

***In-situ* FTIR-ATR spectroscopic investigations of atmospheric-pressure plasma modification of polyolefin thin films – where are the primary amino groups?**

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Abstract

Surface treatment of polyolefines by atmospheric-pressure dielectric barrier discharges (DBDs) in virtually oxygen-free nitrogen-containing gases was studied *in situ* by Fourier transform infrared spectroscopy in the attenuated total reflection mode (FTIR-ATR) in order to follow the plasma-chemical generation of chemical functional groups and their further temporal development in the presence of inert or reactive atmospheres.

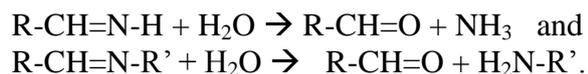
Polyolefin thin films of thicknesses between 50 and 200 nm were prepared directly on ZnS ATR crystals by spin-coating from hot solutions of linear low-density polyethylene (LLDPE), low density polyethylene (LDPE), or polypropylene (PP) in hydrocarbons solvents like xylene or decalin. After the exposure to the afterglows of DBDs in N₂ or in mixtures of N₂ with H₂ or NH₃, infrared spectra were taken *in situ* under inert conditions and after controlled exposure to various reagents, resp., such as water vapor or oxygen. In order to unravel the complex spectra which are generally due to several functional groups with overlapping vibrational bands, exchange reactions with vapor of heavy water (D₂O) was applied in order to identify groups which are known to exhibit a rapid H/D exchange like >N=H (imine), -NH₂ (prim. amine), >NH (sec. amine), -CO-NRH (prim. or sec. amide), using characteristic ratios of wavenumber ratios for corresponding vibrational bands in the deuterated and the protonated moiety.

In addition, reactions of the plasma-treated surface with vapors of 4-(trifluoromethyl)-benzaldehyde (TFBA) or 4-(trifluoromethyl)phenyl isothiocyanate (TPI) were studied by FTIR-ATR *in situ*. Based on these experiments, tentative assignments of the observed vibration bands to imino, amino, and amido groups are made and interpreted in terms of feasible or probable chemical mechanisms.

Keywords: Dielectric barrier discharges, polymer surface modification, *in situ*, FTIR-ATR, derivatization

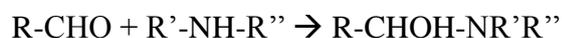
Introduction

Hollahan and Stafford in 1969 [1] and Courval et al. in 1976 [2] were probably the first to investigate the effects of low-pressure radio-frequency (RF) and atmospheric-pressure dielectric-barrier (“corona”) discharges (DBD), resp., in nitrogen or nitrogen-containing gases on surfaces of polyethylene, polypropylene, and other polymers. In both cases the formation of amino groups on the polymer surfaces was inferred – either from the adsorption of negatively charged molecules to quaternary N sites formed by alkylation [1] or by the absorption of acidic dyes [2], resp. In later detailed XPS studies by Foerch et al. [3] and Gerenser [4], the presence of primary and secondary imino groups, C=N-H and C=N-R, on the freshly plasma-treated surface was detected, in parts undergoing hydrolysis upon contact with humid air according to the equations

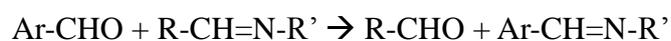


In the recent two decades many more papers were published about the plasma treatment of polymer surfaces in nitrogen-containing gas atmospheres. XPS analysis, frequently combined with chemical derivatization, has become a standard tool for characterization of the resulting surfaces. Everhart and Reilley had in 1991 [5] introduced derivatization with pentafluorobenzaldehyde (PFB) to analyze nitrogen-plasma treated LDPE, assuming that PFB would react with “primary and secondary (!) amines and hydrazines but is not expected to react with amides, imines, nitriles, or nitrogen-containing heterocyclics”. Fally et al. [6] used PFB and 4-(trifluoromethyl)benzaldehyde (TFBA) for “primary amine derivatization” to analyze plasma polymers obtained from primary amines as precursors¹. In the recent years it has become standard to assume that TFBA reacts only with –NH₂ groups of plasma-modified surfaces.

From a chemical point of view this assumption cannot be justified. Quite generally aldehydes may react - among many others - with compounds containing nitrogen-hydrogen bonds [7] and in some cases the product of the first addition reaction, for example of a secondary amine (leading to a hemi-aminal), can be isolated:

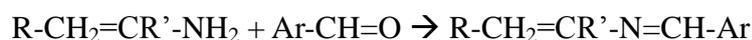


In case of primary amines the subsequent elimination of H₂O generally furnishes secondary imines (aka Schiff bases or azomethines) as products. But aldehydes can also react with imines which are known to be a major product of plasma treatment of polymers in N-containing gases, see above. Aromatic aldehyde may react according to the following scheme, exchanging the aldehyde component of the aldimine [8]:



The uncatalyzed exchange of amine and carbonyl components between imines under moderate conditions has recently gained considerable interest in the field of dynamic covalent chemistry (DCC) as one tool to generate combinatorial substance libraries [9].

Also primary imines R-CH₂-CR'=N-H are expected to react with aldehydes because they are in equilibrium with an enamine:



These considerations show that it is not unreasonable to expect a reaction with TFBA or another aromatic aldehyde also in case of nitrogen-plasma treated surfaces which are virtually free of –NH₂ groups - if only imine functionalities are present, for example.

In fact, in our experiments using *in situ* FTIR-ATR study of LDPE thin films during remote DBD plasma treatment with N₂ + H₂ we are so far unable to find the expected vibrations of primary amino groups and nevertheless we observe a reaction with TFBA, introducing the 4-C₆H₄-CF₃ group to the films.

Experiments

The experimental setup is shown schematically in Figure 1: FTIR-ATR measurements were done on a Nicolet 5700 FT-IR spectrometer with series measurement capability, equipped with an MCT detector and a ZnS ATR crystal (length x height x width = 80 x 4 x 10 mm³, $\theta = 45^\circ$, from *Korth Kristalle GmbH*, Hamburg, Germany,) using unpolarized light with 4 cm⁻¹

¹ The authors noted some reactivity of both aldehydes with secondary amino groups of model compounds.

spectral resolution. LDPE thin films with thicknesses between 50 and 200 nm were obtained by spin coating from hot solutions of purified LDPE (*Goodfellow GmbH*, Bad Nauheim, Germany) in decalin on the preheated ZnS crystal. Polymer purification was done by dissolution in hot xylene and precipitation in isopropanol.

The remote plasma treatment was achieved by a DBD reactor made from glass with an active volume of $70 \times 50 \times 1 \text{ mm}^3$, mounted beyond the ZnS crystal so that the gas flow ($\text{N}_2 + 4\% \text{H}_2$) of typically 16 l/min STP could pass the discharge and reach the polymer surface within a few millisecond after leaving the plasma zone. Gases were purified by an ALPHAGAZ purifier from *Air Liquide*. The discharge was powered by a commercial generator 7010 R from *SOFTAL electronics GmbH*. The voltage and frequency were typically 25 kV (ignition voltage 13.0 kV) and between 20 and 30 kHz, respectively.

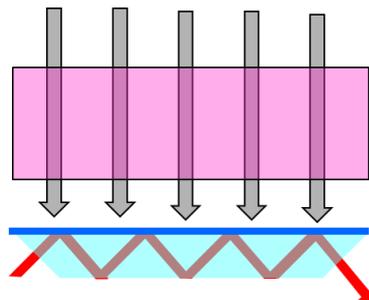
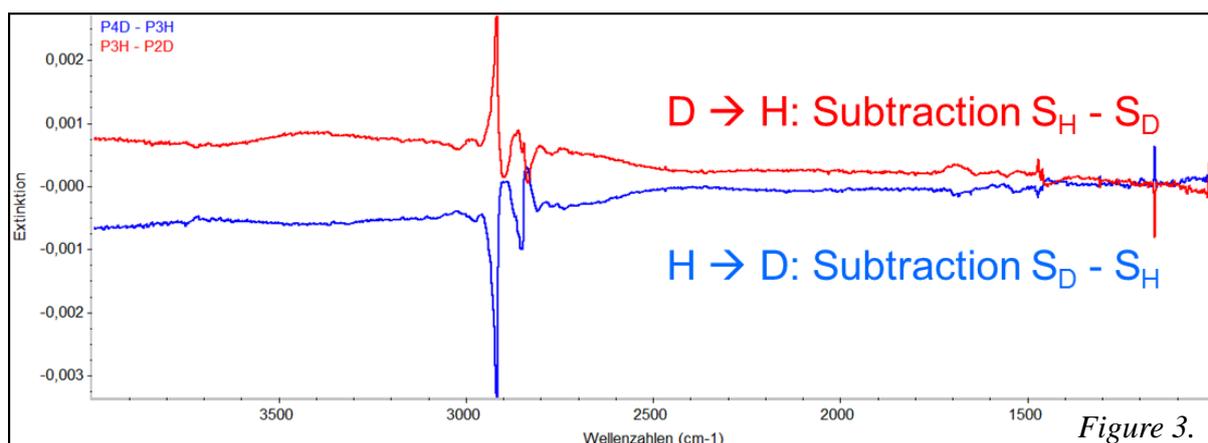
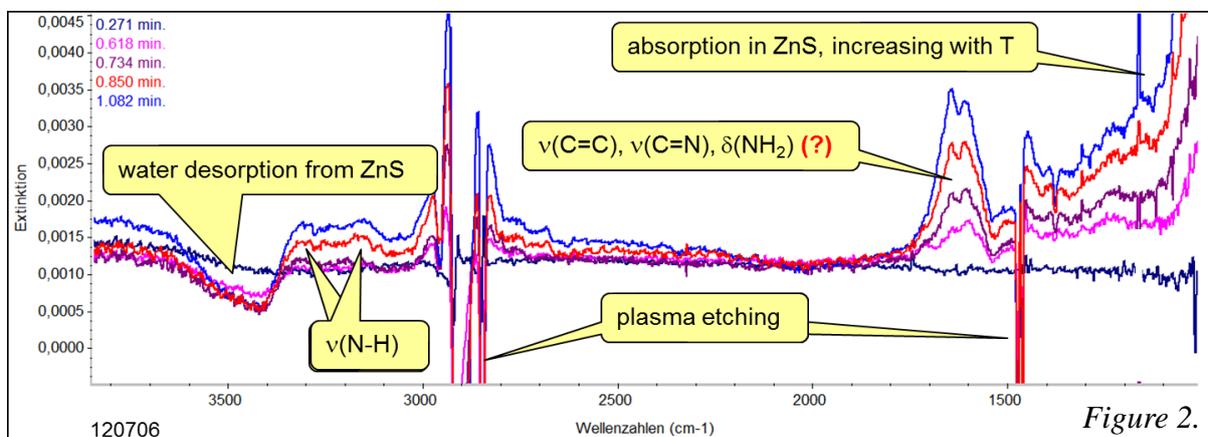


Figure 1. Schematic view of experimental setup: Light blue: ZnS crystal, dark blue: polymer film, violet: discharge zone, grey arrows: gas stream, red arrow: IR light.

First results and preliminary conclusions

The following three figures show the spectral changes observed (i) before, during, and after 30 s remote plasma treatment (Fig. 2, reference: untreated PE), (ii) after several consecutive $\text{H} \rightarrow \text{D}$ and $\text{D} \rightarrow \text{H}$ exchanges, resp. (Fig. 3, reference: spectrum S_{H} or S_{D} before exchange), and (ii) before (red) and after (black) 30 min reaction of the plasma-treated surface with TFBA vapor in N_2 and 20 min dry N_2 purge (Fig. 4, reference: untreated PE).



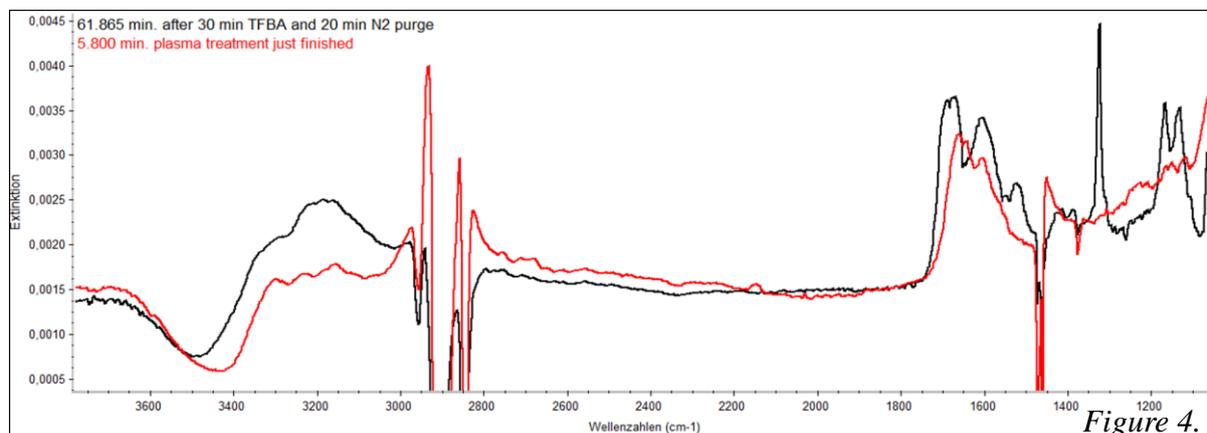


Figure 4.

The following observations can be made:

- During plasma treatment at least four vibrational bands appear in the region of double bond stretching and NH₂ deformation vibrations between 1550 and 1700 cm⁻¹. Beyond 3000 cm⁻¹ ν(NH) bands are developing.
- H→D and D→H exchanges show vanishing ν(NH) (+ possibly ν(OH)) and appearance of deuterated groups and vice versa. There are minor effects in the region between 1700 and 1400 cm⁻¹, probably due to C=NH and amides. There is no significant indication of the presence of amine NH₂ (expected around 1620...30 cm⁻¹) or ND₂ groups (expected around 1225...35 cm⁻¹) within the experimental error range. Expected band areas for 1 NH₂/nm² (1 ND₂/nm²), based on integral intensity values [10] are 0.006 (0.003) cm⁻¹.
- The reaction with TFBA does not proceed along the usually adopted “standard” scheme R-NH₂ + O=CH-Ar → R-N=CH-Ar: At least three new strong bands are developing between 1500 and 1720 cm⁻¹ instead of a single imine vibration expected near 1650 cm⁻¹ (ν(C=N) as measured after adding model primary alkyl amine and TFBA in hexadecane).
- Using isothiocyanate TPI instead of aldehyde TFBA for derivatization (no figures shown here), the amount of bonded reagent is roughly doubled². This may be due to a major role of secondary amines on the surface, smoothly forming thioureas with the reagent.³

From an applicational point of view the presented results do not impair the high value of DBD-based “plasma-amination” of polymer surfaces for subsequent processes such as metallization, printing, gluing, coating or covalent coupling of (bio)molecules. Quite the contrary they give valuable clues how to adapt the subsequent processing in order to exploit the chemical surface functionalities provided by the plasma treatment even more efficiently.

References

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² This was generally observed in recent labeling experiments with TFBA and TPI on N-DBD-treated polyolefin surfaces, also after direct microplasma treatments (“plasma printing”).

³ Imines >C=N-H probably show an analogous reaction. OH groups are not expected to react.