Infrared Spectroscopic Characterization of Plasma-Treated Polyethylene

M. NITSCHKE,[1] A. HOLLÄNDER,[2,*] F. MEHDORN,[2] J. BEHNISCH,[2] and J. MEICHSNER[1]

[1]Technische Universität Chemnitz, Institut für Physik, 09107 Chemnitz, and [2]Fraunhofer-Institut für Angewandte Polymerforschung, Kantstr. 55, 14513 Teltow, Germany

SYNOPSIS

Thin polyethylene films cast on copper or gold were treated with low-pressure oxygen plasma. Changes in the chemical structure of these films were investigated by infrared spectroscopy using a reflection method in combination with chemical derivatization (CD) reactions. The potential of the CD is demonstrated for hydroxyl groups and carbonyl groups by the reaction with trifluoroacetic anhydride and hydrazine. The reaction conditions were varied to check for side reactions. The results of the derivatization are discussed in terms of secondary structures. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The treatment of polymers with low-pressure plasma is a well-established method for improving the surface properties as, e.g., wettability or adhesion. Despite the huge body of scientific articles published on this subject, the elementary processes involved in this type of treatment are not very well known. A low-pressure plasma comprises a complex mixture of particles (ground-state and excited neutrals and ions, molecule and fragments, and electrons) and a broad spectrum of electromagnetic radiation. The interaction of all these components with a polymer surface gives rise to multifarious reactions resulting in a wide variety of different chemical structures in a shallow surface layer. The analysis of the functional groups' concentration and secondary structure is difficult because of their extremely low concentration and the complexity of the mixture that they appear in. Only a combination of a number of complementary methods can provide information about details of the structural composition of a surface. A major improvement of the ability of instrumental surface analytical methods to distinguish chemical

structures was shown to be feasible by using chemical derivatization (CD) reactions. Such reactions are specific for certain functional groups and result in new properties of the surface which can be characterized very well. X-ray photoelectron spectroscopy (XPS), e.g., provides a good elemental analysis of a surface, but has only poor abilities in distinguishing chemical structures. A derivatization reaction can introduce new elements by a reaction with a functional group for which it was designed. The reaction of trifluoroacetic anhydride with hydroxyl groups, e.g., results in the formation of trifluoroacetate groups. The determination of the fluorine concentration allows one to calculate the concentration of hydroxyl groups.

Applying this principle, a number of derivatization reactions for surface analysis have been reported in the literature (e.g., XPS,[1,2] fluorescence spectroscopy,[3,4] and contact angle goniometry[5]). Carlson et al. suggested derivatizations for transmission infrared spectroscopy of the bulk material[6,7] to resolve the very complex carbonyl region of the spectrum. The characterization of the surface structure by IR spectroscopy is limited to films with a total thickness which is not more than one or two orders of magnitude higher than the thickness of the modified layer.

In the present article, we report results of CD–IR investigations on plasma-treated polyethylene.

Infrared reflection absorption spectroscopy (IR-RAS) and attenuated total reflection (ATR) spectroscopy were used to study the potential of this method in obtaining detailed information on chemical structures in the substrate. Due to the multiple reflections, the ATR setup is more sensitive by about one order of magnitude compared with the IRRAS experiment. The results of an oxygen plasma treatment in three different reactors (RF downstream and direct and an MW) are compared.

EXPERIMENTAL

Substances

Copper or gold-coated glass slides were dip-coated with polyethylene (0.5% solution in toluene at 343 K). The film thickness was determined by spectroscopic ellipsometry and ranged from 10 to 50 nm depending on the extraction velocity of the glass slide. Trifluoroacetic anhydride (TFAA, Fluka) and hydrazine (Fluka) were used as received.

Plasma Treatment

The samples were treated in an oxygen plasma in three different reactors: (i) a 27 MHz direct RF reactor with integrated IR–ATR equipment, (ii) in a 13.56 MHz downstream remote reactor, and (iii) a MW (2.45 GHz) downstream reactor equipped with a rf (13.56 MHz) biased sample holder.

(i) In this reactor (described in detail elsewhere[8]), the samples were treated with oxygen plasma at 50 Pa and 30 W. (ii) The rf downstream reactor is described in detail elsewhere.[9] For the experiments reported here, the samples were placed 50 cm away from the main plasma zone. The plasma parameters were kept constant for all the treatments: process gas flow rate 50 sccm, pressure 30 Pa, and rf power 30 W. Oxygen and oxygen/hydrogen (1 : 1) were used as process gases. (iii) This reactor was used in the MW downstream mode (50 sccm oxygen, 5 Pa, 300 W) and in the direct rf mode (50 sccm oxygen, 5 Pa, 30 W).

Derivatization

The derivatization reactions (CD) (see Scheme 1) were carried out in the gas phase. The samples were exposed to the agent for a certain optimum time, following which the excess agent was removed by evacuation. In reactor (i) experiments, the CD were carried out in situ directly after the plasma treatment.
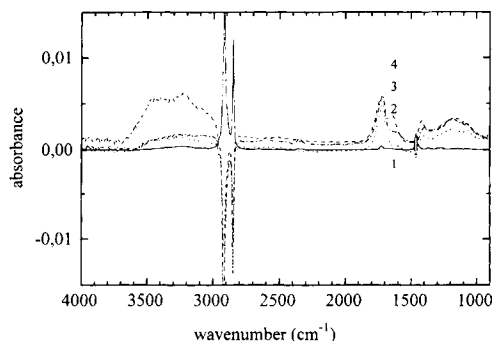

Figure 1 ATR–IR spectra of a 50 nm PE film treated in reactor (i) (curve 2: 0.3 s; curve 3: 1.0 s; curve 4: 1.7 s oxygen plasma, 20 Pa, 30 W) and of an untreated PE (curve 1, divided by 50).

IR Measurements

Reactor (i) is equiped with an internal reflection element (IRE) made of chalcogenide glass Schott IRG100 which is integrated into the rf electrode. One side of the IRE was coated with the PE film. The IRE was placed in the beam of a Bruker IFS66 FTIR spectrometer. This apparatus allows in situ FTIR investigations during low-pressure plasma treatment and gas-phase CD.

Samples treated in reactors (ii) and (iii) were studied with an IRRAS setup. The parallel polarized beam of a Nicolet 800 FTIR spectrometer was reflected at the sample (Cu or Au surface coated with a PE film) under an incident angle of 75°. For the redirection of the beam, two zinc selenide prisms were used.

RESULTS AND DISCUSSION

Using ultrathin films, the oxidation of polyethylene (PE) by oxygen plasma treatment can be followed very sensitively by infrared spectroscopy. Figure 1 shows the ATR spectra of a pristine PE film and the difference spectra which display the changes induced by the plasma treatment. The negative bands below 3000 cm^{-1} and at 1470 cm^{-1} indicate the diminishing of CH_2 groups from the film which is caused by oxidation but also by the complete removal of the material by chain scission followed by desorption of the low molecular weight products formed in this process. The progress of these processes can be observed clearly during the first seconds of the treatment. A broad band at 3500–3000 cm^{-1} is due to hydrogen-bonded hydroxyl groups, the concentration of which is found to be increasing

continuously with the treatment time. In the carbonyl stretching region, a band appears at 1726 cm^{-1}. It is formed very quickly during the first tenths of seconds of the treatment and increases only slightly later on. The missing structuring of this band indicates a rather large number of different structural features of carbon–oxygen double bonds. Ester groups can be included in this band as well as carboxylic acid groups, aldehydes, or ketones. The band at 1644 cm^{-1} represents the stretching vibration of carbon–carbon double bonds which are formed with various substituents that have different characteristic frequencies. Their concentration rises slower than that of the carbonyl groups, which suggests that an important way of double-bond formation are Norrish type II reactions of carbonyl groups. A positive band at 1421 cm^{-1} can possibly be attributed to the shifted deformation vibrations of CH_2 groups in the neighborhood of $C{=}O$ or $C{=}C$ structures.[10] The broad positive peak at wavenumbers down to 950 cm^{-1} is a superposition of a wide variety of vibrations from oxygen-containing species formed during the plasma treatment (OH deformation and $C{-}O$ stretching in alcohols and $C{-}O$ stretching in ether and ester structures).

To obtain a more detailed picture of the functional groups on the surface of the plasma-treated PE, we carried out derivatization reactions. The first one to be discussed here is the conversion of hydroxyl groups with TFAA. The ATR difference spectra (PE is substracted) describing the result are shown in Figure 2. As expected, the OH bands diminish though not completely. New bands are observed at 1250–1100 cm^{-1} ($-CF_3$ stretching) and at 1788 cm^{-1} (ester group). The ester band is well separated from the carbonyl peak observed in the plasma-
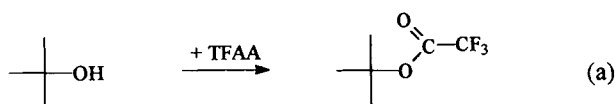
Scheme 1 Derivatization reactions for (a) hydroxyl groups and (b) carbonyl groups.

treated sample and displays two well-distinguished bands which probably are due to different structures of the alcohol part of the trifluoroacetates. The assignment of these peaks is rather difficult and needs more investigations on model substances. However, Table I[11] lists some examples that show how the ester carbonyl vibration frequency is influenced by the structure of the alcohol part. The vibration of aliphatic trifluoroacetic acid ester carbonyl is reported to be at 1785 cm^{-1}. The value observed in our experiments (1788 cm^{-1}) corresponds quite well to these data.

Beside this effect, the TFAA reaction causes a diminishing of the carbonyl peak at 1726 cm^{-1} and a deformation of this peak. Excluding a direct reaction of the agent with $C{=}O$ structures, we have to take other reaction paths into consideration. The reaction of TFAA with ketones via ket-enol tautomerization is a conceivable mechanism. The removal of low molecular weight products from the plasma treatment seems also to be a possible way.

The spectral changes induced by the reaction of hydrazine with aldehyde and ketone structures are shown in Figure 3. The most pronounced effect of this reaction is the diminishing of the carbonyl peak at 1726 cm^{-1} and the formation of a band at 1580 cm^{-1}. The latter represents the carbon nitrogen double-bond stretching and also includes scissor vibrations of the $-NH_2$ group. The dramatic decrease in the carbonyl band intensity after this treatment suggests that a rather large concentration of aldehyde and keto groups is formed by the plasma treatment. This finding is consistent with results reported in the literature[1] obtained by XPS combined with CDs. The intensity decrease at the high-energy site of the peak indicates that the concentration of saturated ester groups after the plasma treatment is essentially zero. No information can be obtained about structures on the low-energy site of the car-
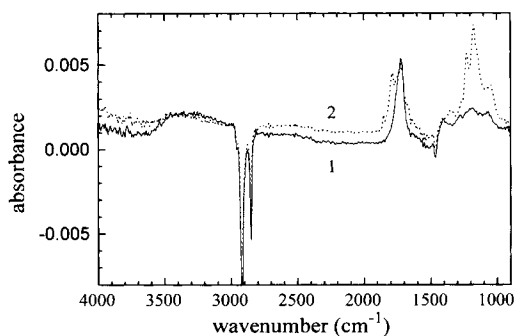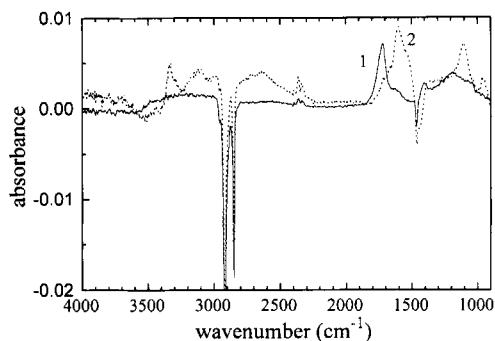
Figure 2 ATR–IR spectra of a 50 nm PE film treated in reactor (i) (curve 1: 0.3 s oxygen plasma, 20 Pa, 30 W) and of the same sample after derivatization (curve 2: 5 min TFAA at 50 Pa).

Table I Examples for Characteristic Vibrations of Acetic Acid and Trifluoroacetic Acid Esters[11]

Structural Feature	C=O Stretching (cm⁻¹)	CH and CF Stretching, Respectively (cm⁻¹)	
CH_3 ester			
—C₁₆H₃₄	1740	1225	
isopropyl	1730	1245	1159
tert-butyl	1725	1250	1150
vinyl	1740	1230	
isopropenyl	1740	1245	
1-propynyl	1782	1198	
cyclooctyl	1735	1245	
benzyl	1740	1220	
o-tolyl	1755	1210	1175
methyl ketone	1735/1750	1235	1173
CF_3 ester			
vinyl	1785	1210	1160/1125

Figure 3 ATR–IR spectra of a 50 nm PE film treated in reactor (i) (curve 1: 1.0 s oxygen plasma, 20 Pa, 30 W) and of the same sample after derivatization (curve 2: 7 min hydrazine at 50 Pa).

bonyl peak because of the overlapping with the $C=N$ streching bands.

The band appearing at about 1100 cm⁻¹ can be attributed to N—N stretching. The N—H stretching can be observed in the 3350 cm⁻¹ region. The broad band covering the region between 3250 and 2300 cm⁻¹ is possibly due to the formation of hydrazonium salts.

To compare the influence of the plasma parameters on the result of the treatment, PE was treated in different systems. The IRRAS spectra were recorded directly after the plasma treatment and after derivatization with TFAA. Beside the experiments described above, four more sets of experimental conditions have been studied: (a) reactor (ii), oxygen plasma; (b) reactor (iii) direct rf mode, oxygen plasma; (c) downstream MW mode, oxygen plasma; and (d) reactor (ii), oxygen plasma followed by hydrogen plasma. For technical reasons, it was not possible to carry out these experiments with very short treatment times as in the experiments discussed above. So, we will discuss only the results of a 10 s treatment for all the experiments.

Figure 4 shows the IRRAS spectra of experiment (a) with a downstream oxygen plasma treatment. Note that in contrast to the ATR spectra the spectra shown here and in the following figures still contain the PE features and that, because the most pronounced changes in the spectrum occur at wavenumbers < 2000 cm⁻¹, only this part of the spectrum is shown. In general, the signal-to-noise ratio is much better in the ATR experiment compared to the IRRAS spectra, which permits only a rather rough comparison. Considering this, one can observe a very similar shape of the absorption shown in Figures 1 and 4: The carbonyl band occurs in both spec-
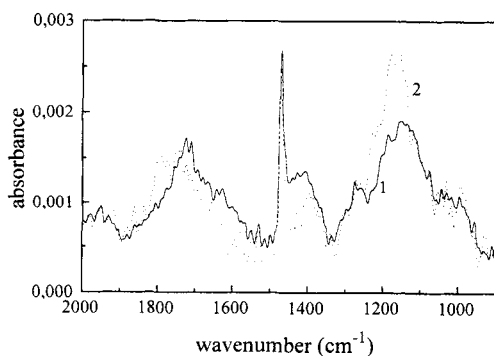
Figure 4 IRRAS spectrum of a 50 nm PE film treated in reactor (ii) (curve 1: 10 s oxygen plasma treatment, 30 Pa, 30 W) and of the same sample derivatized with TFAA (curve 2).

tra, though the peak is found at slightly lower wavenumbers in Figure 4 ($1720\ cm^{-1}$ rather than $1726\ cm^{-1}$). The shoulder of this band representing the carbon double bonds ($1640\ cm^{-1}$) and the broad band between 900 and $1300\ cm^{-1}$ is observed in both experiments. After derivatization with TFAA, a spectrum is observed which differs in the fingerprint region from the one shown in Figure 2: The $1230\ cm^{-1}$ peak (Fig. 2) can only be seen as a shoulder in Figure 4. At the high-energy side of the $1177\ cm^{-1}$ band, an additional peak is to be seen at $1168\ cm^{-1}$ which is displayed in Figure 2 at most as a shoulder.

The treatment in a direct rf oxygen plasma in reactor (iii) (experiment b) produces a very broad absorption between 900 and $1900\ cm^{-1}$, indicating a wide variety of structures. However, the spectral features as observed after the treatments discussed above are still observed (Fig. 5). The TFAA deriv-
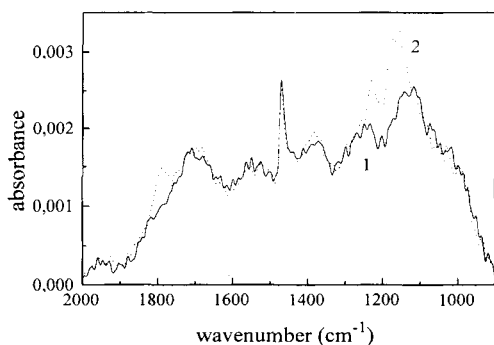
atization results in an absorption which displays in the fingerprint region the same peaks which have been mentioned above. The $1228\ cm^{-1}$ peak is clearly separated and is more intense with respect to the $1160\ cm^{-1}$ peak compared to experiment (a). The carbonyl peak is at the same position ($1788\ cm^{-1}$).

A downstream MW plasma as used in experiment (c) produces products on the PE surface which are distinctly different from those observed in the experiments (a) and (b) (Fig. 6). The poorly resolved spectrum points to a wide variety of different species. In particular, in the fingerprint region, the shape of the spectrum is unlike those observed in the other experiments. However, these variations can hardly be attributed to structural features. The products of the TFAA derivatization are characterized by bands which were also observed in the other experiments (1782, 1220, and $1160\ cm^{-1}$) and by an additional intense band at $1697\ cm^{-1}$. Because the $1220\ cm^{-1}$ band is much more intense than is the analogous ones in Figures 2, 4, and 5, this band seems to originate from the structure that also causes the $1697\ cm^{-1}$ band. The ester carbonyl peak is found at slightly lower wavenumbers ($1782\ cm^{-1}$). According to Table I, one can expect more saturated but linked structures.

The spectrum of PE after a type (d) treatment (Fig. 7) displays slightly narrower bands compared to the ones observed in the downstream oxygen plasma treatment [experiment (a), Fig. 4] and the carbonyl peak is found at $1715\ cm^{-1}$, which is somewhat more energetic, but, in general, the spectra are very similar. After the derivatization, however, slight differences are observed: The fluoroacetate carbonyl peak is found to be shifted to about $1795\ cm^{-1}$, which can possibly be attributed to unsaturations in combination with secondary carbon atoms (Table I).

Figure 5 IRRAS spectrum of a 50 nm PE film treated in reactor (iii) in the direct rf mode (curve 1: 10 s oxygen plasma treatment, 30 Pa, 30 W) and of the same sample derivatized with TFAA (curve 2).
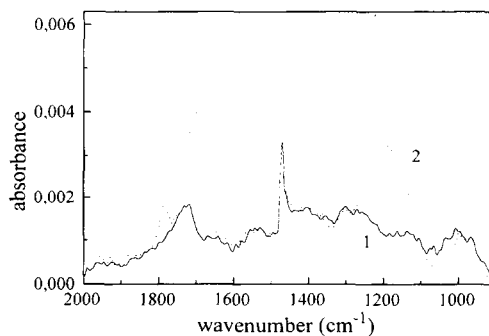

Figure 6 IRRAS spectrum of a 50 nm PE film treated in reactor (iii) in the microwave downstream mode (curve 1: 10 s oxygen plasma treatment, 30 Pa, 30 W) and of the same sample derivatized with TFAA (curve 2).
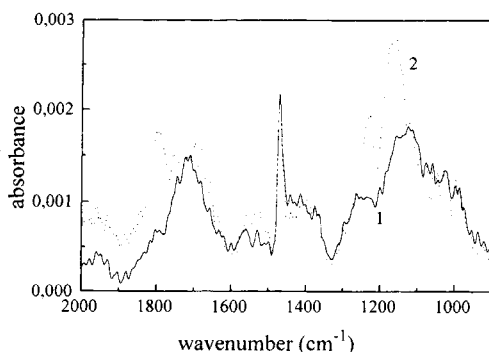
Figure 7 IRRAS spectrum of a 50 nm PE film treated in reactor (ii) (curve 1: 10 s oxygen plasma treatment, hydrogen plasma aftertreatment, 30 Pa, 30 W) and of the same sample derivatized with TFAA (curve 2).

The 1228 cm^{-1} band is relatively intense and well separated from the 1160 cm^{-1} peak in treatment (d) while it is just a shoulder in treatment (a).

CONCLUSIONS

It has been shown that infrared spectroscopy can be a valuable complement for surface analysis of plasma-treated polymers. Using very thin films, the effect of the treatment is detected very sensitively. It was found that different types of treatment also produce differences in the surface structure of PE which is represented by the IR spectra. Chemical derivatization (CD) reactions permit one to obtain more detailed structural information. In particular, secondary structures seem to be accessible if the appropriate model substance spectra are available.

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