

SURFACE COMPOSITION OF GRAFTED THERMOMECHANICAL PULP THROUGH XPS MEASUREMENT

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The purpose of this study is to develop an analytical method to quantify the nitrogen present at the surface of paper by using X-ray photo-electronic spectroscopy (XPS). A sample of softwood thermomechanical pulp (TMP) was treated with a cationic starch containing primary amines, while another one was treated with a cationic polymer containing quaternary amines. We also grafted monomers containing a quaternary amine to the fiber. Sheets were prepared and analyzed by XPS. The technique used allowed us to identify the type of amine and to give a semi-quantitative evaluation.

Keywords: Thermomechanical pulp; TMP; XPS; Cationisation; Grafting; Amine; Fiber surfaces

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INTRODUCTION

The surface of TMP fiber contains cellulose, hemicelluloses, lignin, and extractives. The extractives tend to redeposit on the fiber surface after pulping. They give a hydrophobic surface with only a few oxygen atoms. The chemical composition of the fiber surface affects its reactivity with various chemicals and the interactions between fibers. As for the cellulose and hemicelluloses, they provide the fiber surface mainly with hydroxyl groups and some carboxylic acid groups, making the surface more hydrophilic. On the other hand, the lignin contributes to a hydrophobic surface due to its large amount of aromatic units containing oxygen atoms.

The addition of amine groups onto the fiber would change the surface composition and chemistry. They can be added by grafting or deposition of amine-containing polymers. As a result, they yield surfaces with positive charges. The goal of this study was to characterize the fiber surface composition by XPS to determine the efficiency of such chemical treatments. Mohammed-Ziegler et al. (2006) have demonstrated that Silanization of wood can be follow with XPS.

XPS of Mechanical Pulp

Dorris and Gray pioneered the application of XPS in the pulp and paper domain. They first studied the surface molecular structure of cellulose and lignin (Dorris and Gray 1978a) and thereafter the surface of a mechanical pulp (Dorris and Gray 1978b).

Based on the results of XPS analysis it is possible to separate various carbon groups into four classes (Dorris and Gray 1978a):

- C1: Carbon-Carbon or Carbon-Hydrogen bonding
- C2: Carbon having a simple bond with only one oxygen
- C3: Carbon that bonds to only one oxygen carbonyl or two oxygen atoms, non-carbonyl
- C4: Carbon that bonds to an oxygen carbonyl and an oxygen non-carbonyl

Figure 1 shows an XPS spectrum of cellulose and lignin. The XPS spectrum of cellulose (Dorris and Gray 1978a) exhibits broad C2 bands overlapped by two C1 and C3 bands. Broad bands for oxygen are also observed. It is normal to obtain large C2 bands because cellulose mainly contains carbons related to one oxygen atom.

Lignin presents a different spectrum. The oxygen band is less evident. It has a larger C1 band than cellulose with little evidence of C2 and C3 bands. These observations are in accordance with the basic structure of the Freudenberg lignin (Freudenberg and Neish 1968), $C_9H_{7.95}O_{2.4} (OCH_3)_{0.92}$.

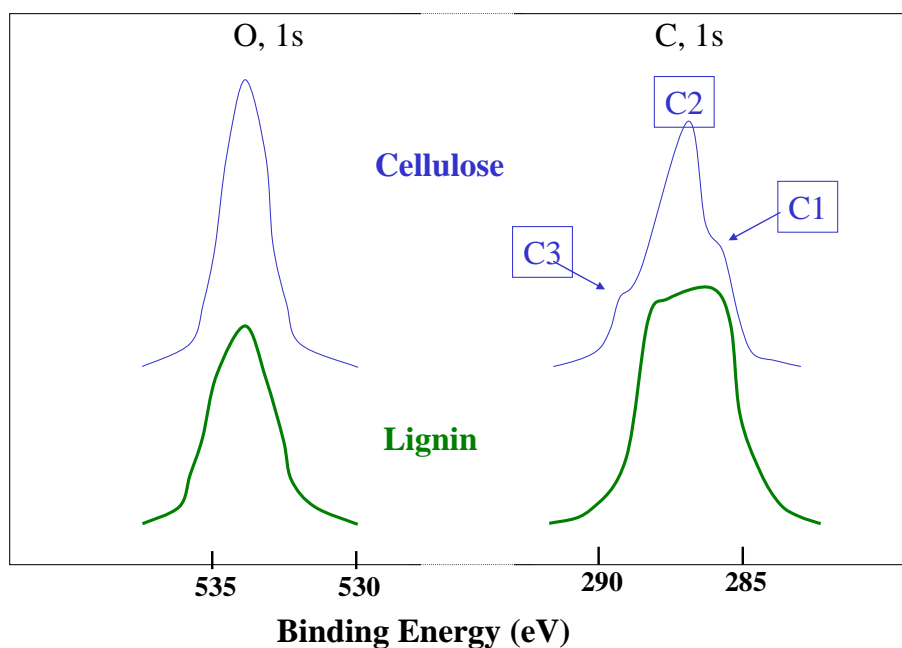


Fig. 1. Lignin and cellulose XPS spectra

An XPS spectrum of mechanical pulp is shown in Fig. 2 (Dorris and Gray 1978b). In this case a significant C2 and a C1 strip are much better defined than in the case of cellulose. On the other hand the C3 strip escarpment is generally less well defined. We thus have a spectrum that seems to be a composite of the cellulose and the lignin spectra.

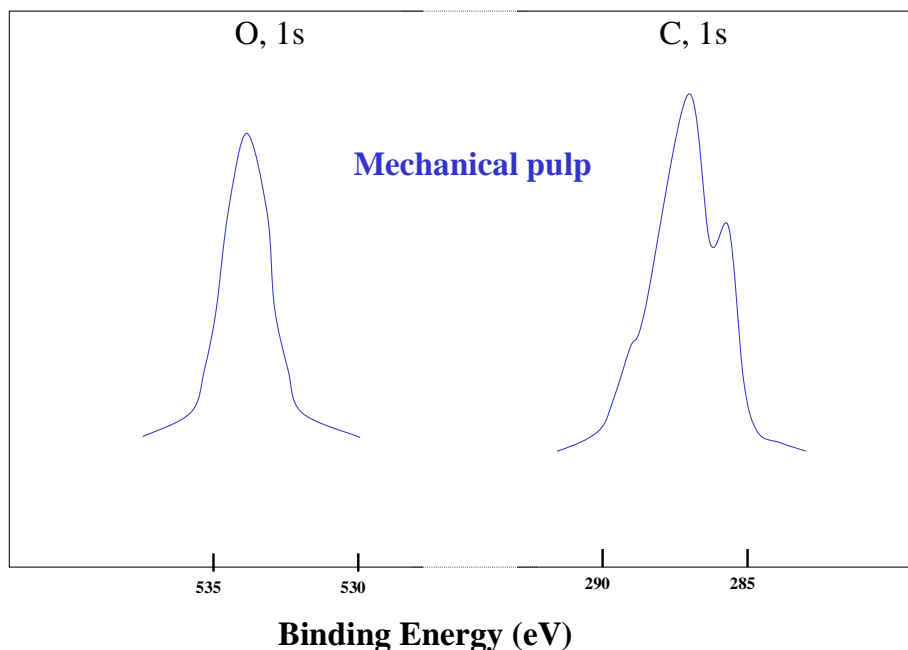


Fig. 2. Mechanical pulp XPS spectrum

Table 1 shows the binding energy for ternary and quaternary amines (Wagner et al. 1979). R can be hydrogen or hydrocarbon and R' can be hydrocarbon. It is thus possible to distinguish quaternary amine easily from other types by determining the binding energies.

Table 1. Amine Binding Energy.

Amine type	Nitrogen 1s
C-NR ₂	399.77
C-NR' ₃	401.46

Cationisation

Adding quaternary amine covalently to polysaccharide is commonly used to produce cationic starch (Wurzberg 1986). This grafting reaction has been applied to cotton fibers to improve anionic dyes fastness (Seong and Koe 1998). Grafting of chemical pulp was also extensively studied (Schempp et al. 1983; Gruber et al. 1996; Gess et al. 1989). It is well established that cationisation of chemical pulp improves both retention and paper strength (Gruber et al. 1997).

It was demonstrated that 2,3-epoxy-propyl-tri-methyl ammonium chloride (EPTMAC) can be grafted onto TMP fiber in aqueous alkaline solution (Montplaisir et al.

2006a). In all cases, including this study, alkali is required to catalyze the reaction. The alkali activates cellulose and hemicellulose to react with the epoxy groups of EPTMAC, forming an ether. A homogeneous hydrolysis of the epoxide can occur as an undesirable side reaction; the glycol produced cannot react further with cellulose or hemicelluloses.

It was shown (Fig. 3) that cationic grafting improved the sheet strength properties and increased the adsorption of anionic fines and fillers (Montplaisir et al. 2006b).

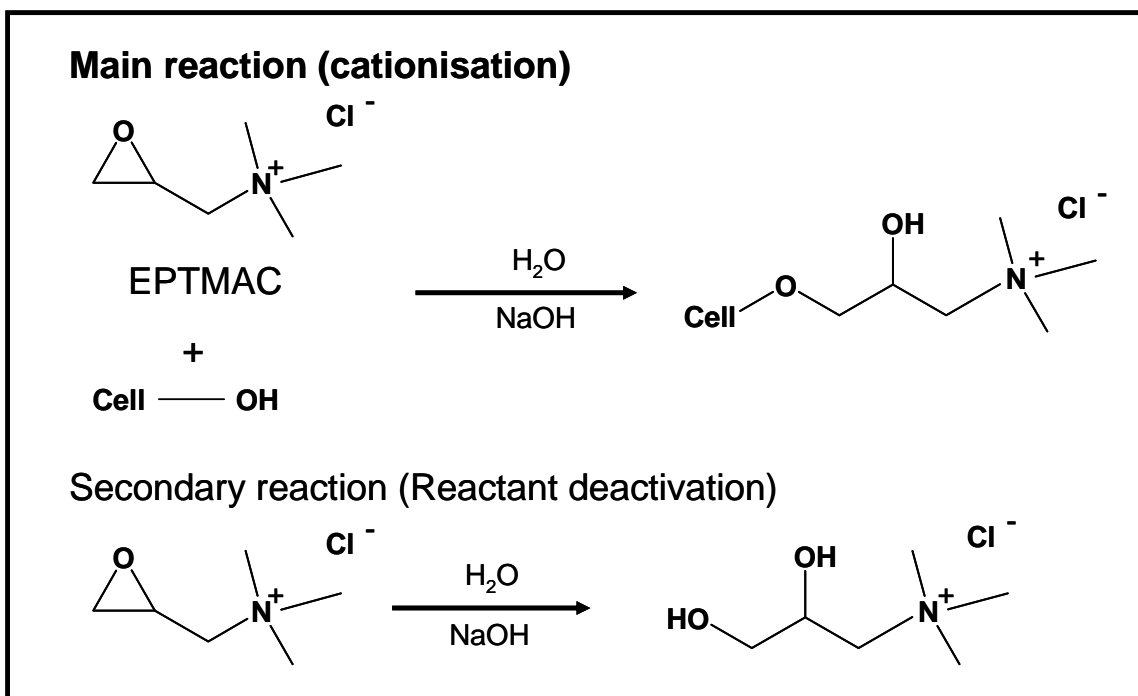


Fig. 3. Grafting reaction mechanism

Oxygen to Carbon Ratio

The important information obtained from XPS analyses is the oxygen-carbon atomic ratio (N_o/N_c), as defined in equation (1):

$$\frac{N_o}{N_c} = \frac{O}{(C1 + C2 + C3 + C4)} \quad (1)$$

For pure cellulose the theoretical value is 0.83 since we have 5 oxygen atoms for 6 carbon atoms. Lignin has a ratio from 0.31 to 0.40 (Toth et al. 2007). For the purpose of this study, we used a ratio of 0.33.

The extractives have a value approaching the theoretical value of 0.1 for abietic acid and 0.11 for oleic acid (Laine et al. 1994). Oxygen to carbon ratio of 0.12 was observed for the extractives of a softwood kraft pulp.

The N_o/N_c ratio for mechanical pulp ranged between 0.4 and 0.5 for the unextracted pulp and between 0.55 and 0.65 for the extracted sample (Laine et al. 1994).

This increase is attributed to the very low level of oxygen of the extractives adsorbed on the fiber surface.

Surface Treatment

Cationic polyelectrolytes can be adsorbed easily on the fiber surface due to its anionic charge. Considering the fact that fibers contain charged groups on their surface, it is predictable that polyelectrolyte adsorption is governed by electrostatic interactions. It has been shown that the adsorption of highly charged cationic polyelectrolyte in electrolyte-free conditions occurs at a 1:1 charge stoichiometry (Winter et al. 1986). Adsorption of cationic starch or polyDADMAC ceases when the charges between the fiber and polyelectrolyte are completely screened (Tanaka et al. 1979; Lindström and Wågberg 1983; Van de Steeg et al. 1993). This adsorption contributes to the fixation of anionic contaminant to the fiber surface (Richardson et al. 2002; Bobacka et al. 1999).

EXPERIMENTAL

A sample of unbleached eastern Canadian spruce/balsam fir (70:30) TMP was taken after the twin-wire press at a Kruger mill in Trois-Rivieres (Quebec). Pulp consistency was approximately 32-38%.

The technique used for grafting the pulp sample was similar to that described earlier (Montplaisir et al. 2006a). The grafting substance was EPTMAC, as shown in Fig. 3. Surface treatment was carried out at room temperature by adding 400 meq/kg of cationic polymer for 30 minutes to the pulp at 4% consistency, followed by standard handsheet preparation according to the PAPTAC standard testing methods. Standard handsheet preparation can be considered as a washing step. The handsheets were all air dried to avoid any variation in the results. Based on Hulten and al. (2006), the XPS oxygen to carbon ratio is sensitive to the drying method. Inari et al. (2006) have demonstrated that applying a heat treatment to beech wood increased the oxygen to carbon ratio at the surface. The cationic polymers used were a cationic starch containing secondary amine groups and a polyDADMAC containing quaternary amine groups.

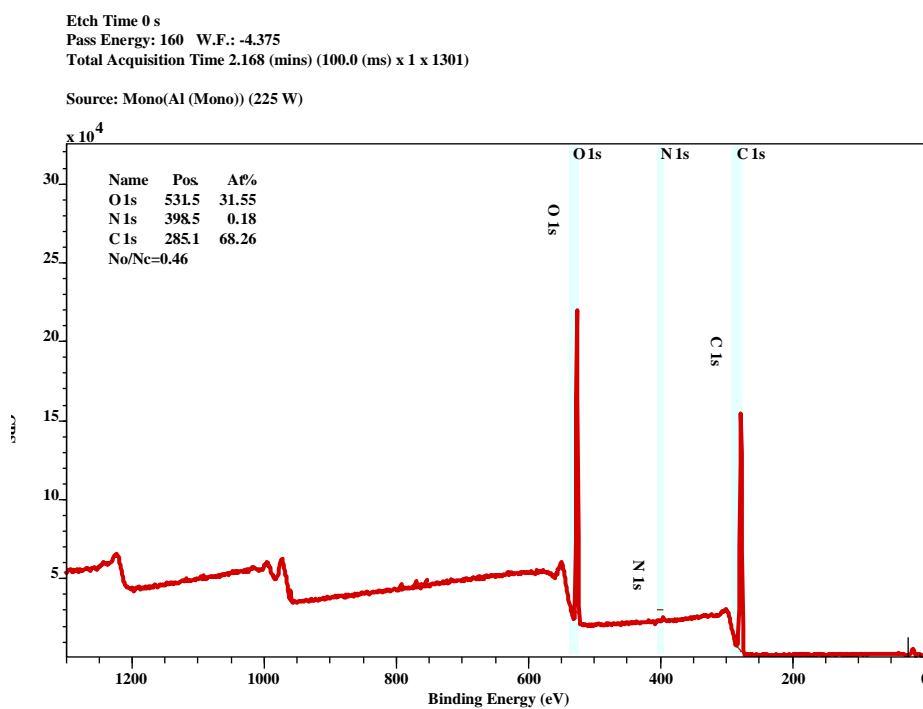
XPS analyses were performed using an "AXIS Ultra" instrument from "Kratos Analytical." A 225 watt monochromatic aluminum source was used. A surface of 2 mm² at 4 positions was analyzed. Emission time was from 180 to 362 seconds with 90° emission angle. Deconvulsion analysis was performed with a SUN Sparc Station IPX computer (Vision 2).

RESULTS AND DISCUSSION

Table 2 summarizes the results extracted from the XPS spectra. As shown in Fig. 4, the three zones studied corresponded to the carbon, oxygen, and nitrogen atoms, respectively. The nitrogen bands were much smaller and required a change of resolution to observe them.

Table 2. Atomic % and Oxygen-to-Carbon Ratio from XPS Spectra.

	TMP	Grafted TMP	Starch TMP	PolyDADMAC TMP
C1	24.63	23.32	39.88	32.95
C2	36.15	35.36	28.27	33.52
C3	7.47	8.70	6.64	6.30
C total	68.26	67.38	74.78	72.77
O	31.55	32.12	24.71	26.56
N1	0.18	0.20	0.43	0.16
N2	0.00	0.30	0.08	0.51
N total	0.18	0.50	0.51	0.67
No/Nc	0.46	0.48	0.33	0.36

**Fig. 4.** XPS analyses of untreated TMP

For all pulps, the oxygen band exhibited the same shape and position when compared to the one shown in Fig. 5. However, the amount of oxygen on the surface was higher for the surface treatments rather than for the untreated TMP and the grafted TMP.

If we compare Figs. 6 and 7, we observe a significant increase in the C1 band. Table 2 also shows a large increase in C1 for the surface treatments comparatively to the grafted or untreated TMP. This phenomenon could be attributed to the fixation of extractives on the surface of the fiber by a coagulant. Extractives are rich in C1 carbon and low in oxygen atoms. It is also shown that the cationic surface charge of the grafted TMP did not contribute to the phenomenon of contaminants fixation. These observations confirm the importance of the polymeric structure in the fixation mechanism.

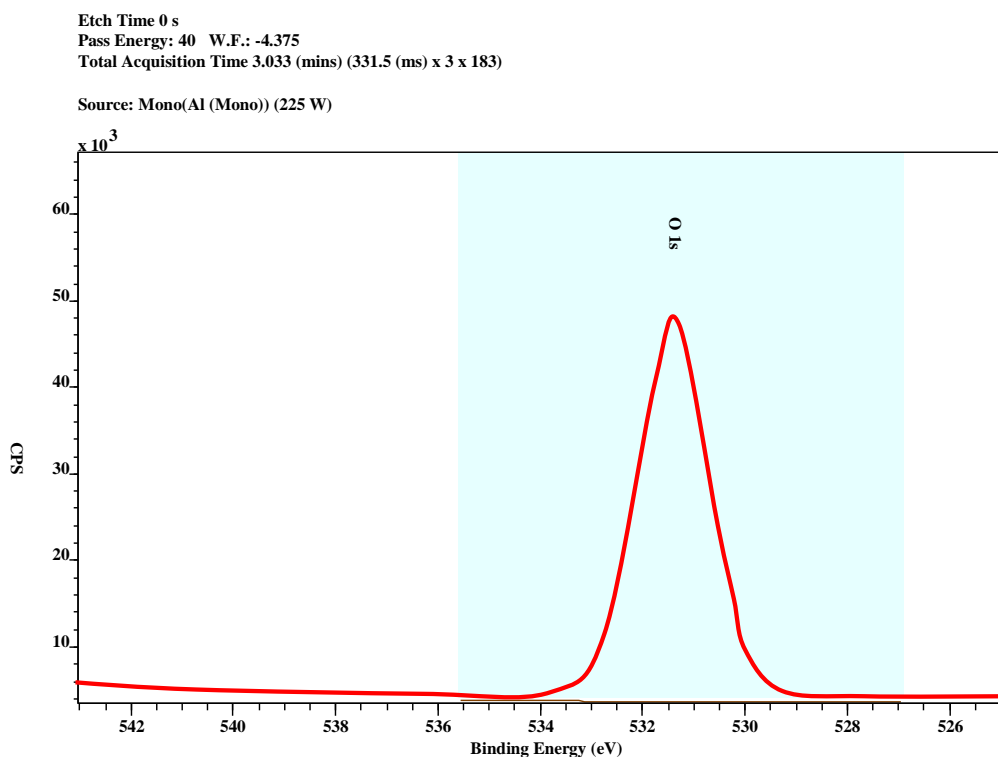


Fig. 5. XPS analyses of TMP-oxygen

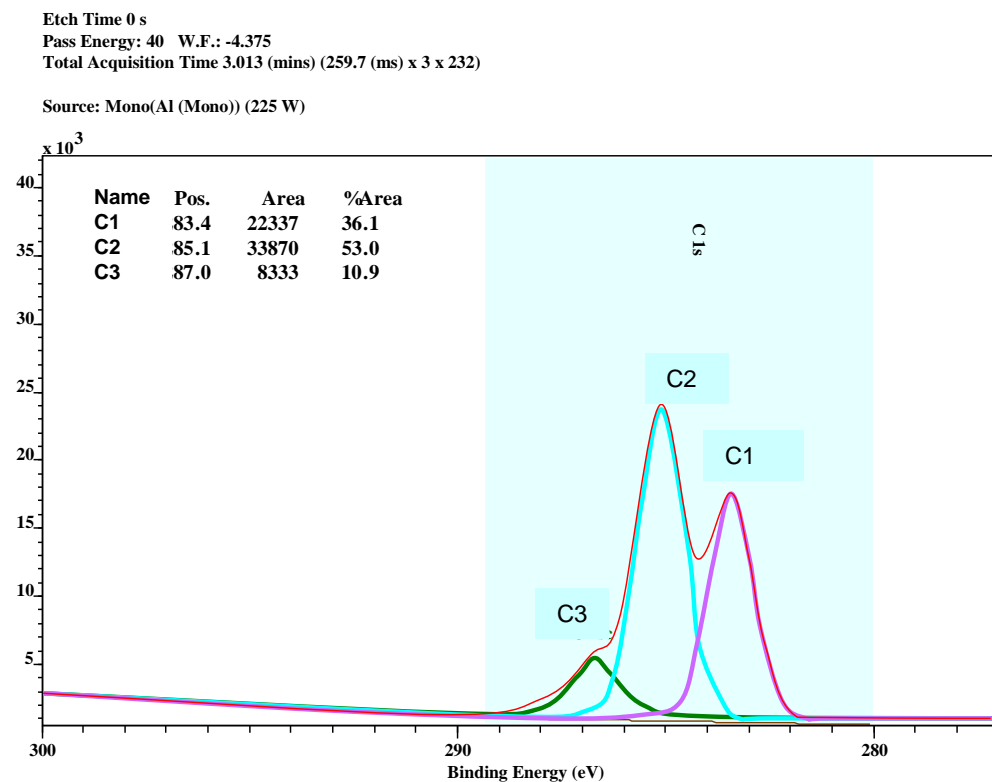


Fig. 6. XPS analyses of TMP-Carbon

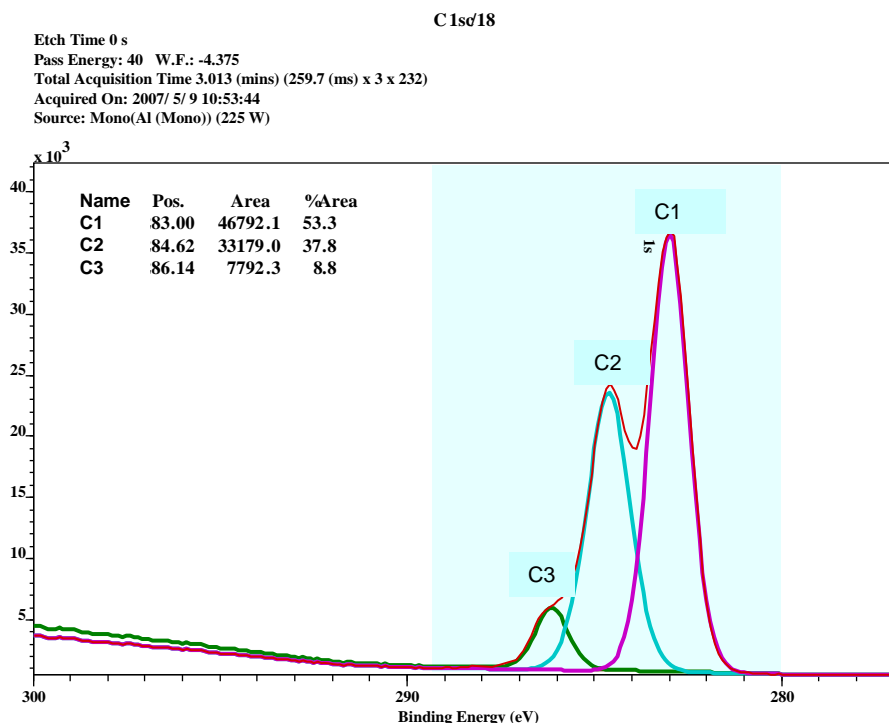


Fig. 7. XPS analyses of Starch-TMP-carbon

Figures 8 to 11 show typical binding energies of nitrogen. Two bands were observed. N1 represents the non-quaternary amines and N2 the quaternary amines. We observed equivalent N1 bands in Figs. 9, 10, and 11 for the untreated TMP, grafted TMP, and the surface treatment with polyDADMAC, respectively. In these cases, the N1 band represented the nitrogen that was already present in the TMP. N1 exhibited a larger percentage for the surface treatment with starch. This observation confirms the attachment of primary amine starch to the fiber surface.

The N2 band was completely missing from the spectra for the untreated TMP and the starch treated TMP. On the other hand, the quaternary addition of amine is obvious with regard to the grafted TMP and the polyDADMAC treatments. It is thus possible to attach more quaternary amine onto the fiber surface with polyDADMAC, compared to grafted TMP samples. Therefore, the polymeric nature of the coagulant allowed a greater concentration of polymer on the fibre surface.

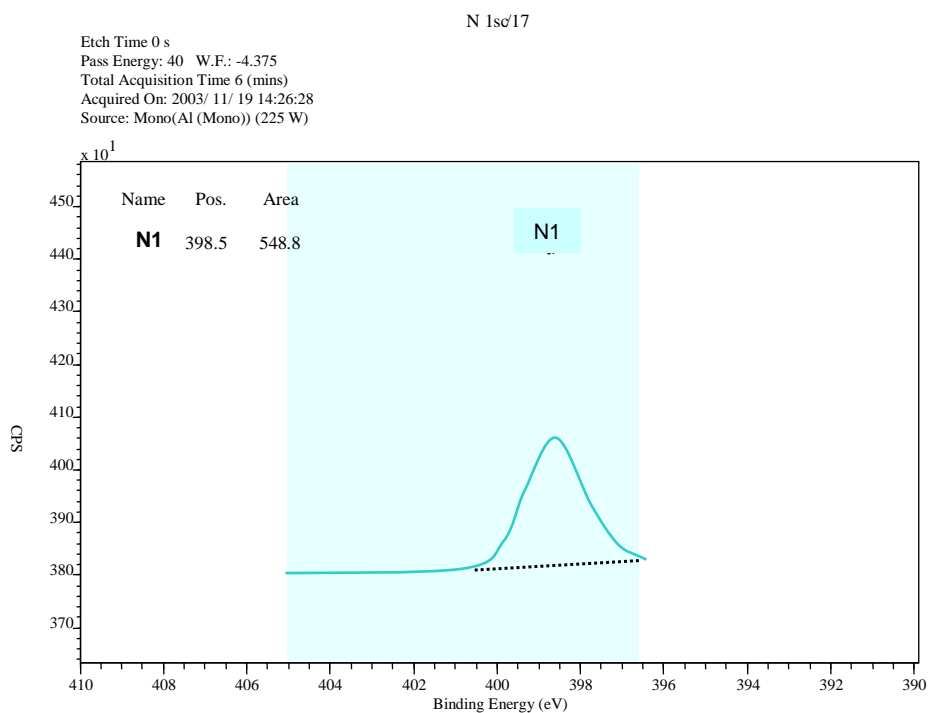


Fig. 8. XPS analyses of TMP-nitrogen

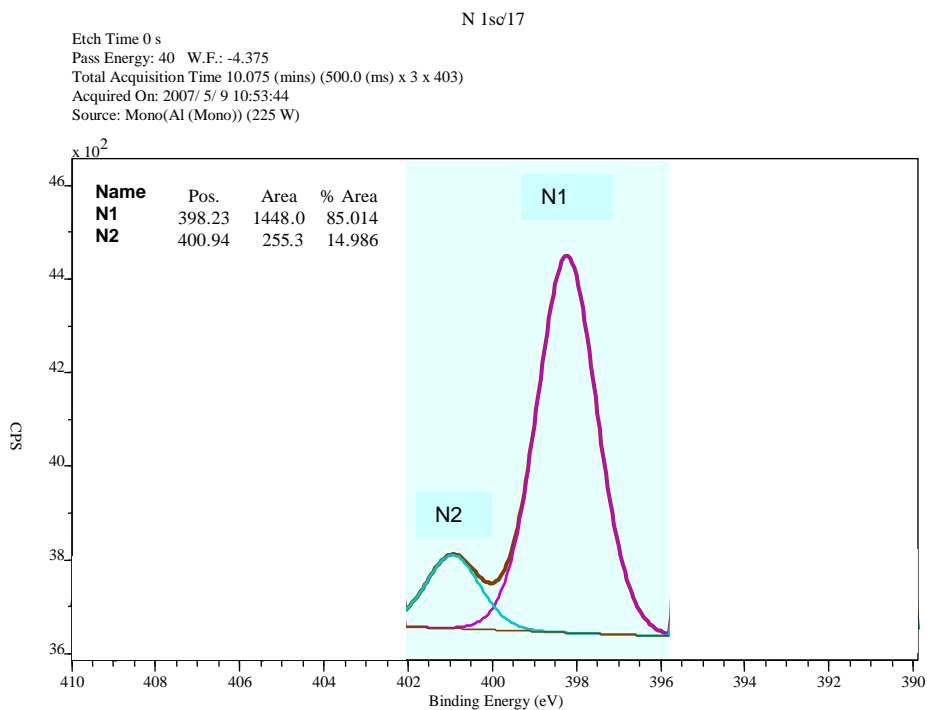


Fig. 9. XPS analyses of starch-TMP-nitrogen

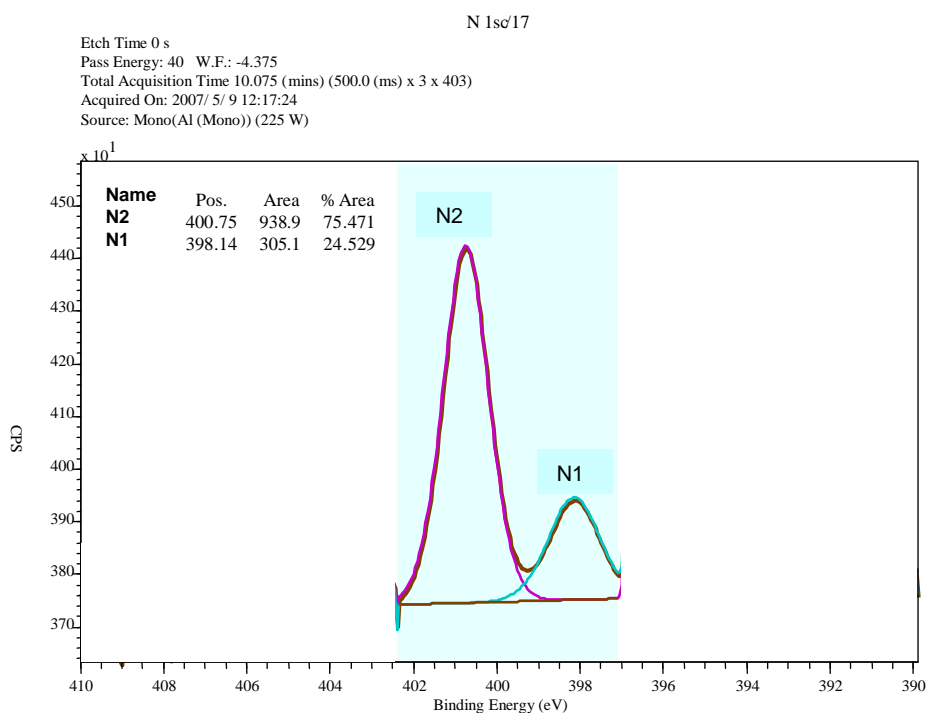


Fig. 10. XPS analyses of PolyDADMAC-nitrogen

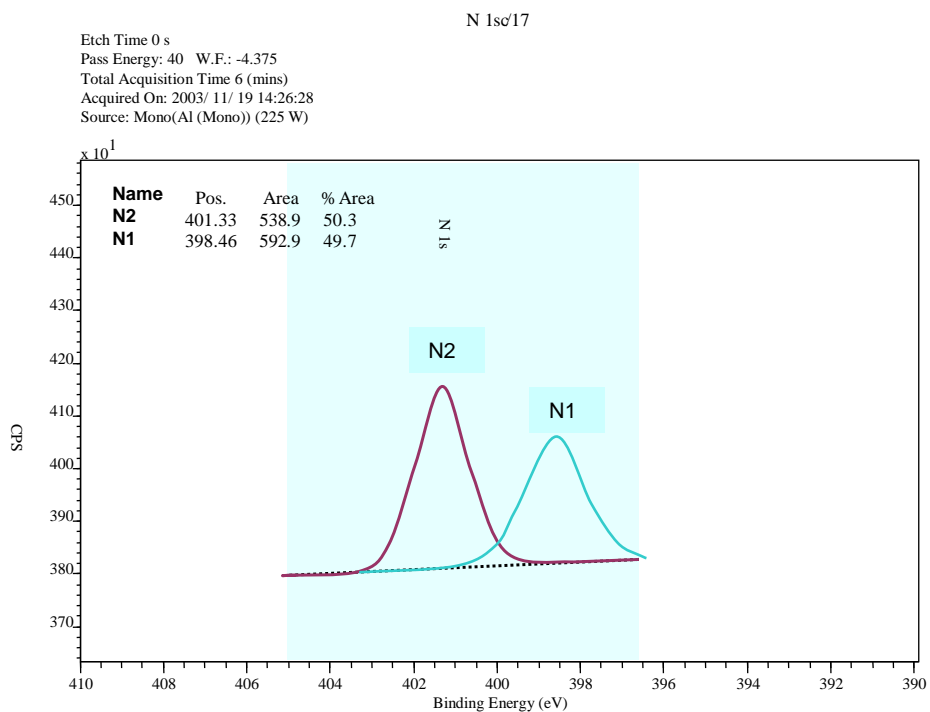


Fig. 11. XPS analyses of Grafted TMP-nitrogen

CONCLUSIONS

XPS is an effective method to determine the changes in surface reaction of fibers. The main observations are:

1. Enrichment of carbons associated with extractives on fiber surface is induced by a coagulant fixation mechanism.
2. Tertiary amine content of the fiber surface is increased by the adsorption of amine-containing cationic starch.
3. Quaternary amine can be grafted onto the fiber surface.
4. Quaternary amine from polyDADMAC is added to the fiber surface through adsorption.

In summary, it is possible to distinguish the non-quaternary from the quaternary amines. This method can be useful for studying any changes in fiber surface chemistry.

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REFERENCES CITED

- Bobacka, V., Kreutzman, N., and Eklund, D. (1999). "The use of a fixative in combination with cationic starch in peroxide-bleached TMP," *J. Pulp Paper Sci.* 25(3), 100-103.
- Dorris, G., and Gray D. (1978a). "The surface analysis of paper and wood fibres by ESCA (Electron Spectroscopy for Chemical Analysis) I. Application to cellulose and lignin," *Cellulose Chem. Technol.* 12, 9-23.
- Dorris, G., and Gray D. (1978b). "The surfaces analysis of paper and wood fibres by ESCA (Electron Spectroscopy for Chemical Analysis) II. Surface composition of mechanical pulps," *Cellulose Chem. Technol.* 12, 721-734.
- Freudenberg, K., and Neish, A. C. (1968). *Constitution and Biosynthesis of Lignin*, Springer-Verlag, Berlin.
- Gess, J. M., Harding, M. J., and Gaines, R. C. (1989). "Cationic cellulose product and method for its preparation," *Can. Pat.* 1,249,585.
- Gruber, E., Granzow, C., and Ott, T. (1996). "New ways for cationizing cellulose," *Papier* 50(12), 729-734.
- Gruber, E., Granzow, C., and Ott, T. (1997). "Cationization of cellulose fibers in view of applications in the paper industry," *Proceeding ACS Meeting*, Orlando.

- Hulten, A. H., Basta, J., Larsson, P., and Ernstsson, M. (2006). "Comparison of different XPS methods for fiber surface analysis," *Holzforschung* 60(1), 14-19.
- Inari, G. N., Petrisans, M., Lambert, J., Ehrhardt, J. J., and Gerardin, P. (2006). "XPS characterization of wood chemical composition after heat-treatment," *Surface and Interface Analysis* 38(10), 1336-1342.
- Laine, J., Stenius, P., Carlsson, G., and Ström G. (1994). "Surface characterization of unbleached kraft pulps by means of ESCA," *Cellulose* 1, 145-160.
- Lindström, T., and Wågberg, L. (1983). "Effects of pH and electrolyte concentration on the adsorption of cationic polyacrylamides on cellulose," *Tappi J.* 66(6), 83-85.
- Mohammed-Ziegler, I., Horvolgyi, Z., Toth, A., Forsling, W., and Holmgren, A. (2006). "Wettability and spectroscopic characterization of silylated wood samples," *Polymers for Advanced Technologies* 17(11-12), 932-939.
- Montplaisir, D., Daneault, C., and Chabot, B. (2006a). "Cationisation of thermomechanical pulp fibres. Part 1: Grafting reaction optimization," *Pulp Paper Can.* 107(10), 29-32.
- Montplaisir, D., Daneault, C., and Chabot, B., (2006b). "Cationisation of thermomechanical pulp fibres. Part 2: Influence on strength and retention," *Pulp Paper Can.*, 107(11), 39-42.
- Richardson, D., Moore, N., Featherstone, A., Parsons, T., Lorz, R., Esser, A., Bauman, P., and Adlam, J. (2002). "The use of chemicals to fix pitch to fibre in newsprint manufacture," *APPITA 2002*, Rotorua, 265.
- Schempp, W., Kaufer, M., and Krause, T. (1983). "Cationization of pulp: Reactions and kinetics," *TAPPI Int. Dissolving Specialty Pulps Conf.*, Boston, 171-175.
- Seong, H. S., and Ko, S. W. (1998). "Synthesis, application and evaluation of cationizing agents for cellulose fibres," *JSDC* 114(4), 124-129.
- Tanaka, H., Tachiki, K., and Sumimoto, M. (1979). "Adsorption of cationic polymers onto bleached kraft pulp," *Tappi J.* 62(1), 41-44.
- Toth, A., Cernakova, L., Cernak, M., and Kunovska, K. (2007). "Surface analysis of groundwood paper treated by diffuse coplanar surface barrier discharge (DCSBD) type atmospheric plasma in air and in nitrogen," *Holzforschung* 61(5), 528-531.
- Van de Steeg, H. G. M., de Keizer, A., Cohen Stuart, M. A., and Bijsterbosch, B. H. (1993). "Adsorption of cationic starches on microcrystalline cellulose". *Nordic Pulp Paper Res. J.* 8(1), 34-40.
- Wagner, C. D., Riggs, W.M., Davis, L. E., Moulder, J. F., and Muilenber, G. E. (1979). *Handbook of X-Ray Photoelectron Spectroscopy*. Perkin-Elmer Corporation, Eden Prairie, Chap. 2.
- Winter, L., Wågberg, L., Odberg, L., and Lindström, T. (1986). "Polyelectrolytes adsorbed on the surface on cellulosic materials." *J. Colloid Interface Sci.* 111(2), 537-543.
- Wurzburg, O. B. (1986). *Modified Starches: Properties and Uses*, CRC Press Inc., Boca Raton, Florida, 113-129.

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