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Surface analysis of different wood species using X-ray photoelectron spectroscopy (XPS)

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X-ray photoelectron spectroscopy (XPS) was used to characterize the surfaces of mechanically treated wood. Microtomed and sanded surfaces of spruce, larch, beech and oak were investigated. Changes due to the sanding process were identified from the survey spectra as well as from the detailed C1s spectra. The changes were quantified with the atomic ratio of oxygen to carbon and with a detailed analysis of the contributions to the C1s peak. The identified changes were explained in terms of the macromolecular wood substances and in terms of density and the amount of extractives.

1. Introduction

Wood consists mainly of three macromolecules: cellulose, hemicellulose and lignin. These polymers are built of hydrogen, carbon and oxygen. From conventional chemical analysis the bulk composition is well known and can be found in the literature [1]. Surface properties are not only determined by bulk composition, but they are heavily influenced by the surface building process. This is true for the morpological character of the built surfaces as well as for changes of the chemical composition. Therefore, information about the properties of a small region on the materials surface is necessary in order to evalute the influence of the building process. A suitable investigation method to characterize changes of the chemical composition of a material surface is X-ray photoelectron spectroscopy (XPS). This method, which analyses the surface to a depth of about 1–20 nm, provides information about the chemical bonding as well as surface composition [2]. It has been previously used to investigate changes after chemical treatment [3–7]. However, investigations of chemically untreated and non extracted wood are quite rare as are investigations which cover the influence of mechanical treatments. Liptáková *et al.* [8] studied the influence of milling and grinding of beech and compared the results to microtomed surfaces. Shen *et al.* [9] used XPS to investigate chipped surfaces of pine and to combine the results with wetting measurements. Moreover, investigations using different softwood and hardwood species are lacking.

In this study we compare the chemical composition of the surface of four different wood species, two softwoods (spruce and larch) and two hardwoods (oak and beech) built by two different mechanical methods. Specimens cut with a sledge microtome and sanded with a random orbit sander, were investigated using XPS in order to quantify the chemical changes at the surfaces. Differences due to the mechanical treatment as well as differences between the wood species are analysed and discussed.

2. Materials

Four different wood species, two hardwoods: oak (*Quercus robur*) and beech (*Fagus sylvatica*) and two softwoods: spruce (*Picea abies* Karst.) and larch (*Larix decidua* Mill.) were investigated in this study.

The samples were cut out radially from the stem and two different types of preparation were chosen:

1. ground with a random orbit sander with sandpaper P400
2. microtomed with a sledge microtome.

The specimens were not extracted or modified otherwise by chemical or thermal treatment. Surface preparation was done on preforms that were stored in a climate chamber (60% relative humidity at 20°C) until preparation.

The radial surface was chosen for investigation with XPS and the sample dimensions were 10 × 10 × 1 mm.

In order to save time during evacuation within the high vacuum chamber of the X-ray-system and to remove the water, the samples were vacuum dried for almost 24 hours within a two stage pumpstand with a rotary pump followed by a diffusion pump. After this the samples were encapsulated in a LDPE-foil and then placed in a container with silicagel to prevent resorption until the measurements were carried out.

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3. Methods

For the XPS investigations a PERKIN ELMER 5500 ESCA System, with a Mg Anode (X-ray-voltage 15 kV, 300 W, X-ray energy 1253.6 eV), was used.

For each sample two spectra in a fixed analyzer mode were measured. The aquisition time of 10 minutes was chosen to obtain sufficient counting statistics.

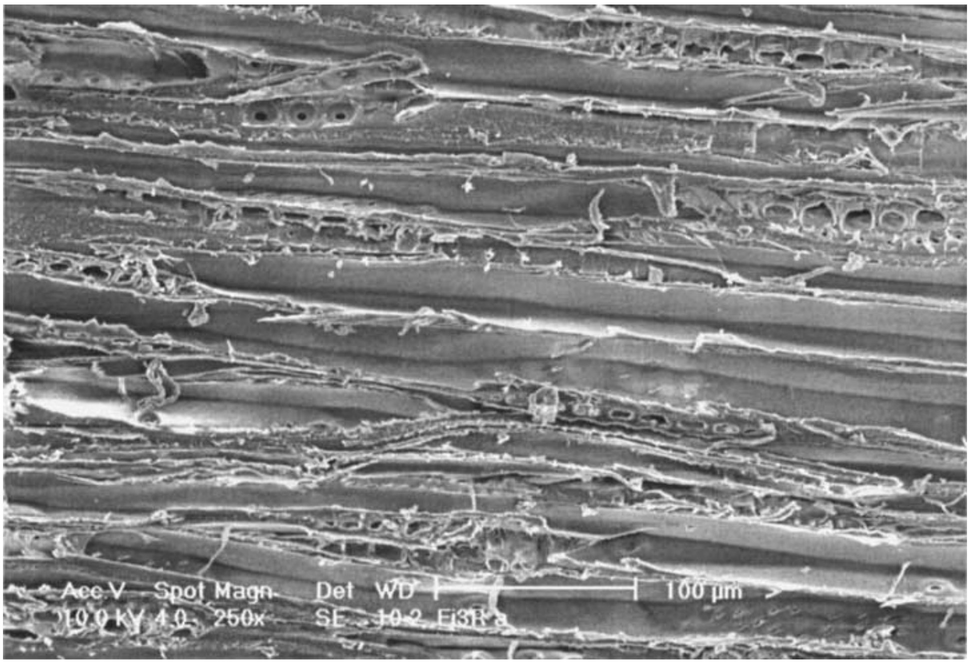
Two spectra were obtained for each sample:

1. A survey spectra from 0 to 1000 eV binding energy (pass energy 90 eV)
2. A high resolution spectra of the C1s region 280–300 eV (pass energy 71.55 eV)

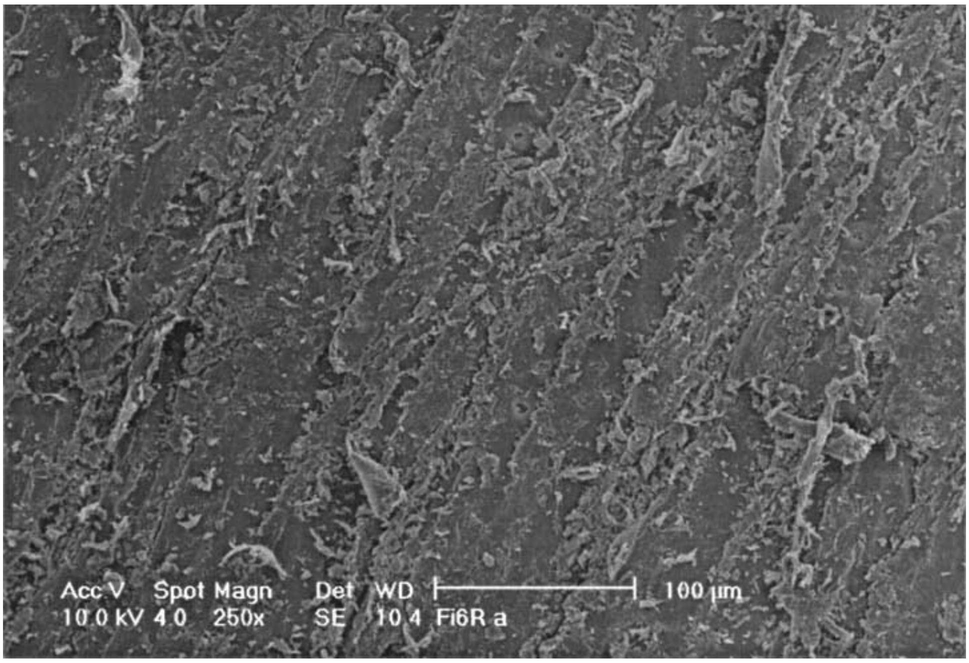
From the survey spectra the ratio of atomic concentration of oxygen to carbon was determined by integrating the area under the curve after a linear background was removed [10]. In order to calculate this ratio the empirical derived atomic sensitivity factors from [11] were used.

Detailed chemical-bond analysis of the carbon was made by curve fitting with a least squares method of the C1s peak area region using the XP-SPEAK Version 4.0 –software from Raymund W.M. Kwok, which is freely available in the Internet (URL: http://chromium.chemie.fu-berlin.de/xpspeak4.zip). According to the classification of carbon atoms in wooden materials, as reported by [10], the C1s peak was deconvoluted into four subpeaks:

1. C1 class of carbon atom that corresponds to carbon atoms bonded only by carbon or hydrogen bonds



(a)



(b)

Figure 1 (a) SEM image of microtomed spruce; (b) SEM image of fine sanded spruce.

2. C2 class which corresponds to carbon atoms bonded to a single noncarbonyl oxygen

3. C3 class of carbon bonded to a carbonyl or two noncarbonyl oxygen

4. C4 class of carbon atoms bonded to a carbonyl and a noncarbonyl oxygen.

For peak fitting, further restrictions were chosen, namely an identical full width at half maximum (FWHM) for each class of carbon and the same curve form (Gaussian-Lorentzian product function).

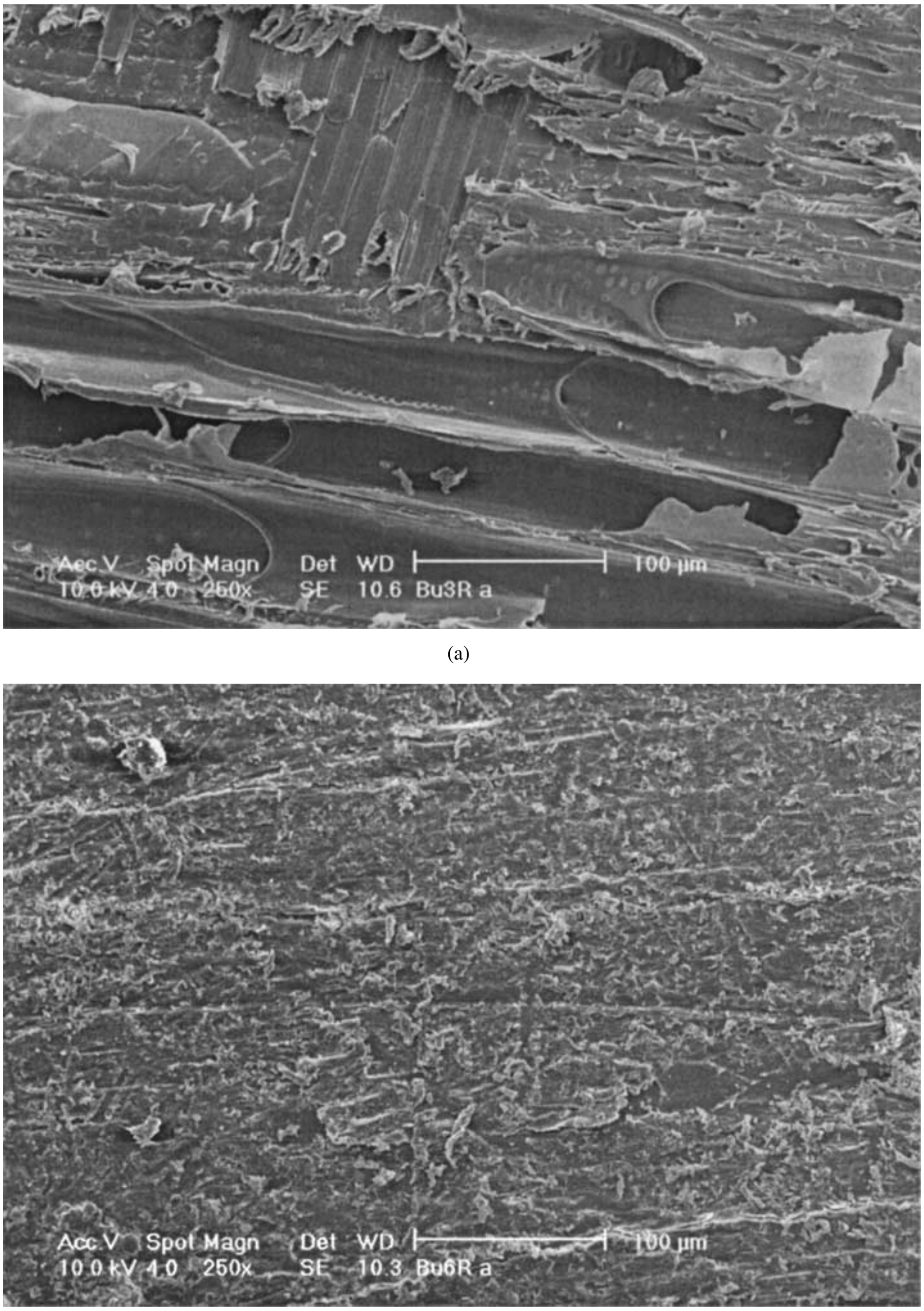
The curve fitting procedure was made by a two step approximation: at the beginning the energy-shift between the four classes of carbon was fixed as follows: $C2 = C1 + 1.4$ eV, $C3 = C1 + 2.8$ eV, $C4 = C1 + 3.75$ eV. The peak position of C1 was arbitrary and chosen in the middle of the C1s peak, at the second step these restrictions were released except the restriction for the FWHM.

For best approximation it was necessary to fit with a further peak called CO with a binding energy about -1.5 eV lower than C1.

Charge compensation was not made during the experiment but line-shift was calculated afterwards.

4. Results

The morphological features of microtomed and sanded spruce are shown in Fig. 1. As can be seen the anatomical characteristica are hardly changed by the microtoming procedure (Fig. 1a). Quite in contrast the anatomical structure of spruce is hard to recognize on the sanded surfaces (Fig. 1b).



(a)

(b)

Figure 2 (a) SEM image of microtomed beech; (b) SEM image of fine sanded beech.

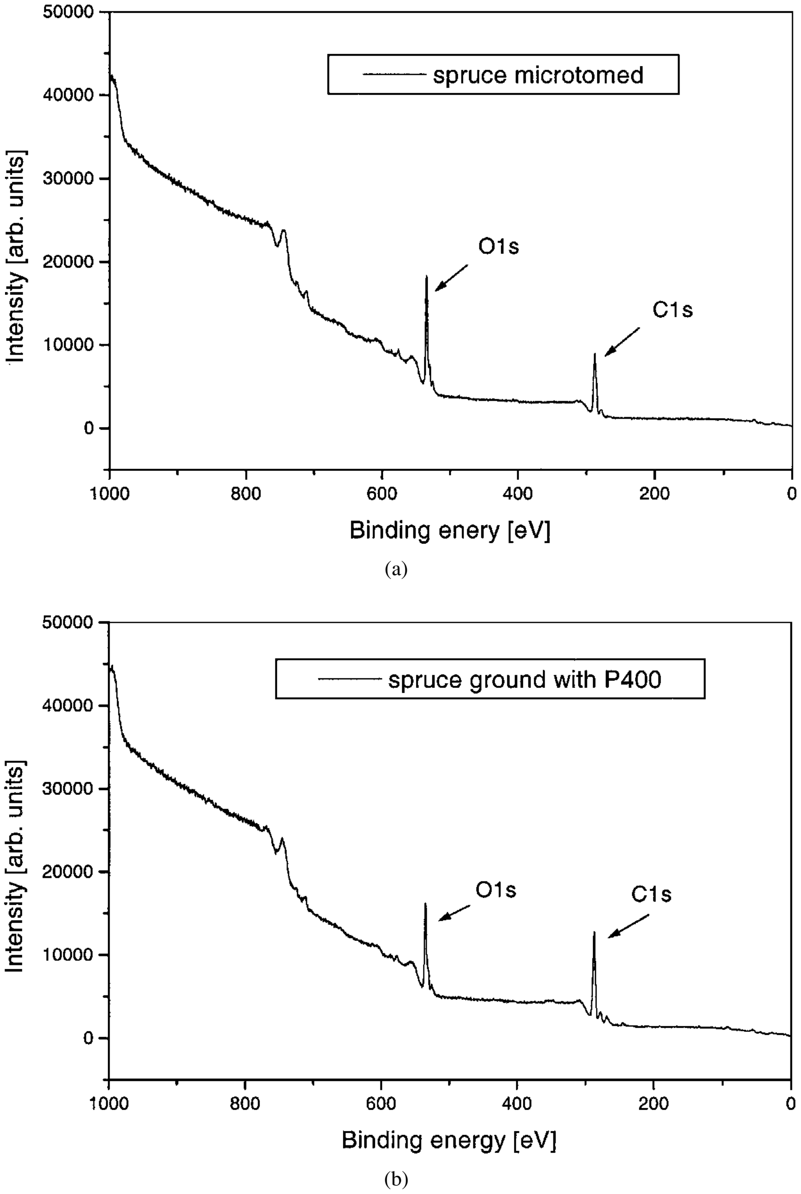


Figure 3 (a) Survey spectra of spruce microtomed; (b) survey spectra of fine sanded spruce.

During sanding the wood fibres are heavily deformed. Moreover, they are mechanically distorted and even crushed. This holds for all four wood species, both softwoods and hardwoods, as can be seen in Fig. 2 where a microtomed surface (Fig. 2a) and a sanded surface (Fig. 2b) of beech are shown.

The survey XPS spectra for spruce is shown in Fig. 3. On all spectra, both from the microtomed (Fig. 3a) and the sanded samples (Fig. 3b) the presence of oxygen and carbon could be identified. By comparing the survey spectra in Fig. 3b with Fig. 3a it can be seen that the carbon C1s peak of the sanded surface is higher than the C1s peak of the microtomed specimen and the oxygen O1s peak is lower. Only these two elements are present to a noticeable amount. The survey spectra of the other wood species exhibited the same findings.

For the four wood species the atomic ratio of oxygen to carbon was higher for the microtomed sections than for the corresponding grounded specimens, (e.g. Fig. 3a and b) except oak, where no significant difference could be identified (Fig. 4).

Although a Gaussian-Lorentzian product function was used for the fitting of the peaks the result showed that only for 16% of all measured samples a small deviation from pure Gaussian behaviour could be found. The lineshape due to the physical process is Lorenzian. However, it is generally assumed that the instrumental contributions to the photoemission peak have a Gaussian lineshape [12]. Therefore the latter influences are dominant.

In Fig. 5 a deconvoluted high resolution spectrum of the C1s peak of microtomed spruce and the different parts contributing to the peak are shown.

Contamination of the samples by carbon is one of the most important problems when using XPS for the investigation of polymers. This is even more problematic for wood than for other materials. First, just the C1s peak is of greatest importance when interpreting XPS data from wood. Second, some handling of the specimens has to be done prior to the measurements (dehydration, encapsulating in a foil, etc.). Therefore the C0 class was introduced. Such a C0 subpeak was also found

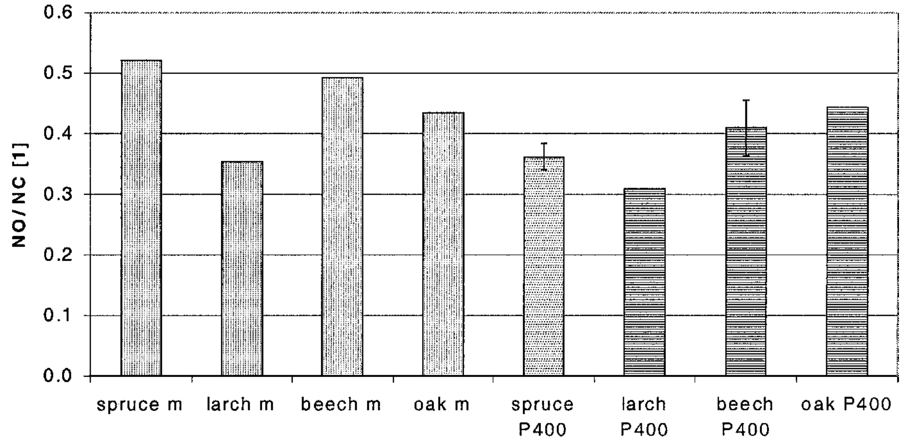


Figure 4 Atomic ratio of oxygen (NO) to carbon (NC).

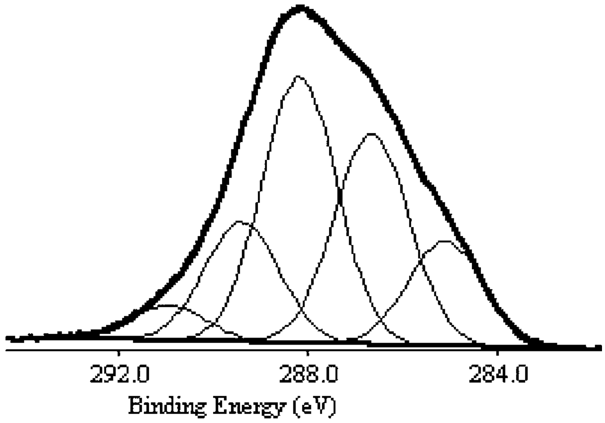


Figure 5 C1s spectra of microtomed spruce; subpeaks separated by deconvolution.

by Torr *et al.* [7] and Dawson [5]. It was interpreted as recondensed polyaromatics respectively as adsorbed hydrocarbon contamination. In this study a C0 class was measured on every specimen resulting from electrical conducting material. Plotting the subpeak position of C0-C1 against C1-285 eV yielded a statistically significant (1% level) linear correlation with a slope near −1 (see Fig. 6) indicating that the subpeak position of C0 is not influenced by charging. Moreover, the standard deviation for the subpeak position when considering all samples was lowest for C0 and nearly fixed at (285.2 ± 0.1) eV. Therefore, the contribution of the C0 class was interpreted as a contamination and was excluded from the further analysis.

Other carbon contamination contributing to the C1 subpeak is not possible to separate. The experimentally necessity to store the prepared samples in a LDPE foil which consists only of $-CH_2-$ chains [13] could contribute to this type of contamination.

A detailed analysis of the C1s region for the sanded surfaces showed that the most important contribution came from the C1 class consisting of C-C and C-H linkage of carbon (Fig. 7). The highest amount was found for spruce (60%) whereas for larch the lowest amount was determined (40%). For all sanded samples the C2 class contributed the second largest amount. For the microtomed samples the contribution of the C1 class was also very important. However, for spruce and beech the C2 class representing the C-O and C-OH groups contributed the greatest amount with 43 and 45%. (Fig. 7).

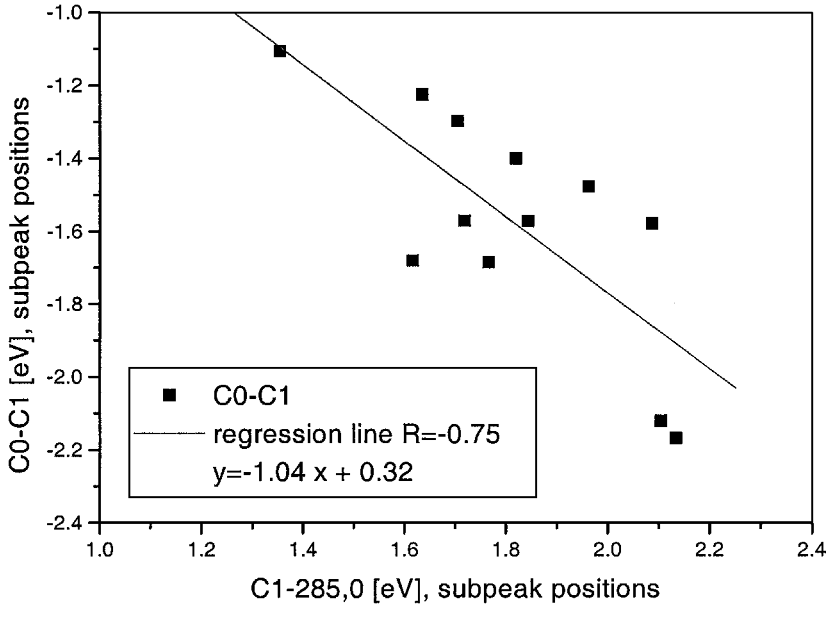


Figure 6 Sample charging.

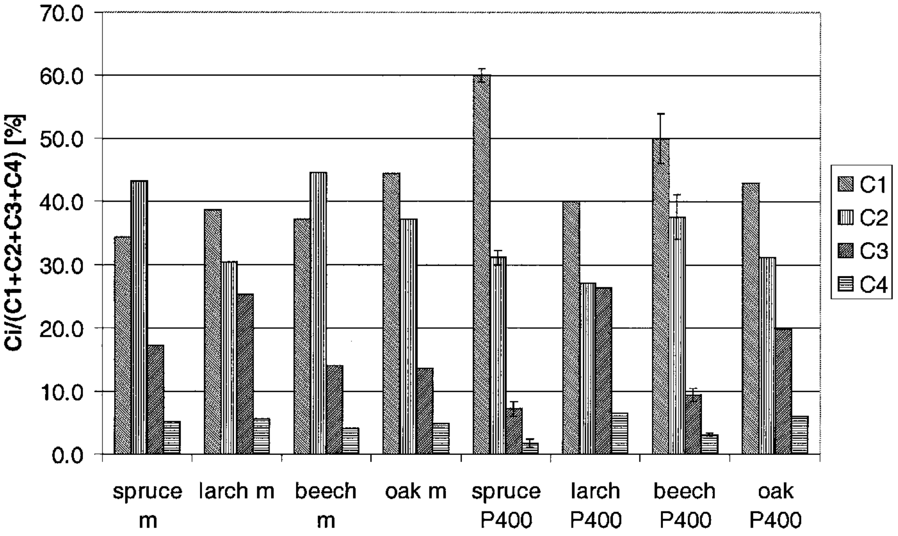


Figure 7 Component peak area contributions: Ci/(C1 + C2 + C3 + C4).

The C3 and C4 class contributed less both for the microtomed and sanded surface. The C3 class contributed between 7 (sanded spruce) and 26% (sanded larch). The C4 class representing carbon atoms bonded to a carbonyl and a noncarbonyl oxygen contributed only between approximately 2–7% to the C1s peak.

5. Discussion

The NO/NC values showed a decreasing trend from the microtomed to the sanded samples (Fig. 4). This indicates that fine sanding process leads to a smooth surface (see Figs 1b and 2b) with the more ductile matrix substances, e.g. lignin, being enriched on the surface. As lignin is known to have a lower NO/NC ratio than cellulose [10, 14], the lower NO/NC ratio for the sanded samples can be explained. This interpretation is supported by the fact that for pure cellulose a NO/NC ratio of approximately 0.83 has been postulated [10, 14, 15] whereas for lignin a ratio around 0.35 has been calculated [10]. When considering the change of the NO/NC ratio from the microtomed to the sanded samples, spruce is modified most, followed by beech, larch and oak. This indicates an influence of the density on the modification due to the sanding process. In Fig. 8 the ratio of NO/NC of the sanded to the microtomed samples is plotted versus the mean measured density of the wood species. Although the number of wood species with different density is not high enough to draw statistically significant conclusions, a trend of decreasing influence of the sanding process with increasing wood density might be indicated. However, more wood species have to be investigated to prove such a relationship. All results are summarized in Table I.

It was shown that the highest contributions to the C1s peak originates from the C1 and C2 class. These two subpeaks are also modified most by the mechanical treatment. Compared to the microtomed samples the contribution of the C1 class is increasing and that of the C2 class is decreasing for the sanded specimens. As cellulose should have a much higher contribution from the C2 class than lignin [16, 17] and a contribution of the C1 class for cellulose should be negligible [16] the same interpretation as for the NO/NC ratio

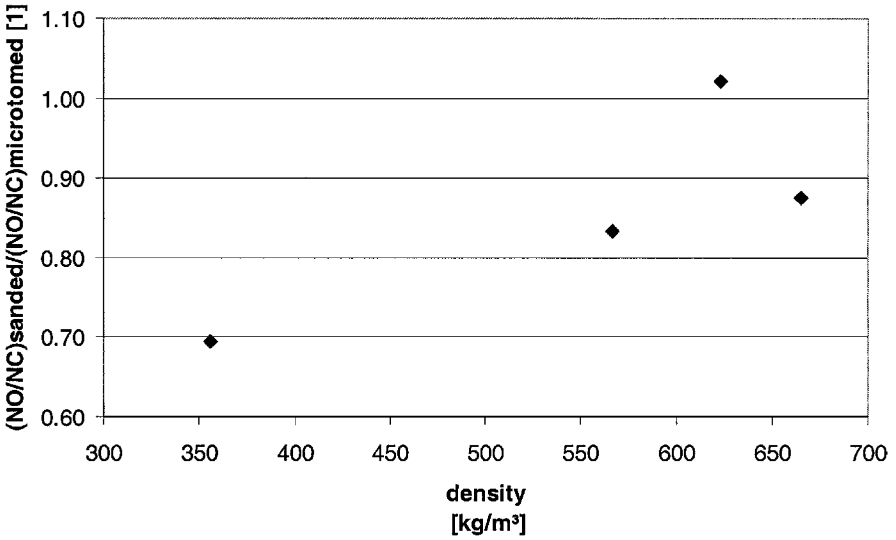


Figure 8 $(NO/NC)_{P400}/(NO/NC)_{microtomed}$ as a function of the density.

TABLE I Density, atomic ratio of carbon to oxygen, subpeak areafractions

Wood species and treatment	Density [kg/m^3]	No. of samples	NO/NC [1]	Area fraction Ci/(Σ Ci) [%]				
				C0	C1	C2	C3	C4
Spruce m		1	0.52	15	29	37	15	4
Spruce P400	356	3	0.36	12	53	27	6	2
Larch m		1	0.35	14	33	26	22	5
Larch P400	665	1	0.31	14	34	23	23	6
Beech m		1	0.49	21	29	35	11	3
Beech P400	567	3	0.41	12	44	33	8	3
Oak m		1	0.44	19	36	30	11	4
Oak P400	623	1	0.44	16	36	26	17	5

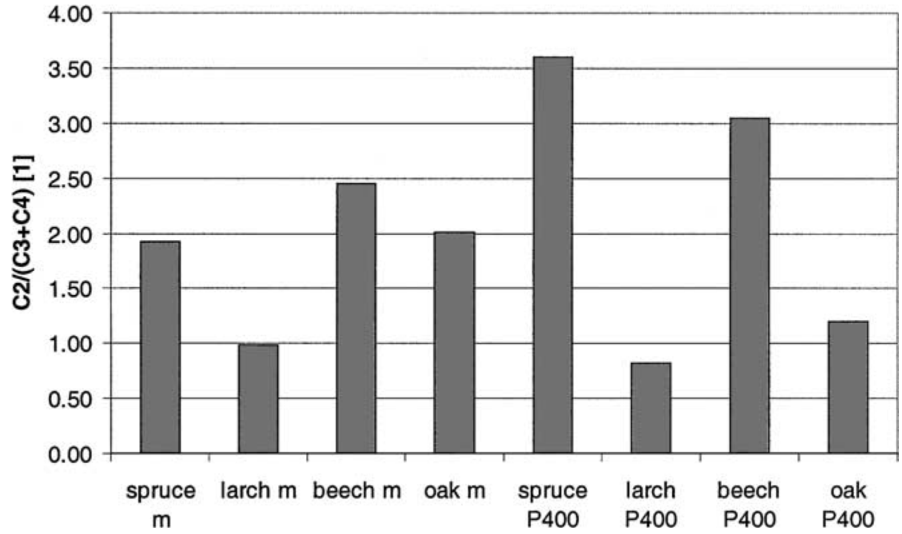


Figure 9 Ratio of carbon bonded only to one oxygen versus carbon bonded to more than one oxygen C2/(C3 + C4).

holds, namely that lignin is enriched on the surface and the cellulose content of the outermost surface layer is reduced. Moreover, contaminations for example from the sanding paper could also contribute to the increased C1 subpeak.

For sanded larch and oak the contribution of the C3 and C4 classes to the C1s peak is about equal to that of the C2 class (see Fig. 9). For sanded spruce and beech the contribution of the C2 class is about three times larger than that of the C3 and C4 classes. This fact might be due to the higher extractive content of larch and oak [1, 18]. These extractives are expected to contribute to the C3 and C4 classes [19]. For the microtomed samples only larch shows a high contribution of C3 and C4 classes compared with the other species.

6. Conclusions

In this paper XPS was used to characterize the surfaces of mechanically treated wood. Microtomed as well as fine sanded specimens of spruce, larch, beech and oak were investigated on the radial surfaces. The atomic ratio of oxygen to carbon NO/NC determined from the survey spectra was found to be lower for the sanded samples. The amount of decrease was influenced by the wood density. A detailed analysis of the C1s peak showed that contributions mainly attributed to cellulose decreased due to the sanding process. In contrast, contributions attributed mainly to lignin or carbon contaminations were increased. This is explained by the fact that the more ductile wood components are enriched on the surface during the sanding process. Moreover, it was shown that the contributions of higher oxidation states were larger for the wood species with more extractives.

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