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**polymer communications**

# Surface analysis of DC oxygen plasma treated or chromium evaporated poly(ethylene terephthalate) foils by soft X-ray absorption spectroscopy (NEXAFS)

**I. Koprinarov, A. Lippitz, J. F. Friedrich and W. E. S. Unger***
*Bundesanstalt für Materialforschung und -prüfung (BAM), D-12200 Berlin, Germany*

**and Ch. Wöll**
*Universität Heidelberg, Institut für Angewandte Physikalische Chemie, Im Neuenheimer Feld 253, D-69120 Heidelberg, Germany*

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Surface modified biaxially stretched poly(ethylene terephthalate) (PET) foils have been analysed by surface sensitive soft X-ray absorption (NEXAFS) spectroscopy. Generally, an orientation of polymer chain segments can be detected by a variation of the angle between the linearly polarized synchrotron light beam and the surface normal of the investigated sample (angle resolved NEXAFS spectroscopy). Biaxially stretched PET foils have been found to be characterized by angle dependent NEXAFS C and O K-edge spectra. This angle dependence was interpreted to be a result of a preferential orientation of the PET chain segments at the surface wherein the plane defined by the benzene ring is parallel to the surface plane. In the course of chromium deposition or low pressure $O_2$ DC plasma treatment that preferential orientation is continuously diminished. This is interpreted to be a structural effect of the respective treatment. © 1997 Elsevier Science Ltd. All rights reserved.

**(Keywords: biaxially stretched poly(ethylene terephthalate); oxygen DC plasma treatment; metallization with chromium)**

## *Introduction*

Recently, we published an X-ray absorption study where the potential of this method to differentiate partially crystalline and amorphous states at the surface of poly(ethylene terephthalate) (PET) was demonstrated[1]. Evidence for a preferential orientation of PET chain segments at the surface of biaxially stretched, partially crystalline foils with the plane, defined by the benzene ring of the PET monomer unit, parallel to the surface was obtained. In this communication the *conformational response* of the preferentially oriented PET foil surface to metallization or oxygen DC plasma treatments is analysed, again using NEXAFS spectroscopy[2]. The results are of importance for a more detailed understanding of adhesion phenomena in polymer/metal composites. The whole matter is, of course, also of technological importance.

As known, plasma treatment is one approach to improve the surface properties of polymers with respect to adhesion of metals or polymers, etc.[3,4]. Important questions are to what extent plasma treatment influences the molecular conformation at the polymer surface and how to analyse it. We found angle resolved NEXAFS spectroscopy to be an instructive tool for monitoring the effects of plasma treatment. The structural damage at the PET surface caused by plasma treatment is a relevant, but, in many practical cases, a hidden parameter in the optimization of its adhesion properties. Moreover, in an adhesion related study of the Al/PET interface De Puydt *et al.*[5] emphasized the importance of the substrate crystallinity for the build-up and quality of a metal/polymer interface.

## *Experimental*

Biaxially stretched 0.5 $\mu$m PET foils (Mylar, Du Pont de Nemours) were used in this study. This polymer is characterized by an average molecular weight of 250 000 g mol$^{-1}$, crystallinity of 60–65% (density measurement) and stretching ratios $\alpha_{\parallel}$ and $\alpha_{\perp}$ of 3.5. The samples were analysed by X-ray photoelectron spectroscopy (X.p.s.) to verify a sufficient purity for surface studies. Narrow X.p.s. C 1s and O 1s scans resulted in spectra very similar to the reference spectra published elsewhere[6]. X.p.s. and $O_2$-DC plasma treatments were carried out in a VG ESCALAB 200X electron spectrometer with a plasma reactor chamber separated by a gate valve. Plasma treatments were carried out at 6 Pa of 99.999% grade oxygen. During the treatment, the sample was 25 mm away from the luminous plasma region. The plasma treated sample was exposed to laboratory atmosphere during the transfer into the NEXAFS apparatus. Chromium evaporation was carried out within a dedicated preparation chamber (base pressure $1 \times 10^{-9}$ mbar, $1 \times 10^{-8}$ mbar during Cr evaporation) of the NEXAFS apparatus using a home-made evaporation system. Chromium covered samples were transferred to the NEXAFS analysis chamber without any exposure to air. To minimize the thermal load of the polymer surface during evaporation the hot filament of the evaporator was thermally shielded. Chromium was sublimed on to the polymer surface from pure Cr (99.997%) through an aperture of this shielding. This aperture was located 7 cm away from the

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* To whom correspondence should be addressed

sample surface. An evaporation rate of $\approx 1$ Å min$^{-1}$ was estimated by using a quartz microbalance. Thermal effects on the polymer sample were ruled out in a separate experiment by using the evaporator without loading it up with Cr and simulating the whole experiment. The result was that no heat effects were found in the NEXAFS spectra of PET samples tested in this way.

Angle resolved NEXAFS spectroscopy experiments were carried out on the HE-TGM2 monochromator beam line at the synchrotron light source (BESSY, Berlin, Germany). Spectra were acquired at the C K-edge and the O K-edge in the partial electron yield (PEY) mode at a retarding voltage of $-150$ V. The monochromator resolution at the C 1s edge was better then 0.8 eV. Raw spectra were divided by the monochromator transmission function, which was obtained with a freshly sputtered Au sample. Energy alignment of the energy scale was achieved by using the C 1s $\rightarrow \pi^*$ resonance, measured with a pyrolytic graphite sample (Advanced Ceramic Corp., Cleveland, OH, USA) which was fixed to the value of 285.4 V[7]. Characteristic features in the flux monitor signals were used to align the energy scales of each spectrum. Reproducibility of the spectra was carefully checked by multiple scanning. Reproducibility is demonstrated by the respective 90° spectra, where two runs are superposed (cf. *Figures 1* and *2*). Spectra are shown with the pre-edge count rate subtracted and after normalization in units of the absorption edge jump[2]. Unfortunately, the second order contribution of the monochromator gives rise to a Cr spectral feature in the region of the C K-edge spectrum. With a pure Cr sample its intensity was measured to be about 6% of the first order contribution; this means, that, at higher Cr coverages, it significantly interferes with the C K-edge spectra. Recently, it was shown that, in principle, these spectra can be corrected for this undesirable overlap[8]. However, in this communication, only C K-edge *difference* spectra were used to draw conclusions wherein this Cr contributions cancel out. Therefore, this correction was not applied.

NEXAFS spectra were recorded at angles of 20, 55 and 90°, measured between the surface plane of the sample and the direction vector of the incident, linearly polarized light beam. An angle of 90° means that the electric field vector **E** lies in the surface plane and 20° that **E** is nearly parallel to the surface normal. The geometry of the experiment is illustrated by an insert in the respective figures.

Absorption spectra were measured by monitoring the non-radiative decay of core holes, created in the sample by the absorption process[2]. Photoelectrons, C-, O-KLL and Cr-L series Auger (after metallization) electrons contribute to the electron yield signal measured by a channeltron detector. Surface sensitivity is achieved by using the PEY mode because low energy electrons, which mostly originate from deeper layers, were suppressed by the pre-set threshold energy from entering the detector. The information depth, which is defined to be the depth, from which 95% of the detected electrons originate[9], is estimated to be $\approx 30$ Å for the C K-edge signal and $\approx 50$ Å for the O K-edge or the Cr L-edge signals[10]. Here it was assumed that the respective Auger electrons dominate the measured partial electron yield signal[2].

## *Results and discussion*

*Figure 1* presents sets of 20, 55 and 90°C K-edge and O K-edge spectra for different states of a biaxially stretched, partially crystalline PET foil. Additionally, '90–20°' difference spectra were given. The first column on the left-hand side of *Figures 1a* and *b* represents the untreated, 'as received' state of the PET sample. The features in these C K-edge and O K-edge spectra were discussed in detail in a previous paper[1]. Essentials are repeated here briefly. The C K-edge spectrum is dominated by the intense resonance (A) at 284.9 eV. It is characterized by a shoulder to higher energies which results from a split component A′. Without a doubt these resonant features are correlated to a C 1s $\rightarrow \pi^*_{\rm ring}$ transition[11,12]. The splitting is to be expected because of the benzene ring symmetry perturbation induced by the polar ester group. High resolution spectra revealed an energy splitting of 0.7 eV (PET C K-edge spectra measured at a resolution of 30 meV with BESSY's HE-PGM3 monochromator[13]). The second intense resonance (B) at 288.3 eV represents a C 1s $\rightarrow \pi^*_{\rm C=O}$ transition, characteristic of the carbonyl bond in the PET molecular unit. The other features (C–G) are related to C 1s $\rightarrow \sigma^*_{\rm C-C}$, $\sigma^*_{\rm C=O}$, $\sigma^*_{\rm C-O}$ shape resonances, superposed by phenyl and carbonyl multi-electron transitions, and the onsets of the continuum for phenyl ring or chain carbons[1,11,12]. The respective O K-edge spectrum, shown in *Figure 1b*, is dominated by an intense O 1s $\rightarrow \pi^*_{\rm C=O}$ resonance which is described in ref. 12 to be split into two contributions, H and I. The other features (J–L) are due to O 1s $\rightarrow \sigma^*$ shape resonances of the C–O and C=O bonds and the respective onsets of the continuum.

Considering the angle dependence of the spectra one should know that the NEXAFS method probes the amplitude and directionality of unoccupied molecular orbitals on the atom characterized by the core hole[2]. Only the spatial orientation (direction of maximal orbital amplitude) of a selected orbital determines the angle dependence of K-edge absorption spectra. In this picture the $\pi$ system of the PET ring can be represented by a vector which is orthogonal to the ring plane. Therefore, the maximal intensity of a transition from C 1s into the $\pi^*_{\rm ring}$ unoccupied orbital should be observed with the **E** vector of the synchrotron light oriented orthogonal to the phenyl ring plane. Because the PET molecular unit is nearly planar[14], the maximum of the C 1s $\rightarrow \pi^*_{\rm C=O}$ transition should occur at the same condition. Considering the left-hand columns of spectra presented in *Figures 1a* and *b* (and in ref. 1) the angle dependence of the key resonance features A, B and H, which were found to have their intensity maxima at glancing incidence of the synchrotron light beam (20°), suggests that the plane of the PET molecular units should be preferentially oriented parallel to the surface plane of the sample[1]; 90°–20° difference spectra were evaluated to clarify the angle dependence of the respective spectra. Furthermore, the area of the C 1s $\rightarrow \pi^*_{\rm ring}$ resonance feature (A) in the C K-edge difference spectra is correlated to a (laterally averaged) degree of orientation of the molecular units in the investigated surface layer. By means of this quantitative parameter the conformational response of the oriented sample to a surface treatment, e.g. plasma functionalization or metallization, can be monitored.

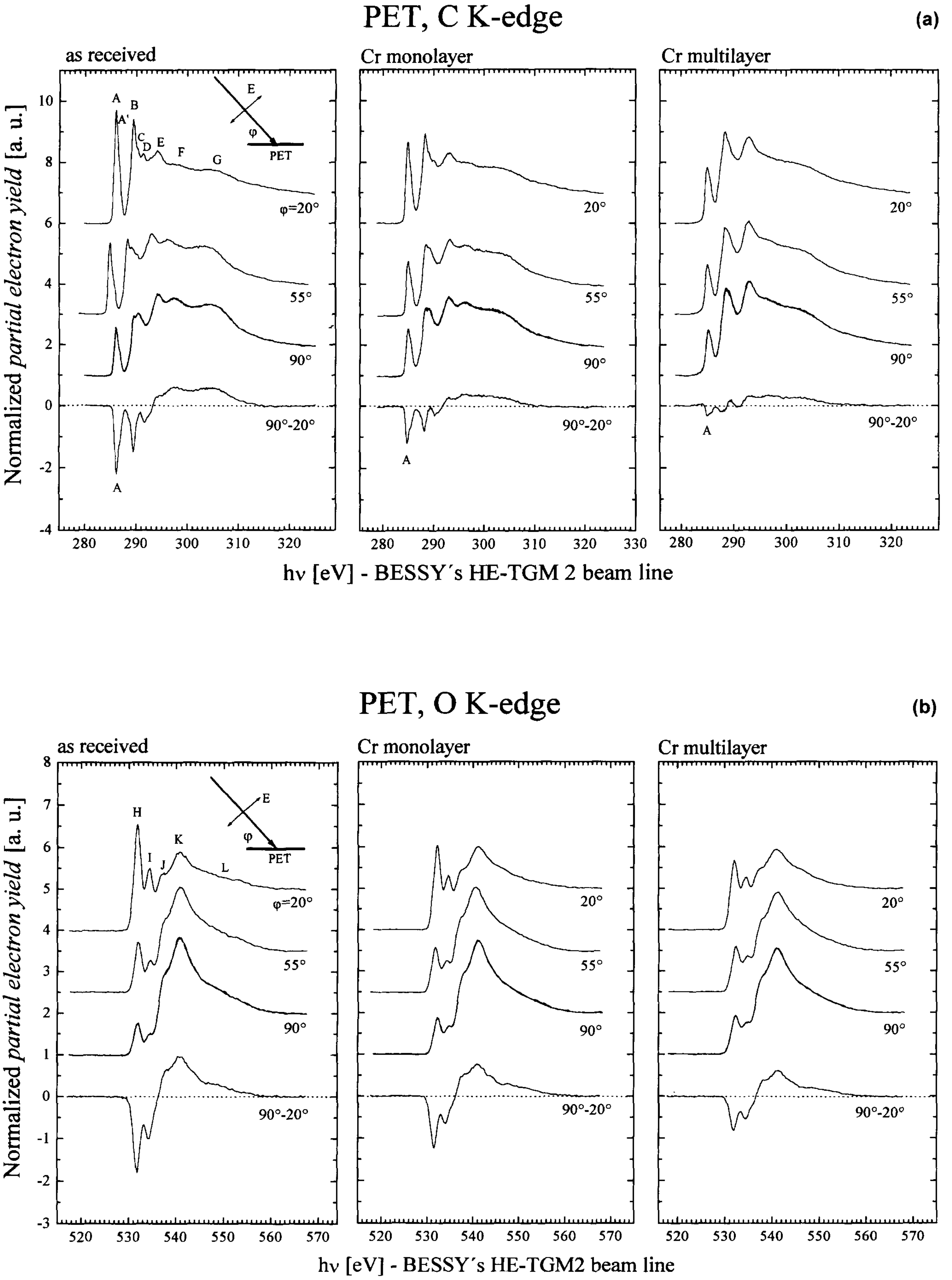

**Figure 1** Angle resolved normalized PEY (a) C and (b) O K-edge X-ray absorption spectra of biaxially stretched PET foils in the 'as received' state and after Cr deposition. The geometry of the experiment is given by the insert. The interpretation of the spectral features marked by capitals is given in the text or in refs. 1, 11 and 12. '90°–20°' difference spectra are evaluated and plotted at the bottom of each set. The 90° spectra were measured at the beginning and at the end of an experiment. Its reproducibility is illustrated by plotting both spectra together in each set of spectra

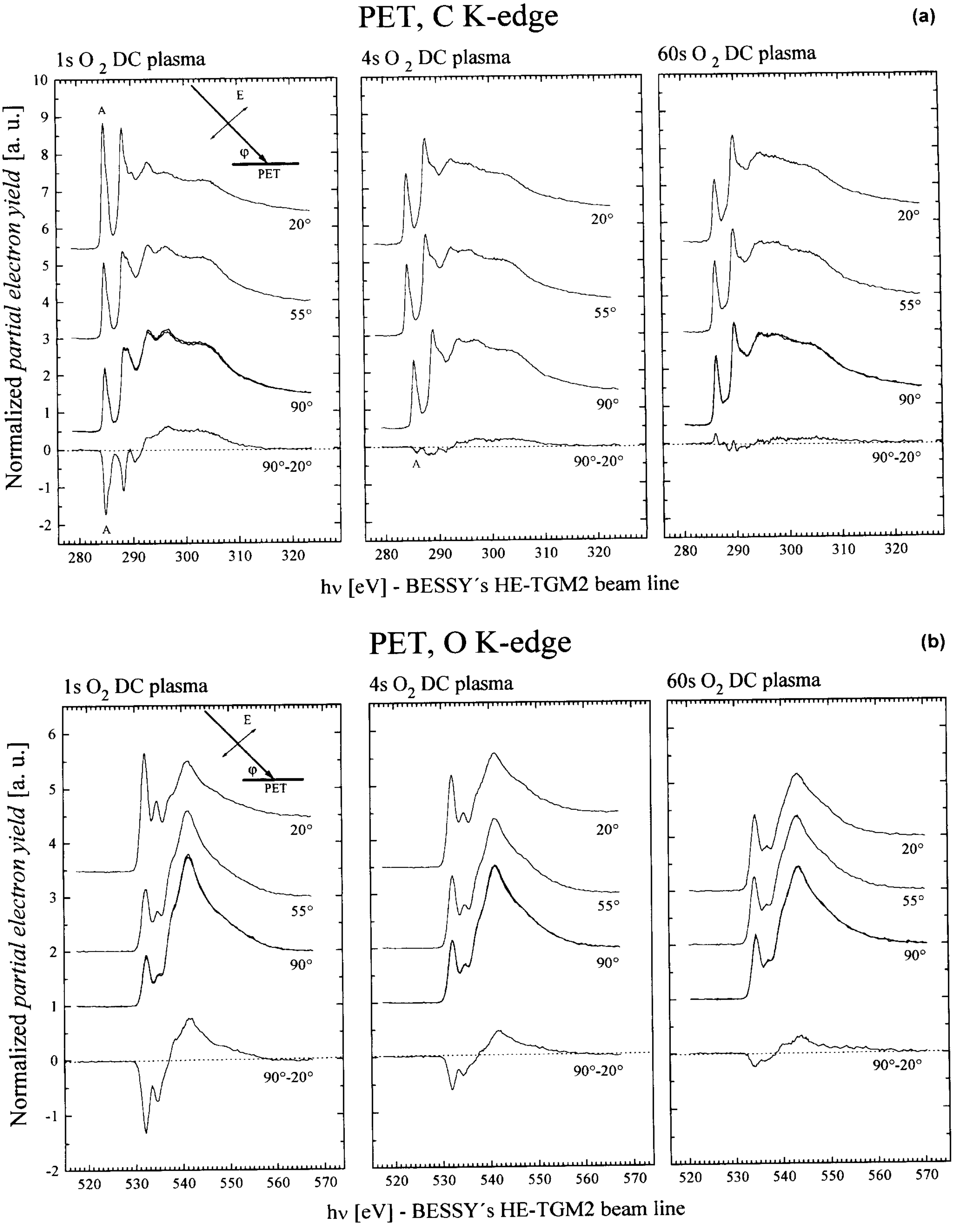

**Figure 2** Angle resolved normalized PEY (a) C and (b) O K-edge X-ray absorption spectra of biaxially stretched PET foils after low pressure-oxygen d.c. plasma treatments

In a first experiment we investigated the response of the biaxially stretched PET foil to metallization with Cr. *Figures 1a* and *b* (middle and right-hand columns) present the respective sets of C and O K-edge spectra together with difference spectra. Obviously, there are chemical effects which alter the spectra in a characteristic manner and are not to be considered further in this communication. In brief, the most prominent effects, i.e. the intensity decrease and broadening of features A and G, and the intensity decrease of feature B, are taken as proof for an interaction of Cr with phenyl rings and carbonyl groups of PET (cf. ref. 8). Considering the difference spectra in *Figure 1a* or *b* and the data presented in *Table 1* a significant decrease in preferential orientation has to be stated for a monolayer coverage of the sample. Multilayer coverage results in a rather strong decrease in orientation. In the latter case the C K-edge spectra reveal only a small residual orientation (≈10% of the original one) whereas the O K-edge spectra are much less affected. This is due to the enhanced information depth obtained when this edge is analysed (cf. Experimental section). Under the conditions applied for multilayer evaporation approximately four layers of Cr were measured with the quartz microbalance. However, nothing is known about the growth mode of Cr on PET or Cr diffusion into the PET bulk. So the details of the Cr covered PET surface are unknown. The experimental data presented above suggest that, besides the chemical interaction of Cr with PET, there is also a driving force, induced by condensing Cr atoms, which turns the surface from a preferentially oriented state to a more or less statistical orientation of the molecular units of the PET substrate. A very similar effect was observed in an earlier study where self-assembling, highly oriented octadecyltrichlorsilane (OTS) films were also evaporated with Cr[15]. In the first case, where these films were evaporated in the 'as received' state, no effect on the orientation of the film was observed by NEXAFS spectroscopy, and Cr was found in the metallic state. This means, that, as to be expected, there was no chemical interaction of this all-*trans*-alkane film with condensing Cr atoms. In a second case, where the OTS film was very carefully treated with an oxygen plasma pulse before Cr evaporation, a completely different behaviour was observed. After plasma treatment the OTS film was oxygen functionalized and, then, as before, oriented (the degree of orientation was only slightly affected by plasma treatment). Evaporation of Cr on this *modified* film immediately eliminates any orientation of the sample. Due to chemical interaction of Cr with O-functionalized sites, Cr(III) species were formed.

**Table 1** Relative areas of the C 1s → $\pi^*_{\mathrm{ring}}$ resonance (A) in the C K-edge 90°–20° difference spectra after Cr metallization of the PET

| PET surface | Relative area of the C 1s → $\pi^*_{\mathrm{ring}}$ resonance feature (A) in the 90°–20° difference spectrum (%) |
|---|---|
| As received | 100 |
| Metallization with Cr monolayer[a] | 35 |
| Metallization with Cr multilayer[a] | 10 |

[a] Layer thicknesses measured by a quartz microbalance under fixed evaporation conditions

The conclusion drawn from these experiments is that interaction of Cr with reactive sites of a polymeric, or, more generally, organic substrate may provide a driving force for alterations of its molecular conformation. Considering PET one may speculate that, e.g. the formation of energetically preferred intra- or intermolecular Cr bisarene complexes provides this driving force (cf. ref. 8).

In a second experiment we monitored the structural response of the surface of biaxially stretched PET foils to low pressure oxygen plasma treatments. Experimental results are summarized in *Figures 2a*, *2b* and *3*. Already at a plasma pulse as short as 1s the preferential orientation of the molecular units is significantly diminished. Relying on the quantitative approach using the integrated feature A of the 90°–20° C K-edge difference spectrum (see above) a decrease of about 30% can be estimated. An increase in the treatment time to 4 s provides further reduction of the degree of orientation down to ≈10% of the original value (cf. *Figure 3*). Longer treatment times result in a surface without detectable preferential orientation. Qualitatively, all these results can be cross-checked by inspection of the respective O K-edge spectra, which represent, as discussed above, a thicker surface layer. Therefore, deeper, not plasma degraded layers may contribute to the spectra (see, e.g. O K-edge spectra of 60 s plasma treated PET with a small but distinct orientation effect). Besides the structural effects discussed so far the shape of the spectra is also altered by chemical effects of the

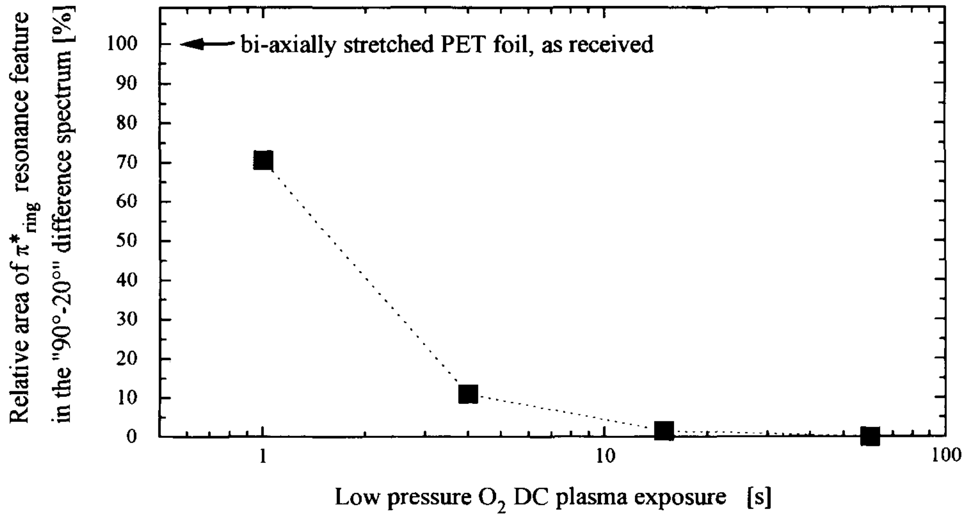

**Figure 3** The decrease of the area of the C 1s → $\pi^*_{\mathrm{ring}}$ resonance related feature (A) in the C K-edge difference spectra of low pressure oxygen plasma treated biaxially stretched PET foils relative to the 'as received' state

plasma treatment. The most prominent one is a strong decrease of the C 1s → $\pi^*_{\text{ring}}$ resonance (A), which is correlated with the degradation of the PET phenyl rings in the course of oxygen plasma treatment. We will investigate this phenomenon in more detail in the future. The conclusion drawn from the plasma treatment experiment is that, as to be expected, plasma exposure degrades the PET surfaces not only in a chemical, but also in a structural way. Application of short plasma pulses is a favoured approach because the structural degradation is, under these circumstances, rather limited. Optimization of plasma treatment conditions should take into consideration surface functionalization and structural degradation to result in stable adhesion properties. Angle resolved NEXAFS spectroscopy can be, provided that the polymer is characterized by an adequate orientation or crystallinity, a tool to control the structural damage of the treated polymer surface produced by a plasma.

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