LOW PRESSURE PLASMA POLYMER MODIFICATION FROM THE FTIR POINT OF VIEW

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Low pressure plasma treatment of polymers is a widely used process to improve surface properties. While x-ray photoelectron spectroscopy (XPS) is the most popular tool to detect chemical changes in the modified surface layer, this paper will focus on the specific advantages of fourier transform infrared (FTIR) spectroscopy as an approach to the diagnostic of low pressure plasma polymer modification. The interactions of selected model polymers (polyethylene, polystyrene) with radio frequency (RF) discharges in argon, hydrogen, oxygen, nitrogen and tetrafluoromethane were investigated. Infrared reflection absorption spectroscopy (IRRAS) and thin film attenuated total reflection (ATR) allow to detect *in situ* surface modifications from plasma treatments of less than one second. The potential of gas phase chemical derivatization as an additional step of the *in situ* FTIR diagnostic is demonstrated. Experiments were performed to understand the contribution of the ion component to the net result of low pressure plasma polymer modification. For this purpose a low energy ion source was operated in the same *in situ* FTIR setup as used for the plasma treatment experiments.

Introduction

Despite many applications in the plasma treatment of polymers, the complex phenomenon of plasma–wall interaction is not understood completely. A large number of elementary processes generates a wide variety of active particles (ions, electrons, radicals, metastable excited species) and vacuum ultraviolet (VUV) radiation. The modification effects at the polymer surface observed as a result of low pressure plasma treatment depend on type, flow rate and energy distribution of the incident species. These values are governed by plasma bulk properties as well as by transport mechanisms in the plasma sheath. In RF discharges with a considerable negative self–bias potential due to asymmetric electrode geometry positive ions can gain several hundred electron volts passing the sheath in front of the smaller RF electrode. Depending on the pressure, the transport of neutral particles is dominated by diffusion or thermal flow respectively. The mean free path of VUV photons ranges from mm to cm.

Plasma diagnostic as well as surface characterization is required to understand plasma–polymer interaction. Due to the small penetration depth of all involved processes (less than some 10 nm), XPS is the most frequently used tool for surface investigation. Beyond this, a lot of other sophisticated methods [1] like electron induced vibrational spectroscopy or ion beam techniques were shown to be successful in polymer surface characterization. But only a few reports were given on the surface diagnostic of plasma modified polymers by means of FTIR spectroscopy. The potential of this widely spread method in combination with special preparation and sampling techniques is demonstrated in the following sections.

Experimental

For the investigation of plasma treated polymer surfaces two *in situ* FTIR sampling techniques (IRRAS, see [2] and ATR) were applied. This paper will focus on the results from the more sensitive ATR experiment (Fig. 1). The IR beam of a Bruker IFS66 FTIR spectrometer is directed trough a 45° internal reflection element (IRE) with 17 reflections on each side made of chalcogenide glass IRG 100 [3]. One side of the IRE is coated with an approx. 50 nm thick polymer film using a dip coating technique [4]. The IRE is sealed to a vacuum chamber. Two electrodes (ground opposite the IRE and RF behind the IRE) are separated by a glass tube. The RF electrode is capacitively coupled to a 27.12 Mhz generator.

The polymer film can be sampled from one side by the evanescent wave at the IRE surface (ATR thin film case [5]) while it is plasma treated from the opposite side. In combination with the number of reflections a film thickness of some 10 nm also ensures, that surface effects can be observed without a huge background from the polymer bulk, possibly exceeding the dynamic range of the spectrometer in strong bands. The acquisition of IR spectra during plasma experiments is performed in the following steps. First a background spectrum I_0 of the coated IRE attached to the vacuum chamber is measured. After the plasma treatment the sample spectrum I of the modified polymer film is acquired. The result spectrum, calculated as $\log I_0/I$, shows *only the changes* at the polymer surface. Positive and negative bands correspond to introduced or removed species respectively.

This basic *in situ* experiment can be extended by gas phase chemical derivatization, a technique well known from XPS [6]. After pumping down the chamber, a derivatization agent like hydrazine or trifluoro acetic anhydride (TFAA) is introduced. Functional groups are labeled selectively. Characteristic bands of structures appearing and disappearing during the reaction become visible in the IR spectrum and allow improved interpretation.

To characterize the contribution of the ion component to the net result of plasma treatment a low energy Kaufmann ion source (ISQ40, IOM Leipzig) was adapted to the *in situ* IRRAS setup [2], originally designed to study RF plasma polymer modification. For the ion beam and the RF discharge the ion current and energy distribution were measured with a Hiden plasma monitor for different parameter sets. At selected parameters it was possible to perform *in situ* FTIR studies of polymer modification effects with roughly the same ion dose and ion energy.

Results and Discussion

Fig. 2 shows the result spectra for polyethylene treatment in different plasmas under the same experimental conditions. All bands appearing in the spectra can roughly assigned to the following two groups. There are bands due to processes like hydrogen abstraction, plasma etching and cross–linking, which appear less or more intense in all experiments. Other bands are characteristic for functional groups only formed in a specific plasma.

The most prominent examples from the first group are the negative bands corresponding to CH_2 stretching and scissoring at 2900 cm^{-1} and 1460 cm^{-1} respectively and the absorption of the vinylene group at 980–965 cm^{-1}. After Ar, H_2 and N_2 plasma treatment there are also positive bands in the CH stretching region, which become fully visible after compensation of the negative structures. In the case of H_2 and N_2 experiments a high wavenumber tail already appears without compensation. These bands can be attributed to stretching vibrations of CH_2 groups, shifted due to conjugation, branching or ring strain in cyclic structures. Especially the last process causes shifts in the observed range. In the case of plasma treated polystyrene the appearence of shifted CH_2 characteristic frequencies is even more pronounced (not shown here). The (full) shape of the positive CH_2 stretching bands remaining after compensation, fits well the characteristic shape of some plasma polymerized a:CH structures [7]. This indicates a structural similarity of this material and the surface layer of a plasma modified polymer.

Oxygen, nitrogen and CF_4 plasma treatment causes bands associated with new atoms introduced into the polymer structure. In the case of O_2 plasma the OH stretching band of the (hydrogen bonded) hydroxyl group appears at 3600–3000 cm^{-1}. Additional information on the hydroxyl content gives a derivatization experiment shown in Fig. 3. In the carbonyl stretching region (1850–1690 cm^{-1}, Fig. 2) a wide variety of C=O containing species (ketones, aldehydes esters ...) form a broad band with maximum at 1720 cm^{-1}. The region 1450–1000 cm^{-1} is covered by a large number of overlapping absorptions originating from hydroxyl CO stretching and OH deformation as well as from COC stretching in esters and ethers. The N_2 plasma experiment exhibits one band with center at 1650 cm^{-1}, which can be assigned to C=N structures. There is no evidence for amine groups even in the case of stoichiometric H_2/N_2 plasma. Tetrafluromethane plasma causes strong CF stretching bands at 1400–1000 cm^{-1}. Because of the effective coupling of this vibration especially with the C–C backbone structure of the polymer, it is difficult to distinguish different CF_X species in the infrared spectrum.

Fig. 4 shows a preliminary result from the ion beam experiments. In the case of oxygen the ion beam modification effects are comparable with the effects caused by the RF plasma with respect to type and intensity of appearing IR bands. Future work will ensure a more precise characterization and control of the ion energy distribution in both processes compared in the experiment.

Conclusions

Special preparation and sampling techniques make FTIR spectroscopy a sensitive tool for the *in situ* diagnostic of low pressure plasma polymer modification. It was demonstrated, that even the structural and chemical changes appearing in the first seconds of plasma treatment can be detected. In comparison with photoelectron spectroscopy FTIR techniques allow to study modification effects in the polymer CH structure like the formation of cross–linked surface layers. Gas phase chemical derivatization was shown to be a useful tool to increase the amount of information accessible by *in situ* FTIR techniques. FTIR spectroscopy offers the chance, to perform semi–quantitative *in situ* studies of the ion component contribution to the net result of RF plasma polymer modification.

Acknowledgements

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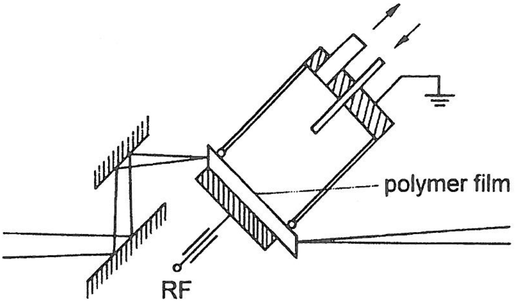

Figure 1: *In situ* ATR setup

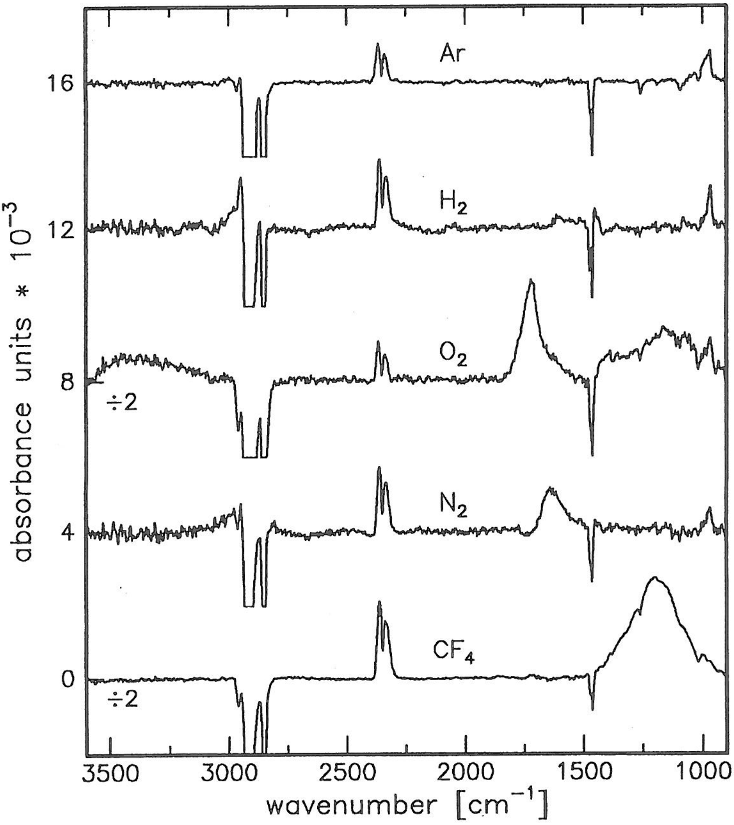

Figure 2: Low pressure plasma modification of polyethylene, all experiments at the same conditions: p = 5 Pa, t = 3 s, *in situ* ATR setup

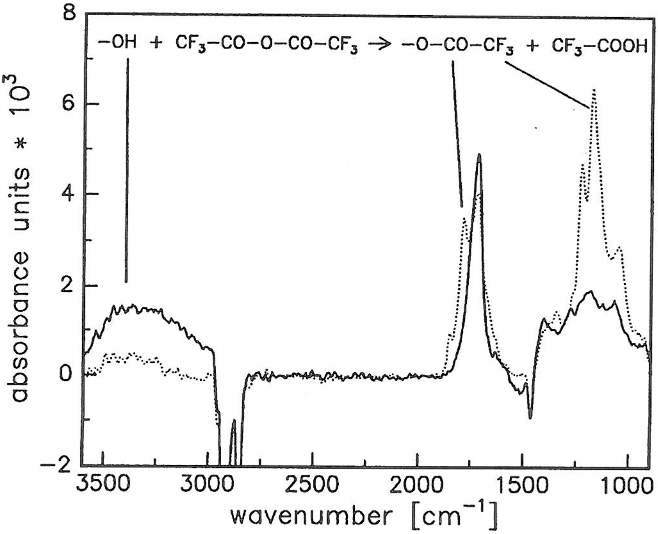

Figure 3: Oxygen plasma modification of polyethylene ($p = 50$ Pa, t = 5 s, solid line) and gas phase chemical derivatization of hydroxyl groups with TFAA ($p = 50$ Pa, t = 5 min, dotted line), *in situ* ATR setup

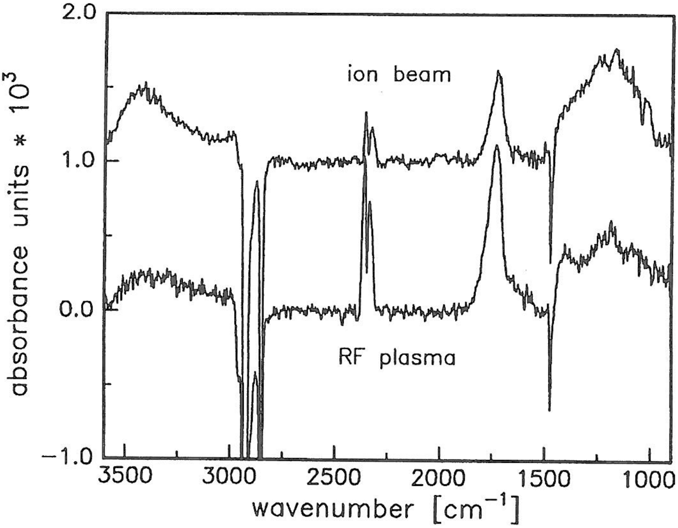

Figure 4: Oxygen plasma modification of polyethylene ($p = 50$ Pa, t = 1 s, compared with low energy ion beam modification ($E = 50$ eV, $t = 5$ s, ion current adjusted to match roughly the ion dose of the plasma experiment), *in situ* IRRAS setup