Investigating surfaces by infrared spectroscopy combined with hydrogen-deuterium isotope exchange: H/D ATR FTIR analysis of amino groups

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Abstract Transmission or attenuated total reflection infrared spectroscopy (ATR FTIR) combined with an exchange of H atoms by D atoms in the presence of D_2O vapour is useful for studying surface chemical compositions. In the present contribution we apply the H/D ATR FTIR technique to the analysis of primary amino groups on polyethylene surfaces plasma-treated in N-containing atmospheric-pressure plasmas and demonstrate how $-NH_2$ in amide and amine groups may be distinguished. Another example is the analysis of amino-silanized surfaces.

Keywords: Infrared spectroscopy, attenuated total reflection, hydrogen-deuterium isotope exchange, amino groups, functionalization, TFBA, silanized surface

1. Introduction

The presence of nucleophilic nitrogen-containing groups on plasma-processed surfaces is desired in many applications, e.g. for immobilization of biomolecules in biomedical applications [1], improving adhesive properties [2] or for wet-chemical metallization of polymers [3]. From the late 1960s the opinion prevailing in the literature was that mainly (primary) amino groups ($-NH_2$) are responsible for the properties of the nitrogenated surfaces (sometimes such surfaces were even called “aminated surfaces”). This view was supposedly justified using chemical reagents which were thought to react selectively with primary amino groups, such as aromatic aldehydes. Secondary and primary amino groups were generally thought to be indicated – aside from hydroxyl groups – by the reaction with trifluoroacetic anhydride, TFAA. Recently it was found by our group that (i) the selectivity of the used reagents was wrongfully assumed and that (ii) the presence of amino groups on surfaces prepared by plasma processes is doubtful at all [4]. In the here presented paper we use an alternative method that can be applied in the search for amino groups without any presumptions on the reactivity of derivatization reagents: hydrogen-deuterium (H/D) isotope exchange in combination with ATR FTIR.

2. ATR FTIR investigations of hydrogen/deuterium exchange on surfaces containing functional groups

H/D isotope exchange is a common technique used in biochemistry where it is often applied for analyzing proteins [5, 6]. Here we will show that H/D isotope exchange in combination with ATR FTIR is also very suitable for investigating the chemical structure of functional groups on functionalized surfaces. Thereby functional group containing surfaces are exposed to atmospheres saturated with vapor of D_2O. Due to the law of mass action hydrogen atoms bonded to heteroatoms (e.g., N in amines, O, S, …) are replaced by deuterium leading to a shift of peaks in the IR spectrum compared to the untreated, i.e., hydrogenated, surface, owing to the higher mass of D compared with H. In the case of primary amino groups ($-NH_2$), $-ND_2$ is formed which has a characteristic deformation vibration around 1200 cm^{-1} [7].

2.1 H/D exchange on plasma treated polymers

First utilization of H/D isotope exchange in combination with ATR FTIR by our group was done using an *in situ* setup to investigate modification of thin layers of low-density polyethylene (LDPE) treated in flowing post-discharges of N_2 (+ H_2) [8]. It was found that virtually no primary amino groups were formed upon plasma exposure, although reactivity towards so-called “amine-selective” reagents was seen, contradicting general assumptions made in the literature and leading to the conclusions that were outlined in the introduction. A detailed discussion on the topic of putative “amine selectivity” and presence of amines on plasma-treated or plasma-polymerized polymers can be found in a recent publication by our group [4]. In our first H/D exchange experiments ultrathin (< 100 nm) polymer films spin-coated onto ATR crystals were measured *in situ* during contact with D_2O vapor. When measuring H/D-exchanged surface-modified polymer foils conventionally by ATR FTIR, care has to be taken to prevent immediate re-exchange (D/H) upon exposure to H_2O vapor in the humid ambient air (i.e., restoring the hydrogenated surface). Consequently, we developed a method allowing ATR FTIR investigations of H/D isotope exchange on any (small) surface. Thereby a piece of the surface is attached to the screw-driven clamper of the ATR accessory and, using a small home-made flushable Perspex^{TM} enclosure encasing the diamond surface and the foil, an atmosphere of light or heavy water vapor was established in the volume between the lifted sample and the ATR crystal, enabling a facile measurement of the foil after contact with the desired gas. A scheme of the measuring setup as well as a photograph is shown in figure 1.

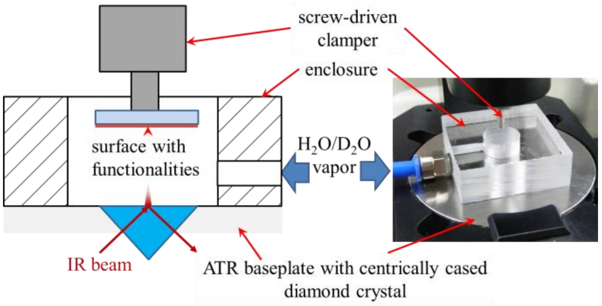

Fig. 1 Setup for ATR FTIR investigations of H/D exchange on any (small) surface. Sizes are not scaled.

Using this method, LDPE foils plasma-treated in a mixture of N_2 + 1% H_2 using a “plasma-printing” setup - a special dielectric-barrier-discharge (DBD) reactor for combinatorial studies described in a recent publication [9] - were investigated. From the spectra taken during exposure of the surface to H_2O or D_2O a difference spectrum (bottom, black curve in figure 2) was obtained by subtracting a spectrum measured after exposing the plasma-treated LDPE sample to H_2O (P:H) from a spectrum measured after exposing the same piece of foil to D_2O (P:D). This spectrum shows the effects of replacing N-H by N-D and O-H by O-D: the broad negative bands between 3000 cm^{-1} and 3700 cm^{-1} can be accounted to vanishing of O-H and N-H vibrations while the broad positive absorption band located between 2250 cm^{-1} and 2750 cm^{-1} is the corresponding deuterated form. These absorptions may originate from a huge variety of functional groups (amines, amides, imines, carboxylic acid, alcohols, etc.) and from adsorbed ambient water on the surface; therefore other vibrations have to be considered to investigate the surface chemistry. One example that shall be mentioned here is the negative band near 1680 cm^{-1} and the positive band near 1600 cm^{-1} which are probably largely due to shifts of amide I bands, i. e., C=O stretching vibrations coupled with N-H deformation, in primary and/or secondary amide moieties formed upon oxidation and/or hydrolysis reactions of the plasma-treated surface. A more detailed investigation of all the observed peaks is beyond the scope of this work. What, however, should be pointed out regarding the focus of this abstract is the presence of a positive band near 1210 cm^{-1} which in principle could be due to ND_2 scissoring vibration of primary amino groups [10].

To further investigate the possible presence of amino groups and to rule out the presence of amides, H/D isotope exchange was combined with derivatization using nucleophilic 4-(trifluoromethyl)benzaldehyde (TFBA).

TFBA is known to undergo a reaction with primary amino groups on surfaces following the scheme depicted in figure 3. Note that the reaction shown in figure 3 was previously presumed to be selective, i.e., it was thought that TFBA would react only with primary amines; the amount of TFBA on the derivatized surface (measured from the amount of $-CF_3$ by XPS or ATR FTIR) was equalized with the amount of amino groups.

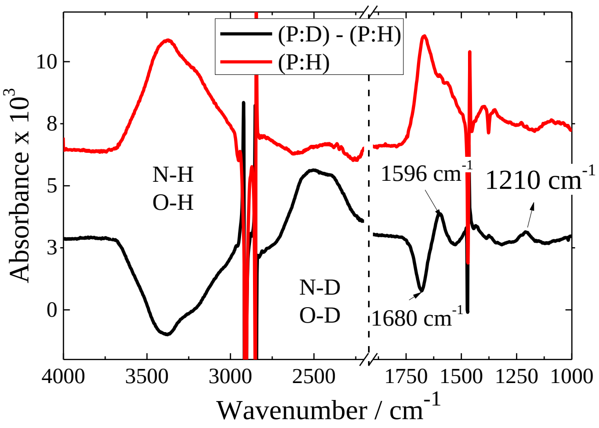

Fig. 2 ATR subtraction spectra of LDPE plasma treated in N_2/H_2 mixtures containing 1% H_2 obtained by spectra measured using the setup shown in figure 1. The red spectrum is from the non-deuterated (i.e. hydrogenated) surface to visualize differences upon deuteration. Spectra have arbitrary offset for clarification.

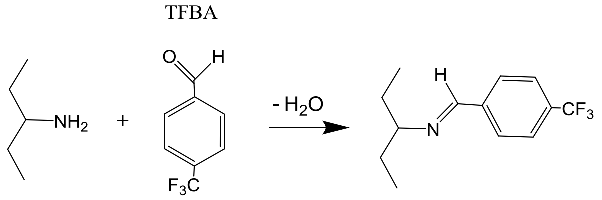

Fig. 3 Reaction between TFBA molecule and amino group on polymer surface.

However as pointed out before in this abstract and by several publications of our group this assumption is not justified and plainly wrong for many plasma-processed polymer surfaces [4, 11, 12]. However, combining TFBA derivatization and H/D isotope exchange the $-NH_2$ moieties in amines and in amides may be distinguished. Thereby the surface is prepared accordingly, e.g. by plasma treatment or plasma polymerization, and subsequently derivatized with TFBA. ATR FTIR measurements using H/D isotope exchange are performed after surface preparation and after TFBA derivatization, respectively. Subtraction spectra according to figure 2 (i.e. spectrum of deuterated surface minus spectrum of hydrogenated surface) before and after derivatization are then compared. In the case of primary amines the absorption band at 1210 cm^{-1} should vanish (or be lowered) after derivatization due to reaction of amino groups with TFBA. Such experiments were performed on LDPE surfaces plasma-treated as the ones shown in figure 2, i.e., using a DBD in a gas mixture of N_2 and 1% H_2. The results are depicted in figure 4. Here the black spectrum (top) is the subtraction of a spectrum from the plasma treated surface after deuteration minus a spectrum of the plasma treated non-deuterated surface. The red spectrum is the same subtraction but with preceding TFBA derivatization. The blue-dotted spectrum shows the plasma treated surface after derivatization, subtracted by a LDPE reference without H/D isotope exchange (reference also underwent derivatization procedure). In the blue spectrum (dotted, bottom) it can be seen from absorptions at 1325 cm^{-1} (ν($C-CF_3$)), 1170 cm^{-1}, 1130 cm^{-1} and 1070 cm^{-1} (all ν(C-F)) that a reaction took place between TFBA and the plasma treated surface. However, this reaction does not seem to take place due to primary amines because the ND_2 absorption at 1210 cm^{-1} is virtually unchanged by derivatization which can be seen by comparison of black (top) and red (middle) spectrum. A significant difference between the spectra before and after derivatization is only seen at 1587 cm^{-1} pointing towards other functional groups than amine undergoing reaction with TFBA. It has to be pointed out that the amount of TFBA bonding to the plasma-treated surface is uncharacteristically low for this kind of treatments (see e.g. ref [13]) - maybe due to contamination of the surface but we believe that the results are nevertheless representative for actual processes occurring on the surface upon plasma treatment.

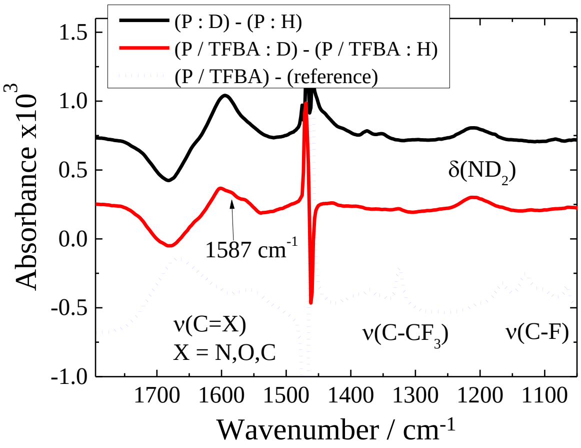

Fig. 4 ATR subtraction spectra of LDPE plasma treated in N_2/H_2 mixtures containing 1% H_2 w/o TFBA derivatization and H/D isotope exchange. Subtractions were obtained by spectra measured using the setup shown in figure 1. Details can be found in the text. Spectra have arbitrary offset for clarification.

2.2 H/D ATR FTIR on amino-silanized surfaces

The H/D isotope exchange combined with ATR FTIR was also used on surfaces that were functionalized wet-chemically by amino-silanization. Thereby a Ge ATR crystal was equipped with a thin layer (<100 nm) of ZnO using the sputtering-annealing method, i.e., sputtering of Zn layer followed by annealing to form ZnO [14]. The coated crystal was then cleaned in an oxygen plasma and dipped in silane solution (mixture of 1% [3-(2-aminoethyl-amino)propyl]-trimethoxylsilane and 99% pure ethanol). After immersion time of 30 minutes crystal was placed in vacuum overnight to remove ethanol from the silanized surface.

Using a homemade flushable enclosure milled from copper placed around the top surface of the crystal, ATR measurement were performed using the silanized Ge ATR crystal while the accessible surface of the film was exposed alternatingly to vapors of H_2O and D_2O. From three H/D-D/H cycles two different spectra taken under D_2O (#1 and #3), and one spectrum taken under H_2O (#2) were used to calculate the difference spectra shown in figure 5. It can be seen that, besides the characteristic shifts of broad bands from 3250 cm^{-1} to 2450 cm^{-1}, there is an exchange of several bands in the range between 1650 cm^{-1} and 1500 cm^{-1} which are shifted upon deuteration. The band at 1637 cm^{-1} may be assigned to δ(NH_2) with the corresponding deuterated peak (δ(ND_2)) emerging at 1205 cm^{-1}. It has to be noted that the silanized surface was measured about 3 hours after preparation, therefore the absorption could be also attributed to asymmetric δ(NH_3^+) [15] of primary amine salt forming upon reaction with CO_2 [16]. In that case the shifting band at 1533 cm^{-1} could be attributed to symmetric δ(NH_3^+) which exhibits a weaker intensity than the asymmetric vibration.

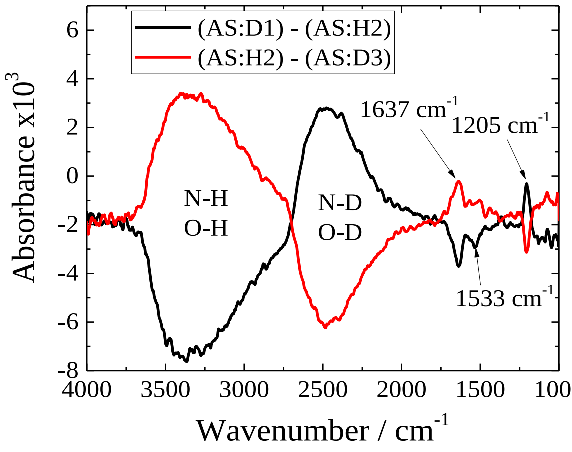

Fig. 5 ATR subtraction spectra of amino-silanized surface exposed to vapors of H_2O and D_2O, respectively.

3. Conclusions

We applied H/D isotope exchange in combination with ATR FTIR to plasma-treated polymer surfaces as well as to wet-chemically amino-silanized surfaces. It was shown that this method (especially in combination with chemical derivatization) can be a powerful tool to investigate the chemistry of chemically functionalized surfaces.

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