Valence band spectroscopy on lignin

Lothar Klarhöfer[1], Burkhard Roos[1], Wolfgang Viöl[2], Oliver Höfft[3], Stefan Dieckhoff[4], Volker Kempter[1] and Wolfgang Maus-Friedrichs[1],*

[1] Institut für Physik und Physikalische Technologien, Technische Universität Clausthal, Clausthal-Zellerfeld, Germany

[2] Hochschule für Angewandte Wissenschaft und Kunst, Fakultät für Naturwissenschaften und Technik, Göttingen, Germany

[3] Institut für Metallurgie, Clausthal-Zellerfeld, Germany

[4] Fraunhofer-Institut für Fertigungstechnik und Angewandte Materialforschung IFAM, Bremen, Germany

*Corresponding author.
Institut für Physik und Physikalische Technologien, Technische Universität Clausthal, Leibnizstraße 4, 38678 Clausthal-Zellerfeld, Germany
E-mail: w.maus-friedrichs@pe.tu-clausthal.de

Abstract

The valence band of lignin and sputtered lignin was studied by X-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS) and metastable induced electron spectroscopy (MIES). The corresponding spectra were compared with those from fingerprint molecules, representing the various chemical groups of lignin. The results of this analysis show that valence band spectroscopy, in particular a combination of XPS, UPS and MIES, allows an identification of hydroxyl, methoxy and phenyl groups at the lignin surface.

Keywords: coniferyl alcohol; lignin; metastable induced electron spectroscopy (MIES); photoelectron spectroscopy (UPS, XPS, ESCA); valence band.

Introduction

X-ray photoelectron spectroscopy (XPS) is a widely used technique in wood science (Johansson et al. 2005). Until now, the main interest has been focused on core level spectroscopy, which provides qualitative and quantitative elemental analysis of a surface and is particularly useful for identification of chemical states located in the topmost molecular layers. However, the valence band region has not been investigated so far in wood science. Valence band spectra provide more detailed information of the chemical states at the surface than XPS core level spectra, which can be used to check or improve surface treatments. The main limitation for XPS valence band spectra comes from poor ionization of cross-sections for p-derived states. Generally, ultraviolet photoelectron spectroscopy (UPS) is sensitive to p-derived chemical states, whereas XPS valence band spectra are dominated by s-derived states.

In metastable induced electron spectroscopy (MIES), metastable helium atoms (He*) are applied which interact only with the outermost wave functions of the surface. Thus, the metastables probe exactly the states on the surface that interact with coatings or environmental substances.

In contrast to infrared or Raman spectroscopy, XPS, UPS and MIES are surface-sensitive techniques with a very small sampling depth of 10 nm, 1 nm or around 0 nm, respectively. This can be of great advantage for the investigation of surface treatments which often affect only the near-surface region, which is the case for plasma treatment, for example (Dénes et al. 1999). It has been shown that plasma treatment of wood at atmospheric pressure in air is a very efficient technique to enhance its surface energy (Rehn et al. 2003; Wolkenhauer et al. 2007, 2008a,b).

The aim of this study was to identify the functional groups in the valence band spectra of lignin with the use of different electron spectroscopic techniques, with the help of which changes could be characterized in the future which are induced to lignin by different treatments.

To interpret and understand valence band spectra of wood surfaces, our investigations begin with the analysis of lignin surfaces (organosolv lignin) and lignin-like monomeric model compounds (benzene, phenol, cinnamyl alcohol) and a precursor (coniferyl alcohol). The studies will be continued by spectroscopy of cellulose and wood surfaces. Unfortunately, the understanding of the lignin valence band spectra is challenging due to the large number of different molecular states and their superposition. Therefore, our strategy is to identify different contributions to the spectra of lignin by investigating the valence band spectra of model compounds These compounds possess similar active groups as lignin in a similar chemical environment. We hope that signals identified for the investigated monomeric models can be useful to identify corresponding structures in lignin.

Experimental

Samples and preparation

All films of lignin or its monomeric models were prepared on Si(100) surfaces after cleaning the surfaces under ultrahigh vacuum (UHV) conditions by heating them up to 1250 K. This procedure provides oxygen and carbon free XPS spectra. The organosolv lignin no. 371017 Lignin from Sigma-Aldrich Co. which was extracted from a hardwood was investigated without further purification.

Thin films of lignin were prepared by spin-coating onto Si(100) wafers, by dimethyl sulfoxide (DMSO) as solvent. On one hand, the lignin films prepared in this way are thick and homogeneous enough to avoid any substrate contribution to XPS, UPS (HeI/II) and MIES. On the other hand, they are sufficiently thin to prevent any sample charging due to low electrical conductivity of the film.

Typical evaporating parameters for the Kentax thermal evaporator.

	Temp. (°C)	Evap. time (min)	Film thickness (nm)
Phenol	30	10	About 1 monolayer
Cinnamyl alcohol	40	5	1.8
Coniferyl alcohol	80	10	3.9

Films of phenol (Sigma-Aldrich Co., >97.0%), cinnamyl alcohol (Sigma-Aldrich Co., >97.0%) and the lignin precursor coniferyl alcohol (Sigma-Aldrich Co., 98%) were prepared in a directly connected preparation chamber (base pressure $<10^{-7}$ Pa), equipped with a thermal evaporator (Kentax 4-cell evaporator). The film thickness was estimated by the attenuation of the substrate signal. Typical evaporating parameters are given in Table 1. The monomeric models are shown in Figure 1.

Sample preparation for the MIES and UPS measurements was checked by XPS core level spectra before each MIES and UPS measurement. In detail, the ratio of oxygen to carbon and the percentage of C1 in total C1s peak was checked and compared with results found in the literature (Johansson et al. 2005).

Analysis

Analyses were performed with an UHV apparatus, which provides facilities for valence band electron emission spectroscopy, MIES, UPS (HeI and HeII) and core level spectroscopy (XPS). The method was described in detail previously (Maus-Friedrichs et al. 1990, 1991; Frerichs et al. 2006).

A cold cathode discharge produces a beam of HeI photons ($E^* = 21.2$ eV) for UPS and metastable He* atoms ($2^3S/2^1S$) ($E^* = 19.8/20.6$ eV) with thermal kinetic energy for MIES. The intensity ratio $2^3S/2^1S$ is found to be 7:1. The metastables approach the surface with near thermal energy and interact only with the outermost surface layer by Auger processes. Different mechanisms depending on the surface electronic structure and work function are possible. Detailed descriptions of the He*-surface interaction processes may be found in reviews (Harada et al. 1997; Morgner 2000). MIES as a non-destructive technique is extremely surface sensitive. For organic molecules and lignin, only Auger de-excitation (AD) occurs. The principle of AD is sketched in Figure 2. An electron from the sample surface fills the 1s orbital of the approaching He*. Simultaneously, the He* 2s electron is emitted carrying the excess energy (E_{kin}). Therewith, MIES provides only information about the outermost wave functions of the surface.

The emitted electrons are analyzed with a hemispherical analyzer (Leybold EA 10) set at a resolution of 220 meV full width at half maximum (FWHM) under normal emission within 280 s. The angle of incidence for the mixed He*/HeI beam is 45°. Considering the excitation energy of 19.8 eV of the 2^3S He*, the
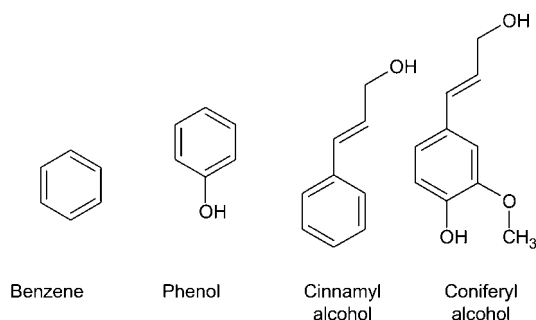
binding energy of the emitted electron can be calculated by the following equation: $E_B = 19.8$ eV$-E_{kin}$. The MIES/UPS (HeI) source is adapted to the UHV chamber via a two-stage pumping system. A time-of-flight technique is integrated to separate electrons emitted due to He* (MIES) or HeI (UPS) interaction with the surface. Thus, MIES and UPS spectra are recorded quasi-simultaneously.

All MIES and UPS spectra are displayed as a function of the electron binding energy with respect to the Fermi level, which is determined by the high energy cut-off obtained on metallic samples in UPS. The surface work function Φ can be determined from the low-energy onset of the MIES or the UPS spectra with an accuracy of ± 0.1 eV.

XPS is performed with a commercial X-ray source (Specs RQ20/38C), which is attached to the MIES/UPS apparatus, located in Clausthal. The spectra are recorded by the same hemispheric analyzer which is also used for MIES and UPS (HeI, HeII) and exhibit a FWHM of 1.9 eV for clean graphite. The photons hit the surface under an angle of 80° to the surface normal. Emitted electrons are analyzed under 10° to the surface normal. Detail spectra are recorded with a resolution of 1.1 eV FWHM and survey spectra with 2.2 eV FWHM, respectively.

XPS valence band and high resolution core level spectra were obtained using a VG ESCALAB 220i-XL spectrometer, located in Bremen at IFAM, equipped with an electromagnetic lens and hemispherical analyzer (Tornow et al. 2005). Monochromatic Al Kα radiation was utilized onto a spot size of 700 μm^2 on the sample surface. Core level and valence band spectra were recorded with a pass energy value of 20 eV in constant analyzer energy mode. Further, the instrument is equipped with a UPS (HeI/HeII) source, providing 21.2 eV (HeI) and 40.8 eV (HeII) excitation energy, enabling cross-referencing of the collected data of the different analytical systems.

To evaluate the XPS measurements, a linear background, caused by inelastic electron processes, was subtracted from the XPS C1s spectra. The peak shape was fitted by Gaussian distributions. The FWHM of the Gaussians curve was estimated by measuring the C1s spectrum of a clean graphite sample. Measurements derived based on a non-monochromatic X-ray source exhibit a FWHM of 1.9 eV, high resolution XPS spectra obtained by a monochromatic source exhibit a FWHM of 1.3 eV.

Figure 1 The structure of investigated molecules.
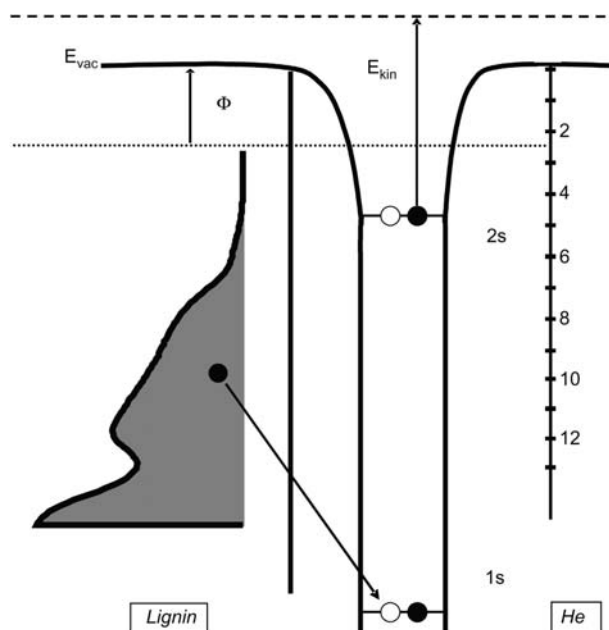
Figure 2 Auger de-excitation process. (Left) Density of occupied states at the lignin surface, (right) approaching metastable He* atom.

The distances of the Gaussians were allowed to be within the intervals of well-known chemical shifts of carbon not bound to oxygen, (C1) at 285 eV, carbon bound to one oxygen atom (C2) with a chemical shift of $\Delta E = 1.5$ eV referred to C1 and carbon double bound to oxygen (C=O) or bound to two oxygen atoms (O-C-O) (C3) with a corresponding peak shift of $\Delta E = 2.9$ eV (see Figure 3) (Dorris and Gray 1978). The additional fourth peak (C*) in the deconvoluted C1s-spectra ($\Delta E = 6.6$ eV) corresponds to the shake-up structure reflecting the $\pi \rightarrow \pi^*$-transition in the aromatic rings (Dilks 1981).

Results and discussion

The absence of any sulfur contribution to the survey XPS core level spectra of lignin (not shown here) reveals the complete disappearance of the solvent DMSO. Furthermore, the absence of any contribution from the substrate (Si) indicates that a fully covering film was prepared and the film thickness must be larger than approximately 10 nm. A spectrum of the C1s emission, obtained by the high resolution VG spectrometer, which was also used for valence band XPS, is presented in Figure 3. It displays well-resolved spectral features, indicating that no differential charging of the sample occurs. The O/C ratio amounts to 0.26 and the ratio of C1 to total C1s to 0.55. The samples were stored in an argon atmosphere during transport to the high resolution XPS spectrometer, which is located at the IFAM, to exclude sample contamination. Nevertheless, it was necessary to expose the samples which were measured at the IFAM to the environmental atmosphere to a certain extent. To exclude contamination by the environmental gases on the samples prepared by evaporation under UHV conditions, cross-referencing to the MIES/UPS apparatus was carried out by UPS (HeI/II) measurements, taken in both spectrometers. Additionally, the O/C ratio and C1 in total C1s was compared to monochromatic and non-monochromatic XPS core level spectra. Careful sample handling provides equal results for the UPS measurements in both apparatuses.

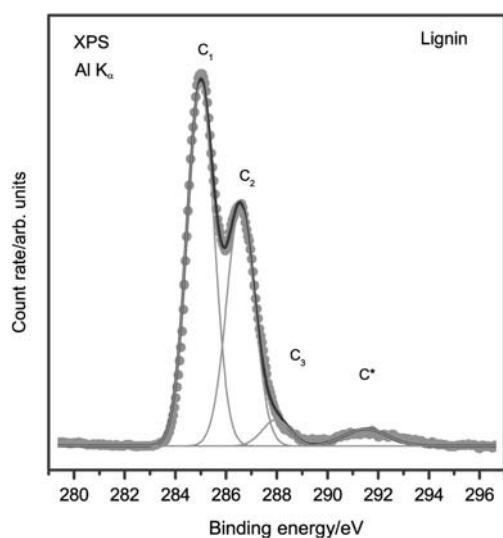XPS valence band spectra of lignin, coniferyl alcohol and cinnamyl alcohol are displayed in Figure 4. The bands can be assigned as an O 2s derived peak, labeled with (g) and the C2s derived structures labeled with (f1), (f2) and (e). The peak labeled with (f2) at around 22 eV, is due to the ionization of the C2s bonding molecular orbital of the molecule's or polymer's backbone. This interpretation is supported by comparison of the spectra with XPS valence band spectra of polyvinyl alcohol (Boulanger 1991) and theoretical results for polyvinylmethylether (Otsuka et al. 2000). The peaks (f1) and (e) are due to the ionization of bonding and antibonding combinations of the C2s molecule orbitals of the molecules skeleton (Galuska and Halverson 1998; Mähl et al. 1999).

As compared to C2s-derived states, C2p states are poorly resolved in XPS owing to the small cross-section of C2p-derived states with Al Kα photons (1486.6 eV). On the other hand, the cross-section for photo-ionization of C2p-derived states by UV photons of 21 eV (HeI) or 40.8 eV (HeII) is approximately 10 times larger than that of C2s-derived states making UPS a useful method to investigate C2p- and O2p-derived valence band states of lignin.

Figure 5 shows MIES and UPS (HeI) spectra of an organosolv lignin and monomeric model compounds, which have similar chemical structure and functional groups as native lignin. The monomers and coniferyl alcohol were analyzed for reliable band assignments. The commercial organosolv lignin is not supposed to be changed too much in comparison to native lignins. Benzene spectrum (Bahr and Kempter 2007) are presented for a reliable identification of the contributions of the benzene ring.

The MIES and UPS spectra of benzene reveal four characteristic spectral features. They are due to the ionization of the highest orbitals of the benzene molecule. In detail, the features can be identified according to the literature (Kimura et al. 1981; Kishimoto et al. 2000; Bahr and Kempter 2007) as: (a) $1e_{1g}$ (π); (b) $3e_{2g}$ (σCH) and $1a_{2u}$ (π); (c) $3e_{1u}$ (σCH), and $1b_{2u}$ (σCC); (c) $2b_{1u}$ (σCH); (d) $3a_{1g}$ (σCH).

Figure 3   X-ray photoelectron spectra, i.e., XPS C1s spectra of an organosolv lignin.
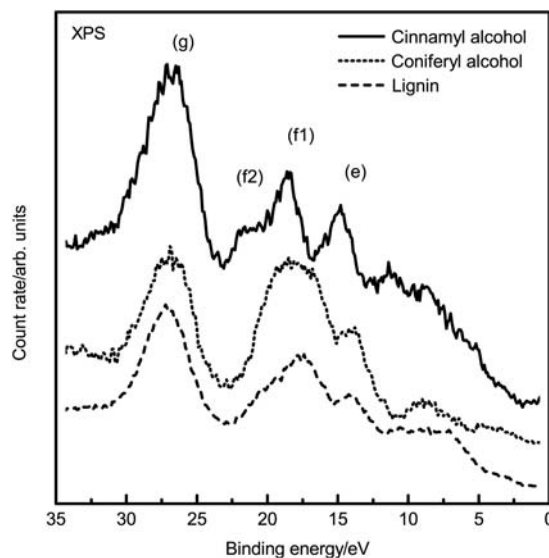
Figure 4   XPS valence band of cinnamyl alcohol, coniferyl alcohol and lignin.
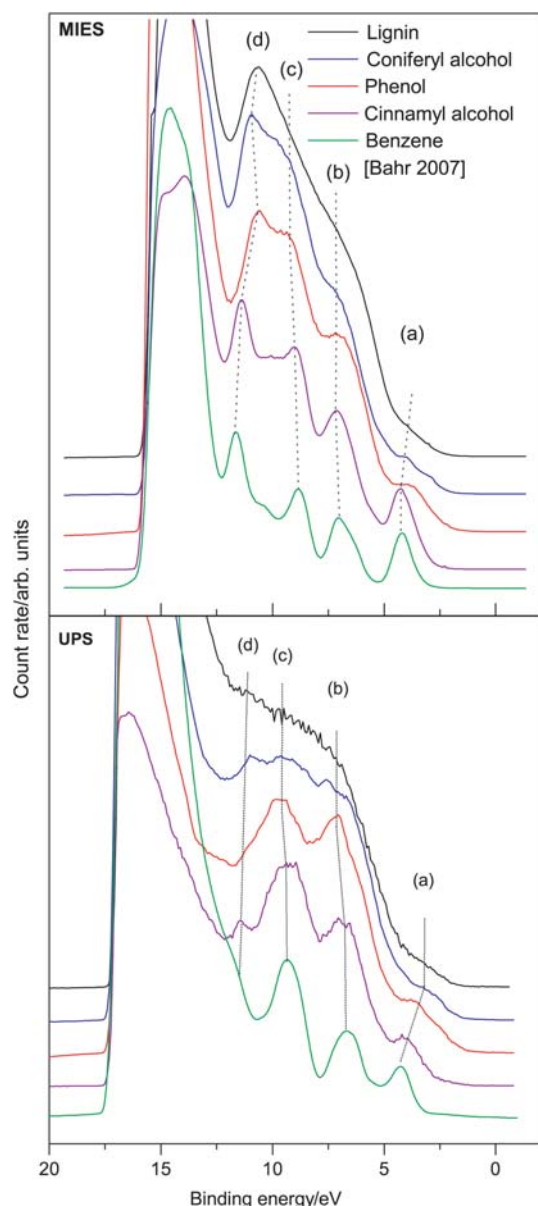
Figure 5 MIES (top) and UPS HeI (bottom) spectra of lignin and monomeric model compounds. MIES, metastable induced electron spectroscopy. UPS, ultraviolet photoelectron spectroscopy. Bands (a) to (d) from benzene, cinnamyl alcohol and phenol show only the ionization of orbitals of the aromatic ring. The shift of band (d) depends on the functional group substituted to the ring. For coniferyl alcohol and lignin structures, (a) to (d) can be assigned to (a) aromatic π orbitals, (b) oxygen lone pairs of the methoxy and hydroxyl groups, (c) mainly carboxyl groups, (d) mainly methoxy groups.

Phenol was prepared on Si(100) at room temperature. A film thickness of 0.4 nm was determined by XPS, corresponding to one monolayer. Corresponding to Kimura et al. (1981) and Kishimoto et al. (2000), the structures of phenol observed in MIES and UPS (HeI/II) can be identified as follows: (a) $4a''$ (π_3) and $3a''$ (π_2); (b) $2a''$ (π_1), $21a'$ and $20a'$; (c) $19a'$ (n_{OII}), $1a''$ (π_0) and $18a'$ $17a'$; (d) $16a'$ and $15a'$. The features (a) to (d) of phenol are less pronounced owing to the small film thickness, but due to the lack of target cooling, no thicker film could be prepared. Nonetheless, all important features of phenol can be recognized. Comparing them with benzene, two

important differences can be seen. First, the structure (a) is broadened towards lower binding energy; second, structure (d) is shifted towards lower binding energy, and both are in agreement with Kimura et al. (1981). These shifts are the consequence of the OH group, which influences the orbitals of the aromatic ring. That shift can be used to identify an OH group bond to the aromatic ring.

Due to the substantial similarities in MIES from cinnamyl alcohol and benzene, only characteristic features of the phenyl group of cinnamyl alcohol are seen in its MIES spectrum. Peaks (a), (b) and (c) of cinnamyl alcohol and benzene are found at the same binding energies. Only peak (d) of cinnamyl alcohol is shifted by 0.4 eV to lower binding energies. Considering that MIES only probes the outermost molecule orbitals and that no contributions from the pendant group are seen, the cinnamyl alcohol molecules must be oriented on the surface with the pendant group towards the substrate and exposing the phenyl ring towards the vacuum side. For that reason, the shift of peak (d) in the lignin spectrum must be a consequence of the corresponding propenol.

The UPS (HeI) spectrum of cinnamyl alcohol in Figure 5 shows four sharp peaks labeled from (a) to (d). Peaks (a) to (c) are again at the same positions similar to (a) to (c) from benzene. In benzene, the contribution of (d) is only visible as a shoulder at 12.2 eV, because it is shifted towards higher binding energy where it overlaps with secondary electrons.

The difference between the MIES and UPS spectra of cinnamyl alcohol is a consequence of the different information depth of the two techniques. Due to the higher information depth, the UPS spectrum contains contributions not only of the phenyl rings but also of the pendant chemical groups located towards the substrate, which explains the differences between the two measurements.

The increase of intensity in the region (a) of coniferyl alcohol, in Figures 5 and 6, between 3.5 eV and 4.8 eV binding energy, in MIES and UPS (HeI and HeII) can only be assigned to the ionization of π bands of the aromatic ring, since other functionalities of lignin do not show any contributions in that region. The other features of the aromatic ring are superimposed by contributions from the other molecular orbitals.

The structure between 5 eV and 12 eV binding energy is due to the ionization of C2p and O2p atomic orbitals. Comparing this energy interval with simulated XPS spectra of polyvinyl alcohol carried out by Boulanger et al. (1991) and the MIES and UPS from phenol and cinnamyl alcohol, the peak seen at position (b) must be due to the ionization of hydroxyl groups. The methoxyl groups of the coniferyl alcohol cause additional contributions in the interval from 5 eV to 12 eV binding energy (Mähl et al. 1999; Otsuka et al. 2000) leading to less pronounced peaks (b), (c) and (d). More precisely, the presence of methoxy groups broadens the structure (d) towards higher binding energy by approximately 0.3 eV in MIES spectrum. Unlike the cinnamyl alcohol molecules, coniferyl alcohol does not show any orientation of the molecules on the substrate since no functionality is preferred to link to the substrate.
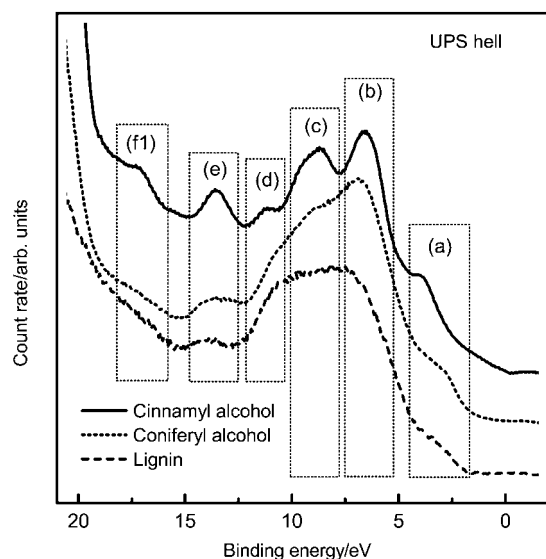
Figure 6 MIES and UPS HeII of lignin as a function of the sputtering time. MIES, metastable induced electron spectroscopy. UPS, ultraviolet photoelectron spectroscopy.

Figure 7 Ultraviolet photoelectron spectroscopy (UPS) HeII of cinnamyl alcohol, coniferyl alcohol and lignin. Peaks (a) to (d) are equivalent to MIES and UPS (HeI) in Figures 4 and 5, peak (e) refers to methoxy and hydroxyl groups.

The peak-like emission seen at binding energies larger than 13 eV binding energy in MIES and UPS (HeI) is due to secondary and/or scattered electrons with small kinetic energy and is therefore not of interest. Due to the overlap of this secondary electron peak with the C2s-derived states, which are scarcely seen, UPS (HeII) and XPS valence band spectra were recorded to obtain more information about higher binding energy states.

In Figure 7, UPS (HeII) valence band spectra of cinnamyl alcohol, coniferyl alcohol and lignin are visible. Bands (a) to (d), discussed already for the MIES and UPS spectra can be clearly recognized. Peak (e) at 13.6 eV is due to the ionization of C2s and O2s molecular orbitals. Because of the lack of methoxy groups, the peak (e) from cinnamyl alcohol must be due to emission from hydroxyl groups. The broader peak (e) of coniferyl alcohol is mainly made up by emissions from hydroxyl and methoxy groups.

Peak (b) of coniferyl alcohol is a result of the ionization of the oxygen lone pairs of the methoxy and hydroxyl groups on the one hand, and small contributions of the π-orbitals of the aromatic ring, on the other hand (Kimura et al. 1981). Peak (c) of coniferyl alcohol involves only contributions from hydroxyl groups and slight contributions from the aromatic ring, but no contributions from methoxy groups are expected, which is consistent with the decrease of intensity.

Peak (d) from cinnamyl alcohol involves only contributions from the aromatic ring, which was described previously. So, peak (d) from cinnamyl alcohol is not due to the ionization of oxygen derived molecular orbitals. The increase of intensity in the region (d) of coniferyl alcohol and lignin can be assigned to the ionization of methoxy groups (Kimura et al. 1981; Okudaira 1998), since no contributions from hydroxyl groups are expected in that region. So, region (d) is a fingerprint for methoxy groups in coniferyl alcohol and lignin.

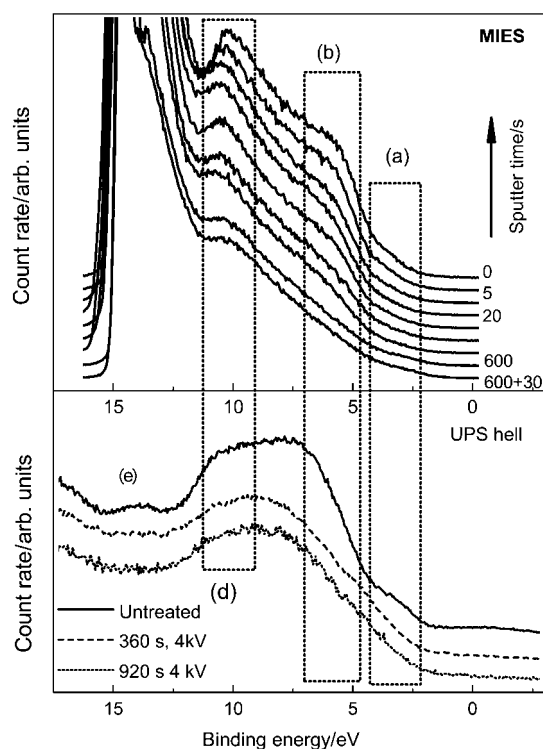Peak (f1) at 17.3 eV corresponds to the C2s molecule orbitals of the molecules skeleton (Salaneck and William

1984; Galuska and Halverson 1998). These 2s derived bands are more pronounced in the XPS spectrum.

The identification of the different functional groups of lignin is of great use to study changes induced by ions or radicals found, e.g., in gas discharges, which can be used to alter the wetting behavior of wood surfaces (Rehn et al. 2003; Wolkenhauer et al. 2007).

To simulate the ion impact of a plasma treatment, we applied a sputter gun for in situ treatment of the lignin surface. Figure 6 displays MIES spectra obtained during sputtering a lignin surface with Ar ions of 1 keV kinetic energy. Changes to the MIES spectra during the sputter process are shown. For the last two spectra, the kinetic energy of the ions was increased to 2 keV and 4 keV, respectively. No significant changes in the O/C ratio of the slightly sputtered surfaces could be observed by XPS. Nevertheless, slight sputtering of the lignin surface causes loss of oxygen derived states in the MIES spectra, which are the regions around peaks (d) and (b), respectively. The fact that the loss of oxygen is only seen in MIES and not in XPS or UPS, demonstrates that slight sputtering alters only the outermost layer of the polymer. Continuing sputtering at higher energy (4 kV) also alters the O/C ratio from 0.30 to 0.15, leading to the disappearance of peak (e) in the UPS spectra, as visible in Figure 6. Simultaneously, the percentage of C1 in C1s increases from 0.54 to 0.81. The disappearance of peak (e) in UPS spectrum with increasing sputter time and the decrease of the O/C ratio confirms the assumptions made on the basis of the model compounds that (e) is made up from methoxy and hydroxyl groups. Continued sputtering leads to the disappearance of structure (a),

which was attributed to the phenyl groups. The ion bombardment seems to destroy the lignin structure at the surface in combination with the loss of oxygen, leading to an amorphous carbon layer at the surface. This interpretation is supported by the similarity of the MIES of the sputtered lignin surface with that of clean graphite presented by Harada et al. (1997).

Conclusions

Lignin and simple monomeric lignin model compounds were investigated by XPS (core level and valence band), UPS (HeI and HeII) and MIES.

It was possible to assign hydroxyl, methoxy and phenyl groups in MIES and UPS spectra of the lignin surface. Furthermore, the time dependent sputter experiment demonstrates well the capability of the combination of XPS, UPS and MIES, by taking advantage of the different information depth of each technique. The ion bombardment seems to destroy the lignin structure at the surface in combination with a preferential loss of oxygen, leading to an amorphous-like carbon layer at the surface.

Further, the combination of UPS and XPS allows the study of the valence band of lignin or modified lignin surfaces, where UPS (HeI and HeII) provides a good performance for the analysis of p-derived states and XPS (Al Kα and Mg Kα) for s-derived states of the valence band.

Acknowledgements

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