

# Surface Analysis by ESCA of Sulfite Post-Treated CTMP

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## Synopsis

Handsheets of post-treated chemithermomechanical pulps (CTMP) and a sample of Whatman paper no. 1 were analyzed using an ESCA spectrometer. All of these samples revealed the presence of the  $C_1$ ,  $C_2$ , and  $C_3$  components in the carbon (1s) peak and the  $O_2$  component in the oxygen (1s) peak; the  $O_1$  peak component which was present in the other samples was missing from the Whatman paper. Pulp sulfonation produced a reduction in  $C_1$  representing the group of carbon not bonded to oxygen, and an increase in  $C_2$  with  $C_3$  remaining relatively constant. These changes imply reductions in lignin and extractives and a corresponding increase in cellulose content on the fiber surface. Extrapolation of the  $C_1$ ,  $C_2$ ,  $C_1/C_2$ , and O/C curves of CTMP to zero percent sulfonation yielded the same values as those obtained for pure TMP. ESCA analysis allows us to monitor the increase of sulfur content as a function of sulfonation in accordance with results obtained from bulk pulp sulfonate content titration.

## INTRODUCTION

Despite the growth in the synthetic polymer industry, products made from wood fibers and cellulose still constitute the most important quantity of organic polymeric materials. Although the chemical composition of those materials are well characterized, much less is known about their surface chemistry, which in turn affects the properties of the final product. In the case of paper, for example, the quality of fiber-to-fiber bonding depends largely on the chemical nature of the fiber surface, which in turn determines the physical strength of paper and even its resistance to weathering and to photo-degradation.

Surface spectroscopic techniques, such as electron spectroscopy for chemical analysis (ESCA), reflectance (ATR) infrared spectroscopy, wettability measurements, and scanning electron microscopy (SEM) have potential of yielding chemical information for interfaces with a resolution of 10 Å or better.<sup>1,2</sup> Since the ESCA technique is based on a direct analysis of the kinetic energy of electrons that have been excited by high energy x-rays and pulled away from their atomic environment, this technique is a powerful tool for the chemical analysis of surfaces of synthetic polymers<sup>3-5</sup> and natural or modified textiles fibers.<sup>6,7</sup> In fact, ESCA has already been employed in the characterization of the surface composition of wood fibers<sup>8,9</sup> and cotton fibers,<sup>10</sup> and the results obtained seem very promising for the pulp and papers industries.

The main objective of this study is to use the ESCA technique to characterize the changes in the surface chemistry of chemithermomechanical (CTMP) fibers when treated to various degrees of sulfonation. ESCA spectra of these fibers were also compared to the spectrum of Whatman paper no. 1, a material which was shown to have a surface composition rather close to that of cellulose.<sup>8-10</sup>

### EXPERIMENTAL

CTMP samples obtained from Kruger Inc. were cooked in a pressure bomb (1 L) for various periods of time ranging from 0 to 8.5 h in order to reach various degrees of sulfonation. The pulp sulfonation was determined by the conductometric titration technique.<sup>11</sup> Each bomb was loaded with 80 g of bone dry pulp and sodium sulfite was dissolved in water (12%) at a liquor to O.D. pulp ratio of 4 : 1. The bombs were then preheated for 30 min in an oil bath to reach the desired cooking temperature (155°C). Once the cooking was completed, it was stopped by cooling under running water. The black liquor was then filtered off and the pulps were washed thoroughly. The latency treatment was carried out in a British desintegrator for 5 min at 1.5% consistency at 95°C. Laboratory handsheets were made for the ESCA analysis according to TAPPI standard methods T205-om-81 and conditioned according to T402-om-70.

The ESCALAB II spectrometer fitted on a microlab system from Vacuum Generators and equipped with a nonmonochromatized dual Mg-Al anode X-ray source was employed in this study. Kinetic energy measurements were made using a hemispherical electrostatic analyzer ( $r = 150$  mm) working in the constant pass energy mode (20 eV). Handsheet samples (15 × 20 mm) were mounted onto an indium disk and introduced into the working chamber: The measurements were made at a vacuum level of  $10^{-8}$ – $10^{-6}$  Torr.

### Treatment of Data

When a sample is irradiated by X-ray photons, the kinetic energy  $E_K$  of the electrons leaving the solid surface is given by

$$E_K = E_X - (E_B + E_C + \Phi) \quad (1)$$

where  $E_X$  = the energy of the incident photons (1253.6 eV for Mg<sub>K</sub> anode source, 1486 eV for Al<sub>K</sub> anode source),  $E_B$  = the binding energy of the electron on its original shell (eV),  $E_C$  = the energy lost in counteracting the potential associated with the steady charging of the surface, and  $\Phi$  = the work function of the spectrometer; it depends only on the nature of the spectrometer.

From eq. (1), the uncorrected binding energy ( $E_B + E_C$ ) is given by

$$E_B + E_C = E_X - (E_K + \Phi) \quad (2)$$

During measurement,  $E_C$  can be minimized by using a floodgun<sup>12</sup> or by wrapping the sample in aluminum foil.<sup>8</sup> We followed the suggestion of Doris and Gray<sup>8</sup> and set the oxygen (1s) peak at 533.2 eV as reference for cellulosic

materials to obtain the absolute value of binding energy,  $E_B$ . The stoichiometric ratio of two elements in the surface region analyzed by ESCA can be estimated from the ratio of their respective peak intensity. For example, the oxygen/carbon atomic ratio,  $N_O/N_C$ , can be obtained from

$$\frac{N_O}{N_C} = \frac{\sigma_C D_C}{\sigma_O D_O} \times \frac{\lambda_C}{\lambda_O} \times \frac{I_{O_{1s}}}{I_{C_{1s}}} \quad (3)$$

where  $\sigma$  refers to the cross sections for photoelectrons generation,  $\lambda$  to the mean free paths of photoelectrons,  $D$  to the spectrometer transmissions, and  $I$  to the integrated peaks intensity.

The oxygen/carbon atomic ratio (O/C) is expressed using the cross sections values reported by Scofield,<sup>13</sup> as

$$\frac{O}{C} = \frac{N_O}{N_C} = \frac{1.00}{2.85} \times \frac{I_{O_{1s}}}{I_{C_{1s}}} \quad (4)$$

### Peak Synthesis and the Evaluation of Chemical Shifts

For all samples the peak synthesis was performed using a product of Gaussian and Lorentzian functions<sup>14</sup> in the ratio G/L of 60%. Table I contains the values of oxygen/carbon atomic ratios O/C calculated from eq. (4), the percentage area of each component of the  $C_{1s}$  and  $O_{1s}$  ESCA lines, the correction  $E_C$  due to charging, and the binding energies of the  $C_{1s}$  and  $O_{1s}$  components.

Furthermore, following Doris and Gray,<sup>9</sup> we evaluated the chemical shifts of  $C_{1s}$  peak components,  $\Delta E_B$ , relative to the value of 285.0 eV for the  $C_1$  component of the  $C_{1s}$  peak. Choosing this value is equivalent to referencing the binding energy scale to the value of 533.2 eV for the  $O_2$  component of the  $O_{1s}$  peak.

The data for chemical shift of  $C_{1s}$  component reported in Table I are in very good agreement with the literature values for woody materials.<sup>3,8,9,15,16</sup> For example the  $\Delta E_B$  values of 0.1, 1.9, and 3.4 for  $C_1$ ,  $C_2$ , and  $C_3$  of Whatman paper, respectively, reported by Doris and Gray,<sup>8</sup> compare reasonably well with the corresponding chemical shifts  $\Delta E_B$  values of 0.3, 1.9, and 3.2 obtained in this work.

## RESULTS AND DISCUSSION

Figure 1 shows some selected  $C_{1s}$  spectra obtained for the untreated thermomechanical pulp (TMP) [Fig. 1(A)], the untreated CTMP possessing 0.3% sulfonate content [Fig. 1(B)], the treated (8.5 h) CTMP having 2.2% sulfonate content [Fig. 1(C)], and Whatman paper no. 1 [Fig. 1(D)]. Figures 2(A), (B), (C), and (D) present the spectra of the same samples in the same order for the  $O_{1s}$  peaks. Both Figures 1 and 2 show peaks synthesis representing the different kinds of carbon and oxygen present on the fibers surfaces. In addition, the ESCA surveys reveal the presence of sulfur, calcium, and probably sodium on the surfaces of the same fibers [Fig. 3(A)–(D)].

TABLE I  
ESCA, C<sub>1s</sub>, and O<sub>1s</sub> Peaks Analysis of Sulfite Post-Treated CTMP Pulp and of Whatman Paper

Sample no.	Time of treatment (min)	Sulfonate content (%)	O/C (ESCA)	E <sub>c</sub> (eV)	C <sub>1s</sub> peak						O <sub>1s</sub> peak																
					Fractional area			Binding energy (eV) corrected			FWHM (eV)			Chemical shifts E (eV)			Fractional area			Binding energy (eV) corrected							
					C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	C <sub>1</sub>	O <sub>1</sub>	O <sub>2</sub>	O <sub>1</sub>	O <sub>2</sub>	O <sub>1</sub>	O <sub>2</sub>				
1	0	0.30	0.46	2.1	0.41	0.52	0.07	285.1	286.8	288.3	1.9	1.9	2.1	+0.1	1.8	3.3	0.04	0.96	531.8	533.2	2.0	2.0					
2	30	0.64	0.48	2.0	0.37	0.56	0.07	284.9	286.7	288.3	2.0	1.9	2.3	-0.1	1.7	3.3	0.17	0.83	532.1	533.2	1.8	1.8					
3	90	1.30	0.51	2.1	0.36	0.54	0.10	284.9	286.9	288.2	1.9	1.9	2.0	-0.1	1.6	3.2	0.14	0.86	532.0	533.2	1.8	1.9					
4	150	1.46	0.54	2.1	0.30	0.61	0.09	284.9	286.7	288.0	1.8	1.9	2.2	-0.1	1.7	3.0	0.09	0.91	531.9	533.2	1.9	1.9					
5	270	1.67	0.53	1.9	0.34	0.59	0.07	284.9	286.7	288.3	1.9	1.9	2.1	-0.1	1.7	3.3	0.10	0.90	531.8	533.2	2.0	1.9					
6	390	2.01	0.52	2.2	0.34	0.59	0.07	285.0	286.8	288.8	1.9	1.9	1.9	0.0	1.8	3.8	0.09	0.91	532.1	533.2	1.7	2.0					
7	510	2.20	0.51	2.0	0.34	0.59	0.07	284.9	286.7	288.2	1.9	2.0	2.1	-0.1	1.7	3.2	0.12	0.88	531.7	533.2	1.8	1.9					
8	Whatman paper		0.80	2.7	0.06	0.83	0.11	285.3	286.9	288.6	2.2	1.8	1.7	0.3	1.9	3.2	0.00	1.00	—	533.2	—	2.0					
Average shifts, CTMP																											
9	Whatman paper <sup>8</sup>																										
10	Wood Sample <sup>9</sup>																										
11	Mechanical pulps <sup>12</sup>																										
13	TMP <sup>13</sup>				0.40	0.50		0.10																			
14	TMP, extrapolated [Fig. 5(D)]				0.41	0.52		0.09																			
15	Pure cellulose (theoretical)				0.00	0.83		0.17																			
										Chemical shifts E (eV)																	
										C <sub>1</sub>			C <sub>2</sub>			C <sub>3</sub>			C <sub>1</sub>			C <sub>2</sub>			C <sub>3</sub>		
										0.05			0.10			1.7			0.1			3.3			0.5		
										-0.1			0.5			1.9			0.3			3.4			0.4		
										0.2			2.0			3.8											
										0.2			0.1			1.8			0.1			3.4			0.3		

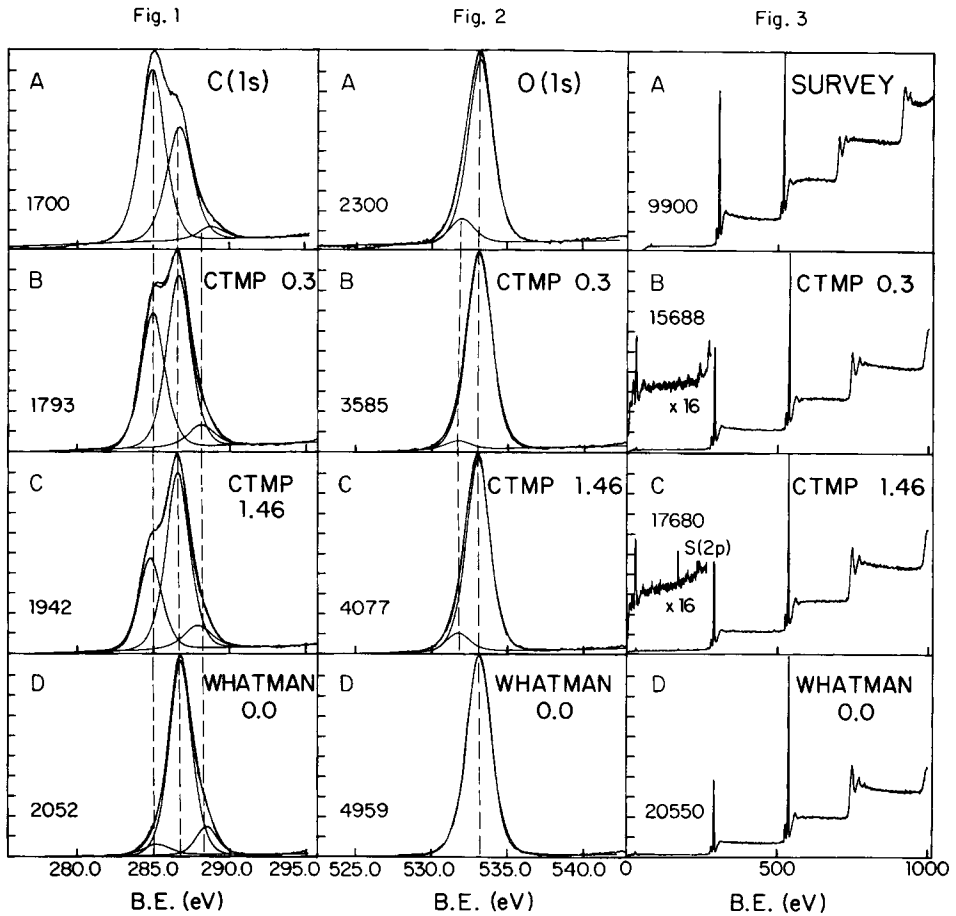


Fig. 1. Examples of C(1s) peaks obtained from the ESCA spectra for TMP pulp (A), for CTMP at two levels of sulfonate content, 0.3% (B) and 1.5% (C), and for the Whatman paper (D). For each spectrum the maximum plotted count rate unit is indicated near the origin of each spectrum. For the CTMP 1.5% it is 1942 counts per second.

Fig. 2. Examples of O(1s) peaks obtained from the ESCA spectra for TMP pulp (A), for CTMP at 0.3% (B) and 1.5% (C) sulfonation, and for the Whatman paper (D).

Fig. 3. Surveys of ESCA spectra for TMP (A), CTMP (B and C), and a Whatman paper (D).

### Interpretation of the Oxygen/Carbon Atomic Ratios, O/C

Table II shows that all pulps have O/C ratios lower than the one of pure cellulose (0.83), but higher than that of pure lignin (0.33). The high carbon content implies the presence of lignin and extractives on the fiber surface. The sulfite treatment of pulps may contribute to the partial elimination of extractives, including resin and fatty acids and their esters, sterols and terpenes, and phenolic material such as lignans and lignin. All of these compounds have a higher carbon content than polysaccharides, and their removal make the holocellulose more accessible on the fiber surface. On the basis of the above considerations, the observed increase of O/C ratio (Table I) upon the sodium sulfite post-treatment of the pulp appears to be a logical consequence of the

TABLE II  
Calculated and Observed Values for Oxygen/Carbon Atomic Ratios (O/C)

Sample no.	O/C theoretical	O/C ESCA	References
Cellulose	0.83		9
Spruce milled-wood lignin	0.33		9
Abietic acid	0.10		9
Whatman filter no. 1		0.80	This work
Whatman filter no. 1		0.79-0.83	9
Chemithermomechanical pulp (CTMP) <sup>a</sup>		0.46	This work
Thermomechanical pulp (TMP)		0.44	12
Refinermechanical pulp (RMP)		0.47	12
Stone groundwood (SGW)		0.49	12
Post-treated CTMP		0.48-0.54	This work
Bleached Kraft pulp	0.62-0.72	1.14	9
Bleached sulfite pulp		0.73	9

<sup>a</sup>0.3% sulfonate content.

increased accessibility of polysaccharides onto the surface of the fibers. The improvement of the mechanical properties of the handsheets made from the treated pulp (increase of breaking length) is also suggestive of a higher exposure of holocellulose on the fiber surface.

Increased exposure of cellulose at the fiber surface upon neutral sulfite pulping has also been suggested<sup>17</sup> as a result of the reduction in glucomannan, glucomannan acetate, xylan and glucuronoxylan as described in Fig. 4. It is evident (Fig. 5) that after 1.5% sulfonation, the O/C ratios remain approximately constant. Figures 5(A) and (B) show that the atomic ratios decrease in the order  $(O/C) < (S/O) < (S/C)$  as functions of the percentage of pulp sulfonation. An extrapolation of the curves to 0% sulfonation [Fig. 5(B)] gives zero values for S/O and S/C, confirming the absence of sulfur in TMP. A similar extrapolation made in Figure 5(A) yields 0.44 for the O/C ratio, which agrees with the value for TMP reported by Doris and Gray<sup>9</sup> and shown in Table II.

Beyond about 1.5% sulfonation (150 min), any additional treatment does not seem to increase the O/C ratio [Fig. 5(A)]. Under neutral or slightly alkaline conditions, sulfonation, as well as the cleavage of ether bonds, leading to lignin fragmentation, is essentially restricted to the phenolic units.<sup>17</sup> Thus, only a medium range degree of sulfonation can be reached. The remainder of the lignin would be sulfonated only in acid medium. At 1.5% sulfonate content, the lignin groups which can be sulfonated under neutral conditions are already sulfonated.

The O/C ratio value for different mechanical pulps reported in Table II are in the order  $TMP < CTMP < RMP < SGW$ . It is well known from literature<sup>18-20</sup> that TMP and CTMP which are produced at 135°C yield surface fractures located in the compound middle lamella. In contrast, in RMP and SGW which are prepared below 100°C, the surface fracture is mainly located within the secondary wall. Consequently, it may be expected that O/C ratios for TMP and CTMP are lower than those of RMP and SGW, in good agreement with the observed  $(O/C)_{ESCA}$  values.

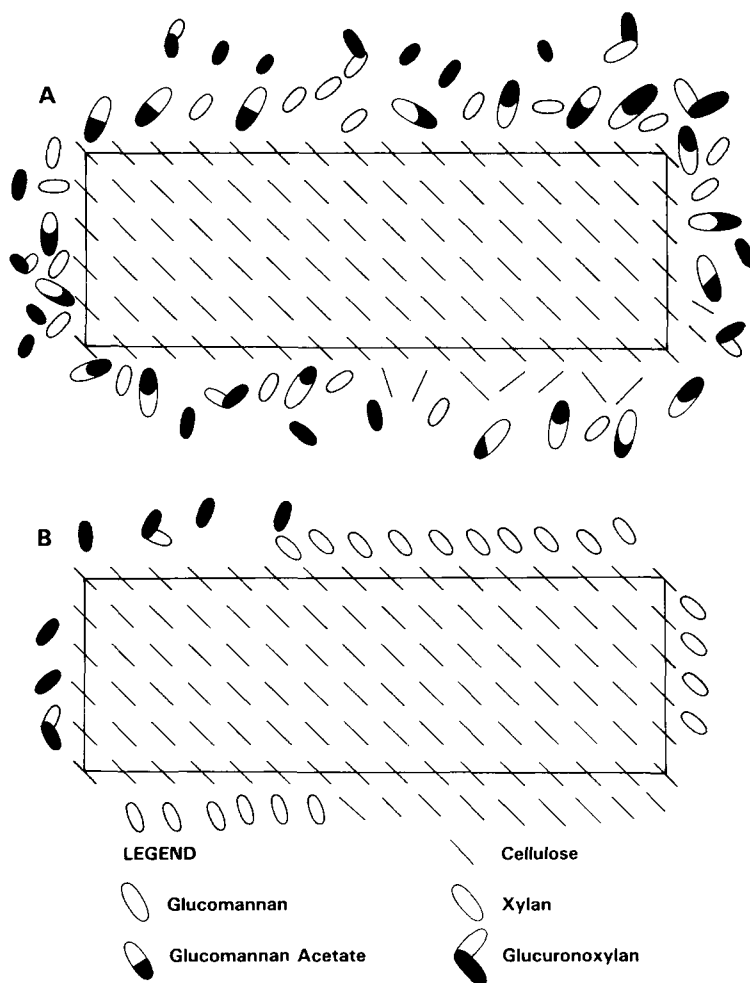


Fig. 4. Cross-sectional representation of the elementary microfibril surrounded by hemicelluloses in the secondary wall of a holocellulose fiber (A) and a two-stage sulfite pulp fiber (B).

Although the bleaching of kraft or sulfite pulps eliminates virtually all of the residual lignin, as well as the residual resin and fatty acids from the fiber surface, it also produces some surface oxidation. Since both phenomena contribute to the increase of O/C ratio, the values for these pulps are much higher than those observed for the sulfite post-treated CTMP samples, as reported in Table II.

The O/C ratio obtained in this work for the Whatman paper (0.80) is in good agreement with those reported previously.<sup>8</sup> It is, however, slightly lower than that calculated for pure cellulose (0.83).

### C<sub>1s</sub> Peaks

On the basis of their chemical shift, the carbon atoms in woody materials have already been classified<sup>8</sup> into four different categories (Table III). Thus, the C<sub>1s</sub> ESCA spectra for all sulfite post-treated and untreated CTMP pulps,

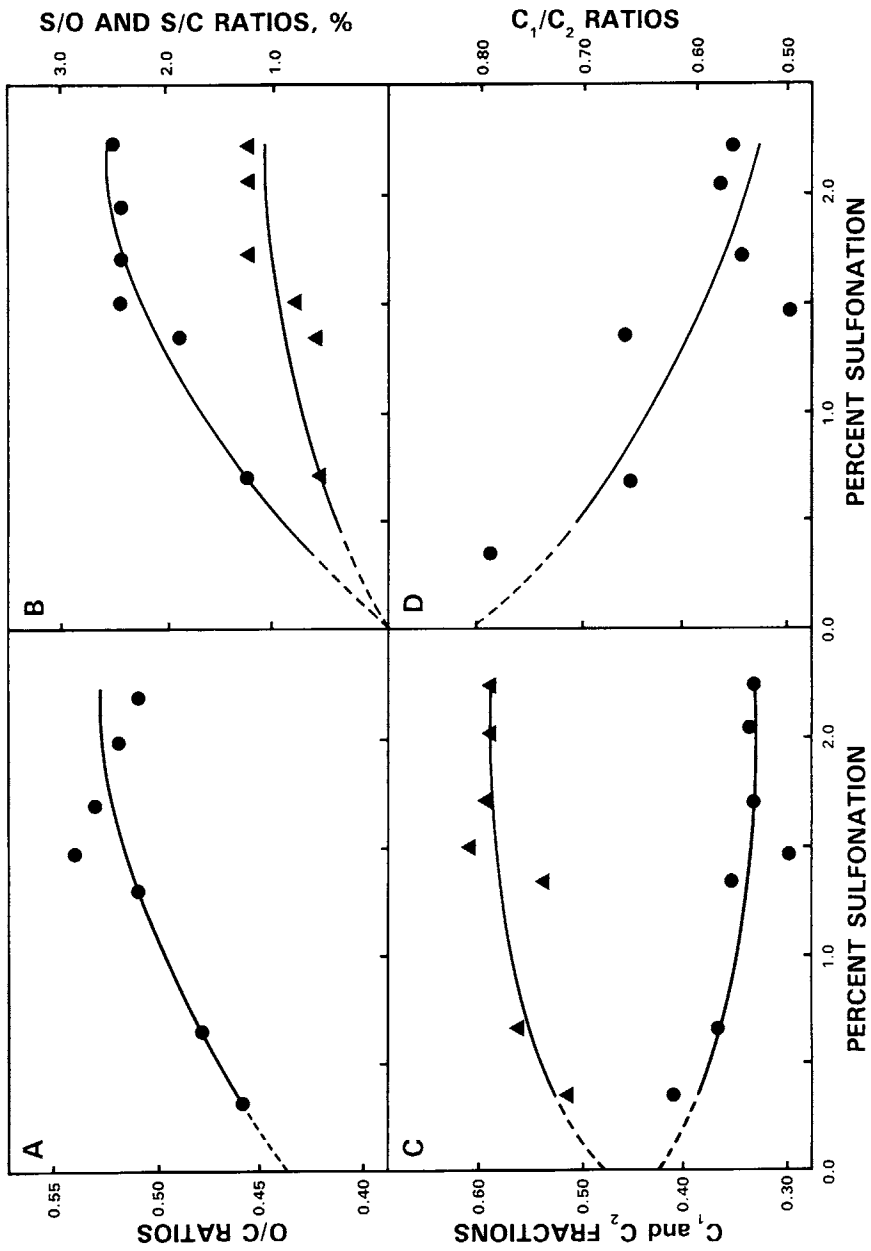


Fig. 5. The effect of sulfonation on the O/C (A), S/O (B), S/C (B), C<sub>1</sub>/C<sub>2</sub> (D) ratios and on the C<sub>1</sub> and C<sub>2</sub> fractions (C).



TABLE III  
Classification of Carbon Components of  $C_{1s}$  ESCA Lines  
for Woody Materials

Group	$\Delta E_B$ (eV)	Symbol	Carbon atoms are bound to
I	0	$C_1$	Carbon and/or hydrogen
II	1.9	$C_2$	A single oxygen via a single bond
III	3.4	$C_3$	Two noncarbonyl oxygens, or to a single carbonyl oxygen
IV	—	$C_4$	A carbonyl and a noncarbonyl oxygen

as well as for Whatman paper samples, were made up of three components:  $C_1$ ,  $C_2$ , and  $C_3$ . Considerable overlap of the ESCA peaks among the test specimen can occur as revealed by the chemical shifts and by the full width at middle height (FWMH) of the peaks reported in Table I.

The fraction area of each component  $C_1$ ,  $C_2$ , and  $C_3$  of the  $C_{1s}$  peaks summarized in Table I are illustrated in Figures 1(A), (B), (C), and (D). As in eq. (4), the fractional areas,  $I_{C_1}/I_C$ ,  $I_{C_2}/I_C$ , and  $I_{C_3}/I_C$ , are equal to the fractions of the surface carbon atoms,  $N_{C_1}/N_C$ ,  $N_{C_2}/N_C$ , and  $N_{C_3}/N_C$ , respectively. Thus, for example, the reference CTMP sample (no. 1) has a surface carbon distribution of 0.41, 0.52, and 0.07 for  $C_1$ ,  $C_2$ , and  $C_3$ , respectively, while the corresponding values in the literature<sup>21</sup> for the TMP pulp are 0.40, 0.50, and 0.10 in the same order (Table I). The slight difference in the surface carbon composition is due to the lower percentage of lignin and extractives in the CTMP fibers, which in turn is a direct consequence of sulfonation.

Figures 5(C) and (D) show the  $C_1$  and  $C_2$  values and the  $C_1/C_2$  ratio as a function of the percentage of pulp sulfonation. An extrapolation of the  $C_1$ ,  $C_2$ , and  $C_1/C_2$  curves to 0% sulfonation (TMP) gives 0.42, 0.49, and 0.80, respectively. The value of 0.09 was obtained for  $C_3$  by subtraction. All of the above values confirm those reported in the literature. Pure cellulose has a theoretical carbon fractions composition of 0.00, 0.83, and 0.17 for  $C_1$ ,  $C_2$ , and  $C_3$ , respectively. The corresponding values for the Whatman paper reported in the literature,<sup>12</sup> as well as those from this study (Table I) are very close to the theoretical values. Note that the spectrum of the Whatman paper [Fig. 1(D)] has a very low fraction of  $C_1$  in contrast to the corresponding value for the CTMP [Figs. 1(A), (B), and (C)].

From the increase of the O/C ratios observed in Figure 5(A), it is logical to expect a corresponding decrease in the  $C_1$  fraction, and a subsequent increase in  $C_2$  with  $C_3$  remaining more or less constant. Beyond about 1.5% sulfonation, the  $C_2$  curve tends to level off, which means that the composition carbon fractions of the surface remains constant [Fig. 5(C)]. Even after 8 h of treatment (2.2% sulfonation), no further change can be observed. Note also that there are large differences in the compositions of the carbon fractions between a CTMP (O/C = 0.54), a bleached kraft (0.72), a sulfite pulp (0.73), and a Whatman paper (0.80). This means that, even after 8.5 h of post-treatment in sodium sulfite solution, CTMP fibers still possess a fiber surface which is considerably richer in lignin and extractives than the kraft or sulfite fibers.

### O<sub>1s</sub> Peaks

Very little is known about the ESCA oxygen (1s) peaks of woody materials. This is probably due to the greater difficulty involved in predicting the O<sub>1s</sub> chemical shifts, as compared to the C<sub>1s</sub> peak.<sup>8</sup> This might also be the reason why the O<sub>1s</sub> peak of pure cellulose reported in the literature is described as a single peak. The results of the present work provide additional data that would be useful in O<sub>1s</sub> peaks assignment.

Figures 2(A), (B), (C), and (D) shows that all O(1s) spectra of the CTMP samples are essentially superimposed. There are two components which could be resolved by the peak synthesis technique. The single oxygen (1s) peak in the Whatman paper spectrum [Fig. 2(D)] at 533.2 eV designated as O<sub>2</sub> is associated with the COH and C—O—C linkages and to glucosidic bonds.<sup>22</sup> The second peak present in the other spectra [Figs. 2(A), (B), and (C)] and designated by O<sub>1</sub> at 532.0 eV represents the benzyl aryl ether and/or the diaryl ether linkages.<sup>23</sup>

As seen in the case of the C<sub>1s</sub> peak, the fractional areas can be equated to the fractional atomic oxygen surface composition of the fibers. Table I shows that a decrease in the O<sub>1</sub> fraction is accompanied by an increase in O<sub>2</sub>. Note, however, that variations of O<sub>1</sub> and O<sub>2</sub> are not well illustrated in Figures 2(A), (B), and (C) due to the unexpectedly low value of O<sub>1</sub> found at 0.3% sulfonation [Fig. 2(B)]. The O<sub>1</sub> fraction can be associated with the lignin and extractives fractions, the elimination of which decreases the O<sub>1</sub> fraction and increases the O<sub>2</sub> fraction by making the cellulose and hemicellulose more accessible on the fibers surface. Our future work is expected to provide additional information concerning the O(1s) peak of cellulosic materials.

### S(2p) Peak

Figure 3 provides information about oxygen and carbon, as well as about other elements present on the surfaces of the CTMP fibers, even though these elements occur in small concentrations. Expansion of the ordinate scale [Fig. 3(C)] by a factor of 16 reveals the presence of sulfur by peaks at 170.4 (S<sub>2p</sub>) and ~ 230 eV (S<sub>2s</sub>) in the spectra of all samples, except for the Whatman paper and the CTMP sample at 0.3% sulfonation [Fig. 3(A)]. Also, the expansion reveals the presence of sodium by the peak at 260 eV (N<sub>1s</sub>) and calcium (Ca<sub>2p</sub>) by the peak at 350 eV.

The same technique of peak synthesis and data treatment used with oxygen and carbon peaks were applied to the S<sub>2p</sub> spectra. This reveals the presence of only one peak at the corrected binding energy of 168.4 eV with a FWHM of  $2.4 \pm 0.1$  eV. In a qualitative approach, the shift in binding energy is taken simply as a measure of the electron density on the atom of interest.<sup>24</sup> Thus, the increase of 2 or 2.2 eV on going from a benzyl methyl sulfide (sulfoxide C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>SCH<sub>3</sub>) to the sulfone (C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>SO<sub>2</sub>CH<sub>3</sub>), or to the sulfonated pulp with S<sub>2p</sub> binding energies of 166.2, 168.2,<sup>25</sup> and 168.4 eV, respectively, indicates a large electron depletion on the sulfur atom in the latter samples. The binding energy found for the sulfur in the sulfonated pulp (168.4 eV) is equivalent to that reported by Craig et al.<sup>25</sup> for the *N*-tosylsulfoximide in which the two nonequivalent sulfur with the same binding energy (168.4 eV) are in the S(VI) state. The same holds true for the sulfone or for the

sulfoximide, which has a binding energy of 168.1 eV. The slight increase in binding energy between these compounds corresponds to an equally small increase of the positive charge on the sulfur atom. It may thus be concluded that the sulfur present in sulfonated pulps is in the S(VI) oxidation state and quite probably ionized.

A progressive increase of pulp sulfur content as measured in ESCA spectra is observed in agreement with bulk degree of sulfonation determined by the titration technique. The very low sulfur content of the sulfonated pulp as illustrated in Figure 5(B) can be increased by a second-stage sulfonation treatment in an acid medium. This second treatment will probably be even easier to monitor through the ESCA analysis.

### CONCLUSION

The ESCA spectra show a progressive change in the surface chemical composition of CTMP fibers as a function of an increasing degree of sulfonation. The  $C_{1s}$  spectra appear to be the most useful tool for this purpose.

A gradual decrease in the atomic carbon fraction not bonded to oxygen  $C_1$  implies a reduction in extractives and lignin content, both of which have low O/C atomic ratio. This implies a corresponding increase of the carbon atomic fractions bonded to oxygen (especially  $C_2$ ), which in turn is an indication of the presence of more cellulose on the fiber surface.

ESCA analysis of the CTMP samples confirms that, even after a 2.2% sulfonation level, the surface chemical composition of the highly sulfonated CTMP fibers is still very different from that of kraft or sulfite fibers with a lower O/C ratio and higher content of  $C_1$  carbon not bonded to oxygen.

ESCA analysis permits us also to detect and to follow very easily the progressive increase of sulfur content as a function of increasing degree of sulfonation. Although the very low sulfur content, with a maximum sulfur/carbon ratio of 1.2%, makes the interpretation of the spectra less precise and probably incomplete, more data from ESCA analysis of sulfur as well as of oxygen of sulfite and kraft pulps would be helpful for the understanding of the chemistry of these processes.

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