

Some Aspects on the Determination of Surface Chemical Composition and Wettability of Modified Wood

Finn Englund¹, Lars Elof Bryne², Marie Ernstsson³, Jukka Lausmaa⁴
and Magnus Wålinder^{1,2}

¹SP Technical Research Institute of Sweden, SP Träteknik, Box 5609, 114 86 Stockholm, Sweden
[email:finn.englund@sp.se]

²KTH, Royal Institute of Technology, Building Materials, 100 44 Stockholm, Sweden
[email:lars-elof.bryne@byv.kth.se]

³Institute for Surface Chemistry, Box 5607, 114 86 Stockholm, Sweden
[email:marie.ernstsson@yki.se]

⁴SP Technical Research Institute of Sweden, Chemistry and Materials Technology, Box 857,
501 15 Borås, Sweden [email:jukka.lausmaa@sp.se]

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ABSTRACT

Recent advances in spectroscopy methods used in the surface science field may provide new valuable information about the surface chemical composition of engineering materials. Our idea is to apply such methods combined with wettability analysis in the development of well designed adhesives and coating systems for newly developed and commercially available modified wood materials. The main objective of this paper is to demonstrate and present some aspects on the application of two different state-of-the-art spectroscopic methods for surface chemical composition studies of a complex material such as modified wood. The methods are X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (ToF-SIMS), the former generating more quantitative data and the latter more qualitative data. The spectroscopic data are also combined with wettability data obtained from contact angle measurements using the Wilhelmy method. Modified wood samples were prepared from pilot plant or commercially produced acetylated, furfurylated and heat treated wood. Effects of wood surface ageing, *i.e.* the time after machining, on the surface chemical composition and wettability were also studied. Results clearly indicate a hydrophobization process due to ageing of the unmodified and certain modified wood, probably mainly related to a migration and reformation of extractives in the surface. The surface composition and wettability of acetylated wood was not appreciably affected by the ageing process. Such findings could be quantified by the XPS measurements, which is further discussed and related to the different wood modification routes. ToF-SIMS is a powerful tool and complementary to XPS for identification of *e.g.* specific hydrophobic substances in the wood surfaces. Additionally, this method provides ion images, mapping the lateral distribution of selected secondary ions signals within an analyzed wood surface area.

INTRODUCTION

Modified wood is often used in combinations with other materials, *e.g.* with adhesives in more complex engineered products or with coatings for protective or aesthetic purposes. Surface properties, and most notably the wetting behaviour, then becomes a very decisive factor for the performance of the combined material. The wetting properties are indirect expressions on a macroscopic scale of surface characteristics on a

microscopic scale, governing adhesion phenomena and hence the interfacial forces between materials. They are, in turn, dependent on the chemical composition in the outermost layers of the surface. It is also well known that the chemical composition of wood, unmodified or modified, is subject to changes with time and that these changes may occur very rapidly on fresh surfaces (Back 1991, Nussbaum 1999, Nguyen and Johns 1979, Hse and Kuo 1988, Nuopponen *et al.* 2003).

Wood is a three-dimensional natural biopolymer composite composed of varying proportions of the main polymer components – cellulose, hemicellulose, and lignin – in different cell layers. The chemical characteristics of an exposed wood surface may therefore depend on the exact position of the cutting plane and the cutting technique when a fresh surface is created. The changes with time are results of mainly oxidative reactions in the polymers, but also of translocation of mobile, naturally occurring extractives. For modified wood, additional components are present, such as non-fixed impregnation residues and monomers or oligomers of polymerisable treatment chemicals, which can also migrate to the surface and alter its chemical characteristics.

Well established techniques for investigations of surface phenomena and wettability of lignocellulosic materials include contact angle measurements, where the Wilhelmy plate technique has been proved to deliver more consistent and reproducible data than the traditional sessile drop methods (see *e.g.* Wålinder and Ström 2001). Such data is useful for predicting interaction parameters between *e.g.* wood and water or wood and other polymeric materials. The theory and procedures around these determinations of wettability and acid-base interaction parameters is further described by Wålinder and Johansson (2001), Wålinder and Ström (2001), and Wålinder and Gardner (2002).

Conclusions about the chemical composition of the outermost 5-10 nm of a lignocellulosic surface can be drawn from the elements and functional groups detected and quantified by X-ray photoelectron spectroscopy (XPS) (Ström and Carlsson 1992, Gindl *et al.* 2004). Molecular fragments, and often also intact molecular ions, in the surface can be identified with time-of-flight secondary ion mass spectrometry (ToF-SIMS). This method, which has recently been used with or without combination with XPS, has an information depth of only 1-2 nm, and it has a lateral resolution in the order of 100 nm (Tokareva *et al.* 2007, Kangas and Kleen 2004).

MATERIALS AND METHODS

Veneer samples of pine (*Pinus sylvestris*) sapwood with mainly radial sections and dimensions of approximately 10 x 5 x 0.5 mm³ were prepared from wood sticks cut into smaller blocks according to the description in Bryne (2008). Before cutting the veneer replicates, the wood blocks were wrapped in clean aluminum foil and then placed in plastic zip-lock bags. The final veneer preparation was made with a steel chisel, carefully cleaned with hexane between each use. Veneers prepared for the ageing test series were placed in glass Petri dishes and stored in normal indoor climate for 4-5 weeks.

These studies embraced, in addition to unmodified pine, also samples of acetylated pine with 18-23% acetyl content, heat treated spruce (*Picea abies*, Thermowood D process), and furfurylated radiata pine (*Pinus radiata*). The latter had been treated according to the process described by Lande *et al.* (2004) to a weight gain of ~30%.

The Wilhelmy method, was applied to estimate apparent contact angles on the veneer, measured along the wood grain. A Sigma 70 tensiometer from RSV Instruments was used with a test velocity of 12 mm/min. The veneers were immersed in the liquid (advancing stage) to a depth of 6 mm and then withdrawn (receding stage) to about 4 mm above the surface, and thereafter immersed a second time. The measurements were performed at about 22 °C and about 50% relative humidity. Five independent wood veneer replicates were tested, and in each case new liquid was used. Each replicate was then conditioned to approximately its original weight and tested in the 'wetting-out-liquid' octane to determine the perimeter of the veneer. The determination of perimeters and the estimation of apparent water contact angles followed the procedures described by Wålinder and Ström (2001). Values for the surface tensions, viscosities and densities of the probe liquids were taken from Bryne and Wålinder (2008).

The XPS measurements were made on a Kratos AXIS HS X-ray photoelectron spectrometer (Kratos Analytical, Manchester, UK). The samples were analyzed in the fixed analyzer transmission mode using a monochromatic Al K α X-ray source operated at 300 W (15 kV/20 mA) for high resolution carbon spectra 1s spectra. For survey spectra and detail spectra used for quantification of atomic concentrations, a non-monochromatic Mg K α X-ray source operated at 180 W (12 kV/15 mA) was used. Each wood sample was analyzed in 2-3 positions (one location on each of 2-3 different sample pieces). The area analyzed was 700 x 300 micrometers, and the take-off angle of the photoelectrons was perpendicular to the sample surface.

The ToF-SIMS analyses were made on a ToF-SIMS IV instrument (IONTOF GmbH, Münster, Germany). Mass spectra (1-1800 u) of positive and negative secondary ions were acquired from randomly selected areas of 500 x 500 μm^2 on each sample. At least two samples from each group were analysed. 25 keV Bi $_3^+$ primary ions at an average beam current of 0.1 pA were used in all cases. The ion gun settings used typically produced a mass resolution $M/\Delta M$ between 3000-5000 (depending on surface topography) and a beam diameter (lateral resolution) of 4-5 μm . Low energy electron flooding was used for charge compensation. All analyses were done under so-called static SIMS conditions, *i.e.* the primary ion dose was kept well below that where significant damage starts to occur on the surface.

RESULTS

Contact angles

A typical Wilhelmy test cycle of immersion and withdrawal of a thin plate in a probe liquid results in separate apparent contact angles for the advancing stage and for the receding stage. In practice, no finite receding water contact angles exists on high surface roughness, porous and hygroscopic substrates, such as wood, mainly due to liquid sorption effects in the surface. This phenomenon can easily be demonstrated by the immersion of the wood veneer sample a second time in direct conjunction with the first test cycle. If no hysteresis is found between the second advancing and previous receding force versus immersion depth curves, this corresponds to a zero contact angle, or in other words, complete wetting at the receding stage. This behaviour was indeed the case here for all wood samples, which means that no receding contact angles were found. Table 1 presents the apparent advancing contact angles measured from the very first part of the advancing curve, when sorption effects are not yet influencing the values.

Table 1 reveals that the heat treated material shows a similar behaviour to that of the unmodified reference. The original contact angles are close, and they increase with almost the same amount on ageing. This increase is explained by the exudation of mobile hydrophobic substances from the interior to the surface, and this migration is driven by a minimization of system energy won by exposing a more non-polar surface towards the air, which is regarded as a non-polar (hydrophobic) phase. The furfurylated wood has a lower intrinsic contact angle, and after ageing it remains relatively low and with a larger spread. The presence of small amounts of unreacted furfuryl alcohol and other byproducts or process additives is the most likely explanation for the lower values. Acetylated wood, by contrast, shows no significant change in wettability with ageing. Among the fresh samples it has the highest of all contact angles, and upon ageing they remain at the same level and attain the same level as those of unmodified and heat treated, *i.e.* apparently slightly lower but not with statistical significance. The results are in good agreement with earlier reported results (Gardner *et al.* 1991, Gindl *et al.* 2004).

Table 1: Apparent contact angles θ (advancing) measured by the Wilhelmy method for water on different wood samples. Average values are given, based on five replicates, with standard deviations within parentheses.

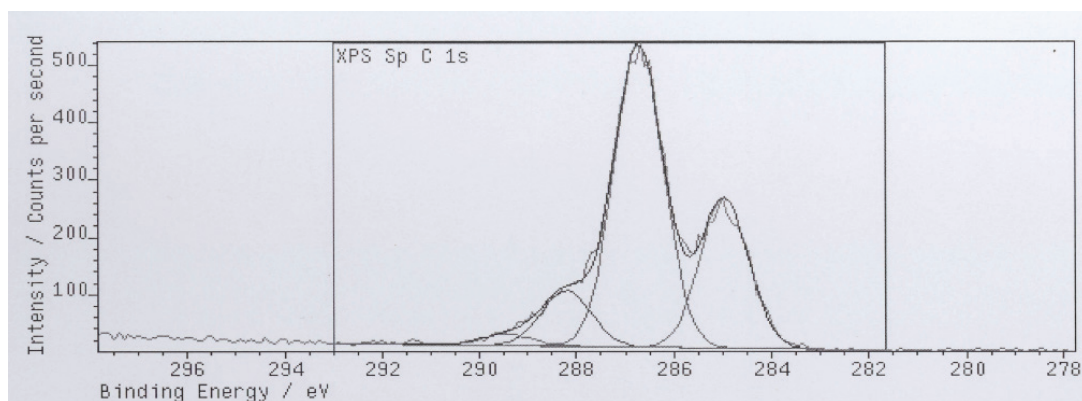
Sample	Unmodified	Heat treated	Furfurylated	Acetylated
Fresh	68.6 (6.2)	66.7 (3.8)	56.7 (4.2)	82.6 (2.1)
Aged	86.5 (2.7)	83.0 (3.4)	72.8 (10.6)	81.2 (2.6)

It is important to remember that the immediate wetting properties of wood do not infer similar differences with regards to its hygroscopicity and equilibrium moisture contents or uptake rates of moisture or liquid water.

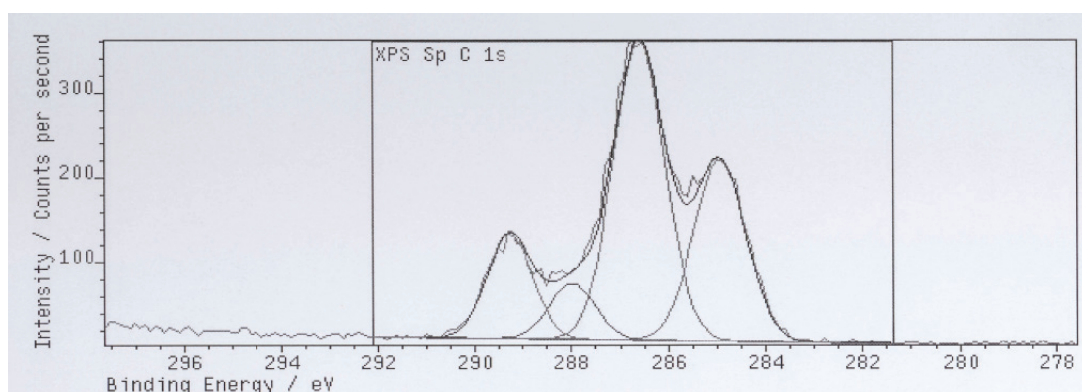
XPS results

The high resolution mode of XPS offers the possibility of quantitative determinations of various atomic species in different oxidation states, via so called chemical shifts that occur in the electron binding energy in different chemical compounds. For *e.g.* a carbon atom, the energy of the emitted photoelectrons depends on the electronegativity of the adjacent atoms to which it is covalently bonded, and the number of bonds to oxygen is here of central interest. The overall C1s signal (Figure 1) can be resolved into different carbon peaks corresponding to different functional groups, called C1-, C2-, C3-, and C4-carbon with increasing binding energy. The C1 peak represents unoxidised carbon with bonds to C or H (C-C, C-H, C=C functional groups, such as found in hydrocarbon chains / aromatic groups). The C2 peak corresponds to carbon with one bond to oxygen (C-O, C-O-C), the C3 peak to carbon with two bonds to oxygen (C=O, O-C-O), and the C4 peak to carbon with three bonds to oxygen (O-C=O, C(=O)OH). The C4 carbon peak thus represents the carboxylic functional groups, including esters, and is expected to be particularly strong for the acetylated wood. The majority of the carbon atoms in the cellulose structure are C2 type of carbons, and because the spectra are normalized to C2, no depression of the C2 peak can be seen. The dominance of the C2 carbon is consistent for all samples, with 42-64% of the total carbon signal (Table 2). The C1 carbon amounts to 22-44% of the total, C3 to 7-13%, and C4 to 1-15%.

As expected, the C4 signal is particularly strong in the acetylated samples, mostly owing to the esters formed by the modification and with a possible contribution from residual acetic acid.



a.



b.

Figure 1. XPS high resolution C1s spectra of unmodified (a) and acetylated (b) wood, fresh surfaces. The different peaks correspond to: C1 at 285 eV: C-C, C-H, C=C; C2 at 286.7 eV: C-O, C-O-C; C3 at 288.1 eV: C=O, O-C-O; C4 at 289.3 eV: O-C=O, C(=O)OH

Table 2: O/C atomic ratios and chemical shift distribution in high resolution carbon spectra for fresh and aged samples. Values from deconvolution of total carbon signal. Min and max values given for the 2-3 positions analysed.

Sample		Atomic ratio O/C	C1s tot=100%			
			C1	C2	C3	C4
Unmodified	Fresh	0.54-0.62	22-28	59-64	11-12	2
	Aged	0.48-0.50	31-36	50-56	10	3-4
Heat treated	Fresh	0.56-0.57	27-30	56-60	11-12	1
	Aged	0.51	32-33	53-55	12-13	2
Furfurylated	Fresh	0.58-0.59	29	56	12-13	2-3
	Aged	0.45-0.55	30-44	42-56	11-12	2
Acetylated	Fresh	0.53-0.58	29	47-48	8-9	15
	Aged	0.49-0.54	32-37	42-46	7-8	13-15

On ageing, the distribution of differently bonded carbon atoms is affected in all samples by a decrease in C2-carbon and a concurrent increase in C1-carbon (Table 2). This can be seen as a dehydration reaction, or migration of extractives, but the analysis does not reveal which of the biopolymers that are mainly involved. Another measure of

interest is the O/C ratio, which follows a similarly consistently decreasing trend on ageing. The changes in the O/C ratio fit well with the shifts in emphasis from C2- towards C1-carbon, and they also give an explanation in part to the observed increase in apparent contact angles. The only exception is the acetylated wood, where the chemical differences are not manifested as a surface with enhanced hydrophobicity, in this case the reason most likely being the high amount of oxidised C4-carbons.

ToF-SIMS

All spectra were dominated by organic peaks of the types C_xH_y and $C_xH_yO_z$. Due to given limitations, this paper shows only negative spectra (Figure 2). The spectra are shown in two panels, one representing the mass range 9-220 u (left), and the other 200-650 u (right). The identification of some of these signals is discussed below.

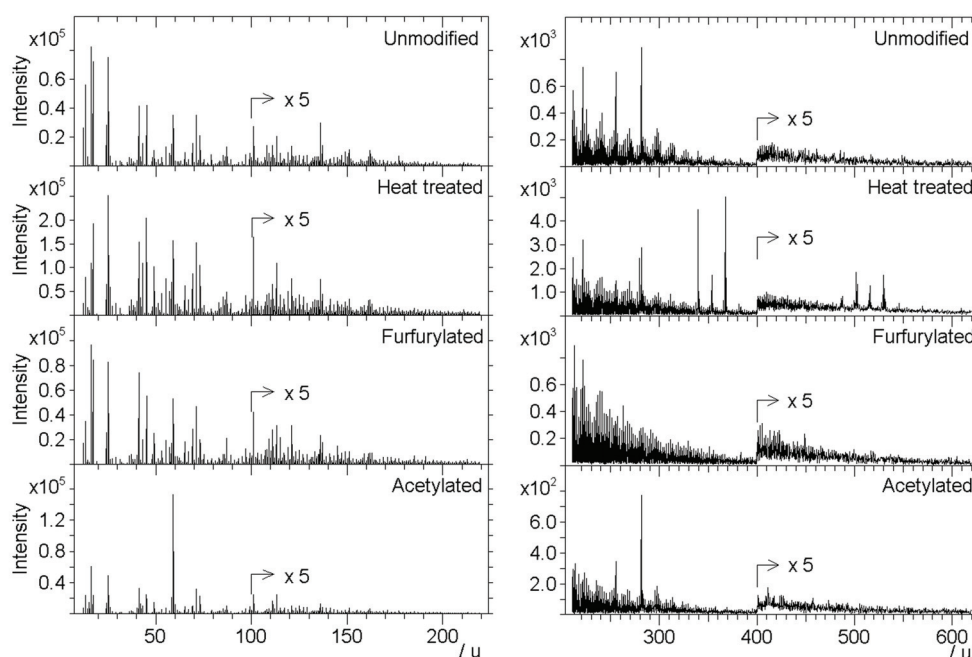


Figure 2. Negative ion ToF-SIMS spectra of from fresh samples, mass ranges 9-225 u (left) and 200-650 u (right). Note the differences in intensity scale for the different samples.

The positive spectra (not shown) reveal some characteristic fragment ions from hemicellulose (xylan at 115 u, mannan at 127 u) and from lignin (137, 151 u). The negative spectra showed clear signals at 71, 87, 113 and 221 u, which can be assigned to different fragments of cellulose. Ion images (not shown) indicate that the signals from these wood components were homogeneously distributed over the analysis areas. The acetylated wood shows a marked difference in positive spectra by the presence of a strong peak at 43 u (CH_3CO^+ , acetyl) and peaks at 139 and 169 u (acetylated glucoside), and at 331 u (tetraacetylated glucoside). The negative ion spectra at masses up to 200 u do not show any clear differences between the differently treated samples.

Sterols and steryl esters show positive ions between 383 to 429 u (Kangas and Kleen 2004, Kangas 2007), but they are less evident in the furfurylated samples, and relatively stronger in the heat treated samples. In the negative ion spectra (masses above 200 u), all samples except the furfurylated ones show clear signals from the fatty acids oleic acid (C18:1 at 281 u) and palmitic acid (C16:0 at 255 u). For the heat treated samples

strong signals are also observed at 339 u (tentative assignment behenic acid, C22:0) and at 367 u (tentative assignment tetracosanoic or lignoceric acid, C24:0).

Semi-quantitative comparisons of fresh and aged samples showed that the relative signal intensities for the different substances varied considerably, also within the sample groups. This is a common observation in ToF-SIMS analyses, where signals intensities are strongly influenced by surface topography and the presence of spurious surface contamination. Due to the variations in signal intensities, no firm conclusions are attempted here about changes occurring at the surfaces during ageing. The results underline the necessity of sample preparation with methods that minimize surface topography, as ultramicrotoming (Tokareva *et al.* 2007) or excimer laser ablation (Seltman 1995, Bryne *et al.* 2008).

CONCLUSIONS

All of the three employed methods provide useful and complementary information about wettability, surface chemical composition and ageing effects of the investigated modified wood.

While XPS provides quantitative data about functional groups in the surface layer, ToF-SIMS can provide further insights into the specific molecular composition of differently treated samples. The imaging possibilities also makes ToF-SIMS especially valuable in combination with electron microscopy for the localisation of specific compounds to specific wood tissues, but very careful surface preparation is necessary for optimal surface smoothness.

The heat treatment affects the spatial distribution of extractives in the wood. On ageing, all samples show decreased oxygen/carbon ratios in the surface and become less polar. This is also reflected by decreased wettability, except for the acetylated wood, where the contact angles did not change appreciably due to ageing.

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