

Surface Analysis of Press Dried-CTMP Paper Samples by Electron Spectroscopy for Chemical Analysis

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SYNOPSIS

The effect of press-drying temperature on the surface chemistry of chimicothermomechanical pulp fibers has been studied using electron spectroscopy for chemical analysis (ESCA). The chemical composition showed no significant variation for press-dried samples at temperatures between 25 and 140°C. On the other hand, ESCA showed that lignin content increased whereas hemicelluloses content decreased on the surface of press-dried samples at 175°C. By its hydrophobic nature, lignin gives to paper and paperboards better dimensional stability and resistance to moisture and water. However, lignin does not intervene in fiber bonding because the specific bond strength does not vary with press-drying temperature. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Press drying is a process in which external pressure is applied to the wet web while it dries at temperatures in excess of 100°C. At these temperatures, the fiber components become softer and the compressibility of the moist sheet is enhanced. This leads to increased sheet density, fiber bonding, and overall strength.¹⁻⁶ The improvement in bonding by press drying is mainly attributed to the increase in the contact area between fibers. However, changes in fiber surface chemistry might play an important role because it determines the physical strength of paper and even its resistance to weathering and photodegradation.

Electron spectroscopy for chemical analysis (ESCA) was found to be a powerful tool for the chemical analysis of surfaces of synthetic polymers,⁷⁻⁹ natural and modified textile fiber,^{10,11} and wood and cotton fibers.¹²⁻¹⁶ The results obtained seem very promising for the pulp and paper industries. In fact, some recent studies¹⁷⁻²⁰ showed that ESCA can characterize the surface chemistry changes of pulp fibers as a result of chemical treatments.

The main objective of this study is to characterize the changes in the surface chemistry of press-dried papers at various temperatures using ESCA. It is expected that the results of this study will help us to better understand the role of temperature in fiber bonding and the mechanism of bond formation in press-dried papers and paperboards.

EXPERIMENTAL

Handsheets Preparation

Standard handsheets of 60 g/m² were made from bleached white birch (*Betula Papyrifera* Marsh.) and white spruce (*Picea Glauca* (Moench) Voss) chimicothermomechanical pulps (CTMP). Series of handsheets from each pulp were wet pressed and air dried at 25°C according to the Canadian Pulp and Paper Association (CPPA) standard method, whereas others were press dried at a constant pressure (0.75 MPa) and at three different temperatures (105, 140, and 175°C). We used a hydraulic press with two heated platens to dry the handsheets under pressure according to the arrangement shown in Figure 1. The moisture content of a sheet before press drying is critical to the development of its strength.^{2,21,22} In our experiments, handsheets had

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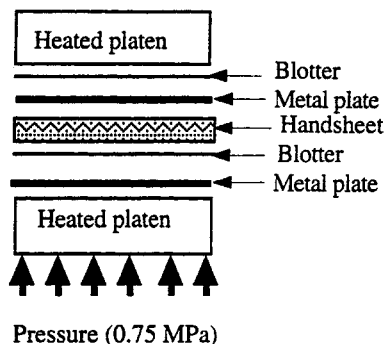


Figure 1 Experimental arrangement for press drying.

a moisture content from 100% to 150%. After press drying, the moisture content ranged from 6% to 9%. The time of press drying varied with platen temperature.

Evaluation of the Handsheet Properties

Among the various handsheet properties, the apparent density, the wet breaking length, and the bond strength were determined. The apparent density (ρ) and the wet breaking length were measured according to the CPPA standard methods. For the wet breaking length, handsheet samples were soaked in distilled water for 24 h before testing at solid contents from 26% to 30%.

The bond strength (BS) was measured in J/m^2 according to the delamination test carried out on a free rotating wheel.²³ The specific bond strength (SBS, J/m^2) was calculated from eq. 1, which is based on the assumption that a completely bonded sheet has the same density (ρ) as the fiber wall ($1540 \text{ kg}/\text{m}^3$).

$$\text{SBS} = \frac{\text{BS}}{\rho} \times 1540 \quad (1)$$

ESCA Experiments

The ESCA analyses of handsheet samples were carried out on the ESCALAB II spectrometer fitted on a microlab system from vacuum generators. This spectrometer is equipped with a nonmonochromatized dual Mg-Al anode X-ray source. Kinetic energy measurements were made using a hemispherical electrostatic analyzer ($r = 150 \text{ mm}$) working in the constant pass energy mode (20 eV). The handsheet samples were mounted onto an indium disk and introduced into the working chamber. The measure-

ments were made at a vacuum level of 10^{-8} – 10^{-6} Torr.

When a sample is irradiated by X-ray photons, the kinetic energy E_k of electrons leaving the solid surface is given by eq. 2. The uncorrected binding energy ($E_b + E_c$) is given by eq. 3. To minimize E_c , one can use a floodgun²⁴ or wrap the sample in aluminum foil.¹² In our experiments, we corrected the binding energies by setting the binding energy of C_1 at 285.0 eV. This leads to a binding energy of O_2 from 533.2 to 533.3 eV. This is exactly the expected value for the binding energy of O_2 for cellulosic materials.¹⁴

$$E_k = E_x - (E_b + E_c + \Phi) \quad (2)$$

$$E_b + E_c = E_x - E_k - \Phi \quad (3)$$

where E_b is the binding energy of the electron on its original shell (eV), E_x is the energy of the incident photons (1253.6 eV for Mg_k anode source and 1486 eV for Al_k anode source), E_c is the energy counteracting the potential associated with the steady charging of the surface, and F is a correction factor that depends of the nature of the spectrometer.

The stoichiometric ratio of two elements in the surface region analyzed by ESCA can be estimated from the ratio of their respective peak intensities. For example, the oxygen/carbon atomic ratio (O/C) can be obtained from eq. 4. Using the cross-section values reported by Scofield,²⁵ we can express O/C by eq. 5:

$$\frac{\text{O}}{\text{C}} = \frac{\sigma_{\text{O}} D_{\text{O}} \lambda_{\text{O}} I_{\text{O}}}{\sigma_{\text{C}} D_{\text{C}} \lambda_{\text{C}} I_{\text{C}}} \quad (4)$$

$$\frac{\text{O}}{\text{C}} = \frac{1.00}{2.85} \times \frac{I_{\text{O}1s}}{I_{\text{C}1s}} \quad (5)$$

where σ is the cross-section for photoelectrons generation, λ is the mean free path of photoelectrons (in practice, λ is proportional to $E_k^{0.7526}$), D is a function of the spectrometer transmissions, and I is the integrated peak density.

RESULTS AND DISCUSSIONS

Physical and Mechanical Properties

Figure 2 shows the effect of press drying temperature on ρ , BS, and SBS. For both pulps, ρ and BS increase with press-drying temperature. This is due to the softening action of temperature on fibers that become

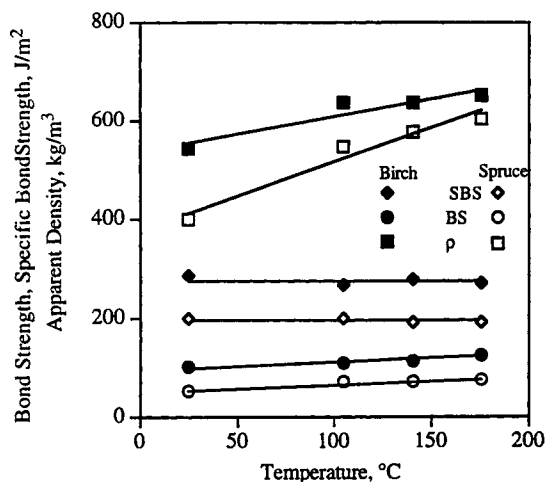


Figure 2 Effect of press-drying temperature on apparent density (ρ), bond strength (BS), and specific bond strength (SBS) of birch and spruce CTMP.

more flexible and come into closer contact under pressure. However, the SBS remains constant for both pulps. These results suggest that the improvement in BS is attributed to the increase in the bonded area and not to a change in the nature of fiber-to-fiber bonds. These are thought to be hydrogen bonds²⁷⁻²⁹ that break easily under the action of water.

In contrast, the exponential variation of the wet breaking length with press-drying temperature (Fig. 3) suggests the possibility of changes in the nature of fiber-to-fiber bonds when handsheets are press dried at 175°C. At this temperature, the increase of the wet breaking length is very important compared with that from 25 to 140°C. This increase can be explained by the formation of covalent bonds resistant to water.³⁰ However, the formation of such bonds requires specific chemical and thermal conditions³⁰ and is unlikely to happen between pulp fibers. This affirmation is supported by Figure 2, where the SBS of press-dried handsheets does not change significantly over the entire temperature scale.

The important increase in the wet breaking length at 175°C (Fig. 3) may be explained by the flow of lignin on fiber surface because its glass transition temperature is exceeded.³¹ The following chemical surface analysis by ESCA may provide additional information and explain the mechanism of flow and adhesion between fibers under various thermal conditions.

ESCA Results

Table I presents the apparent concentrations of the elements present on the fiber surface and the error

($\pm s$) associated to their measure. In addition to the peaks associated with oxygen and carbon, the ESCA survey reveals the presence of sulfur, calcium, aluminum, and nitrogen on the fiber surfaces of some samples. Table II presents the values of oxygen/carbon (O/C) atomic ratios, the binding energies, the percentage and the full width at middle height (FWMH) of the C_{1s} and O_{1s} components. Figure 4 shows examples of survey spectra and C_{1s} and O_{1s} peaks given by ESCA.

C_{1s} Peak

Dorris and Gray¹³ classified the carbon atoms in woody materials in four different categories based on their chemical shifts (Table III). There is a general agreement on the assignment of the components C_1 , C_2 , C_3 , and C_4 of spectrum C_{1s} of woody and methacrylate materials.^{12,13} For the CTMP samples, ESCA showed that the C_{1s} peak is made up of three components only: C_1 , C_2 , and C_3 .^{12-15,17,18} The C_{1s} peak of all CTMP samples analyzed in this study showed these three components [Fig. 4(b)]. Furthermore, the chemical shifts and binding energies found in this study (Tables II and III) are in very good agreement with the literature values for woody materials.^{7,12-15,17,18}

The C_1 component arises from lignin and wood extractives^{13,15,24,32} and corresponds to a carbon bound to a hydrogen ($-C-H$) or a carbon atom ($-C-C$). The C_2 component arises from both the carbohydrate and lignin constituents of wood and corresponds to a carbon atom bound to an oxygen ($-C-O$). The C_3 component arises from cellulose and is due to a carbon atom bound to one carbonyl

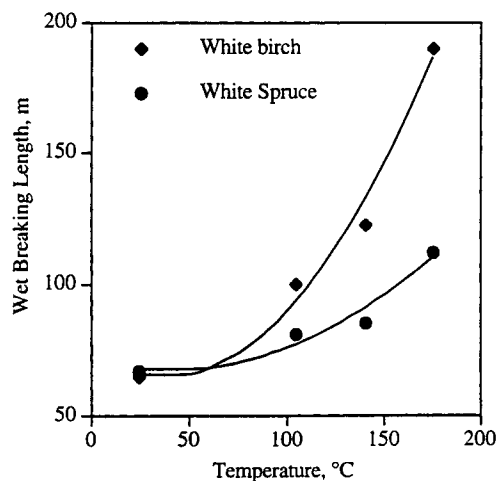


Figure 3 Effect of press-drying temperature on the wet breaking length of birch and spruce CTMP.

Table I Apparent Concentrations of Elements Detected on Fiber Surfaces of Birch and Spruce Press-Dried CTMP

Species	Press-Drying Temperature (°C)	Apparent Concentrations in Atomic Percentage ($\pm s$) (%)							
		Al	S	Si	N	Ca	Cl	C	O
Birch	25	0.4 (0.1)	—	—	—	—	0.2 (0.04)	64.5 (0.2)	34.6 (0.2)
	105	—	—	—	—	—	0.2 (0.04)	65 (0.2)	34.4 (0.2)
	140	—	—	—	0.40 (0.17)	0.26 (0.12)	0.20 (0.04)	65.2 (0.2)	33.8 (0.2)
	175	—	—	0.10 (0.07)	0.26 (0.12)	—	0.14 (0.03)	67 (0.2)	32.2 (0.2)
	Spruce	25	—	—	—	—	—	0.10 (0.04)	65.1 (0.2)
Spruce	105	—	—	0.20 (0.08)	0.26 (0.12)	—	0.25 (0.04)	64.8 (0.2)	34.1 (0.2)
	140	—	—	0.30 (0.1)	—	—	0.10 (0.04)	64.7 (0.2)	34.5 (0.2)
	175	—	—	—	0.40 (0.15)	—	0.30 (0.05)	66.6 (0.2)	32.4 (0.2)

oxygen atom ($-\text{C}=\text{O}$) or two noncarbonyl oxygen atoms ($-\text{C}(\text{O})_2$).

Figure 5 shows the variation of the C_1 and C_2 fractional areas with press-drying temperature. No significant variation between 25 and 140°C is found for the C_1 fractional area for both pulps. However, a considerable increase of that area is obtained at 175°C. Because C_1 is associated to lignin and wood extractives, the presence of either one of these constituents or both on the fiber surface explains this increase. Lignin is a logical candidate because of its glass transition temperature.³¹ In fact, at 175°C, this temperature is largely exceeded, causing the lignin to flow.

On the other hand, the fractional area of C_2 increases slightly with press-drying temperature and reaches a maximum between 105 and 140°C. At 175°C, C_2 fraction shows a considerable decrease. If the increase of C_1 is associated to the presence of lignin on fiber surface, then the decrease of C_2 suggests that the carbohydrates content on this surface has decreased. The fractional area of C_3 does not vary with press-drying temperature. This shows that in the range studied, temperature does not affect the cellulose content on the fiber surface.

O_{1s} Peak

Few studies have dealt with O_{1s} peak of wood-derived materials. Even in the field of simple organic compounds, O_{1s} core level binding energy data are rel-

atively sparse in the literature, because of its complex shift behavior compared with the C_{1s} peak.³³ This is mainly attributed to the electronegativity and polarizability of substituents interacting directly or indirectly with the oxygen atom.^{14,25} In addition, it is difficult to distinguish between simple or double bonds between this atom and carbon.¹⁵ Ahmed et al.¹⁵ suggested the decomposition of this peak and compared it to known models. For example, for Whatman paper, only one peak is reported and all oxygen atoms of cellulose are attributed to O_2 component. This component has a binding energy of 533.2 eV.

In the same way, using the O-biphenol spectrum, Ahmed et al.¹⁵ ascribed the phenolic oxygen to O_3 . This component has a binding energy of 534.3 ± 0.4 eV. In woody materials, phenolic oxygen is mainly associated with lignin. Consequently, the presence of O_3 component in ESCA spectra indicates the presence of lignin on fiber surface.

The O_1 component has a binding energy of 531.6 ± 0.4 eV. Ahmed et al.¹⁵ attributed this component to oxygen atoms between two phenolic groups. However, Kamdem et al.¹⁸ suggested that the O_1 peak comes from an oxygen bound to a carbon through double bond or a ketonic oxygen as in acrylate and acetate. Hua et al.¹⁹ associated this component to lignin. They suggested that because oxygen atoms of hemicelluloses have similar chemical environments to those of cellulose, any increase in the surface of O_1 indicates a decrease in carbohy-

Table II ESCA C_{1s} and O_{1s} Peaks Analysis of Birch and Spruce CTMP

Species	Press-Drying Temperature (°C)	C _{1s} Peak									O _{1s} Peak									
		Binding Energy (eV)			Fractional Area			FWHM (eV)			Binding Energy (eV)			Fractional Area			FWHM (eV)			
		O/C	C ₁	C ₂	C ₃	C ₁	C ₂	C ₃	C ₁	C ₂	C ₃	O ₁	O ₂	O ₃	O ₁	O ₂	O ₃	O ₁	O ₂	O ₃
Birch	25	0.54	285	286.8	288.7	0.31	0.62	0.06	1.9	1.9	1.6	531.8	533.3	535.2	0.12	0.87	0.02	1.9	1.9	1.9
	105	0.53	285	286.8	288.8	0.31	0.64	0.05	2.0	1.9	1.6	531.9	533.3	535.1	0.12	0.85	0.02	1.9	1.9	1.9
	140	0.52	285	286.7	288.8	0.33	0.62	0.05	2.1	2.0	1.6	531.7	533.3	535.2	0.12	0.86	0.01	2.0	2.0	2.0
Spruce	175	0.48	285	286.7	288.6	0.38	0.56	0.06	2.0	1.9	1.6	531.6	533.2	535.2	0.11	0.86	0.01	1.9	1.9	1.9
	25	0.53	285	286.8	288.7	0.33	0.61	0.05	2.0	1.9	1.6	531.7	533.3	535.5	0.10	0.89	0.01	1.9	1.9	1.9
	105	0.53	285	286.9	288.8	0.32	0.65	0.04	1.9	1.9	1.4	531.8	533.3	535.4	0.10	0.89	0.01	1.9	1.9	1.9
140	0.53	285	286.8	288.5	0.32	0.60	0.07	1.9	1.8	1.7	531.7	533.2	535.3	0.09	0.90	0.01	1.9	1.9	1.9	
	175	0.48	285	286.8	288.7	0.36	0.60	0.05	2.0	1.9	1.6	531.7	533.2	535.0	0.13	0.85	0.03	1.9	1.9	1.9

drates on the fiber surface and an increase in lignin and extractives. This observation agrees with that of Barry et al.,¹⁷ who stated that eliminating lignin and extractives from the fiber surface by chemical treatments decreases fractional area of O₁ and increases that of O₂.

Figure 4(c) and (d) shows examples of the O_{1s} spectra found in this study. These illustrations show three components: O₁, O₂, and O₃. The spectra analyses give to O₁ and O₂ binding energies of 531.7 ± 0.2 eV and 533.2 ± 0.1 eV, respectively (Table II). These values are in an excellent agreement with those reported in the literature for the O₁ and O₂ of woody material.^{15,17-19} The O₃ component has binding energy of 535.3 ± 0.4 eV. This value is somewhat higher than that reported for aspen (*Populus Tremuloides* Michx.) wood residues.¹⁵ However, the intensity of this peak is negligible for most samples [Fig. 4(c)] except for that of spruce press dried at 175°C, where the intensity of the O₃ component is significant [Fig. 4(d)]. Its binding energy is similar to that reported by Ahmed et al.¹⁵

The analysis of the effect of temperature on the O_{1s} spectra of birch CTMP samples showed no significant variation. This can be attributed to the low resolution of oxygen peak decomposition. However, the analysis of spruce CTMP spectra showed that the fractional areas of the O_{1s} components are constant between 25 and 140°C (Fig. 6). At 175°C, O₁

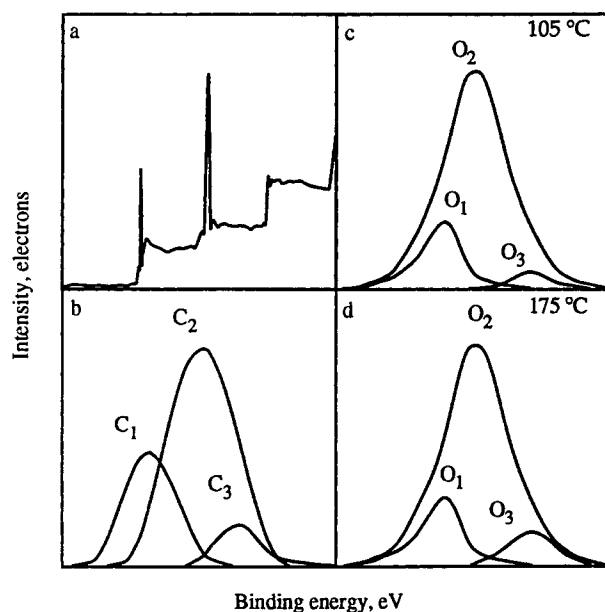
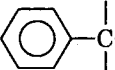
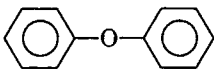
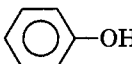
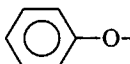
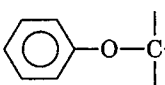



Figure 4 Examples of survey spectra and C_{1s} and O_{1s} peaks. (a) Survey spectra; (b) C_{1s} peak; (c) O_{1s} peaks for spruce sample press dried at 105°C; (d) O_{1s} peaks for spruce sample press dried at 175°C.

Table III Classification of Carbon and Oxygen Peak Components: C_{1s} and O_{1s} ESCA Lines for Woody Materials^{12,15,34}

Group	Chemical Shifts		Carbon or Oxygen Bound to
	Literature	This work	
Carbon			
C ₁	0.0 ± 0.4	0.0	C—C, C—H
C ₂	1.5 ± 0.4	1.8 ± 0.1	C—O, C=O
C ₃	3.0 ± 0.4	3.6 ± 0.1	C=O, —C $\begin{matrix} \diagup O \\ \diagdown O \end{matrix}$
C ₄	4.5 ± 0.4	—	O—C=O
Oxygen			
O ₁	-1.5 ± 0.4	-1.4 ± 0.2	O—C=O,  , 
O ₂	0.0 ± 0.4	0.1 ± 0.1	C=O, C—O, C—O—C, O—C=O
O ₃	1.5 ± 0.4	2.0 ± 0.3	 ,  ,  , 

and O₃ increased, whereas O₂ decreased. Because O₁ and O₃ are associated to lignin and O₂ to hemicelluloses (Table III), we can affirm that press drying of paper at 175°C increases the lignin content and decreases that of hemicelluloses on fiber surface.

O/C Interpretation

A high oxygen carbon atomic ratio (O/C) reflects high cellulose and hemicelluloses contents on fiber surface. However, a low O/C indicates the presence of lignin on fiber surface. For example, ESCA showed that Whatman paper rich in cellulose has

an O/C of approximately 0.80.^{15,17} On the other hand, O/C of lignin ranges from 0.25 to 0.40.^{12,13,15} Table IV presents some O/C ratios for the different samples analyzed in this study and those reported in the literature. The values found in the present study for CTMP samples are in same order of magnitude of those reported in the literature.^{17,34}

Figure 7 shows that O/C is constant between 25 and 140°C but decreases considerably at 175°C. The initial constancy of O/C suggests that carbohydrates and lignin contents are constant. However, the decrease in O/C at 175°C suggests that the lignin con-

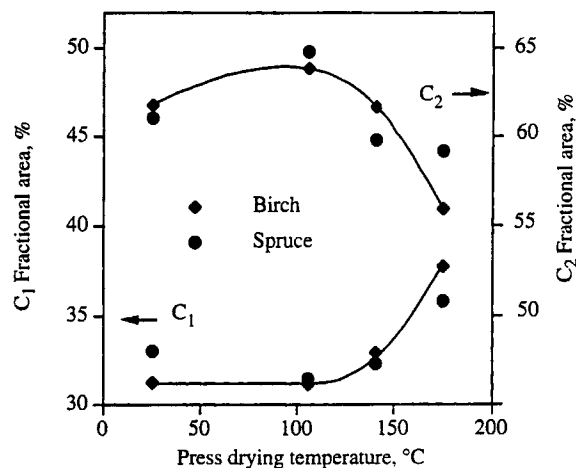


Figure 5 Effect of press-drying temperature on the C₁ and C₂ fractional areas of birch and spruce CTMP.

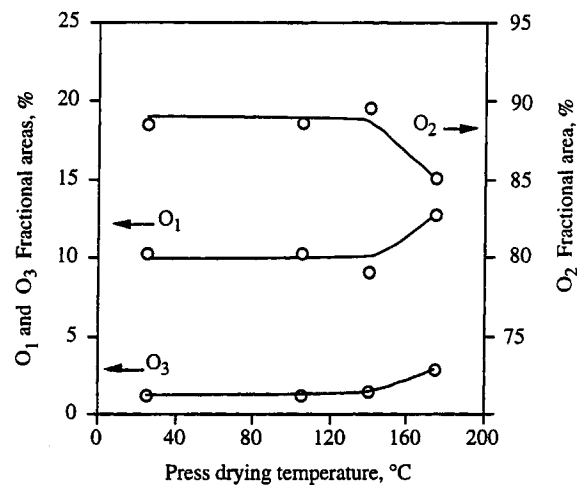


Figure 6 Effect of press-drying temperature on the O₁, O₂, and O₃ fractional areas of spruce CTMP.

tent increases whereas the hemicelluloses content decreases on the fiber surface.

Flow and Adhesion

The nonsignificant variations of O/C, C_{1s}, and O_{1s} components between 25 and 140°C suggest no difference in the flow of the fiber components. In fact, the wet carbohydrates in the amorphous state are already plasticized at 25°C.³⁰ Thus, an increase in temperature should not modify the flow of these components. In addition, the glass transition temperature of lignin was reported to be 90–110°C.³⁰ To flow, any material should have a temperature of 60–70°C higher than its glass transition temperature. Consequently, lignin should not flow at 140°C or less. On the other hand, the glass transition temperature of lignin is largely exceeded at 175°C. Consequently, in the presence of water, this component passes from a glass state to a rubber state. In this state, lignin flows and its presence on fiber surface is abundant. This explains the decrease in O/C and increases in C₁, O₁, and O₃.

By its presence on the fiber surface, lignin may play two roles. First, by its hydrophobic nature, lignin protects the hydrogen bonds that link adjacent fibers from water and moist conditions. The important improvement in the wet breaking length of press-dried CTMP samples at 175°C supports this affirmation (Fig. 3). Second, after flowing and cooling, lignin may freeze between adjacent fibers and acts as a thermoplastic glue. The occurrence of such phenomenon is difficult to prove. However, the variation of the SBS with press-drying temperature suggests that this phenomenon is not likely to happen (Fig. 2). Consequently, lignin does not intervene in fiber bonding. This finding agrees with previous

Table IV O/C Ratios Given by ESCA for Different Pulps

Pulp or Paper Type	O/C (ESCA)	Reference
Birch CTMP	0.48–0.54	This work
Spruce CTMP	0.48–0.53	This work
CTMP	0.46–0.54	17
CTMP	0.37	34
Whatman paper	0.79–0.83	13, 15, 17
Refiner mechanical pulp	0.47	24
Groundwood pulp	0.49	24
Thermomechanical pulp	0.44	24
Kraft	0.62–1.14	13
Bleached sulfite	0.73	13
Lignin	0.31–0.40	15

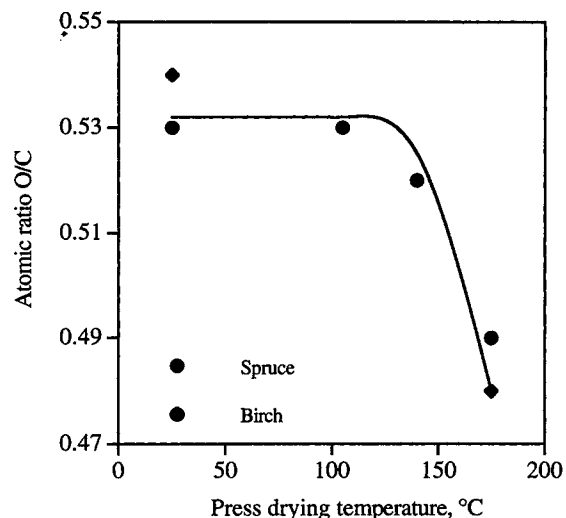


Figure 7 Effect of press drying temperature on the O/C ratio of birch and spruce CTMP.

studies^{35,36} that reported that adding lignin to chemical pulps does not affect the bonding strength in paper.

CONCLUSIONS

Increasing press-drying temperature improves softwood and hardwood CTMP properties. This is mainly attributed to the softening action of temperature on the fibers that collapse easily under the compression action of pressure. The contact area between fibers is then enhanced, thereby increasing the number of hydrogen bonds.

ESCA analysis shows no significant change in the surface chemistry of CTMP handsheets press dried at temperatures between 25 and 140°C. However, at 175°C, O/C ratio and the fractional areas of C₂ and O₂ components increase, whereas the fraction areas of C₁, O₁, and O₃ components decrease. These suggest an increase in lignin content and a corresponding decrease in hemicelluloses content on the fiber surface. At this temperature, lignin flows but does not intervene in fiber bonding because the SBS is not affected by press-drying temperature. Thus, the role of lignin is to protect the hydrogen bonds from water and moist conditions. This gives paper better dimensional stability.

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Received November 28, 1995

Accepted January 23, 1996