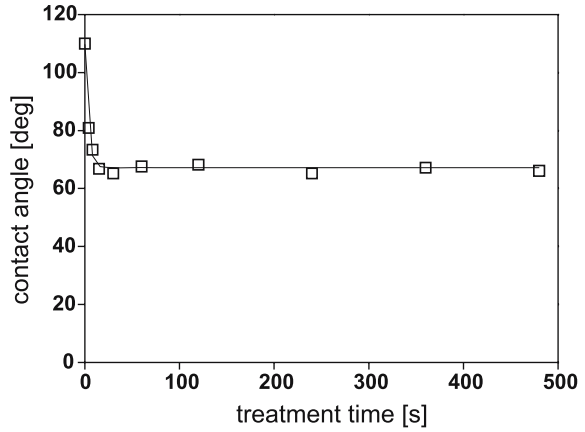


Fig. 10.2 Advancing (solid lines) and receding (dashed lines) water contact angles of NH₃ plasma treated FEP (squares) compared to untreated FEP (circles). Reprinted with permission from [1]

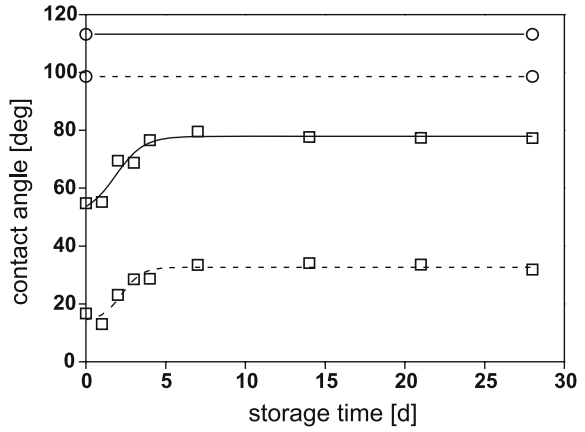
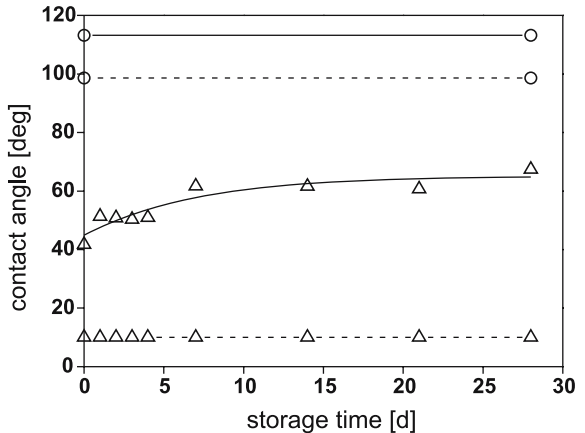


Fig. 10.3 Advancing (solid lines) and receding (dashed lines) water contact angles of NH₃ plasma treated and poly(sodium 4-styrenesulfonate) exposed FEP (triangles) compared to untreated FEP (circles). Reprinted with permission from [1]



In other applications, the purpose of low pressure plasma treatment is to provide a particular type of functional group on the polymer surface. In this case more sophisticated surface sensitive analytical techniques are necessary. For semi-quantitative results Fourier transform infrared (FTIR) attenuated total reflection (ATR) spectroscopy can be applied. Quantitative results can be obtained by X-Ray photoelectron spectroscopy combined with labelling techniques (Figs. 10.4–10.7).

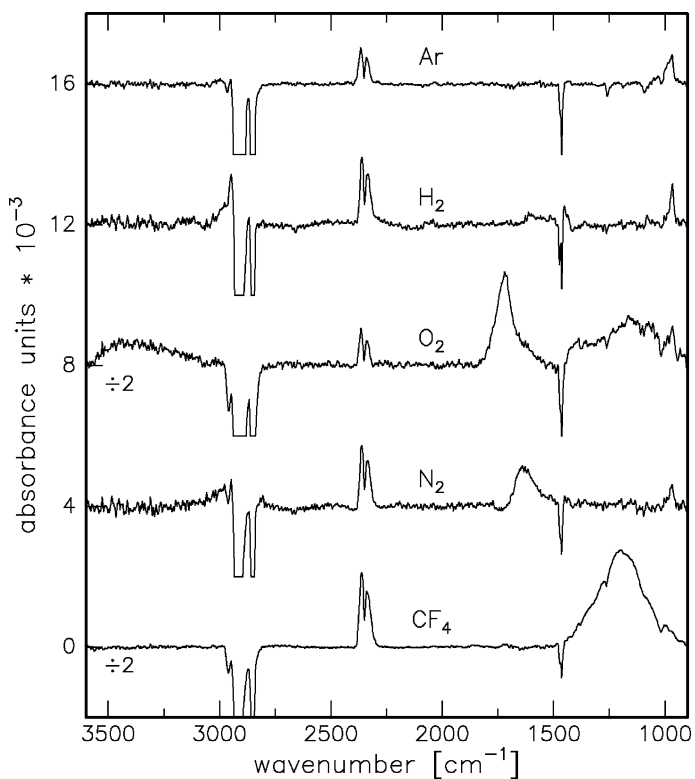


Fig. 10.4 FTIR-ATR difference spectra for the treatment of polyethylene in Ar, H_2 , O_2 , N_2 and CF_4 plasmas. Reprinted with permission from [2]

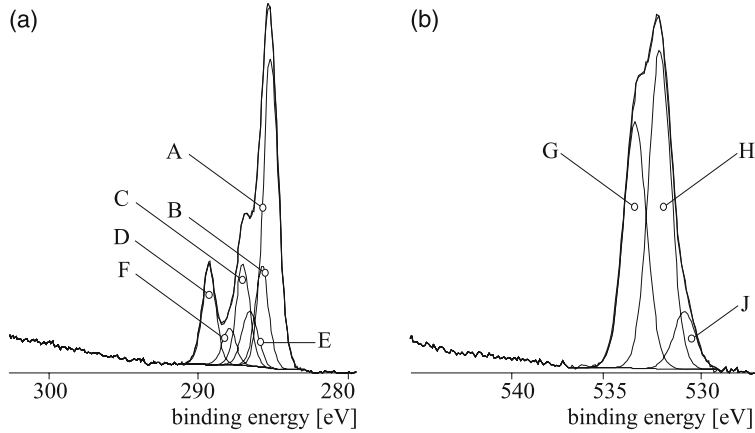
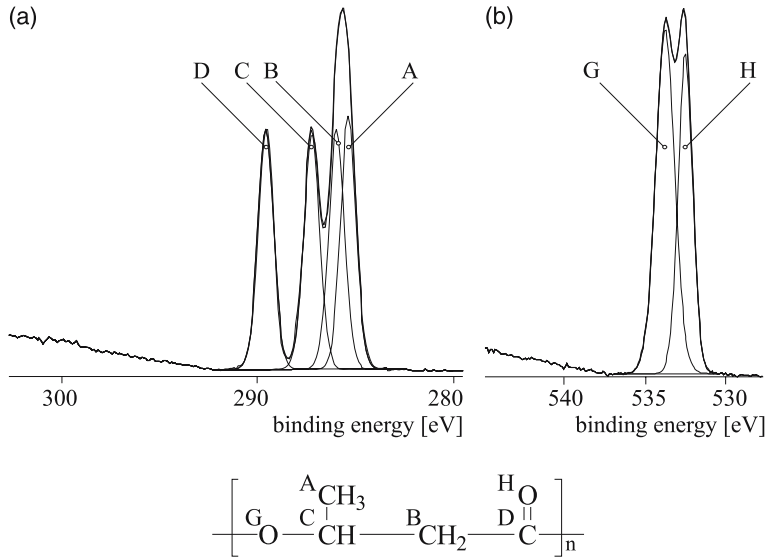


Fig. 10.5 XPS C_{1s} and O_{1s} spectra of poly (3-hydroxybutyrate) before (top) and after NH₃ plasma treatment (bottom). Reprinted with permission from [3]

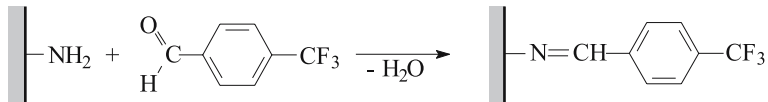


Fig. 10.6 Labelling of NH₂ groups with trifluoromethyl benzaldehyde (TFBA)

Fig. 10.7 Total nitrogen content (squares) and nitrogen in NH_2 groups (circles) after plasma treatment as determined by XPS and TFBA labelling. Reprinted with permission from [3]

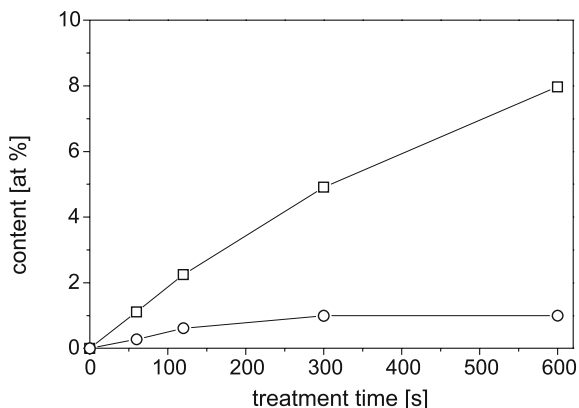


Table 10.2 Examples of polymer surface modification by low pressure plasma

| Plasma | Application |
|---|--|
| Ar, He, H_2 | Surface cross-linking, generation of radicals for grafting processes, plasma immobilization of pre-deposited molecules or thin films |
| O_2 , CO_2 , H_2O | Improvement of the wetting behavior, generation of $\text{C}=\text{O}$, $\text{O}-\text{H}$, etc. |
| NH_3 | Improvement of the wetting behavior, generation of NH_2 groups |
| CF_4 | Fluorination |

10.2 Plasma Polymerization

10.2.1 Why Use Plasma Polymerization?

Electrical gas discharges can initiate monomers to form polymeric products. When a low pressure plasma is operated under appropriate conditions with a substance like styrene or acrylic acid as a process gas, the formation of thin polymer films on the reactor walls is observed. This effect is called plasma polymerization.

The concept of atomic polymerization (one of the proposed mechanisms for plasma polymerization) suggests, that the elemental reactions are the fragmentation of monomer molecules, the formation of radical sites and the recombination of the activated fragments (in the gas phase as well as in the growing film).

According to this concept, plasma polymerization is not restricted to unsaturated monomers as used in conventional polymerization. This was proven in many experiments with process gases consisting of saturated organic molecules. For example, plasma polymerization leads to similar results when a unsaturated monomer is replaced by its saturated counterpart.

Advantages

- The variety of organic substances that can serve as a monomer makes plasma polymerization an extremely versatile tool for the deposition of polymeric thin films.
- Functional groups of the monomer can be transferred into the plasma polymer film.
- Due to the adjustable degree of cross-linking, plasma polymers can have exceptional mechanical properties.
- Plasma polymers can be prepared as thin as a few nanometres while the films are pin hole free and have good adhesion to most substrates.
- Vertical gradients of the film properties can be obtained by changing the process parameters *during* the deposition process.

Disadvantages

The major disadvantages of plasma polymerization are the same as those mentioned for low pressure plasma surface modification.

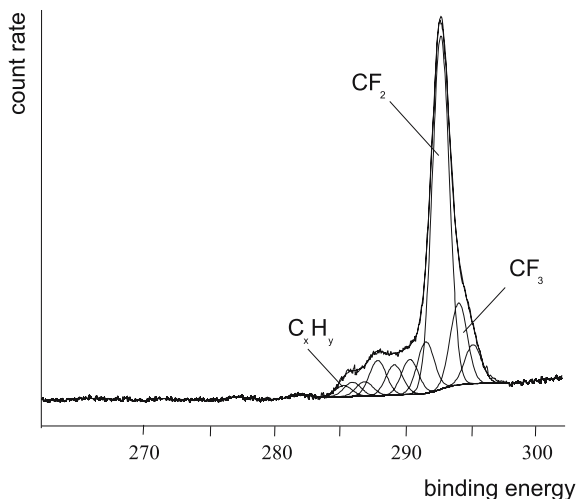
10.2.2 *How to Apply Plasma Polymerization*

A number of process parameters allows to adjust the deposition rate and the properties of the obtained thin film:

- Depending on the monomer, hydrocarbon, fluorocarbon or silicon organic films can be fabricated. The process gas can be either a pure monomer gas or a small amount of monomer mixed with a carrier gas (e. g. argon).
- Pressure and flow rate of the process gas are essential parameters to control plasma polymerization. The deposition rate passes through a maximum when a monomer sufficient regime is gradually shifted into a monomer deficient regime.
- The applied power determines the degree of fragmentation of the process gas. This can change the properties of the obtained polymer film over a very wide range. For example, the film obtained by plasma polymerization of hexamethyldisiloxane can vary from a low molecular weight silicone polymer to silicon oxide depending on the applied power.
- The structure of the obtained film can be altered significantly when the position of the substrate is changed from inside the plasma excitation volume to a remote position in the outward gas flow. This is due to gas phase reactions of activated species and differences with respect to flux and energy of ions hitting the growing film. Beyond that, a remote substrate position can be shielded from high energy vacuum ultraviolet photons emitted by the plasma.
- Flux and energy of the ion bombardment at the substrate position can be changed by electrical potentials (bias voltages). This allows to control the deposition rate and the structure of the plasma polymer film.

10.2.3 Example

Fig. 10.8 XPS C_{1s} spectrum of a plasma polymer film obtained from a RF discharge operated with a mixture of argon and C_2F_4 . Contrary to most plasma polymers, the film has a structure close to PTFE, characterized by a low degree of cross-linking. Reprinted with permission from [4]



10.3 Recommended Literature

There is a huge amount of literature on low pressure plasma techniques. Some text books and review articles are recommended here. The book by Chapman [5] gives an easy to read introduction to low pressure plasma (DC, RF). Microwave plasmas are discussed in detail in the book by Ferreira and Moisan [6]. Selected techniques of polymer surface modification and characterization are presented by Chan [7, 8]. By comparison, the book by Sabbatini and Zambonin [9] covers a wider range of techniques but it is not exclusively dedicated to plasma induced surface effects. Briggs and Seah [10] give a general introduction to X-Ray photoelectron spectroscopy (XPS) while the book by Beamson and Briggs [11] addresses the specific problems of XPS polymer characterization. Beyond XPS, infrared (IR) spectroscopy is one of the most popular techniques to study plasma modified polymer surfaces. The book by Garton [12] is an excellent introduction to this method. Among the surface sensitive IR sampling techniques attenuated total reflection (ATR) is especially important. This subject is covered in depth by Harrick [13]. General introductions to plasma polymerization are given by d'Agostino, Biederman and Inagaki [14–16].

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