

## **Surface analysis of explosion pulps by ESCA**

### **Part 1. Carbon (1s) spectra and oxygen-to-carbon ratios**

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**Summary.** The surface composition of explosion pulp and conventional CMP and CTMP underwent ESCA spectroscopy. Explosion pulps exhibited a higher oxygen-to-carbon ratio and less C1 peak areas compared to conventional CMP/CTMP. Based on the theoretical O/C ratios and C1 contents for the main components of wood fibers (i.e., carbohydrates, lignin and extractives), a triangular graph was used to illustrate the relative amounts of the three components on the surface. This analysis indicated that explosion pulps had more carbohydrates exposed on their fiber surface, which may explain their high physical strength. A bulk analysis indicated that these differences could not depend on their bulk compositions, since the latter were similar.

### **Introduction**

Recently, a pulping process, referred to as the Steam Explosion Pulping Process (SEP) or S-pulping, was proposed for both softwoods and hardwoods (Kokta et al. 1986, 1987a, 1987b, 1989, 1991). The steam explosion pulping process consists of the chemical impregnation of chips, short duration steam cooking at temperatures varying from 170°C to 210°C, pressure release, refining and bleaching (if necessary). In this process, impregnation and cooking conditions were aimed at minimizing yield and brightness loss, maximizing resulting paper properties and decreasing specific refining energy. Explosion pulping produced ultra-high-yield (87%+) pulp with paper properties superior to conventional chemimechanical pulps (Barbe et al. 1990; Hua et al. 1991b). To explain the high physical strength, fiber length and sulfonate content, cellulose crystallinity as well as crystallite size were studied (Hua et al. 1991b; Focher et al. 1991). However, surface chemical properties of pulps were not examined.

The structural and chemical composition of pulp fiber surface are important for the paper strength since those properties strongly influence the bonds between fibers in a paper sheet. The objective of this study was to apply the ESCA technique, electron spectroscopy for chemical analysis, to analyze the surface chemical properties of explosion pulps and conventional CMP/CTMP pulps prepared with the same raw materials and the same cooking chemical charges.

The ESCA-technique, developed by Kai Siegbahn et al. (Briggs et al. 1983), was also used in biomass-like wood fibers, cellulose, lignin, pulp and paper science (Dorris

et al. 1978 a, 1978 b; Gray 1978; Mjöberg 1981; Takeyama et al. 1982; Hon 1984; Clark et al. 1976). Dorris and Gray (Dorris et al. 1978 a, 1978 b; Gray 1978) analyzed the surface of cotton filter paper, mechanical pulps and spruce dioxane lignin using ESCA spectroscopy. They interpreted  $C_{1s}$  peak by a deconvolution method, which determines chemical shifts of the peak. Mjöberg (1981) studied the surface of the wood fibers with ESCA. Ahmed et al. (Ahmed et al. 1987 a, 1987 b, 1988, 1989; Grandmainson et al. 1988) carefully analyzed the ESCA of wood solid residues after vacuum pyrolysis and supercritical extraction residues. ESCA was compared with the bulk chemical analysis. A tentative assignment for the component peaks of  $O_{1s}$  peak was proposed. Barry et al. (1990) studied the ESCA of sulfite post-treated CTMP. The ESCA technique was also used in alkaline sizes on paper surface and grafting of wood fibers (Brinen et al. 1989; Kamdem et al. 1991). The principle and detailed applications of ESCA in wood and paper science were reviewed elsewhere (Hua et al. 1991 a).

## Experimental conditions

### 1. Raw material and pretreatment

Aspen (*Populus tremuloïdes* Michx.) chips were spray-impregnated at Hymac Co. in a solution of  $Na_2SO_3$  alone or with NaOH. The ratio of liquor/wood during impregnation was 2:1.

### 2. Cooking

The explosion pulp was produced with a Stake continuous reactor with a 48 ton/day capacity at the University of Sherbrooke. Pulps were submitted to two cooking conditions. The first one was 190°C for 2 min, while the second was 195°C for 1 min. Conventional cooking was carried out under typical CTMP and CMP pulping conditions: 128°C during 10 min for CTMP, 150°C during 30 min for CMP in the pilot plant unit of the École de papeterie, CEGEP de Trois-Rivières. The percentages of chemical charges during cooking appear in Table 3.

### 3. Refining

The pulp tested by ESCA was produced by refining cooked chips using a domestic blender OSTERIZER B-8614 at a 2% consistency level.

### 4. Bulk elemental analysis

A bulk elemental analysis was carried out with a type 1160 Carlos Erba Elemental Analyzer.

### 5. Lignin content

The lignin content was expressed as a sum of Klason lignin and acid soluble lignin. The Klason lignin measurement was performed according to TAPPI Standard T13. The acid soluble lignin was measured using a ZEISS Spectrophotometer PM2 D.

### ESCA spectroscopy

The ESCA spectrometer was an ESCALAB MKII spectrometer fitted on a Microlab system from V.G. Scientific and equipped with a non-monochromatized dual Mg-Al anode X-ray source. Kinetic energies were measured using a hemispherical electrostatic analyzer with 150 mm radius working in the constant pass energy mode (20 eV for C<sub>1s</sub> and O<sub>1s</sub> peak, 50 eV for survey spectra). No flood gun was used. The vacuum in the test chamber was maintained at a pressure of 10<sup>-8</sup> mbar. Liquid nitrogen was used for cooling the sample.

A small piece of pulp pad was pressed in an indium disk with maximum care to prevent sample contamination. Spectra were produced using a Mg anode at 300 W with typical accumulation time of 270–300 seconds for carbon C<sub>1s</sub> peak, 130–210 seconds for oxygen O<sub>1s</sub> peak and 288 seconds for survey spectra. To check the stability of the fiber surface with exposure time, repeated spectra acquisitions were performed. The sample area exposed to the X-ray was 10 × 15 mm. The spectrometer was operated in a computer-controlled scanning mode.

For peak synthesis, which is a curve fitting technique for resolving the complex spectra, a computer with VGS 1000 software was used. The ratio of Gaussian to Lorentzian function was 60% for C<sub>1s</sub> and O<sub>1s</sub> peak. The FWHM (Full Width at Half Maximum) was 2.0 ± 0.1 eV.

After peak synthesis the raw data were reported as uncorrected binding energy defined as

$$E_b + E_c = h\nu - E_k - \phi \quad (1)$$

where E<sub>b</sub> is the binding energy of photoelectrons, E<sub>c</sub> is the energy loss in counteracting the electronic charge on the sample surface, hν is the photon energy of X-rays, E<sub>k</sub> is the kinetic energy of photoelectrons, φ is the work function of the spectrometer. The use of a known reference is necessary to obtain an absolute scale of binding energy E<sub>b</sub>.

The quantitative analysis of ESCA is based on peak area sensitivity factors. The number of photoelectrons per second in a specific spectral peak, I, can be given by (Wagner et al. 1970),

$$I = K n \sigma \lambda T \quad (2)$$

where n is the number of atoms of the element per cm<sup>3</sup> of sample, σ is the photoelectric cross-section for the atomic orbital of interest, λ is the inelastic mean free path of the electron, K is a proportionally constant, T is the detection efficiency for electrons emitted from the sample. This can be rewritten as,

$$n = I / K \sigma \lambda T \quad (3)$$

The denominator in equation (3) can be assigned the symbol  $S$ , defined as the atomic sensitivity factor. If we take another element  $R$  as reference, then the atomic ratio of the element  $X$  we are interested in, to the element  $R$  is

$$n_x/n_r = (I_x/S_x)/(I_r/S_r) \quad (4)$$

Therefore, the atomic ratio on the surface can be estimated from corresponding peak intensities using equation (4). Using Scofield's cross sections (Scofield 1976) for oxygen  $O_{1s}$  and carbon  $C_{1s}$  peaks, corrected for angular asymmetry, electron attenuation length, and instrument transmission (Reilman et al. 1976), we can obtain the following equations:

$$O/C = I_o/(2.85 I_c) \quad (5)$$

where  $O/C$  is the atomic ratio of oxygen to carbon,  $I_o$  is the normalized integrated area of  $O_{1s}$  peak,  $I_c$  is the normalized integrated area of  $C_{1s}$  peak. Based on this equation, the oxygen-to-carbon atomic ratios were calculated from corresponding normalized peak areas.

## Results and discussion

The spectra of  $C_{1s}$  and  $O_{1s}$  were recorded. Peak synthesis techniques were applied for  $C_{1s}$  and  $O_{1s}$  peaks and resulted in three carbon and two oxygen components. The peak positions (uncorrected binding energy) appear in Table 1.

Since our wood fiber samples were electric insulators, a charge built-up on the sample surface due to X-ray bombardment acted as an additional retarding potential, which reduced the kinetic energy of photoelectrons. To get true binding energies, a reference whose binding energy is known with accuracy had to be chosen. In the case of cellulose and bleached pulp and paper, Dorris and Gray suggested that the  $O_{1s}$  peak of cellulose can be used as a reference at 533.2 eV (Dorris et al. 1978 a, 1978 b). According to Ahmed et al. (1978 a), the O2 peak in the  $O_{1s}$  spectra is considered equivalent to the  $O_{1s}$  peak of cellulose, the O2 peaks in this study were therefore chosen as the reference, at a binding energy of 533.2 eV. The corrected binding energies are shown in Table 2.

The binding energy of  $C_{1s}$  and its peak deconvolution have been well documented. There is a general agreement of the assignment of components C1, C2, C3 and C4 of  $C_{1s}$  peak in wood-derived material (Dorris et al. 1978 a, 1978 b; Gray 1978; Mjöberg 1981; Takeyama et al. 1982; Hon 1984). C1 corresponds to carbon only linked to hydrogen or to carbon ( $-C-H$ ,  $-C-C$ ), C2 has one link to a single oxygen ( $-C-O$ ), whereas C3 bonds to two non-carbonyl oxygen ( $-C \begin{smallmatrix} \diagup O \\ \diagdown O \end{smallmatrix}$ ), or to a single carbonyl oxygen ( $-C=O$ ). C4 representing carbons linked to a carbonyl and a non-carbonyl ( $-C \begin{smallmatrix} \diagup O \\ \diagdown O \end{smallmatrix}$ ) is absent in our spectra due to the low concentration of carboxylic groups on the fiber surface which makes them undetectable when using the

**Table 1.** Uncorrected binding energy of C<sub>1s</sub> and O<sub>1s</sub>

Sample	Type of pulping	C <sub>1s</sub> (eV)			O <sub>1s</sub> (eV)	
		C1	C2	C3	O1	O2
A-3	SEP	288.5	290.3	292.1	535.7	536.9
A-4	SEP	288.5	290.3	292.1	535.5	536.8
B-7	SEP	288.3	290.1	292.0	535.4	536.6
B-8	SEP	288.7	290.5	292.3	535.8	537.0
C-11	SEP	288.5	290.2	292.1	535.6	536.8
C-12	SEP	288.5	290.2	292.1	535.6	536.8
D-1	CTMP	288.8	290.6	292.4	535.9	537.1
D-2	CMP	288.9	290.6	292.4	535.8	537.1
E-5	CTMP	288.5	290.3	292.2	535.6	536.8
E-6	CMP	288.8	290.6	292.4	536.0	537.2
F-9	CTMP	288.5	290.2	292.0	535.6	536.8
F-10	CMP	288.3	290.0	291.9	535.3	536.5

**Table 2.** Corrected binding energy of C<sub>1s</sub> and O<sub>1s</sub>

Sample	Type of pulping	E <sub>c</sub> (eV)	C <sub>1s</sub> (eV)			O <sub>1s</sub> (eV)	
			C1	C2	C3	O1	O2
A-3	SEP	3.7	284.8	286.6	288.4	532.0	533.2
A-4	SEP	3.6	284.9	286.7	288.5	531.9	533.2
B-7	SEP	3.4	284.9	286.7	288.6	532.0	533.2
B-8	SEP	3.8	284.9	286.7	288.5	532.0	533.2
C-11	SEP	3.6	284.9	286.6	288.5	532.0	533.2
C-12	SEP	3.6	284.9	286.6	288.5	532.0	533.2
D-1	CTMP	3.9	284.9	286.7	288.5	532.0	533.2
D-2	CMP	3.9	285.0	286.7	288.5	531.9	533.2
E-5	CTMP	3.6	284.9	286.7	288.6	532.0	533.2
E-6	CMP	4.0	284.8	286.6	288.4	532.0	533.2
F-9	CTMP	3.6	284.9	286.6	288.4	532.0	533.2
F-10	CMP	3.3	285.0	286.7	288.6	532.0	533.2

ESCA technique. In the solid phase, the binding energy of C1 is 285.0 eV, those of C2 and C3 are usually close to 286.8 and 288.0 eV (Gelius et al. 1970).

As one can see in Table 2, data in this study are in good agreement with those reported in the literature (Dorris et al. 1978 a, 1978 b; Gray 1978; Hon 1984; Ahmed et al. 1987 a, 1987 b, 1988, 1989; Grandmaison et al. 1988; Barry et al. 1990; Brinen et al. 1989; Kamdem et al. 1991; Young et al. 1982). For example, the binding energy of C1, C2 and C3 on the cellulose surface in the report of Hon (1984) were 285.0, 286.5 and 288.3 eV respectively, 284.9, 286.9 and 288.4 eV in the work of Young et al. (1982), corresponding to our data, 284.8–285.0, 286.6–286.8 and 288.4–288.6 eV. In other words, it is justifiable to take O2 peak as reference at 533.2 eV. The binding energies of O<sub>1s</sub> are also consistent with those previously reported.

**Table 3.** O/C ratios and C<sub>1s</sub> areas of explosion and conventional pulps

Type of pulping	Chemical charge	O/C Atomic ratio	C <sub>1s</sub> area (eV)		
			C1	C2	C3
CTMP	8%Na <sub>2</sub> SO <sub>3</sub> +1%NaOH	0.47	34.2	59.4	6.4
CMP	8%Na <sub>2</sub> SO <sub>3</sub> +1%NaOH	0.41	43.1	50.8	6.1
Explosion-1 <sup>a</sup>	8%Na <sub>2</sub> SO <sub>3</sub> +1%NaOH	0.51	32.5	60.7	6.8
Explosion-2 <sup>b</sup>	8%Na <sub>2</sub> SO <sub>3</sub> +1%NaOH	0.52	32.5	61.3	6.2
CTMP	4%Na <sub>2</sub> SO <sub>3</sub> +1%NaOH	0.46	39.8	54.2	6.0
CMP	4%Na <sub>2</sub> SO <sub>3</sub> +1%NaOH	0.44	41.5	52.3	6.2
Explosion-1	4%Na <sub>2</sub> SO <sub>3</sub> +1%NaOH	0.49	37.2	58.0	4.8
Explosion-2	4%Na <sub>2</sub> SO <sub>3</sub> +1%NaOH	0.50	36.7	57.5	5.8
CTMP	8%Na <sub>2</sub> SO <sub>3</sub>	0.36	52.1	41.6	6.3
CMP	8%Na <sub>2</sub> SO <sub>3</sub>	0.34	56.5	38.9	4.6
Explosion-1	8%Na <sub>2</sub> SO <sub>3</sub>	0.39	51.5	42.5	6.0
Explosion-2	8%Na <sub>2</sub> SO <sub>3</sub>	0.40	50.4	44.4	4.6

<sup>a</sup> Explosion-1: 190 °C, 2 min

<sup>b</sup> Explosion-2: 195 °C, 1 min

### *Oxygen-to-carbon ratios*

The main components of wood fibers are polysaccharides, lignin and extractives. Polysaccharides include cellulose and hemicellulose, extractives include resin and fatty acids and their esters, sterols and terpenes. The atomic ratio of oxygen to carbon in pure cellulose is 0.83. For simplification, it could be assumed that hemicellulose has the same O/C ratio since the presence of pentose sugar and uronic acids introduces little error in this assumption (Dorris 1978 b). Dorris and Gray analyzed the surface of lignin and abietic acid. Theoretically, their O/C atomic ratios were respectively 0.33 and 0.10 (Dorris et al. 1978 a, 1978 b; Gray 1978). The abietic acid is a principal constituent of wood extractives. Consequently, the O/C ratio will reflect the content of lignin and extractives on the surface. The results (see Table 3) show that explosion pulp has a higher O/C ratio than CMP and CTMP. This implies that explosion pulp has less extractive and lignin, and more polysaccharide on the fiber surface.

### *Carbon (1s) spectra*

Based on equation (4), it is easy to understand that the peak area ratio is exactly the atomic ratio for the components in the same spectral band. Areas of the three components of C<sub>1s</sub> are also shown in Table 3. There are remarkable differences between explosion pulp and CMP. The explosion pulp has much more C2 components and less C1 components. It is believed that C1 mainly comes from lignin and extractives, because the carbohydrates only contribute to C2 and C3 peak (Ahmed et al. 1987 a; Kamdem et al. 1991). Theoretically, there are 83% C2, 17% C3 and no C1 in pure cellulose, and hemicellulose has a similar carbon bond structure to cellulose, that is, all the carbons in hemicellulose are linked to at least one oxygen. According to Freudenberg's (Dorris et al. 1978 a) spruce lignin empirical model, lignin has higher

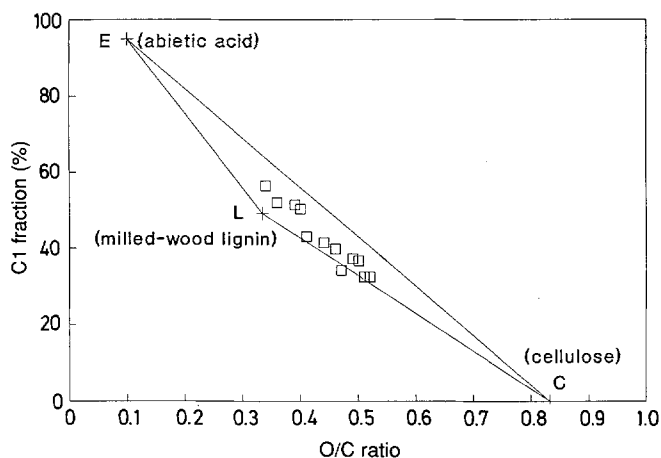


Fig. 1. Variation in C1 component area as a function of O/C atomic ratio

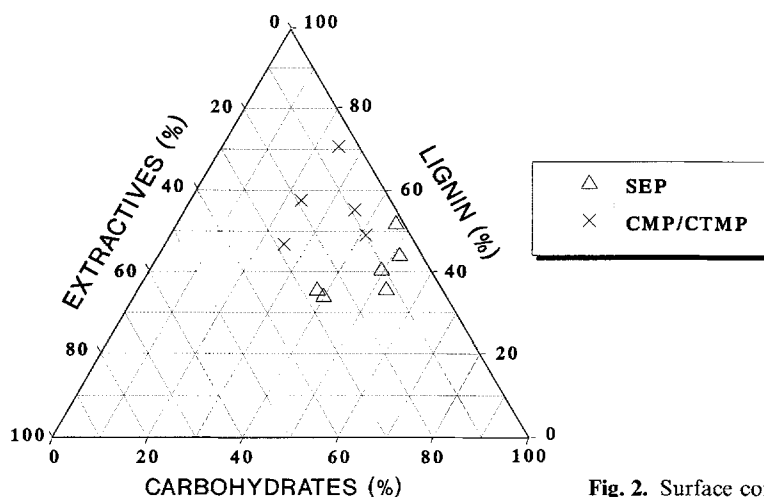
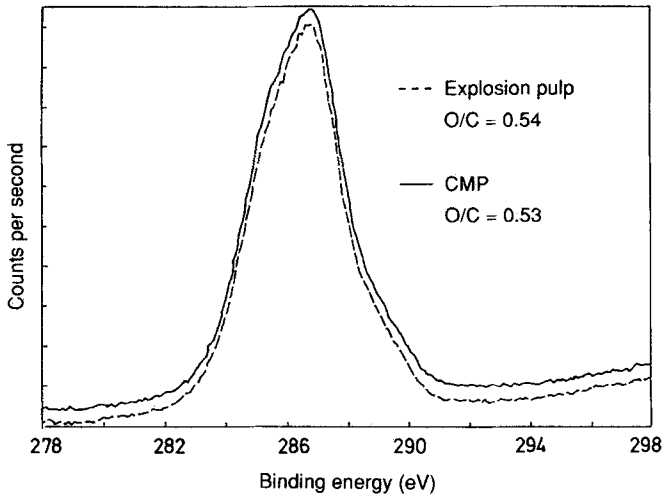


Fig. 2. Surface component fraction

C1 components. Its C1, C2 and C3 contents are 49.2%, 48.8% and 2% respectively. As for the extractives, they should have the highest C1 percentage since they are mainly hydrocarbons; for example, abietic acid has 95% C1 components. Hence, the lower C1 content in the explosion pulp indicates there were more polysaccharides exposed on the fiber surface, less lignin and extractives, confirming the result from the oxygen to carbon ratio.

Figure 1 shows the O/C ratio and the C1 percentage of the samples. The points at L, E and C are the theoretical values for spruce milled wood lignin, abietic acid and cellulose respectively. If we assume these values to be those of lignin, extractive and carbohydrate in our samples, the weight percentage of the three components can be estimated according to their O/C ratio and C1 content. If this assumption is true, then all the points should fall within the triangle LEC of Figure 1. In fact, only one point



**Fig. 3.**  $C_{1s}$  spectra of powder samples

is dropped out, which might be due to the structure of aspen lignin which is slightly different from that of spruce. It was reported (Faix et al. 1980) that milled wood lignin of aspen has a formula of  $C_9H_{6.84}O_{1.57}(OH)_{1.39}(OMe)_{1.46}$  which produces a higher O/C ratio and a lower C1 percentage. The results based on this assumption could still be considered a relative quantitative estimation for our samples where a precise chemical structure of aspen lignin is not available. Figure 2 indicates that explosion pulp has more carbohydrate and less lignin on the fiber surface compared to CTMP and CMP, though the range of extractive content is the same. A rise in exposure for carbohydrates means more exposure for hydrophilic groups on the fiber surface, which facilitates the formation of hydrogen bonding between fibers during paper making. This might partially explain why explosion pulps show greater strength compared to conventional CMP and CTMP.

#### *Bulk composition*

To distinguish the surface composition from its bulk, the samples were ball-milled to a fine powder. Ball-milling subdivides the fibers into progressively smaller portions so that the fiber structure disappears. It was suggested that the surface composition of the powder sample should approach the bulk composition of the fiber (Dorris et al. 1978 b). Figure 3 is the  $C_{1s}$  spectrum of the two powder samples. Taking into account data from the integral fiber samples, an increase in O/C ratio reveals more lignin and extractives on the fiber surface. Consequently, the bulk composition of the fibers is not representative of their surface composition. Furthermore, the powder samples of the explosion pulp and CMP have very similar spectra of  $C_{1s}$  and very close O/C ratios, 0.54 to 0.53. This indicates that they have similar bulk compositions. An elemental analysis confirmed this conclusion (see Table 4). Table 5 shows bulk lignin contents. Again there is no significant difference between explosion pulp and conventional pulps.



**Table 4.** Bulk oxygen/carbon ratio

Sample	Chemical charge	O/C ratio
CTMP	8% Na <sub>2</sub> SO <sub>3</sub> + 1% NaOH	0.52
CMP		0.53
SEP-1		0.53
SEP-2		0.53
CTMP	4% Na <sub>2</sub> SO <sub>3</sub> + 1% NaOH	0.49
CMP		0.50
SEP-1		0.51
SEP-2		0.48
CTMP	8% Na <sub>2</sub> SO <sub>3</sub> alone	0.51
CMP		0.54
SEP-1		0.53
SEP-2		0.52

Elemental analysis was carried out with CARLOS ERBA 1160

**Table 5.** Lignin contents of explosion and conventional pulps

Type of pulping	Chemical charge	acid insoluble lignin (%)	acid soluble lignin (%)	total lignin (%)
CTMP	8% Na <sub>2</sub> SO <sub>3</sub> + 1% NaOH	17.1	3.8	20.9
CMP	8% Na <sub>2</sub> SO <sub>3</sub> + 1% NaOH	16.0	4.3	20.3
Explosion-1 <sup>a</sup>	8% Na <sub>2</sub> SO <sub>3</sub> + 1% NaOH	15.6	4.4	20.0
Explosion-2 <sup>b</sup>	8% Na <sub>2</sub> SO <sub>3</sub> + 1% NaOH	15.0	4.4	19.4
CTMP	4% Na <sub>2</sub> SO <sub>3</sub> + 1% NaOH	16.8	3.6	20.4
CMP	4% Na <sub>2</sub> SO <sub>3</sub> + 1% NaOH	16.1	3.9	19.9
Explosion-1	4% Na <sub>2</sub> SO <sub>3</sub> + 1% NaOH	16.2	3.9	20.1
Explosion-2	4% Na <sub>2</sub> SO <sub>3</sub> + 1% NaOH	15.6	3.6	19.2
CTMP	8% Na <sub>2</sub> SO <sub>3</sub>	17.1	3.2	20.3
CMP	8% Na <sub>2</sub> SO <sub>3</sub>	16.4	3.6	20.0
Explosion-1	8% Na <sub>2</sub> SO <sub>3</sub>	14.8	4.1	18.9
Explosion-2	8% Na <sub>2</sub> SO <sub>3</sub>	15.0	4.1	19.1

<sup>a</sup> Explosion-1: 190°C, 2 min

<sup>b</sup> Explosion-2: 195°C, 1 min

## Conclusion

ESCA analysis shows that explosion pulp has a higher oxygen-to-carbon ratio and less C1 peak areas compared to conventional CMP/CTMP. It is suggested that explosion pulp has more carbohydrates exposed on its fiber surface, which has therefore more hydrophilic groups, facilitating hydrogen bonding during paper formation. This may explain why the paper sheet made of explosion pulp provides much greater strength than in the case of conventional pulp. These differences could not be explained on the basis of their bulk compositions since the latter were similar.

## References

- Ahmed, A.; Adnot, A.; Grandmaison, J. L.; Doucet, J.; Kaliaguine, S. 1987a: ESCA analysis of cellulosic materials. *Cellulose Chem. Technol.* 21: 483–492
- Ahmed, A.; Adnot, A.; Kaliaguine, S. 1987b: ESCA study of the solid residues of supercritical extraction of *Populus tremuloïdes* in methanol. *J. Appl. Polym. Sci.* 34: 359–375
- Ahmed, A.; Adnot, A.; Kaliaguine, S. 1988: ESCA analysis of partially converted lignocellulosic materials. *J. Appl. Polym. Sci.* 35: 1909–1919
- Ahmed, A.; Pakdel, H.; Roy, C.; Kaliaguine, S. 1989: Characterization of vacuum pyrolysis of *Populus tremuloïdes*. *J. Anal. Appl. Pyrolysis* 14: 281–294
- Barbe, M. C.; Kokta, B. V.; Lavallée, H. C.; Taylor, J. 1990: Aspen pulping: a comparison of Stake explosion and conventional chemimechanical pulping processes. *Pulp Paper Can.* 91: T395–T403
- Barry, A. O.; Koran, Z.; Kaliaguine, S. 1990: Surface analysis by ESCA of sulfite posttreated CTMP. *J. Appl. Polym. Sci.* 39: 31–42
- Briggs, D.; Seah, M. P. 1983: A perspective on the analysis of surfaces and interfaces. In: Briggs, D.; Seah, M. P. (Eds.): *Practical surface analysis by auger and x-ray photoelectron spectroscopy*. Chapter 1, pp 1–16. New York: John Wiley & Sons
- Brinen, J. S.; Calbick, J. C.; Cody R. D. 1989: Quantitative determination of alkaline sizes on paper surfaces by ESCA. *Surf. Interface Anal.* 14: 245–249
- Clark, D. T.; Peeling, J.; O'Molloy, J. M. 1976: Application of ESCA to polymer chemistry VIII: Surface structures of AB block copolymers of polydimethylsiloxane and polystyrene. *J. Polym. Sci., Polym. Chem. Ed.* 14: 543–551
- Dorris, G. M.; Gray, D. G. 1978a: The surface analysis of paper and wood fibers by ESCA I. *Cellulose Chem. Technol.* 12: 9–23
- Dorris, G. M.; Gray, D. G. 1978b: The surface analysis of paper and wood fibers by ESCA II. *Cellulose Chem. Technol.* 12: 721–734
- Focher, B.; Capretti, G.; Marzetti, A.; Hua, X.; Kaliaguine, S.; Kokta, B. V. 1991: Effect of vapor phase cooking temperature on the structure of sulfonated aspen fibers. *Proceedings of Cellulose 91* (in press)
- Faix, O.; Lange, W.; Beinhoff, O. 1980: Molecular weights and molecular weight distributions of milled wood lignins of some wood and bambusoideae species. *Holzforschung* 34: 174–176
- Gelius, U.; Heden, P. F.; Hedman, J.; Lindberg, B. J.; Manne, R.; Nordberg, R.; Nordling, C.; Siegbahn, K. 1970: Molecular spectroscopy by means of ESCA. *Phys. Scr.* 2: 70–80
- Grandmaison, J. L.; Ahmed, A.; Kaliaguine, S. 1988: Solid residues from supercritical extraction of wood. In: Soltes, E.; Millne, T. (Eds.): *ACS Symposium series No. 376, Pyrolysis oils from biomass: producing, analyzing and upgrading*. Chapter 14, pp. 139–155. Washington: American Chemical Society
- Gray, D. G. 1978: The surface analysis of paper and wood fibers by ESCA III. *Cellulose Chem. Technol.* 12: 735–743
- Hon, D. N.-S. 1984: ESCA study of oxidized wood surfaces. *J. Appl. Polym. Sci.* 29: 2777–2784
- Hua, X.; Ben, Y.; Kokta, B. V.; Kaliaguine, S. 1991 a: Application of ESCA in wood and pulping chemistry. *China Pulp & Paper* 10: 52–57
- Hua, X.; Kokta, B. V.; Kaliaguine, S. 1991 b: Explosion pulping of aspen. *Proceedings of Cellulose 91* (in press)
- Kamdern, D. P.; Riedl, B.; Adnot, A.; Kaliaguine, S. 1991: ESCA spectroscopy of poly(methylmethacrylate) grafted onto wood fibers. *J. Appl. Polym. Sci.* 43: 1901–1912
- Kokta, B. V. 1987a: Process for preparing pulp for paper making. *Can. Pat.* #1,230,208
- Kokta, B. V. 1987b: Improved process for preparing pulp for paper making. *Can. Pat. Appl.* #542,643
- Kokta, B. V. 1989: Process for preparing pulp for paper making. *U.S. Pat.* #4,798,651
- Kokta, B. V. 1991: Process for preparing pulp for papermaking. *Can Pat.* #1,287,705
- Kokta, B. V.; Vit, R. 1986: Method, process and apparatus for converting wood, wood residue and/or biomass into pulp. *Can. Pat.* #1,212,505
- Mjöberg, P. J. 1981: Chemical surface analysis of wood fibers by means of ESCA. *Cellulose Chem. Technol.* 15: 481–486

- Reilman, R. F.; Msezane, A.; Manson, S. T. 1976: Relative intensities in photoelectron spectroscopy of atoms and molecules. *J. Electron Spectrosc.* 8: 389–394
- Scofield, J. H. 1976: Hartree-Slater subshell photoionization cross-sections at 1257 and 1487 eV. *J. Electron Spectrosc.* 8: 129–137
- Takeyama, S.; Gray, D. G. 1982: An ESCA study of the chemisorption of stearic acid vapor on cellulose. *Cellulose Chem. Technol.* 16: 133–142
- Wagner, C. D.; Riggs, W. M.; Davis, L. E.; Moulder, J. F.; Muilenberg, G. E. 1979: *Handbook of X-ray Photoelectron Spectroscopy*. pp. 1–28. Eden Prairie, Minnesota: Perkin-Elmer Corporation
- Young, R. A.; Rammon, R. M.; Kelley, S. S.; Gillespie, R. H. 1982: Bond formation by wood surface reactions: Part I, Surface analysis of ESCA. *Wood Sci.* 14: 110–119

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