

# polymer communications

## Valence band region XPS, AFM and NEXAFS surface analysis of low pressure d.c. oxygen plasma treated polypropylene

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Biaxially stretched polypropylene (PP) foils treated with oxygen plasma at low pressure were analysed by core level and valence band region X-ray photoelectron spectroscopy (XPS), atomic force microscopy and near edge X-ray absorption fine structure (NEXAFS) spectroscopy. Applying short treatment times the XPS O/C atomic ratios are  $\leq 0.1$ . Valence band electron spectroscopy for chemical analysis (ESCA) and NEXAFS spectroscopy reveal that a certain number of C–O and a smaller amount of C=O functionalities together with C=C bonds exist at a short-time treated PP surface. These species were not observed or resolved by a standard core level XPS analysis of the same surface. The surface is smoothed by the plasma treatment and the C–O and C=O bonds are slightly non-statistically oriented (parallel to the surface plane). Considering the results obtained after prolonged plasma treatment, NEXAFS spectroscopy provides a direct indication for the formation of conjugated carbon double bonds in the surface region of the PP samples. (Keywords: polypropylene; plasma treatment; spectroscopy)

### Introduction

Plasma chemical surface modification of polyolefins is a well established technique to improve their adhesion properties. Recently it has been found that good adhesion results can also be obtained at rather short treatment times (a few seconds). We confirmed this effect for the model composite oxygen plasma treated polypropylene (PP)–isocyanate terminated polyurethane (PUR)<sup>1</sup>. We obtained an enhancement of the lap shear strengths from zero for untreated biaxially stretched PP foils to  $\approx 4$  MPa for these foils when only one d.c. oxygen glow discharge pulse of 1 s was applied to the PP surface. Quantitative X-ray photoelectron spectroscopy (XPS) surface analysis of these short-time treated PP samples resulted in O/C atomic ratios of  $< 0.1$ . Comparison of the XPS C 1s peak shape observed with short-time treated and untreated PP revealed a full width at half maximum (FWHM) broadening by  $\approx 25\%$  for the CH<sub>x</sub> peak. No signal intensity was obtained in the binding energy (BE) region where O–C=O or C=O C 1s signals are usually observed. Considering the O/C atomic ratio a certain, small amount of C–O species should exist at the treated surface. Unfortunately, this cannot be verified with sufficient accuracy by analysis of the C 1s photoemission because of the overlap with the broadened CH<sub>x</sub> peak and the fact that the C 1s photo peak of virgin PP itself is asymmetric towards higher BEs due to vibration effects<sup>2</sup>. Obviously, a more detailed characterization of a short-time oxygen plasma treated PP surface requires the

application of additional surface analytical methods. In this communication we present some X-ray excited valence band (VB) region spectra, near edge X-ray absorption fine structure (NEXAFS) spectra and atomic force microscopy (AFM) results which may provide more insight into the situation at the surface under consideration. NEXAFS spectroscopy is a surface analytical method providing molecular specific information (the excitation of electrons into unoccupied molecular orbitals (MOs) via dipole transition from core levels are probed) together with data on the orientation of macromolecules or parts of it<sup>3</sup>.

### Experimental

Biaxially stretched 30  $\mu\text{m}$  Hoechst PP foils were used as test samples. The polymer is characterized by a s.e.c. average molecular weight of 250 000, a crystallinity of 55–65% (density measurement) and stretching ratios of  $\alpha_{\parallel} = 5$  and  $\alpha_{\perp} = 8$ –10. The surface of the foils was cleaned from O and Si residuals by rinsing in ether. After cleaning the XPS O/C ratio was  $< 0.01$ ; there was no oxygen peak in the survey scans. The PP samples were exposed to a low pressure (6 Pa) oxygen d.c. plasma. The plasma treatments were carried out in a reactor system described in ref. 4. After treatment the samples were exposed to laboratory air. The influence of this post-plasma laboratory air exposure was checked in the following way. PP samples were plasma treated within an ultra-high vacuum chamber directly attached to an electron spectrometer. A treated sample was transferred into the spectrometer chamber without exposure to air and

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analysed by XPS. Subsequently the sample was exposed to laboratory air in different steps, beginning with 2 min and ending with 1 week, before it was analysed by XPS again. We checked the following parameters: carbon functionalization, C 1s *FWHM*, O 1s BE, O 1s *FWHM*, O/C surface concentration ratio and the X-ray excited VB region. As a result, we did not find any alteration. Therefore, the results presented in this communication should be, to some extent, characteristic of the plasma treatment effect itself.

VB spectra were obtained employing an SSX 100 photoelectron spectrometer. We used monochromatized Al K $\alpha$  radiation, a fixed energy pass at 50 eV and a take-off angle of 55° versus surface normal. Under these conditions, the Au 4f $_{7/2}$  *FWHM* (BE=83.98 eV) was 1.08 eV. The spectrometer energy scale was calibrated following ref. 5. To reduce charging a flood gun releasing 2 eV electrons was used. Additionally, the analysis chamber of the spectrometer was filled up with 99.9999% pure Ar up to  $3 \times 10^{-5}$  Pa. We found that charging was minimized at these conditions<sup>6</sup>. The valence band spectra were fitted employing Gauss–Lorentz sum functions where the Gaussian fraction was fixed at 80%. A linear background was subtracted before peak fitting was applied. The number of peaks to be fitted was established relying on the respective theoretical and experimental results published in refs 7–9. The information depth (95% criterion) of this method can be estimated with the help of ref. 10 to be 35 Å.

Total electron yield (TEY) X-ray absorption experiments were carried out on the HE-TGM 2 beam line at BESSY (Berliner Elektronenspeicherring-Gesellschaft Für Synchrotronstrahlung mbH, Berlin, Germany) at a resolution better than 0.8 eV at the C 1s edge. The angle of incidence of the photon beam was varied between 90° (i.e. the electric field vector *E* lies in the surface plane) and 20° (*E* nearly parallel to the surface normal). To obtain difference spectra all spectra were scaled to the same value before and far behind the absorption edge jump<sup>3</sup>. The energy scale was calibrated by setting the C–H\* resonance peak of a paraffin reference sample to 285.7 eV (ref. 11). Characteristic features in the flux monitor signal were used to align the energy scales of all spectra relative to this value. The information depth (95%) of this approach can be estimated to be 20–30 Å assuming that C KLL Auger electrons (including inelastic scattering events) predominantly contribute to the signal<sup>3</sup>. Low energy electrons cannot leave the positively charged surface of the irradiated foils. Fluorescence yield NEXAFS experiments were carried out on BESSY's HE-PGM 2 beam line at a resolution of 1.5 eV at the O 1s edge. The spectra were divided by the transmission, scaled and aligned as in the former case. The oxygen fluorescence signal was detected with the help of a Ge-detector (Explorer, Noran Instruments, Middleton, WI, USA). The resulting information depth obtained with fluorescence photons is estimated to be roughly 2000 Å, i.e. the whole oxygen functionalized PP layer should contribute to the NEXAFS signal.

The surface topography was monitored with the help of an air atomic force microscope (Omicron-Vakuumphysik, Taunusstein, Germany). The Si $_3$ N $_4$  cantilever (ultra lever, feather constant 0.03–0.06 N m $^{-1}$ , top radius 10 nm) was used in the constant force mode. No differences in the AFM pictures were obtained when

the same area was scanned several times. Therefore, a substantial damage effect on the probed PP surfaces can be ruled out.

### Results and discussion

Characteristic X-ray excited VB region spectra of PP samples are presented in *Figures 1a–c*. With the clean PP sample we obtained a spectrum very similar to those published in refs 7 and 8. Signals related to backbone C 2s–C 2s bonding (peak 1) and anti-bonding (peak 2) molecular orbitals (MOs), a methyl side group C 2s level (peak 3), methyl group (peak 4) and backbone carbon (peak 5) C 2p–H 1s bonds can be observed<sup>7,8</sup>.

Analysis of the spectrum of the short-time plasma treated PP surface (XPS O/C atomic ratio =  $0.05 \pm 10\%$ ) reveals several new peaks together with the peaks observed with virgin PP. The new features were interpreted by employing the theoretical results reported in ref. 9. The most prominent new oxygen-related feature is an O 2s signal (peak 10). The formation of C–O bonds is indicated by a shifted C 2s signal (peak 8), which fills the valley between features 1 and 3. Additionally,  $\pi$ - and  $\sigma$ -contribution C–O bond oxygen lone electron pair signals<sup>9</sup> (features 7 and 6, respectively) were probably detected. Thus we can unequivocally state the existence of a small number of C–O functionalities on the basis of feature 8 in the VB region spectrum.

Inspection of the VB region spectrum observed with longer-treated PP foils (XPS O/C atomic ratio =  $0.22 \pm 10\%$ ) reveals a new intense feature due to a carboxyl bonding MO (peak 11) and a feature (9), interpreted as being related to carbonyl group oxygen lone electron pairs<sup>9</sup>. The latter fills the valley between features 2 and 4.

Considering our VB region analysis results we conclude that features 8, 9, 10 and 11 can be used as finger-prints for a qualitative analysis, whereas an interpretation of the photoemission between 0 and  $\approx 10$  eV BE cannot be very straightforward. For that range only an overall increase in intensity due to an oxygen treatment can be stated.

Additional information on the state of the surface was obtained with the help of AFM and NEXAFS. AFM revealed, for the untreated PP foil, the ripple topography (r.m.s. roughness = 4 nm evaluated for a 500 nm  $\times$  500 nm section) usually observed with stretched PP foils. Short time (1 s, XPS O/C =  $0.05 \pm 10\%$ ) oxygen plasma treatment results in an efficient smoothing of this surface. The ripples mostly disappear and the surface seems to be rather flat (r.m.s. roughness decreased down to 1.3 nm). Longer treatment times did not result in an improvement in smoothness.

The C K-edge X-ray absorption spectra of the cleaned PP foil (see *Figure 2a*) revealed a sharp resonance feature at 287.5 eV labelled *B*. With paraffin we found a very similar feature at the same energy position. This feature was also found in the spectra of highly oriented polyethylene<sup>3</sup> or oriented films of long chain alkanes<sup>11</sup> and was attributed to a C–H\* resonance. Comparison of the PP spectra (difference spectrum), obtained at different electric field polarizations (90° or 20°) relative to the surface normal, reveals a weak but distinct non-isotropic character for this C–H\* feature. The same effect, but more pronounced, was found with highly oriented PE and was interpreted as an effect of the

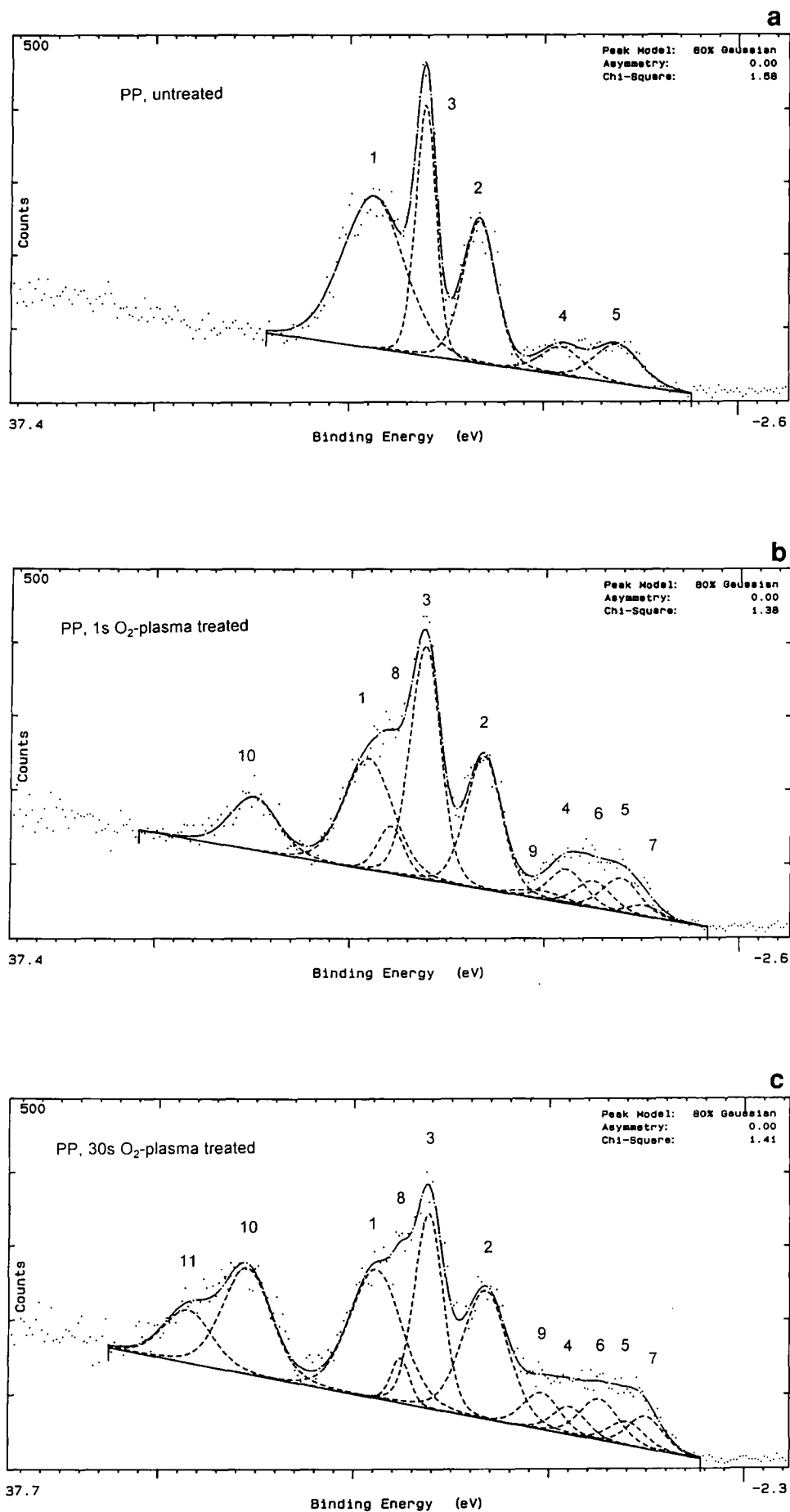
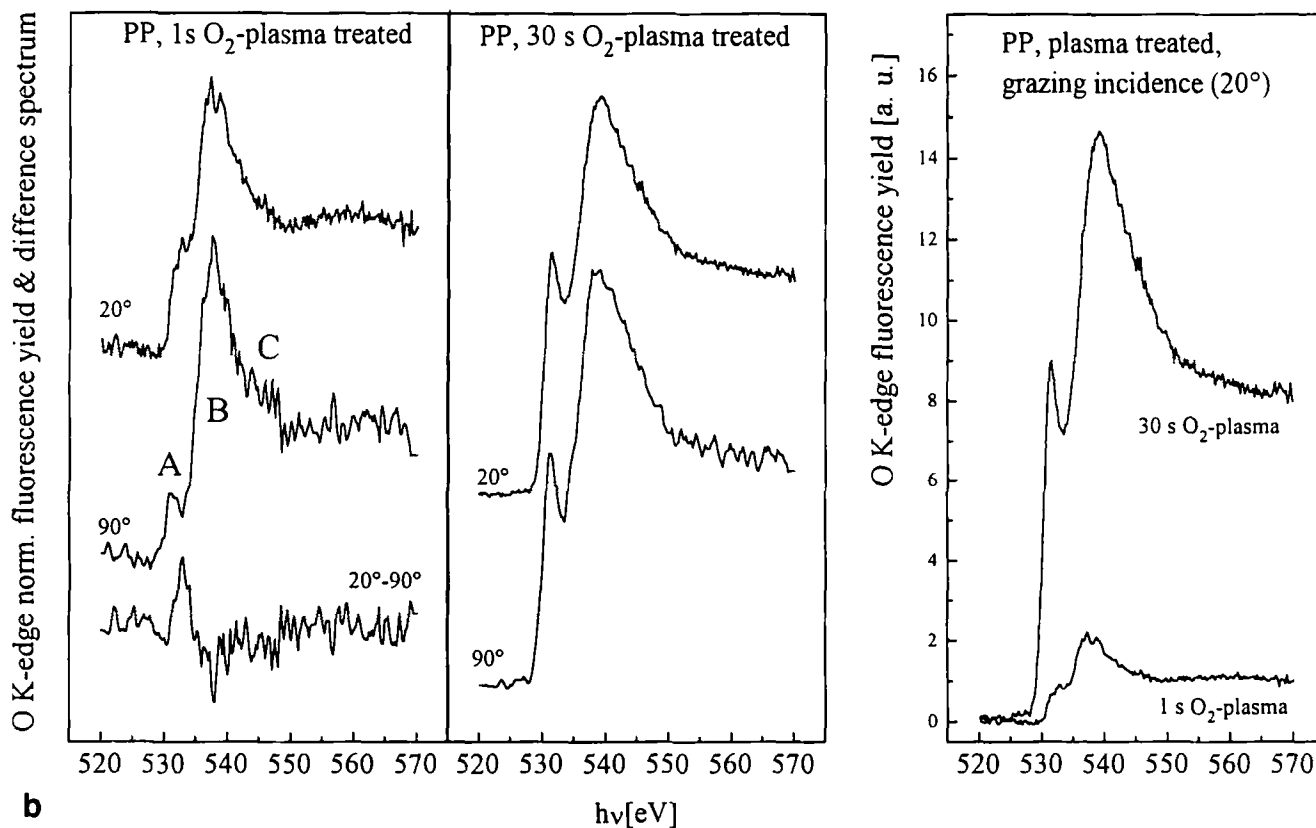
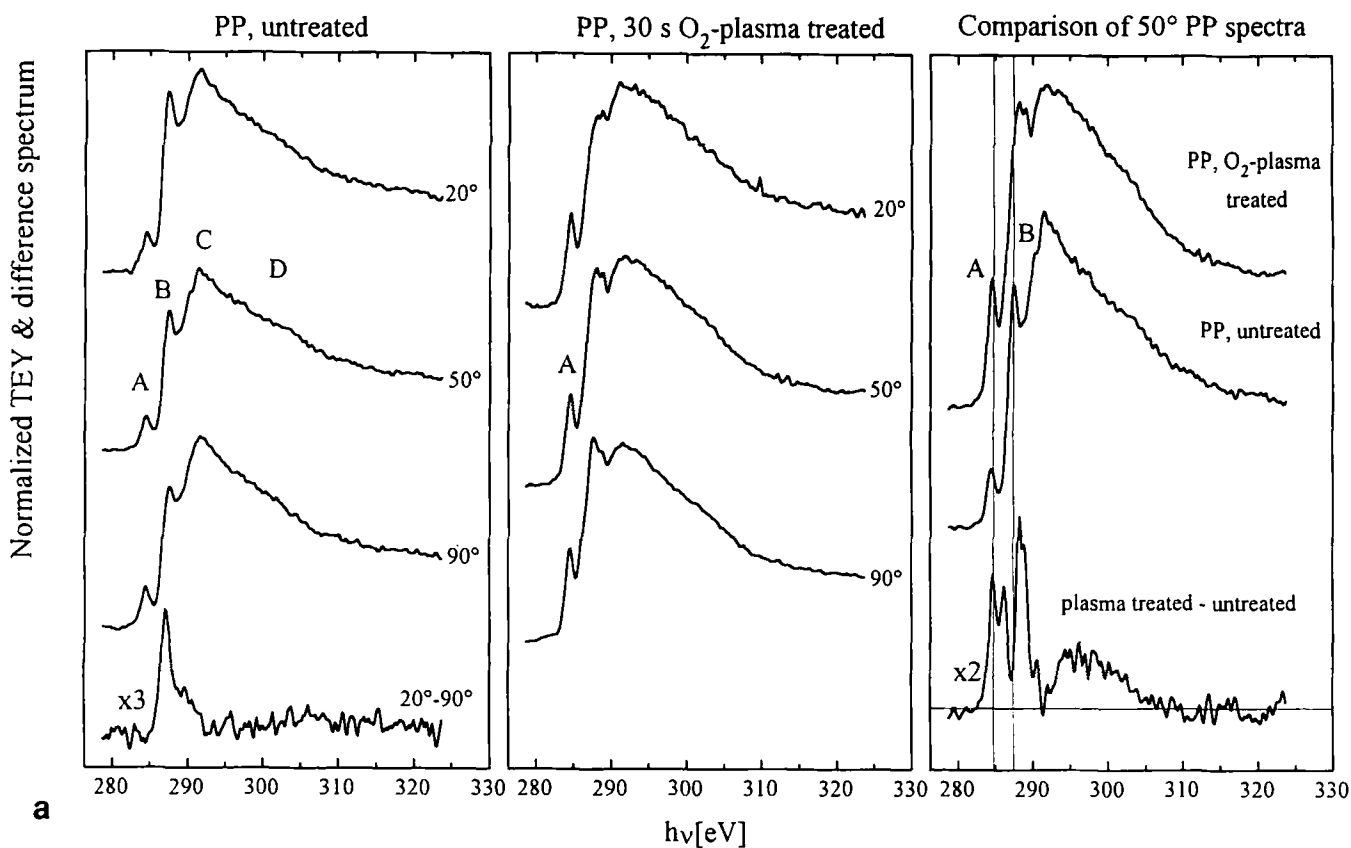


Figure 1 Valence band region spectra of plasma treated and untreated PP surfaces excited by monochromatized Al K $\alpha$  radiation (●, data; ---, sub-bands obtained by fitting; ---, sum of all these sub-bands). The interpretation of the spectral features is given in the text



**Figure 2** (a) Total electron yield NEXAFS C K-edge spectra and (b) fluorescence yield NEXAFS O K-edge spectra of untreated and low pressure oxygen d.c. plasma treated PP samples for different beam light incidence angles relative to the surface plane. The interpretation of the spectral features is given in the text. In the right box of part a, the vertical lines labelled A and B indicate the position of the C=C  $\pi^*$  and C-H\* resonances at the energy scale; the horizontal line marks zero for the difference spectrum

orientation of long, rotationally disordered all-*trans* hydrocarbon chains parallel to the surface<sup>3</sup>. Because stretched PP foils are known to be also partially crystalline samples, the effect could be an indication of a similar, slightly non-statistical, overall orientation of PP chain segments within the surface. Considering the features *C* and *D*, which are attributed to a broad C–C  $\sigma^*$  resonance split due to an interaction of adjacent C–C  $\sigma$  bonds<sup>3</sup>, we found (in contrast to the PE results reported in ref. 3) an isotropic behaviour. Replacing H with CH<sub>3</sub> distorts the PE *trans* conformation, resulting in a non-planar PP chain conformation. Thus the formation of an effective transition dipole moment for the C–C  $\sigma^*$  resonance, which is colinear with the chain axis<sup>11</sup> and which provides a way to discuss NEXAFS polarization effects in relation to an orientation of the chain axis, should be ruled out. Finally, we found a C=C related, isotropic  $\pi^*$  resonance, labelled *A*. The reason for the occurrence of this C=C  $\pi^*$  resonance should be olefinic double bonded end groups terminating the PP chains.

In comparison to the former case, analysis of short-time treated (1 s, XPS O/C = 0.05 ± 10%) PP samples reveals some changes: the most prominent are a decrease of the C–H\* resonance intensity, an increase of the C=C  $\pi^*$  resonance intensity and a disappearance of the non-isotropic behaviour observed with the C–H\* feature. Analysis of the O K-edge fluorescence yield NEXAFS spectra, obtained at high sensitivity, provides more details (see Figure 2b). We found several features in the spectra, labelled *A*, *B* and *C*: *A* is attributed to a weak C=O  $\pi^*$  resonance, *B* to a dominating C–O  $\sigma^*$  resonance and *C* to a C=O  $\sigma^*$  resonance<sup>3</sup> which is also weak. The respective difference spectrum reveals small anisotropy effects. The maximum C=O  $\pi^*$  intensity at an *E* polarization perpendicular to the surface plane clearly suggests a preferential orientation of the C=O bond axis parallel to the surface plane because a C 1s → C=O  $\pi^*$  transition has maximum intensity when *E* points along the direction of maximal orbital amplitude<sup>3</sup>. The same, slightly non-statistical orientation of the C–O bond axis is obtained when the angular dependence of the respective  $\sigma^*$  resonance intensity is considered.

C K-edge NEXAFS spectroscopy of a PP sample after extended plasma treatment (XPS O/C atomic ratio = 0.22 ± 10%, see Figure 2a) reveals a strong decrease of the C–H\* resonance intensity, a strong increase of the C=C  $\pi^*$  resonance intensity and the appearance of some new, unresolved features around  $h\nu = 289$  eV. These  $\pi^*$  resonances are attributed to co-existing, more complex C=O containing species usually interpreted (on the basis of XPS results) as being formed in the course of oxygen plasma treatments. Obviously, there is also a certain angle dependence of the spectrum, but it is not very straightforward to discuss it for the given, chemically poorly defined PP surface. Comparison of the 50° C K-edge spectra of untreated PP and PP after extended plasma treatment (see the respective difference spectrum in Figure 2a) clearly reveals the occurrence of new  $\pi^*$  resonances at *E* > 287.5 eV, the energy characteristic of the C–H\* resonance (*B*), and new  $\sigma^*$  resonance contributions between 292 and 305 eV. Additionally, a splitting of the C=C  $\pi^*$  resonance is obtained, which is usually observed with conjugated  $\pi$ -systems<sup>3</sup>. For an X-ray incidence angle of 54.7° (magic angle) the measured NEXAFS intensity distribution is independent of the molecular orientation<sup>3</sup>, therefore the

comparison of our 50° spectra is well suited to look for only chemical effects. O K-edge fluorescence yield NEXAFS spectroscopy on a similarly treated sample (XPS O/C atomic ratio = 0.25 ± 10%) reveals an intense, sharp C=O  $\pi^*$  resonance and a broad feature between ~535 and 550 eV covering the  $\sigma^*$  resonance contributions of the oxygen functionalities formed by plasma treatment. Note that in this case the whole modified PP layer contributes to these spectra. Additionally an illustration for the increase in the O K-edge fluorescence yield after prolonged plasma treatment of PP is given. With untreated PP we did not measure O related signals.

### Conclusions

We conclude from our VB electron spectroscopy for chemical analysis and NEXAFS spectra, that a certain number of C–O and a smaller amount of C=O functionalities together with C=C bonds exist at a short-time low pressure oxygen plasma treated PP surface. These species were not observed or resolved by a standard core level XPS analysis of the same surfaces. Moreover, the surface is smoothed by the plasma treatment and the C–O and C=O bonds are slightly non-statistically oriented (parallel to the surface plane). A discussion of the improvement in adhesion data in terms of adhesion models should take these results into account. Considering the results obtained after prolonged plasma treatment, NEXAFS spectroscopy provides a direct indication for the formation of conjugated carbon double bonds in the surface region of the PP samples.

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### References

- 1 Friedrich, J. F., Unger, W., Lippitz, A., Gesang, Th., Wöll, Ch., Rohrer, P., Saur, W., Erdmann, J. and Gorsler, H.-V. Paper presented at International Symposium on Polymer Surface Modification: Relevance to Adhesion, Skill Dynamics — IBM Corp., Las Vegas, 1993
- 2 Beamson, G. and Briggs, D. 'High Resolution XPS of Organic Polymers', Wiley, Chichester, 1992, p. 56
- 3 Stöhr, J. 'NEXAFS Spectroscopy', Springer Verlag, Heidelberg, 1992
- 4 Friedrich, J., Elger, J., Unger, W., Lippitz, A., Gesang, Th., Höper, R., Erdmann, J. and Gorsler, H.-V. Proceedings of Plasmatec '93, Universität-GH-Duisburg, Germany (Ed. H. Hansmann), Print Service, Mühlheim, 1993, p. 109
- 5 Anthony, M. T. and Seah, M. P. *Surf. Interface Anal.* 1984, **6**, 95
- 6 Yu, X.-R. and Hantsche, H. *J. Electr. Spectrosc. Relat. Phenom.* 1990, **50**, 19
- 7 Seah, M. P. and Dench, W. A. *Surf. Interface Anal.* 1979, **1**, 2
- 8 Hähner, G., Kinzler, M., Wöll, Ch., Grunze, M., Scheller, M. K. and Cederbaum, L. S. *Phys. Rev. Lett.* 1991, **67**, 851
- 9 Foerch, R., Beamson, G. and Briggs, D. *Surf. Interface Anal.* 1991, **17**, 842
- 10 Gelius, U., Wannberg, B., Nakayama, Y. and Baltzer, P. in 'Photoemission: From the Past to Future' (Eds C. Coluzza, R. Sanjinés and G. Margaritondo), Ecole Polytechnique Fédérale de Lausanne, Lausanne, 1992, p. 143
- 11 Orti, E., Virruela, R., Bredas, J. L. and Pireaux, J. J. Proceedings of International Conference on Polymer–Solid Interfaces, Namur, 1991 (Eds J. J. Pireaux, P. Bertrand and J. L. Bredas), Institute of Physics Publishing, Bristol, 1992, p. 325