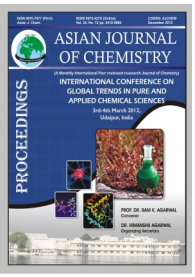
Asian Journal of Chemistry; Vol. 24, No. 12 (2012), 5476-5480

ASIAN JOURNAL OF CHEMISTRY

www.asianjournalofchemistry.co.in



XPS Characterization of Fiber Surface of Chemithermomechanical Pulp Fibers Modified by White-Rot Fungi†

CHONGXING HUANG*, QIFENG YANG and SHUANGFEI WANG

College of Light Industry and Food Engineering, Guangxi University, Nanning 530004, P.R. China

*Corresponding author: E-mail: huangcn21@163.com

AJC-11672

In the present paper, the fiber surface chemistry of eucalyptus chemithermomechanical pulp fibers before and after fungal modification was studied with X-ray photoelectron spectroscopy. The results show that the fungal modified chemithermomechanical pulp fibers had a higher O/C ratios and lower C1 percentage than the control pulp fibers and the C1s peak shifted to high binding energy direction. This implies that fungal modified fibers have less lignin and extractives and more hydrophilic groups and carbohydrate on the surface, which is preferred in helpful to forming hydrogen bond. The X-ray photoelectron spectroscopy quantified analysis of surface lignin and extractives contents showed that the content of lignin and extractives contents of fungal modified fiber decreased by 8.3 % and 55.9 %, respectively. However, bulk lignin and extractives contents of fungal modified fiber decreased only by 2.5 % and 11.1 %, respectively. This indicated that the degradation of lignin and extractives mainly took place on fiber surface.

Key Words: Bio-modification, Chemithermomechanical pulp fibers, Surface chemistry analysis, XPS.

INTRODUCTION

X-ray photoelectron spectroscopy is a practical surface analysis method, which is used for qualitative analysis, quantitative analysis and structural identification of solid surface and it has been widely applied in the fields of chemistry, chemical engineering, materials, machinery, electronic materials, *etc.*[1]. X-ray photoelectron spectroscopy technique has been used to identify the chemical composition of wood surface[2,3]. It is also very helpful in pulp fibers surface analysis and can be employed to reveal the contents and distribution of carbohydrates, lignin and extractives in the pulp surface[4-11].

In our experiment, the surface chemistry of fibers in eucalyptus chemithermomechanical pulp before and after fungal modification and acetone extraction was studied with X-ray photoelectron spectroscopy. This study focused on the O/C ratio and the C1s peak's carbon valence and then the contents of lignin and extractives on the eucalyptus chemithermomechanical pulp (CTMP) fiber surface after fungal modification was quantitatively analyzed. The purpose was to unveil that fungal modification can change the surface chemistry of fibers in eucalyptus chemithermomechanical pulp fiber by removing lignin and extractives and other chemical components from the pulp fiber surface.

EXPERIMENTAL

Eucalyptus chemithermomechanical pulp fiber: It was provided by Nanjing Forest Chemical Industry Chinese Academy of Forestry, with a whiteness 49.6 %, free degrees of 700 mL. The eucalyptus Bio-CTMP pulp is eucalyptus CTMP fiber after modification by white-rot fungus 19-6, homemade, with an incubation temperature of 28 ºC and an processing time of 7 days, the initial pH value of 4.5. The ucalyptus CTMP-E fiber is eucalyptus CTMP fiber after acetone extraction, according to T204 Tappi standard. The eucalyptus Bio-CTMP-E fiber is eucalyptus Bio-CTMP fiber after acetone extraction, according to T204 Tappi standard.

The chemical compositions of the pulps are summarized in Table-1.

TABLE-1
CHEMICAL COMPOSITIONS OF THE EUCALYPTUS CTMP FOBERS IN THE EXPERIMENTS

Name	Cellulose content	Lignin content	Acetone extract content
Eucalyptus CTMP fiber	50.3	25.1	0.45
Eucalyptus Bio-CTMP fiber	51.4	24.4	0.40
Eucalyptus CTMP-E fiber	50.2	24.1	-
Eucalyptus Bio-CTMP-E fiber	51.2	23.7	-

†Presented at International Conference on Global Trends in Pure and Applied Chemical Sciences, 3-4 March, 2012; Udaipur, India

TABLE-2
CTMP PULP FIBER SURFACE OXYGEN-CARBON RATIO AND C1s PEAK AREA ON THE SURFACES OF FIBERS IN DIFFERENT CTMP PULP

Pulp	O/C	C1 (%)	C2 (%)	C3 (%)	C4 (%)	FWHM (eV)	
						C1	C2-C4
Eucalyptus CTMP Pulp	0.497	36.9	51.2	7.5	4.3	1.86	1.74
Eucalyptus Bio-CTMP Pulp	0.534	30.8	54.9	10.0	4.3	1.86	1.74
Eucalyptus CTMP-E Pulp	0.548	29.9	58.0	10.2	1.9	1.86	1.74
Eucalyptus Bio-CTMP-E Pulp	0.570	27.6	55.7	12.2	4.5	1.86	1.74

X-ray photoelectron spectroscopy analysis: Firstly, Eucalyptus CTMP fiber was made into quantitative handsheet of 80-100 g/m^2 (30 mm in diameter) in the Buchner funnel and dried naturally in a clean environment. And then handsheets were extracted for 4 h in the soxhlet extractor with acetone and deionized water respectively and sealed in a plastic bag, finally.

X-ray photoelectron spectra were obtained using Leybold Max200 type instrument, equipped with a monochromated AlK_α X-ray source, operated at a power of 15 kV/15 mA of power. The hand sheets were placed on the sample stage in the vacuum chamber, whose analysis area was 1 mm × 7 mm and a photoelectron collection was at 90º in relation to the sample surface. Three different spots were measured in pulp hand sheets. As the electronic excitation of the paper surface required a charge compensator to counteract the charge of paper surface, the calibration scope of spectrometer was as following: Ag 3d5/2 peak = 368.3 eV, Cu 2p3/2 pesk = 932.7 eV. The calibration of the binding energy was related to O1s peak at 532 eV. O/C ratio (pass energy was 192 eV) was obtained in low resolution mode, including oxygen and carbon sensitivity of 0.75 and 0.32, respectively. C1s peak (pass energy for 48 eV) of the convolution spectrum was obtained in high resolution mode, then processed by curve fitting procedures, a curve which had a deviation value of 0.65 compared with the Gaussian/Lorenzian ratio was gained. The chemical shift of C-O(C2), O-C-O or C=O(C3) and O=C-O(C4), relative to C-C(C1), were (1.7 ± 0.1), (3.1 ± 0.1) and (4.4 ± 0.2), respectively. Other detailed experimental methods were described by Li[12].

RESULTS AND DISCUSSION

For the pulp fiber, only oxygen and carbon atoms can be detected by X-ray photoelectron spectroscopy. C1s has four kinds of combining ways on fiber surface, which is C1, C2, C3 and C4: (1) C1 represents the carbon atom which only connect to carbon and hydrogen (-C-H,-C-C). C1 comes from lignin and extractives of the fiber surface. (2) C2 represents the carbon atoms, which connects with a non-carbonyl oxygen atom *via* σ bond(-C-O). C2 comes from cellulose, which linked to hydroxyl or ether groups in the lignin. (3) C3 represents the carbon atom which connect to a carbonyl or two non-carbonyl oxygen atoms (C=O or O-C-O). C3 is mainly derived from ketone and aldehyde of lignin molecule or oxidation products of cellulose. (4) C4 represents the carbon atom which connect to a carbonyl oxygen atoms and non-carbonyl oxygen atom (O=C-O). As the content of C4 is low on the fiber surface, it is difficult to detect in X-ray photoelectron spectroscopy[13]. The Gelius's studies[14] suggest that different valence states of carbon in fiber materials have different electronic binding energies in the X-ray photoelectron spectroscopy spectra. Typically the standard binding energy of C1s is 285 eV, in which C1, C2, C3 and C4 are located in the binding energy of 285 eV, 286.5 eV, 288.3 eV, 289.5 eV. Generally chemical shift of O1s is small and its standard electron binding energy of O1s is 532 eV, with the reference of O1s peak. O1s has two kinds of valence states: O1 and O2. O1 with low binding-energy is from lignin (C = O) and O2with high binding-energy is mainly from carbohydrates (C-O). The area ratio of C1, C2, C3 and C4 is the ratio of its carbon atoms. Thus, the number of C1 atom reflects the quantity of non-carbohydrate bindings in the materials. Fig. 1 shows a typical spectra of C1s.

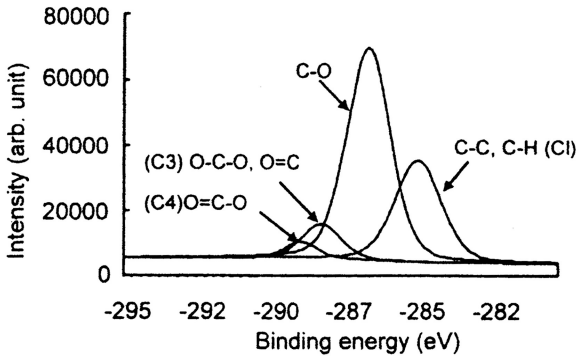


Fig. 1. High-resolution decomposition map of C1s peak

In the experiment the fiber surface chemistry of fibers in eucalyptus chemithermomechanical pulp before and after fungal modification and extraction was studied using X-ray photoelectron spectroscopy. The results are shown in Table-2.

Surface O/C analysis of fiber in eucalyptus CTMP fiber after fungal modification: O/C is the ratio of oxygen and carbon atoms that X-ray photoelectron spectroscopy can detect within the scope of depth on fiber surface. In many literatures it has been confirmed that there are no such chemical bond in which carbon atom only connected with carbon or hydrogen. In other words there are no single C-C and C-H bonds. Therefore, C1 peak exists only in lignin and extractives[4,5] based on this principle, if the peak area of C1 gets larger, the areas of C2, C3 and C4 peaks will become smaller; As oxygen atom only connects with C2, C3 or C4, the less the number of oxygen atoms, the lower the content of carbohydrate. Thus, O/C ratio can reflect the contents on lignin and extractives fiber surface. A lower O/C ratio means that a higher content of lignin and extractives and middle lamella on fiber surface; instead, a higher O/C ratio shows a higher content of carbohydrate on fiber surface.

Figs. 2 and 3 are the low-resolution X-ray photoelectron spectroscopy spectra of the fiber in eucalyptus CTMP fiber before and after fungal modification. In Figs. 2 and 3, only carbon and oxygen peaks are clear, besides, no other peak is found. For general organic compounds, standard binding energy of carbon and oxygen are 285 eV (C1s) and 532.0 eV (O1s). However, due to chemical shift, the binding energy may be different. In the two figures, there are some shifts in the binding energy of carbon and oxygen compared with their standard binding energy.

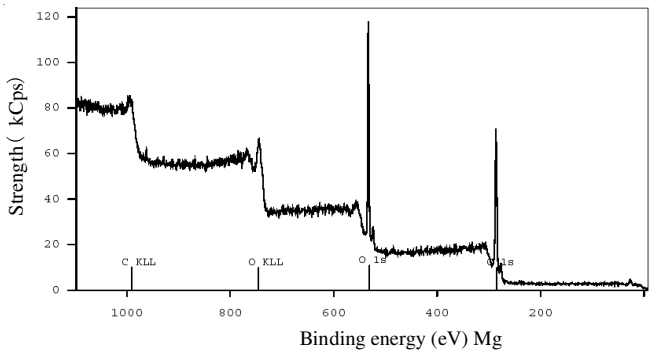


Fig. 2. Low-resolution X-ray photoelectron spectroscopy spectrum of eucalyptus CTMP fiber before fungal modification

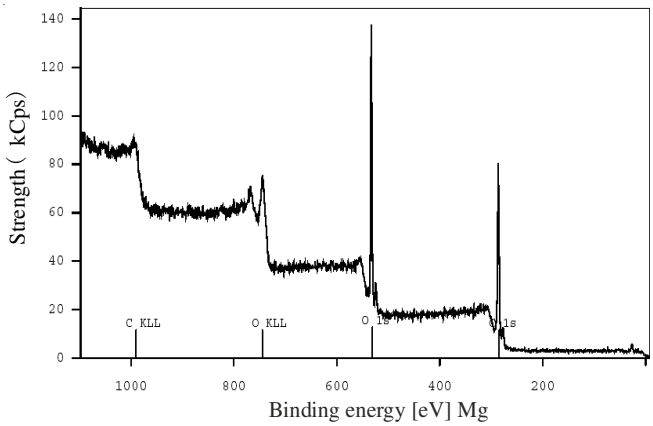


Fig. 3. XPS low-resolution scan spectrum of eucalyptus CTMP fiber after fungal modification

Table-2 (Figs. 2 and 3) suggested that the surface O/C ratio of the fibers surface modified by fungi increased significantly (from original 0.497 to 0.534, 7.4 % growth) and the C1s peak shiftes to high binding energy direction at the same time. These show that fungal modification, the carbohydrate content get higher and lignin and extractives contents get lower on the fiber surface. This should be due to white-rot fungi modification which degradates the lignin and extractives on the fiber surface and make more carbohydrate-rich structure of the S1 layer exposed in the surface. This indicates that white-rot fungi can remove lignin and extractives from fiber surface.

Analysis of the carbon valence on the fiber surface in eucalyptus CTMP fiber before and after fungal modification: As white-rot fungus can remove various components from fibers in eucalyptus CTMP fiber, especially lignin and extractives, it may also change changes the proportion of C1s valence. According to literature[15,16], C1 was mainly from lignin and extractives, C2 and C3 were mainly found in carbohydrates. Theoretically, 83 % of the carbon atoms in pure cellulose are C2, 17 % are C3 and none are C1. The carbon connection in hemicellulose is similar to that in cellulose, which means every carbon atom in hemicellulose is connected to at least one oxygen atom. Lignin generally has more C1, while extractives have the highest contents of C1. This is because extractives are mainly composed of a number of hydrocarbons. Figs. 4 and 5 show the points peak curve of C1s on fiber surfaces in eucalyptus CTMP fiber before and after fungal modification respectively.

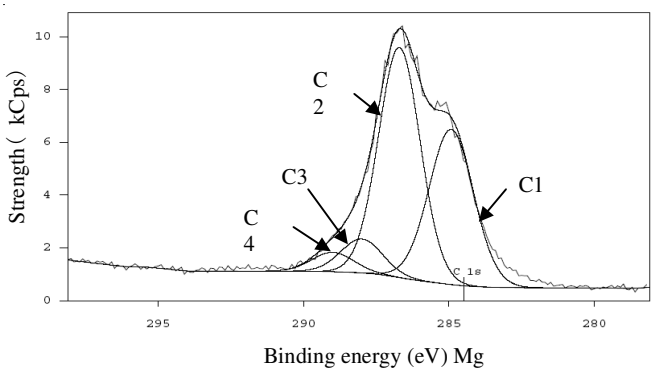


Fig. 4. Points peak curve of C1s on fiber surfaces in eucalyptus CTMP fiber before fungal modification

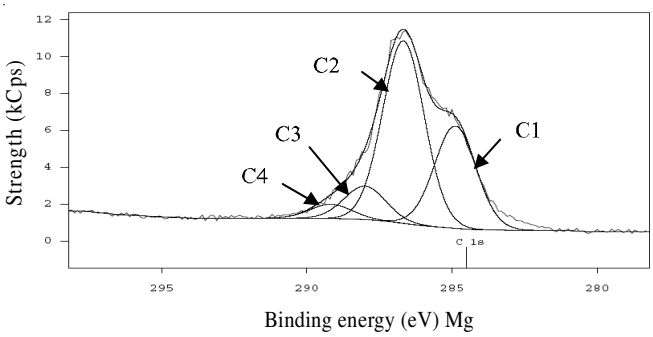


Fig. 5. Points peak curve of C1s on fiber surfaces in eucalyptus CTMP fiber after fungal modification

Table-2 (Figs. 4 and 5) showed that the peak area of C1 on the surface of fungal modified fiber decreased from the original 36.9 to 30.8 %. The peak area of C2 and C3 increased by 7.2 and 33.3 % respectively, while that of C4 did not change. As we mentioned previously, a lower C1 percentage meant that on the modified fiber surface there were less had lower lignin and extractives and more carbohydrate content. The increase in the peak area of C2 and C3 suggest this too, and the result agree with O/C ratio trends. Therefore, through comparing the carbon valence on fiber surface before and after fungal modification, it further indicated fungal modification could remove lignin and carbohydrate from fiber surface and make the S1 layer exposed more on the fiber surface.

In addition, high carbohydrate contents on the fiber surface meant there are more hydrophilic groups exposed on the fiber surface, which was helpful in the forming of hydrogen bonds. Therefore, this result can better explain why the physical strength performance of the fibers in fungal modified eucalyptus CTMP fiber is improved significantly.

TABLE-3
CONTENT OF LIGNIN AND EXTRACTIVES ON THE SURFACE OF EUCALYPTUS CTMP FIBERS (%)

Pulp	C1	C2	C3	C4	Lignin content	Extraction content
Eucalyptus CTMP fiber	36.9	51.2	7.5	4.3	56.9	10.9
Eucalyptus Bio-CTMP fiber	30.2	55.2	9.6	5.0	54.1	2.6
Eucalyptus CTMP-E fiber	30.8	54.9	10.0	4.3	52.2	4.8
Eucalyptus Bio-CTMP-E fiber	28.9	52.9	13.3	4.8	51.8	2.2

Quantitative analysis of lignin and extraction from the surface of CTMP fiber before and after modification by white rot: Besides the analysis of the proportion of carbon valence from O/C and C1s peaks of the surface from plant fiber, X-ray photoelectron spectroscopy can also be used for quantitative analysis of the contents of lignin and extraction from fiber surfaces. As mentioned above, because C1s peaks do not appear in pure fiber as well as in hemicellulose, for the fibers after extraction, the C1 peaks can be considered almost come from lignin. This feature of plant fiber offers us a method to quantitatively determine the contents of lignin and extractives from fiber surface through the information given by C1 peaks. Attention should be paid to that analysis needs using the patterns after extraction when we quantitative analyzed the contents of lignin and extractives from fiber sueface. The common solvents for the extraction are acetone and dichloromethane.

According to the literatures, if the proportion of O/C on fiber surface or the numbers of carbon of different valence have been given, the contents of lignin and extractives on fiber surface can be estimated through eqn. (1)-(4).

$$\phi_{lignin} = \frac{O/C_{extracted\,pulp} - O/C_{carbohydrates}}{O/C_{lignin} - O/C_{carbohydrates}} \times 100\% \quad (1)$$

$$\phi_{extractives} = \frac{O/C_{extracted\,pulp} - O/C_{pulp}}{O/C_{extracted\,pulp} - O/C_{extractives}} \times 100\% \quad (2)$$

In the equations, O/C_{pulp} -the proportion of O/C of pulp that hasn't been extracted; $O/C_{extracted\,pulp}$ -the proportion of O/C of pulp that has been extracted; $O/C_{carbohydrates}$ -the proportion of O/C of carbohydrates; O/C_{lignin} -the proportion of O/C of lignin.

$$\phi_{lignin} = \frac{C1_{extracted\,pulp} - \alpha}{49} \times 100\% \quad (3)$$

$$\phi_{extractives} = \frac{C1_{pulp} - C1_{extracted\,pulp}}{C1_{extractives} - C1_{extractted\,pulp}} \times 100\% \quad (4)$$

In the equations, $C1_{pulp}$ - the percentage of C1 of pulp the hasn't been extracted; $C1_{extracted\ pulp}$ -the percentage of C1 of pulp that has been extracted; 49 -the percentage of C1 of milled wood lignin; $C1_{extractives}$ -the percentage of C1 of extractives; α -the measurements of C1 in pure fiber, generally dereferenced as 2 %.

In the above 4 equations, eqns. (1) and (2) were first set up by Ström and Carlsson[17]. Equation (3) was first set up by Österberg[18]. Afterwards, Risén *et al.*[19] and Zhou *et al.*[20] expanded eqns. (1)-(3) respectively, then set up equation (4). According to Koljonen's research[7], when we quantitatively analyze the contents of lignin and extractives on fiber surface, if each experimental condition is strictly controlled, the algorithmic method of taking the percentage of C1 as the baseline (using eqns. 3 and 4) is better than that of taking the proportion of O/C as the baseline (using equation 1 and 2), for using the former one we can get good reproducible results[7]. That's because for the second method, the fiber surface is easy to soak up water, meanwhile the proportion of O/C is quite sensitive to the chemical changes on fiber surfaces during the process. These will influence the results finally[21-23]. Therefore, we suggest that eqns. (3) and (4) are used in calculating the content of lignin and extractives on fiber surfaces.

In this research, we used acetone to extract and process the CTMP fiber in eucalyptus pulp and eqns. (3) and (4) to calculate the contents of lignin and extractives on fiber surface. Based on the data in Table-2, the contents of lignin and extractives on fiber surface calculated are listed in Table-3.

It is shown in Tables 1 and 3 that, no matter before or after the modification of white rot fungi, the contents of lignin and extractives on the surface of eucalyptus CTMP fiber are always far higher than the total contents of lignin and extractives. For example, the total content of lignin of the fibers in eucalyptus CTMP fiber which haven't been modificated is 25.1 %, however, the content of lignin on its surface reach up to 56.9 %. Thus it indicates that the lignin and extractives of fibers in eucalyptus CTMP fiber mainly concentrate on the surface. That's because the separation of fibers mainly happens in middle lamella during CTMP pulping and the major chemical composition of middle lamella are lignin and extractives, which has been proved in our previous works using SEM and AFM.

In Table-3, the content of lignin on the surface of fibers in eucalyptus CTMP decreases from original 56.9 to 52.2 % after modification, reduced by 8.3 %, while the total content of lignin only decrease by 2.5 %. This means shows the delignification by white rot fungi mainly happened on fiber surfaces Meanwhile, the content of extractives on the surfaces of fibers in eucalyptus CTMP fiber decreases from original 10.9 % to 4.8 % after modification, reduced by 55.9 %, while the total content of extractives just reduce by 11.1 %. It suggested that the removing of extractives caused by white rot fungi modification mainly concentrates on fiber surfaces.

Conclusion

The X-ray photoelectron spectroscopy analysis of oxygen-carbon ratio (O/C) on the surfaces of fibers in eucalyptus CTMP fiber before and after the modification of white rot fungi showed that the oxygen-carbon ratio (O/C) on the surfaces of fiber in eucalyptus CTMP fiber after modification by white rot fungus increased by 7.4 %, meanwhile C1s peak shift to higher binding energy, which means, the surface of fibers in eucalyptus CTMP fiber are high in carbohydrate content, low in lignin and extractives content. That's caused by white-rot fungus which removes part of lignin and extractives

from the fiber surface and makes more carbohydrate-rich components exposed in S1 layer structure.

Through the studies of C1s peaks of fiber surfaces in eucalyptus CTMP fiber, the area of C1 peaks of fiber surface decreases by 16.5 % after the white rot fungus modification. While the areas of C2 and C3 peaks increase by 7.2 % and 33.3 %, the area of C4 peak does not change. The drop in the area of C1 peak means hydrophilic groups are exposed on the fiver surfaces in the eucalyptus CTMP fiber after white rot fungus modification, the content of carbohydrate increased, lignin and extractives are deduced. That will promote the formation of hydrogen bonding between the fibers during papermaking.

In the quantitative X-ray photoelectron spectroscopy analysis of the contents of lignin and extractives on the fiber surface, the contents of lignin and extractives in the fiber surface in eucalyptus CTMP fiber after white rot fungus modification decreased by 8.3 % and 55.9 % reseparately, while the total lignin content and total extraction content of pulp decrease by only 2.5 % and 11.1 %, which proves that the delignification by white rot fungi and the degradation of extractions mainly happened on fiber surfaces.

ACKNOWLEDGEMENTS

The authors gratefully acknowledged the financial support of this study by the Science and Technology Project of Guangxi Province (10100025) and the fund of Guangxi University.

REFERENCES

1. D. Guanben, Wood Industry, **13**, 17 (1999).
2. J. Buchert, G. Carlsson, L. Viikari and G. Ström. *Holzforschung*, **50**, 69 (1996).
3. G. Fang, *Wood Industry*, **13**, 24 (1999).
4. G.M. Dorris and D.G. Gray, *Cellulose Chem. Technol.*, **12**, 9 (1978).
5. X. Hua, S. Kaliaguine, B.V. Kokta and A. Adnot, *Wood Sci. Technol.*, **27**, 449 (1992).
6. Q. Yang, H. Zhan and S. Wang, *Paper Sci. Technol.*, **23**, 22 (2006).
7. K. Koljonen, M. Österberg, L.-S. Johansson and P. Stenius, *Colloid. Surf. A*, **228**, 143 (2003).
8. P. Fardim, *Colloid. Surf. A*, **255**, 91 (2005).
9. J. Laine, P. Stenius, G. Carlsson and G. Ström, *Cellulose*, **1**, 145 (1994).
10. A.L. Seisto, *Paperi ja Puu-Paper and Timber*, **81**, 54 (1999).
11. Z. Jian and H. Hu, *Chin. Paper*, **26**, 53 (2007).
12. K. Li, *J. Pulp Paper Sci.*, **28**, 369 (2002).
13. S. Takeyama and D.G. Gray, *Cellulose Chem. Technol.*, **16**, 133 (1982).
14. U. Gelius, P.F. Heden, J. Hedman, B.J. Lindberg, R. Marine, R. Nordberg, C. Nordling and K. Siegbahn, *Phys. Scripta*, **2**, 70 (1970).
15. K. Li, *Cellulose Chem. Technol.*, **38**, 197 (2004).
16. D.P. Kamdem, B. Riedl, A. Adnot and S. Kaliaguine, *J. Appl. Polym. Sci.*, **43**, 1901 (1991).
17. G. Ström and G. Carlsson, *J. Adhes. Sci. Technol.*, **6**, 745 (1992).
18. M. Österberg, Stockholm, Sweden:The Royal Institute of Technology, (2000).
19. J. Risén, A.H. Hultén and M. Paulsson, *J. Wood Chem. Technol.*, **24**, 307 (2004).
20. Q. Zhou, M.J. Baumann, H. Brumer and T.T. Teeri, *Carbohyd. Polym.*, **63**, 449 (2006).
21. L.S. Johansson, *Microchim. Acta*, **138**, 217 (2002).
22. L.S. Johansson, J.M. Campbell and P. Fardim, *Surf. Sci.*, **584**, 126 (2005).
23. L.S. Johansson, J. Campbell and K. Koljonen, *Surf. Interf. Anal.*, **36**, 706 (2004).