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Determination of surface functional groups in lignocellulosic materials by chemical derivatization and ESCA analysis

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Abstract

Simple and convenient methods for determining surface chemical composition of lignocellulosic materials are described. The methods are based on vapor phase fluorine surface derivatization with either trifluoro acetic anhydride (TFAA), tri-fluoro ethanol (TFE) or pentafluorophenyl hydrazine (PFPH) and subsequent Electron Spectroscopy for Chemical Analysis (ESCA). Model cellulosic surfaces with well defined functionalities were used to optimize the derivatization reaction conditions. Detection and accessibility of surface hydroxyl functional groups were investigated in cotton and regenerated cellulose as models. Carboxymethyl cellulose (CMC) was used as a model surface for detection and quantification of carboxylic acid groups. Theoretical conversion curves for derivatization reactions were calculated and used to evaluate the extent of the reactions on the model surfaces. It was found that the conversion was higher for the regenerated cellulose and CMC than for cotton. The protocols developed using the model surfaces were applied to a case study on wood fibers with different degrees of complexity, namely dissolving and chemithermomechanical (CTMP) pulp. Untreated and oxygen-plasma modified pulps were compared with respect to the surface composition of functional groups. According to the derivatization reactions, functionalities containing oxygen were significantly increased on the plasma-treated samples. The effect of the treatment was found to be dependent on the type of pulp. Fluorine derivatization is shown to be an unambiguous method for clear assessment of the chemical functionalities of cellulosic surfaces.

Introduction

The surface properties of lignocellulosic materials are of great importance in applications ranging from paper and tissue products to composite materials. Interfacial interactions, such as inter-fiber bonding, paper sheet strength, wetting and liquid penetration rate and adhesion to non-polar materials (polyolefine-cellulose fiber composites, for example), are all controlled to a large extent by

the chemical composition and morphology of the surface of the lignocellulosic material (Felix and Gatenholm 1991; Ström and Carlsson 1992; Börås and Gatenholm 1999).

It is well known that many surface properties of materials depend chiefly on the chemical composition at the surface, dictated by the presence and type of polar and non-polar components, and on the physical state, such as crystallinity and surface roughness. Lignocellulosic surfaces are extremely

complex because they are composed of different chemical components such as cellulose, hemicellulose, lignin and extractives. In addition, the different processes by which pulp and paper products are obtained result in such chemical modifications as the introduction of carboxylic groups, sulfates, chain scission etc. (Fengel and Wegener 1989). The lignocellulosic surfaces also have different states and surface areas, which affect the total concentration of chemical moieties. Re-precipitation and migration of extractives, hemicelluloses and low molecular weight lignins make the determination of the surface chemistry of pulp and paper products elusive.

Methods for determination of chemical composition and functional groups in pulp have been extensively reported in the literature (Sjöström and Haglund 1961; Sumi et al. 1964; Sjöström and Enström 1966; Wågberg et al. 1985; Stenius and Vuorinen 1998). These methods, based mainly on wet chemistry, probe the entire lignocellulosic sample. Upon surface treatment of pulp fibers only a very small fraction of the sample is modified, typical treatment depth is only a few nm (Garbassi et al. 1998). Surface modifications are therefore very difficult to analyze by bulk analysis methods. Many attempts have been made to shed light on the chemical surface composition of pulps and paper products. Studies on the surface of lignocellulosics date back more than 20 years and the more recent introduction of sophisticated techniques and ease of computing data have resulted in a clearer depiction of the surface of lignocellulosics. Infrared (IR) and nuclear magnetic resonance (NMR) spectroscopic techniques are sensitive to bulk properties, although studies done to describe the chemical changes after surface treatments have included IR analysis (Goring 1967). The identification of the chemical structure of the surface by these techniques, attenuated total reflection or solid state NMR for instance, is difficult however because of superimposed signals in IR and low signal-to-noise ratios in solid state NMR; moreover, the probing depth is rather high. More sensitive surface techniques, such as time of flight secondary ion mass spectroscopy and X-ray photo electron spectroscopy analysis, have been used to assess structural changes in lignocellulosic surfaces (Connors and Banerjee 1995).

The chemical derivatization of these surfaces has been overlooked, from the earliest paper

describing the chemical composition of cellulosic surfaces by ESCA (Dorris and Gray 1978a), where the carbon binding values were assigned, up to the most recent papers describing the changes in the structure of the surface of lignocellulosic after special treatments. Dorris and Gray (1978a, b) described their application of the ESCA technique to cellulose, lignin and high yield pulps. They reported that the elemental surface composition and the bulk composition of both lignin and cellulose showed good agreement, while the shape of the high resolution C_{1s} was described in qualitative terms. The relative abundance of the class of carbons that make up the shape of the C_{1s} was estimated by Gray (1978) by a deconvolution method. He found that the deconvolution of C_{1s} in cellulose surfaces gave results in reasonable accordance with the oxygen-to-carbon ratios and the chemistry of the samples. These papers stressed the importance of the O/C ratio as an index for describing the different components that might be part of the surface.

Since that time the ESCA technique has been routinely used to describe the surface elemental composition of pulp and paper and lignin, especially after having been subjected to chemical modification of the surfaces (Carlsson and Ström 1991; Belgacem et al. 1995; Laine et al. 1996; Börås and Gatenholm 1999; Gellesterd and Gatenholm 1999; Toriz et al. 2000; Henriksson and Gatenholm 2001; Koljonen et al. 2003; Toriz et al. 2004).

Although well resolved high resolution carbon $1s$ (C_{1s}) peaks have specific binding energies for the bonds usually found in cellulosic materials, it is well known that some of the functional groups superimpose upon each other (ether to alcohol; carbon double bond to carbon single bond; carbonyl and amino groups to the anomeric carbon in cellulose etc.), which results in an ambiguity in the determination of functionalities. For example, ESCA has been used to characterize the modified surface after oxygen plasma treatments of chemical and high yield pulps (Ström and Carlsson 1992; Carlsson et al. 1994, 1995) based solely on the shape of the C_{1s} spectra. It is well known that cold plasma treatments are complex, heterogeneous reactions that affect the surfaces of even the most inert materials in a random fashion. Simultaneous processes of etching, deposition, degradation, recombination and crosslinking take place on the surface of materials that are plasma treated.

Carlsson and Ström (1991) pointed out that plasma treatments can result in chain scission, cross-linking and production of hydroperoxides; however, these authors only proceeded to determine hydroperoxides with SO_2 . With the exception of another paper that described hydroxyl accessibility on cellulose surfaces (Tasker and Badyal 1994), the papers mentioned above lack any other type of chemical tagging. Despite these facts, numerous studies have used ESCA to determine the surface coverage of lignin and extractives, even after surface treatments, based on theoretical O/C ratios (Ström and Carlsson 1992; Shen and Parker 1999).

Börås and Gatenholm (1999) addressed the heterogeneity of CTMP fiber surfaces and proposed a model of the fiber on the basis of findings in ESCA and identification of surface morphology by atomic force microscopy. It was found that the ratio of C1/C2 correlated well to the amount of extractives and the contact angle. Gellerstedt and Gatenholm (1999) found that cellulose fibers modified with succinic anhydride resulted in the introduction of carboxylic acid functionalities mainly at the fiber surface, as determined by ESCA. In that case, the O/C ratio was not illustrative of the changes; rather the degree of surface modification was indicated by the changes in the C4 region of the high resolution C_{1s} spectra.

To unambiguously identify different functional groups by ESCA, the core level binding energy shifts of the species that are present must be large enough to be resolved by curve-fitting. Chemical derivatization allows labeling with a molecular or elemental tag not present at the original surface (Andrade 1985; Batich 1988). Strategies for tagging functionalities containing oxygen include derivatization with compounds containing fluorine, among other chemicals. A series of derivatization reactions for polyethylene modified with plasma was proposed by Everhart and Reilley (1981). Trifluoroacetic anhydride has been shown to have a high selectivity for hydroxyl groups; it does not label alkenes, ethers, ketones or esters, either aromatic or aliphatic (Dickie et al. 1982; Gerenser et al. 1985; Chilkoti et al. 1990, 1991; Chilkoti and Ratner 1991). Carbonyl tagging with hydrazine and pentafluoro phenol hydrazine and carboxylic acid tagging with trifluoroethanol have both been discussed (Everhart and Reilley 1981; Chilkoti et al. 1991) and shown to proceed efficiently.

The aim of the work reported in this paper was to describe a relatively simple method for determining functional groups at lignocellulosic surfaces using chemical derivatization and ESCA analysis.

Experimental

Materials

The model substrates used were cotton, regenerated cellulose (cellophane) and carboxymethylated cellulose (CMC). Cotton filter paper (Munktel No 5) was purchased from Stora, Sweden. A sheet from the middle of the fresh stack was selected and used for the studies without further preparation. Unplasticized cellophane (Prod. No. 350POO) was kindly provided by UCB Films, UK. The cellophane was acetone extracted prior to use in a Soxhlet apparatus in order to remove impurities. The extraction was allowed to proceed overnight with approximately eight evacuations per hour. The samples were left to dry in ambient conditions. The crystallinity ratio (Cr.R.) of the cellulosic samples were 0.85 (Cellulose I) for the cotton and 0.80 (Cellulose II) for the cellophane film. CMC (cekol 50.000; batch no. G1706) was obtained from Noviant, The Netherlands; the degree of substitution was 0.9 and contained approximately 0.05% of NaCl and Na-glucolate. The CMC was dissolved in deionized water to a concentration of 0.5% and then dialyzed with 0.2 M HCl to convert the sodium carboxylate to carboxyl acid and to remove the sodium. The dialyzed solution was then spin coated on a glass slide.

Dissolving and CTMP pulps were used as received to prepare sheets. These sheets were stored in a climate controlled room at 50% humidity and 23 °C before further use. The dissolving pulp (MoDoCrown dissolving) was kindly submitted by Domsjö Sulphite Mill, Sweden. This is a softwood sulphite pulp produced in a two stage cooking procedure which is followed by TCF bleaching. Sheets with a grammage of 100 g/m² were formed in a Büchner funnel. The sheets were pressed between filter papers and left to dry overnight in room conditions. CTMP (tissue grade V07) was kindly provided by Östrand Pulp Mill, Sweden. The pulp is made from chipped spruce wood that is impregnated with sodium sulphite

prior to refining and then bleached with hydrogen peroxide. Sheets were made according to the SCAN test standard (SCAN C26:72 and SCAN M 5:76).

All derivatization agents, trifluoroacetic anhydride 99% (TFAA), trifluoroethanol 99.5% (TFE), pentafluorophenyl hydrazine 97% (PFPH) and tert-butylcarbodiimide 99%, were purchased from Aldrich Chemicals (Milwaukee, WI) and used without further purification.

Methods

Crystallinity measurements

The type and degree of crystallinity of the cellulose materials were investigated using wide-angle X-ray diffraction (WAXD). Diffractograms were recorded in the reflection geometry on a Siemens D5000 diffractometer using CuK_α radiation. Diffractograms were taken at 5° and 40° (2θ) at a rate of 1° (2θ) per minute and a step size of 0.1° (2θ). The crystallinity ratio (Cr.R.) was calculated by a formula used by Buschle-Diller and Zeronian (Buschle-Diller and Zeronian 1984):

$$\text{Cr.R.} = 1 - \frac{I_1}{I_2}$$

where I_1 is the intensity at the minimum (between $2\theta = 18^\circ$ and 19° for cellulose I and between $2\theta = 13^\circ$ and 15° for cellulose II) and I_2 is the intensity of the crystalline peak at the maximum (between $2\theta = 22^\circ$ and 23° for cellulose I and between $2\theta = 18^\circ$ and 22° for cellulose II).

Plasma treatment

Oxygen plasma treatments were carried out in a parallel plate reactor (Technics Plasma 40G) at 2.45 GHz. The sheet samples (dissolving and CTMP pulps) were placed on the lower electrode and the chamber was evacuated to a base pressure of 0.18 mbar. Oxygen was then introduced into the chamber to obtain a pressure of 0.70 mbar, and the plasma discharge was ignited. The power delivered to the upper electrode was 300 W for a treatment time of 45 s.

Hydroxyl derivatization procedure

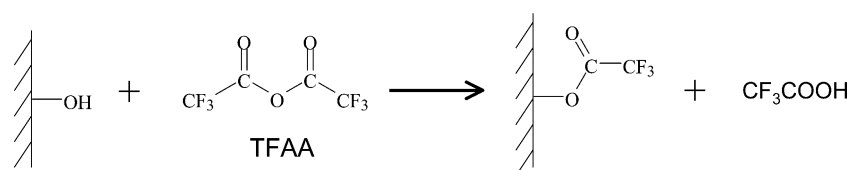
The labeling of hydroxyl groups with TFAA vapor was carried out at atmospheric pressure according to Scheme 1. The procedure described by (Chilkoti et al. 1991) was followed with minor adjustments.

Carboxyl derivatization procedure

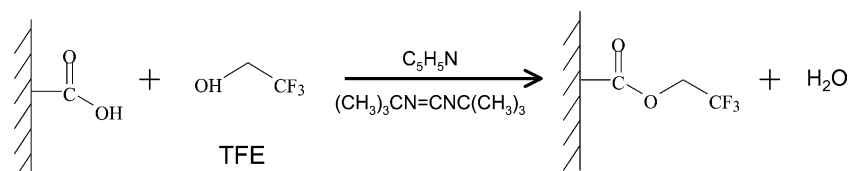
We followed the methodology for the derivatization of carboxylic groups in vapor phase (Scheme 2) given by (Chilkoti et al. 1991). The time needed for labeling was studied by allowing the reaction to proceed for different time periods at room temperature. Reaction times from two up to 24 h were investigated.

Carbonyl derivatization procedure

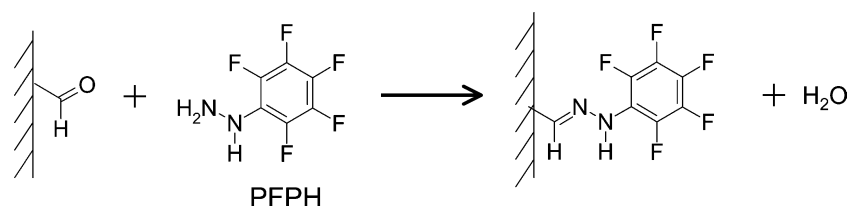
The protocol for carbonyl derivatization in liquid phase by Everhart and Reilly (1981) was modified, using tert-butylcarbodiimide as a coupling agent to allow gas phase derivatization (Scheme 3). Pentafluorophenolhydrazine was dissolved in ethanol (4% by weight) and tert-butylcarbodiimide



Scheme 1.



Scheme 2.



Scheme 3.

were placed in a dessicator under the samples for 5 h at 60°C.

Electron spectroscopy for chemical analysis

After derivatization, the samples were recovered and immediately analyzed using ESCA. Survey and high resolution ESCA multiplex spectra were obtained with a Quantum 2000 from Physical Electronics equipped with a monochromatic Al K α X-ray source (15 kV, 20 W, beam size 100 μ m) and a neutralizer to avoid electrostatic charging. An area of 500 \times 500 μ m was analyzed at a take-off angle of 45°. Survey spectra were taken from 0–1100 eV binding energy, with a resolution of 1 eV. The pass energy of the electron energy analyzer was set at 187.85 eV. The high resolution multiplex spectra were collected for each of the elements identified from the survey scan (C_{1s}, O_{1s}, for untreated samples; and, in addition, F_{1s} for the treated samples). The energy resolution for a multiplex scan was 0.25 eV with a pass energy of 29.35 eV. The surface atomic composition was calculated with MultiPak software from Physical Electronics based on peak intensity, corrected for atomic sensitivity factors. Survey scans were collected only at the start of the study and then

cancelled, since it has been shown that fluorine intensities decrease over prolonged X-ray exposure ([Hutt and Leggett 1997](#)).

Results and discussion

Model studies

Model cellulosic surfaces with known chemical functionalities were used to ensure the accuracy of the chemical derivatization of cellulosic materials. Native and regenerated cellulose were used to verify the surface accessibility of hydroxyl groups. A cellulose derivative – CMC-with known carboxylic acid functionality served to ascertain the effectiveness and selectivity of the chemical tags.

ESCA survey spectra of unmodified and TFAA chemically tagged cellophane surfaces are shown in Figure 1. C_{1s} and O_{1s} were easily identified, and the presence of F_{1s} was confirmed on the surface of the tagged sample. Optimal tagging conditions were found by reacting cellophane with TFAA at 24°C and 35°C and varying the time from 5 to 120 min. Figure 2 shows the evolution of the reaction over time. It can be

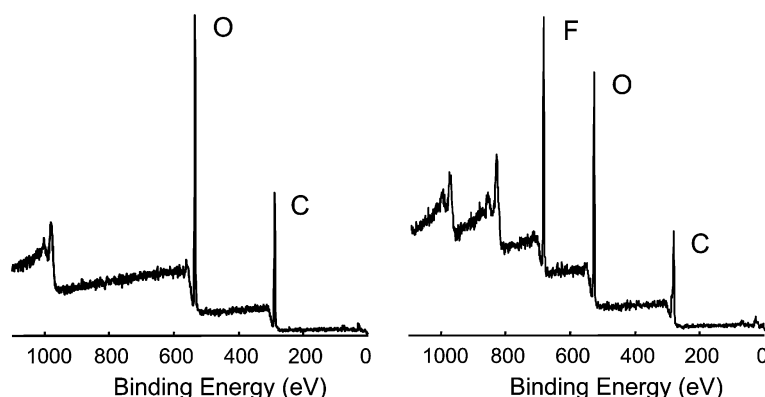


Figure 1. Survey spectra of cellophane (left) and TFAA-derivatized cellophane (right).

seen that 40 min of reaction is sufficient to achieve almost total conversion. As expected, the anhydride reacted more slowly at 24 °C than at 35 °C, and full conversion was not reached even after 120 min. The optimization trials showed that 40 min of TFAA exposure at 35 °C was required to achieve close to full conversion in cellophane samples.

The high resolution C_{1s} ESCA spectra of untreated and TFAA cellophane derivatized surfaces are shown in Figure 3. Figure 3a shows the untreated cellophane. The usual carbon peaks were found: the ubiquitous C1 from hydrocarbon

impurities, C2 from carbon bonded to one oxygen and C3 from carbon bonded either to two oxygen atoms, keto or aldehyde groups. The TFAA derivatized cellophane is shown in Figure 3b. In addition to the peaks found in Figure 3a, two more peaks at 289.7 eV and at 292.8 eV were found, corresponding to the central carbon in the trifluoroacetate group ($O-C=OCF_3$) and the trifluoromethyl carbon ($O-C=OCF_3$), respectively. The theoretical atomic concentrations of chemically derivatized cellophane can be calculated as a function of the conversion factor (ξ) of the hydroxyl group in the repeating unit of cellulose.

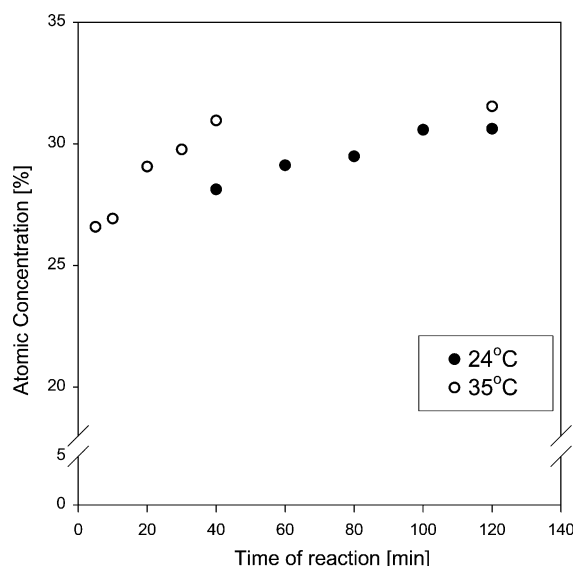


Figure 2. Fluorine atomic concentration as a function of time for TFAA-derivatized cellophane surfaces at 24 °C (●) and 35 °C (○).

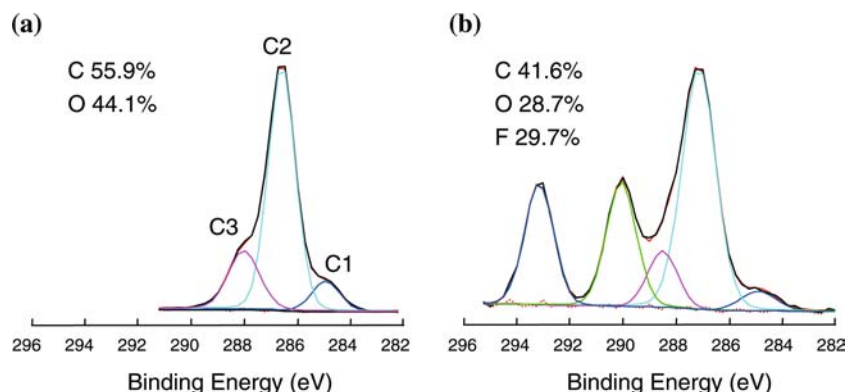


Figure 3. Deconvoluted C_{1s} spectra of cellophane (a) and TFAA-derivatized cellophane (b).

ξ can take values from 0 (unreacted) to 3 (100% substitution of the cellulose repeating unit).

$$[F] = \frac{3\xi}{\alpha} \quad (1)$$

where $\alpha = 11 + 6\xi$ (which is the total amount of atoms in the molecule at a given conversion factor). Coefficient 3 in the numerator of Equation (1) corresponds to the number of fluorine atoms incorporated for each chemical tag; 11 is the number of atoms other than hydrogen in the cellulose repeating unit and coefficient 6 corresponds to the total number of atoms incorporated in the chemical tag.

Similarly, the theoretical oxygen concentration is given by

$$[O] = \frac{5 + \xi}{\alpha} \quad (2)$$

Factor α was defined in Equation (1); 5 in the numerator represents the number of oxygen atoms, and ξ is the oxygen atoms added with the tag.

The carbon concentration is:

$$[C] = \frac{6 + 2\xi}{\alpha} \quad (3)$$

Equations (1–3) were plotted and are shown in Figure 4. It can be seen that the theoretical maximum concentration of fluorine (conversion

factor = 3) is 31%. As seen in Figure 3, the fluorine surface composition of the tagged cellophane was 29.7%, revealing very high surface hydroxyl accessibility in the regenerated cellulose.

CMC was a very appropriate model surface for testing both hydroxyl and carboxylic acid functionalities; Figure 5 shows the high resolution C_{1s} spectra of underivatized, TFE and TFAA exposed CMC surfaces. The theoretical elemental composition of CMC surfaces after the chemical derivatizations can be easily calculated from Equations (4) to (9).

For TFAA derivatization:

$$[F] = \frac{3\xi}{\beta} \quad (4)$$

where ξ ranges from 0 to 2.1 (since the degree of substitution of the CMC is 0.9) and $\beta = 11 + 6\xi + 4(0.9)$.

The elemental oxygen concentration can be obtained as:

$$[O] = \frac{5 + 1.8 + \xi}{\beta} \quad (5)$$

β was defined before, and 5 is the original number of oxygen atoms. 1.8 is the number of oxygen atoms originating from the carboxymethyl group.

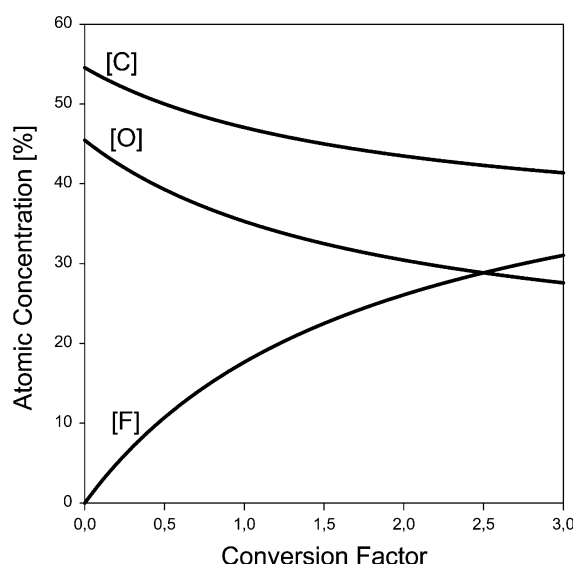


Figure 4. Theoretical atomic concentration of a TFAA-derivatized cellulose surface as a function of extent of reaction.

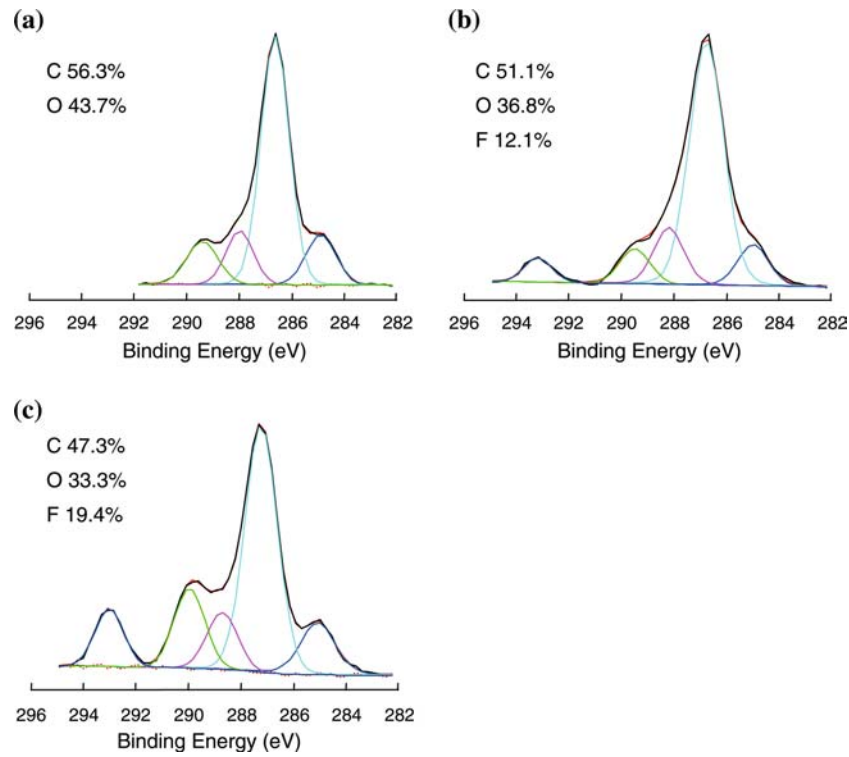


Figure 5. Deconvoluted C_{1s} spectra of CMC (a), TFE-derivatized CMC (b) and TFAA-derivatized CMC (c).

The elemental concentration of carbon is given by:

$$[C] = \frac{6 + 1.8 + 2\xi}{\beta} \quad (6)$$

In the case of TFE derivatization it can be shown that the elemental composition of an element is given by:

$$[F] = \frac{3\xi}{\gamma} \quad (7)$$

$$[O] = \frac{5 + 1.8}{\gamma} \quad (8)$$

$$[C] = \frac{6 + 1.8 + 2\xi}{\gamma} \quad (9)$$

Here, ξ has values from zero to 0.9 and $\gamma = 11 + 4(0.9) + 5(\xi)$.

Figure 6 shows the elemental concentration profiles for both reactions on CMC, based on

Equations (4–9). The elemental surface concentrations obtained for these derivatization reactions are shown in Figure 5. It can be seen from Equation (4) that the maximum theoretical fluorine concentration for TFAA on CMC is 23% while the observed fluorine atomic concentration was 19.4%. According to those figures the extent reaction is nearly 80%, which demonstrates a great surface hydroxyl accessibility of the cellulose derivative. On the other hand, the maximum theoretical fluorine concentration for TFE derivatization is 14%, given by Equation (7). The atomic concentration of fluorine that was detected was 12.1%, which indicates more than 80% conversion. The theoretical fluorine concentration ratio of TFE to TFAA derivatized models is 0.61 (resulting from dividing the fluorine concentration in fully derivatized models), while the actual ratio obtained from ESCA analysis of the samples was 0.62. These calculations are evidence of efficient and selective chemical derivatization of these two functionalities in model cellulosic surfaces.

Surface accessibility

Cellulose from cotton can be considered a model substrate; it was thus subjected to chemical tagging according to the previous results. Table 1 shows the atomic concentrations of untreated and TFAA and TFE derivatized cellulose cotton. The fluorine concentration for the TFAA tagging reaction represented 57% of the hydroxyl conversion to the ester. This denotes a lesser accessibility to surface hydroxyl groups. The underivatized sample showed a peak in the high binding energy region that can be assigned to carboxylic acid functionality. Although the surface composition of the carboxyl group on untreated cellulose accounted for 3%, attempts to tag that group resulted in only a 0.3% fluorine concentration, which is negligible. Figure 7 shows a comparison between the cellophane and cotton derivatized samples. It can be seen that the greater changes on cellophane are caused by its higher surface accessibility (Tasker and Badyal 1994).

Case study: surface modification of lignocellulosic fibers

Once the suitability of the derivatization reactions had been established, lignocellulosic fiber surfaces were oxygen plasma treated and the chemical functional groups were determined according to the previous protocols. PFPH was used in the analysis series to determine carbonyl functional

groups, since lignin and hemicellulose could be expected to have carbonyl groups.

Figure 8 shows a series (a–h) of high resolution ESCA spectra of dissolving sulfite pulp. The spectrum of the untreated and underivatized sample resembles the usual spectrum for cellulose (Figure 8a), with the adventitious C1 contamination peak, the regular C2 and C3, and a low area high binding energy peak, C4. Figure 8b–d shows that only TFAA rendered significant values of fluorine atomic concentration (22.3%), indicating a moderate accessibility of the hydroxyl at the surface (conversion of 72%). Negligible amounts of fluorine for carboxylic groups and carbonyl groups indicate that untreated dissolving pulp cellulose is barely oxidized and does not have these functional groups from hemicellulose.

The C_{1s} spectrum of the plasma treated sulfite pulp (Figure 8e) resembles that of the untreated sample but has higher carboxyl functionality; the oxygen-to-carbon ratios for the untreated and plasma treated were 0.77 and 0.89, respectively, indicating an incorporation of oxygen on the surface. The series of derivatization reactions was done on this sample (Figure 8f–h). It was found that the fluorine concentration after TFAA derivatization was greater than in the untreated sample, which indicates that more hydroxyl groups are accessible after plasma treatment; fluorine from TFE tagging was found in 2.3%, which shows that oxidation to carboxylic groups took place. PFPH derivatization resulted in noticeable amounts of both fluorine and nitrogen

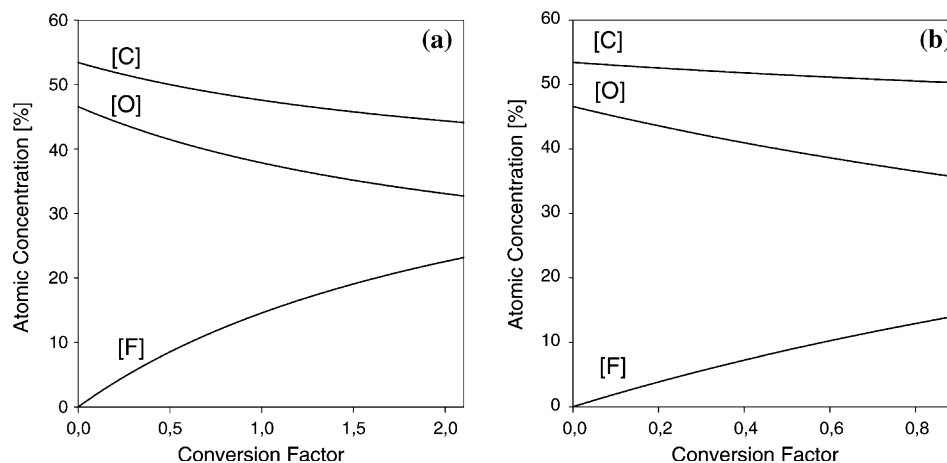


Figure 6. Theoretical atomic concentrations of TFAA-derivatized (a) and TFE-derivatized (b) CMC ($DS = 0.9$) as a function of extent of reaction.

from the derivatizing agent. This suggests that carbonyl groups were generated during the treatment via chain scission or rupture of the pyranosic ring (Hua et al. 1997). These results are not easily seen in the C_{1s} spectrum of the underivatized plasma treated sample (Figure 8e). Results of the deconvolution of that spectrum and comparison with the C_{1s} spectrum of the untreated sample (Figure 8a) show that hydroxyl groups diminished while carboxyl groups increased; C3 was slightly increased. C3 represents, besides carbonyl and keto groups, the anomeric carbon in cellulose. From these results it is not clear that carbonyl groups are generated. In addition, it would be very easy to make a mistake in curve fitting, since deconvolution processes are very sensitive to small changes in parameters and the calculated areas could be increased by a few percentages for instance by changing the tailing of the curves.

The plasma treated dissolving pulp was subjected to further chemical derivatization. Tagging hydroperoxides, which might form as a result of pyranosic ring opening and chain scission, with SO_2 resulted in insignificant amounts of incorporated sulfur on the surface. HCl was used to chemically derivatize epoxides; however, the

results showed only negligible amounts of chlorine on the surface.

CTMP paper was also oxygen plasma treated and fully characterized by tagging and ESCA. Figure 9 shows the high resolution C_{1s} spectra of all CTMP samples. The untreated untagged sample (Figure 9a) shows the typical spectra of a CTMP fiber surface, which contains all the main chemical components of wood and accounts for all the peaks found (C1 for lignin and extractives; C2 for hydroxyl in polysaccharides and hydroxyl and ether groups in lignin and extractives; C3 for the anomeric carbon in polysaccharides and carbonyl groups in lignin and extractives; and C4 for carboxyl and ester groups in lignin and extractives). The chemical derivatization of the untreated CTMP sample is shown in Figure 9b–d. Fluorine was detected in different amounts in all derivatized samples; a 25% fluorine atomic concentration after TFAA derivatization suggest a greater hydroxyl accessibility in this pulp as compared to the dissolving pulp. Carboxylic acid groups are found in this pulp, since 1.1% fluorine was detected after TFE derivatization.

The oxygen plasma treated CTMP samples are shown in Figure 9e–h. Simple conclusions can be drawn in comparing Figures 9a and e, the underivatized samples. Both figures show a tetramodal pattern in the C_{1s} envelope; it can be seen that the relative C1–C4 areas changed as a result of the plasma treatment. The C1 and C3 relative surface areas are smaller while C2 and C4 increased with the oxygen plasma treatment. Owing to the derivatization reactions, hydroxyl, carbonyl and carboxyl functional groups were all increased. It can be seen that there was a twofold increase in the carbonyl and carboxyl content after plasma treatment.

Table 1. Atomic concentration of carbon, oxygen and fluorine for untreated, TFAA-derivatized and TFE-derivatized cellophane and cotton.

	Cellophane			Cotton		
	Untreated	TFAAf	TFE	Untreated	TFAA	TFE
C	55.9	41.6	55.4	55.7	45.3	56.6
O	44.1	28.7	43.4	44.3	37.1	43.1
F		29.7	1.2		17.6	0.3

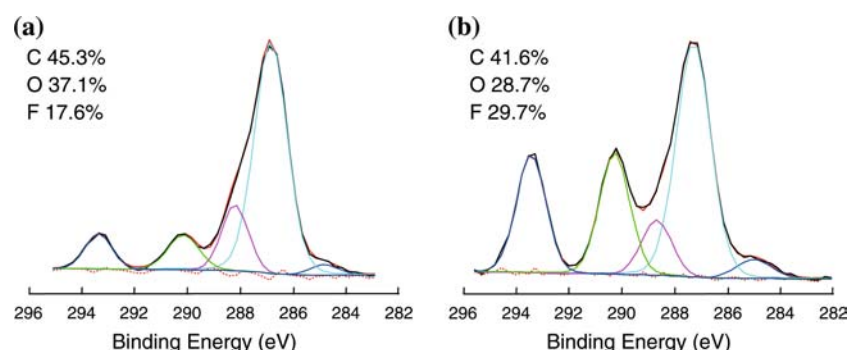


Figure 7. Deconvoluted C_{1s} spectra of cotton (left) and cellophane (right) TFAA-derivatized for 40 min.

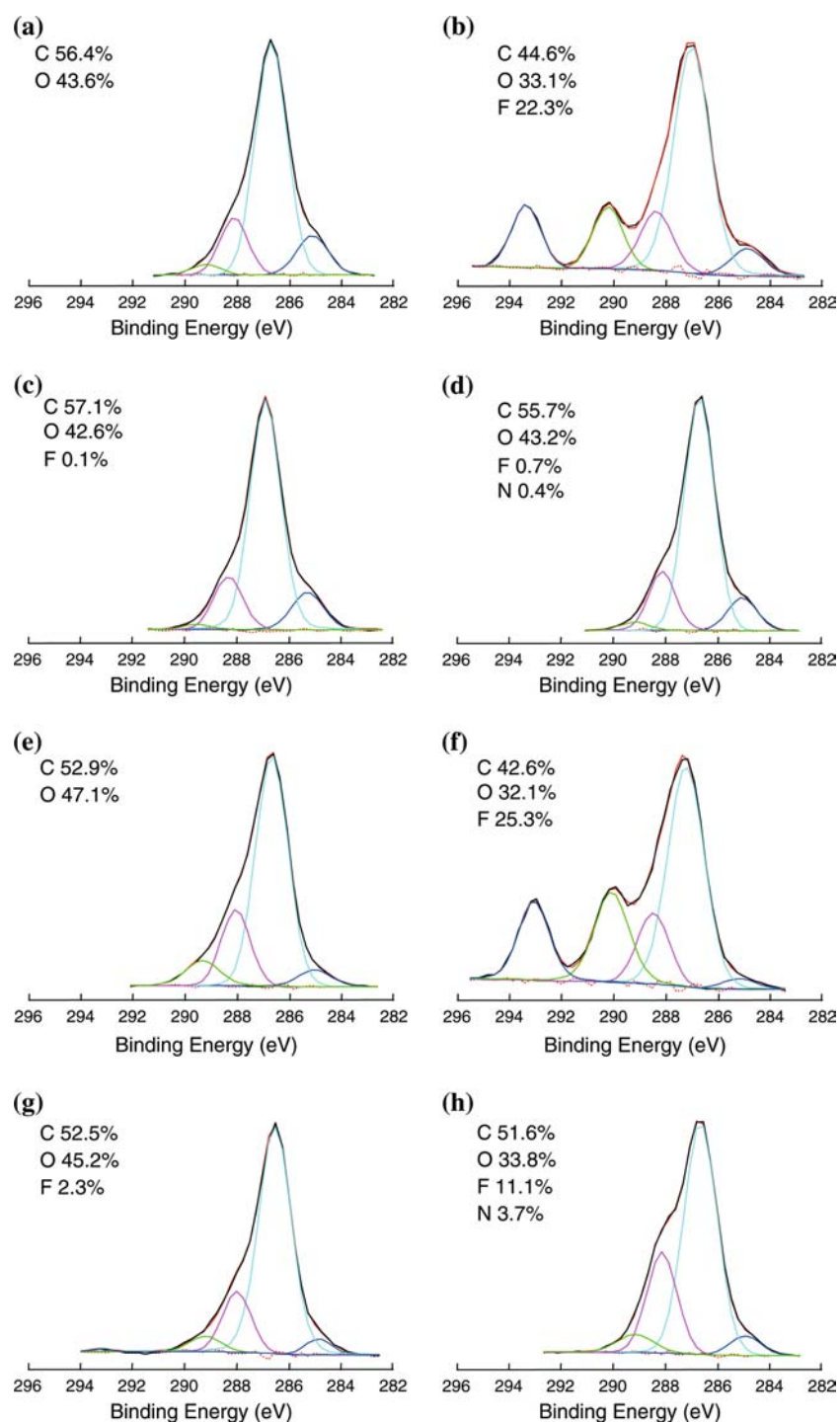


Figure 8. Deconvoluted C_{1s} spectra of sulfite pulps. Untreated: (a) underivatized; (b) TFAA-derivatized; (c) TFE-derivatized; and (d) PFPH-derivatized. Plasma treated: (e) underivatized; (f) TFAA-derivatized; (g) TFE-derivatized; and (h) PFPH-derivatized.

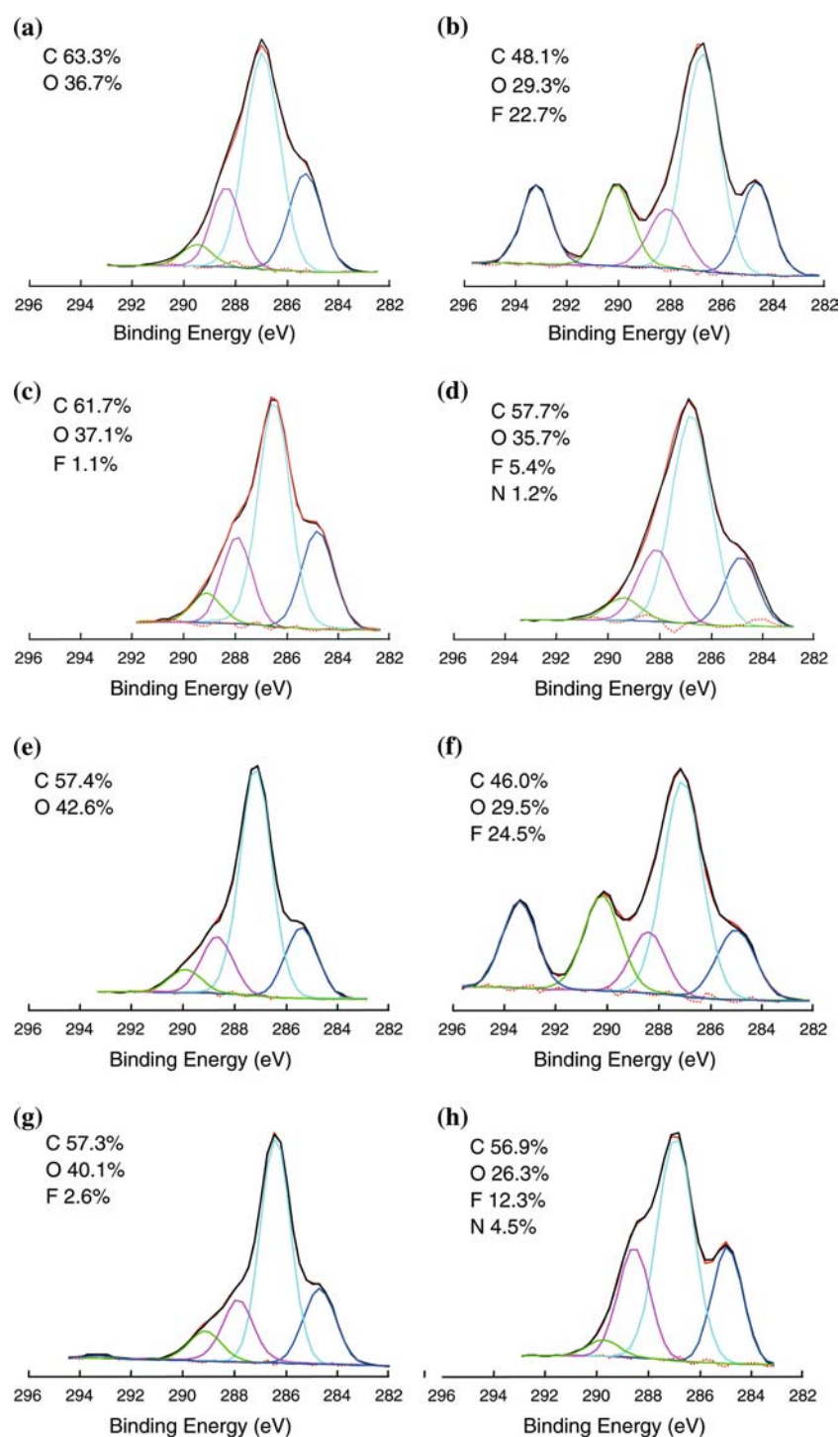


Figure 9. Deconvoluted C_{1s} spectra of CTMP pulps. Untreated: (a) underivatized; (b) TFAA-derivatized; (c) TFE-derivatized; and (d) PFPH-derivatized. Plasma treated: (e) underivatized; (f) TFAA-derivatized; (g) TFE-derivatized; and (h) PFPH-derivatized.

Conclusions

Vapor phase chemical derivatization with fluorine followed by ESCA was used to identify different functional groups on lignocellulosics. Reagents containing fluorine that efficiently and selectively tagged specific functional groups were selected. Regenerated cellulose and CMC were chosen as models to test the different chemical derivatization protocols. A high conversion of the chemical derivatization reactions was found according to theoretical calculations. Cotton filter paper was also used as model surface that contains hydroxyl groups. Comparison of cotton and regenerated cellulose revealed a limited surface accessibility in cotton. Differences in the crystallinity of the models should explain the better surface accessibility in the regenerated cellulose.

The methods were applied in lignocellulosic fibers with different levels of complexity, both before and after oxygen plasma treatment. The fibers studied were dissolving pulp and CTMP pulp. Oxygen plasma treatment resulted in increased oxygen content, as quantified by ESCA, in both pulps. TFAA and TFE tagging of the treated dissolving pulp showed that hydroxyl and carboxyl functional groups were moderately increased while the carbonyl content was noticeably increased, as shown by PFP tags. The higher carbonyl content denotes chain scission and/or rupture of the pyranosic ring. Untreated CTMP pulp showed a slightly higher surface accessibility of functional groups than the untreated dissolving pulp. The availability of the different functional groups must be due both to the chemical and to the morphological heterogeneity of the substrate. Plasma treatment of CTMP resulted, as in the case of the dissolving pulp, in an increment in the quantity of tagged functionalities, which was seen mainly for carboxyl and carbonyl groups.

We report here on gas phase fluorine surface derivatization of functional groups on lignocellulosic fibers. The advantages of using these methods can be summarized as follows:

- Introduction of an easily detected foreign element.
- High conversion and selectivity of functional groups.
- Minimal sample preparation.
- No use of solvents.

- Gas phase reactions (the surface remains relatively uncorrupted; only the surface is probed and the use of reagents is minimized).
- Rapid and simple reactions.
- The core level binding energy shifts of the derivatized samples are sufficiently separated, allowing unambiguous determination of functional groups.

However, protocols developed for surface derivatization of one type of sample, i.e. polyolefines, are not directly applicable to all samples. An optimization study, using relevant model surfaces, is not only desirable but necessary. The time that elapses between derivatization and ESCA analysis should be consistent and as short as possible. The method does not automatically provide absolute quantification since reactions seldom achieve full conversion.

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