

BINDERLESS FIBERBOARD MADE FROM PRIMARY AND SECONDARY PULP AND PAPER SLUDGE

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Abstract. Pulp and paper sludge is valuable in fiberboard manufacturing because primary sludge (PS) contains fibers and secondary sludge (SS) has adhesive properties. We evaluated properties of binderless fiberboard made from conventional pulp and paper mill sludge sources using a factorial design in which the factors were SS:PS ratio (1:9, 2:8, and 3:7) and pulping process (thermomechanical [TMP], chemical–thermomechanical [CTMP], and kraft). Sludge was collected, refined, dried, and characterized for chemical composition and fiber length. Internal bond strength of CTMP panels increased 90% and thickness

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swell of TMP panels improved 92% with increasing SS content from 10–30%. IR Fourier transform and X-ray photoelectron spectroscopy analyses were conducted to better understand these results. Increased bonding was attributed to presence of proteins and lignin on the sludge fiber surface, which enhanced adhesion during hot pressing, whereas surface contamination decreased bonding efficiency. The TMP formulation at SS:PS ratio 3:7 met the ANSI requirement for basic hardboard. All other formulations were not dimensionally stable enough to meet the standard. The CTMP source resulted in the highest mechanical properties, and thickness swell was similar for the TMP and CTMP pulping processes. The kraft source produced low-integrity and dimensionally unstable panels.

Keywords: Fiberboard, industrial waste, adhesion, material characterization, recycling.

INTRODUCTION

Water treatment processes in pulp and paper mills generate solid residues called pulp and paper sludge. The most common sludge disposal methods are landfilling, incineration for power production, and land application for soil amendment (Amberg 1984; Smook 2002; Mahmood and Elliott 2006; Ochoa de Alda 2008). Current disposal alternatives are affected by shrinking space, public opposition, increasing regulatory pressure, and, above all, poor economics (Amberg 1984; Mahmood and Elliott 2006). Valuing sludge as a commercial product would be a beneficial way to recycle this residue.

A typical pulp and paper mill water treatment process comprises primary treatment followed by secondary treatment (Smook 2002). Primary treatment removes suspended solids from wastewaters. The solid residue obtained after thickening is called primary sludge (PS). Wastewaters from primary treatment go to secondary treatment, also called biological treatment. The solid residue obtained after thickening is called secondary sludge (SS). The main organic components are microbial extracellular polymeric substances (EPS), nonbiodegraded materials, and microbial cell biomass (Bitton 2005). In most mills, PS and SS are mixed to form a combined sludge. SS:PS ratio varies among mills and within the same mill (Amberg 1984; Smook 2002).

The pulping process impacts the pulp's chemical composition and consequently fiber properties (Clark 1985; Smook 2002). For example, the chemical composition of fibers from high-yield pulping processes such as thermomechan-

ical pulping (TMP) is roughly similar to that of nonprocessed wood. Low-yield pulping processes such as the chemical kraft process remove most of the lignin from the fiber cell wall. Chemical composition and properties of fibers from intermediate-yield pulping processes such as chemithermomechanical pulping (CTMP) lie between those of TMP and kraft fibers. Because sludge contains fibers, its chemical composition also varies with pulping process (Zerhouni et al 2009; Migneault et al 2010).

Geng et al (2006) studied the effect of hot-pressing parameters on properties of fiberboard made from paper mill sludge. Dry-formed binderless fiberboard panels were hot-pressed at different densities, temperatures, and pressing times. Optimal parameters were 1100 kg/m³, 210°C, and 8 min. Properties of medium-density fiberboard (MDF) and particleboard made from pulp and paper sludge have been investigated (Davis et al 2003; Taramian et al 2007; Geng et al 2007a; Migneault et al 2010). These studies concluded that inorganic content of sludge negatively affected panel properties. Deinked sludge produced lower quality panels than combined sludge (Geng et al 2007a). Industry quality standards were met at 25% sludge content (Migneault et al 2010), although properties decreased with increasing sludge content (Geng et al 2007a; Migneault et al 2010).

The wood industry benefited from the advent of protein glues in the early 1900s (Pizzi and Mittal 2003; Rowell 2005), but these natural adhesives were replaced by higher-performance, lower-cost petroleum-based adhesives such as urea-formaldehyde and phenol-formaldehyde resins. In recent years, interest in biobased adhesives

has increased because of stricter regulations for synthetic adhesives and growing environmental concerns. Biobased adhesives are derived from natural materials such as proteins, carbohydrates, and lignin. SS contains some of these substances and shows good bonding properties (Geng et al 2007b; Zerhouni et al 2009). Polar groups of proteins and carbohydrate molecules can interbond and possibly bond with the high energy surface of wood (Pizzi 1989). However, for effective adhesion, the native protein structure generally has to be denatured to expose polar groups (Pizzi 1989). PS and SS were used as filler in phenol-formaldehyde resin formulations for plywood (Geng et al 2007b), resulting in higher shear strength compared with a control resin formulation made with a commercial filler. Use of SS alone, without synthetic resin, resulted in reasonably good shear strength. This suggests that SS has bonding properties. Zerhouni et al (2009) formed paper handsheets using combined pulp and paper sludge and found increased bonding strength with increasing SS content.

Pulp and paper sludge could be recycled for fiberboard manufacturing because it contains wood fibers and has adhesive properties. Before attempting industrial application, common sources of industry-generated sludge must be evaluated. The adhesive ability of sludge has been demonstrated but not understood. Therefore, objectives of this study were to 1) characterize and compare PS and SS from different pulping processes; and 2) study adhesive properties of SS.

MATERIALS AND METHODS

Sludge Collection and Refining

Pulp and paper sludge samples were collected from three pulp processes: TMP, CTMP, and kraft. The TMP mill (White Birch Paper Stadacona Division, Québec, Canada) produces newsprint and directory-grade papers. The CTMP mill (Abitibi-Bowater Dolbeau-Mistassini, Canada) produces book-grade and supercalendered papers. The kraft mill (SFK Pulp Fund, Saint-Félicien,

Canada) produces commercial bleached pulp. All mills process softwood chips from commercial eastern softwood species (mainly spruce and balsam fir and, to a lesser extent, pine). PS and SS were collected from each mill and combined in three SS:PS mass ratios of 1:9, 2:8, and 3:7 corresponding to 10, 20, and 30% SS content, referred to as low, medium, and high SS content, respectively. Combined sludge was refined in an Andritz (Graz, Austria) 0.56-m single disk refiner at the FPInnovations-Forintek Division MDF pilot plan (Québec, Canada). Material was preheated for 1.5 min at vapor pressure of 750 kPa in a cooking screw (digester) and then refined at disk plate speed of 2000 rpm. Refined sludge was discharged through a blowline, dried by a flash tube dryer to $15 \pm 5\%$ MC, and dried to $3 \pm 1\%$ MC in a rotary dryer.

Sludge Characterization

Samples were characterized for chemical composition (Table 1) as described in Migneault et al (2010). Briefly, cellulose content was determined by Kürschner and Hoffer's nitric acid method. Pentosan content was obtained according to TAPPI T 223 cm-84. Lignin content was determined according to TAPPI T 222 om-98 and TAPPI useful method UM-250. Extractive content was determined according to TAPPI T 204 cm-97 and T 207 om-93. Ash content was determined according to TAPPI T 211 om-93. Nitrogen content was determined using a Perkin Elmer (Waltham, MA) 2410 Series II nitrogen analyzer. Pulp from each mill was characterized for comparison, and two repetitions were conducted for chemical analysis. Fiber length distribution was measured using an OpTest Equipment (Hawkesbury, Ontario, Canada) Fiber Quality Analyzer.

Diffuse reflectance IR Fourier transform spectroscopy (FTIR-DRIFTS) and X-ray photoelectron spectroscopy (XPS) were performed to obtain information on chemical reactions during hot-pressing. This study focused on three possible types of adhesive bonds: protein crosslinking, mechanical bonding by lignin entanglement

Table 1. Chemical composition of pulp, primary sludge (PS), and secondary sludge (SS) from the three pulping processes.

Pulping process	SPF ^a	TMP				CTMP		Kraft		
Material type	Wood	Pulp	PS	SS	Paper	PS	SS	Pulp	PS	SS
Ash (%)	0.2-0.4	0.3 (0.0)	19.6 (0.2)	12.0 (0.1)	5.2 (0.1)	30.2 (0.1)	18.0 (0.2)	0.3 (0.0)	49.1 (0.4)	41.3 (1.4)
Cellulose (%)	43-46	49.7 (0.5)	36.5 (0.5)	19.7 (0.2)	52.7 (4.8)	44.6 (0.2)	26.6 (0.3)	87.9 (1.1)	41.4 (1.2)	18.9 (0.4)
Pentosans (%)	11-13	15.5 (0.2)	5.2 (0.4)	3.0 (0.1)	17.6 (0.1)	6.7 (0.0)	2.2 (0.0)	6.6 (0.5)	8.1 (0.0)	3.4 (0.0)
Lignin (%)	27-30	25.3 (0.3)	23.6 (0.2)	50.2 (0.5)	29.9 (0.9)	22.6 (0.4)	50.0 (1.1)	0.0 (0.0)	20.3 (0.6)	36.4 (1.0)
Extractives (%)	5-8	7.3 (0.2)	15.5 (0.4)	21.5 (0.6)	4.6 (0.2)	2.9 (0.1)	1.7 (0.2)	3.4 (0.6)	0.4 (0.0)	7.9 (0.0)
Nitrogen (%)	—	0.1 (0.0)	0.5 (0.0)	7.7 (0.0)	0.1 (0.0)	0.2 (0.0)	5.4 (0.0)	0.0 (0.0)	0.1 (0.0)	1.3 (0.0)

^a SPF, minimum and maximum values for balsam fir, jack pine, black, red, and white spruce wood (Rowell 2005).

TMP, thermomechanical pulping; CTMP, chemicothermomechanical pulping.

(modification of lignin polymer concentration on fiber surface would be a clue), and hydrogen bonding. However, XPS cannot give information on hydrogen bonds and interference of water makes analysis with FTIR difficult. DRIFTS was conducted using a Tensor 27 FTIR system (Bruker Optics, Ettlingen, Germany) equipped with a deuterated triglycine sulfate detector. Spectra of each sample were recorded by collecting 128 scans in the 4000–400 cm^{-1} range at 4 cm^{-1} resolution. Samples were mixed with KBr as a reference material at 1% by weight. XPS was performed using an Axis Ultra HSA (Kratos Analytical, Ltd., Manchester, UK). The X-ray source was a monochromatic Al with an $800 \times 400\text{-}\mu\text{m}$ analysis area. Pressure during analysis was in the 10^{-8} torr range. Survey scans were recorded at 160 eV pass energy and 1 eV step size. Survey scans were used for elemental analysis and to calculate apparent element concentrations. Detailed high-resolution C_{1s} spectra were recorded at 20 eV pass energy and 0.025 eV step size. Two repetitions were conducted for FTIR and XPS measurements.

Panel Manufacturing and Testing

Sludge panels were hot-pressed (dry process) according to a 3^2 factorial design in which factors were mill pulping process (TMP, CTMP, and kraft) and SS:PS ratio (1:9, 2:8, and 3:7). Each experimental condition was repeated three times. Panel target density was 1100 kg/m^3 , pressing temperature was 210°C , and pressing

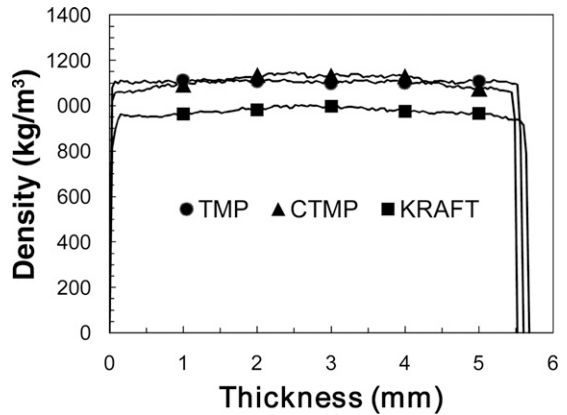


Figure 1. Typical density profiles for binderless panels made with sludge from the three pulping processes (examples at SS:PS = 2:8). SS, secondary sludge; PS, primary sludge.

cycle was 8 min (including closing and opening time). These parameters were optimized in Geng et al (2006). High density and lengthy pressing time were selected because no binder was used and to obtain better response to SS content. Target panel thickness was 6 mm, and pressing schedule was optimized for panels with a flat vertical density profile (Fig 1). Mats were manually formed in a $460 \times 560\text{-mm}$ wood box and pressed in a Dieffenbacher hydraulic press with $1000 \times 1000\text{-mm}$ plates.

Physical and mechanical properties of panels were measured according to ASTM D 1037-99. A sample cutting outline is shown in Fig 2. Analysis of variance with multiple comparisons (contrasts) was conducted using SAS 9.2. Panel properties were adjusted using Eq 1, in which

target density is 1100 kg/m³ and measured density is given in Table 2.

Adjusted property = $\frac{\text{measured property}}{\text{measured density}} \times \text{target density}$ (1)

RESULTS AND DISCUSSION

Sludge Chemical Composition and Fiber Length Distribution

Table 1 shows the chemical composition of the three pulps. Bleached kraft pulp has the highest

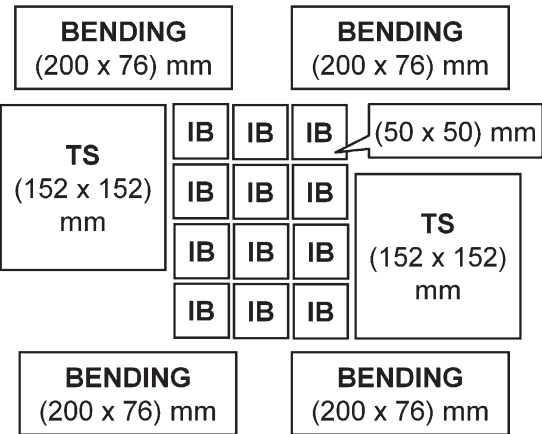


Figure 2. Panel cutting outline. TS, thickness swell; IB, internal bond strength.

carbohydrate content and the lowest lignin content (Clark 1985; Smook 2002). Ash content in TMP and kraft pulps is similar to those typically found in SPF wood, whereas it is higher in the CTMP sample because of the filler used in paper formulation. Although some differences in chemical composition are attributable to wood species, pulping processes induced much greater variation (Table 1).

Ash content differs between PS and pulp (Table 1). Only a small fraction of ash originates from wood. The majority of ash originates from nonwoody materials rejected in wastewaters at any stage of pulp and paper processing or inert solids rejected during the chemical recovery process (Smook 2002; Ochoa de Alda 2008). As previously reported (Davis et al 2003; Geng et al 2007a; Ochoa de Alda 2008), ash content is an indicator of the nonfibrous proportion of sludge or the inorganic content. Assuming that ash content negatively impacts panel performance, TMP PS is the best candidate for panel manufacturing and kraft PS is the worst. In addition to ash, carbohydrates and lignin were found in PS (Table 1). Because these compounds are found in wood, they provide potential for PS as a fiber source in fiberboard manufacturing. Lignin and carbohydrate contents of kraft pulp differ from those of the two other pulps. Kraft PS has the lowest carbohydrate content within PS because it has the highest ash content. However, lignin content is roughly similar within PS.

Table 2. Panel properties (standard deviation in parentheses) made with primary sludge (PS) and secondary sludge (SS) from the three pulping processes.

Pulping process	SS content (SS:PS ratio)	IB (MPa)	MOE (GPa)	MOR (MPa)	Density (kg/m ³)	TS ^a (%)
TMP	Low (1:9)	0.96 (0.16)	2.03 (0.03)	11.4 (0.1)	1048 (4.4)	50 (0.6)
	Medium (2:8)	1.19 (0.05)	1.96 (0.15)	11.6 (1.3)	1105 (26)	34 (1.8)
	High (3:7)	1.29 (0.10)	2.58 (0.09)	14.4 (1.3)	1133 (34)	26 (1.4)
CTMP	Low (1:9)	0.86 (0.16)	2.57 (0.27)	15.0 (2.3)	1085 (37)	39 (3.3)
	Medium (2:8)	1.61 (0.14)	2.74 (0.30)	16.0 (2.4)	1126 (35)	32 (1.1)
	High (3:7)	1.63 (0.06)	2.36 (0.30)	13.4 (1.7)	1106 (34)	32 (5.0)
Kraft	Low (1:9)	0.060 (0.01)	1.10 (0.01)	6.7 (0.08)	925 (2.8)	245 (1.4)
	Medium (2:8)	0.074 (0.01)	0.97 (0.04)	5.6 (0.40)	985 (14)	153 (7.8)
	High (3:7)	0.072 (0.01)	0.60 (0.01)	4.0 (0.05)	951 (6.4)	187 (4.2)

Properties adjusted according to Eq 1.
^a Twenty-four-h water immersion.
IB, internal bond strength; MOE, modulus of elasticity; MOR, modulus of rupture; TS, thickness swell; TMP, thermomechanical pulping; CTMP, chemithermomechanical pulping.

Lignin and carbohydrates found in PS may also originate from underfiberized chips. However, the characterization methods were designed for wood and pulp, not sludge. Neutralizing agents such as large quantities of ash decrease efficiency of carbohydrate removal during acid extraction and may overestimate lignin content (Jackson and Line 1997). Extractive content is lower in PS than in pulp except for TMP. An extractive content of 6.37% was reported for chemimechanical sludge (Taramian et al 2007). Low extractive content in kraft and CTMP pulp could be explained by the fact that these processes involve chip chemical treatments. In the kraft pulping process, wood extractives are processed in black liquor, which is normally recovered, recycled, and burned. However, there is no chemical recovery in the TMP process. The TMP mill also uses higher proportions of balsam fir wood chips (50% spruce, 50% fir) compared with CTMP (95% spruce) and kraft (70% spruce, 30% fir and pine). Balsam fir has higher extractive content than spruce (Smook 2002). These are among the plausible explanations of lower extractive contents of kraft and CTMP sludge samples compared with TMP samples. Extractives are undesirable for panel manufacturing because they may evaporate during hot-pressing and create delamination and decrease resin crosslinking (Maloney 1993).

SS has lower ash content than PS for the three pulping processes (Table 1). This suggests that some nonfibrous substances such as suspended solids were removed in primary water treatment. In good agreement with previously reported data (Smook 2002; Geng et al 2007b), carbohydrate content was lower in SS than in PS indicating that SS contains fewer wood fibers than PS. Lignin content was higher in SS than in PS for the three pulping processes. This could be explained by the fact that chemical tests not only detected lignin from the cell wall, but also microbial and chemical byproducts such as polyphenols. TMP SS had the highest extractive content, and kraft sludge had the highest ash proportion (among SS). Because kraft PS had the lowest extractive content within PS and the

highest within SS, extractives in kraft SS may have originated from the biological water treatment process. In good agreement with previous findings (Cetin and Erdinçler 2004; Bitton 2005), SS had high nitrogen content, suggesting the presence of proteins. Protein-rich SS was expected to have a positive effect on internal bond strength (IB), as shown by the use of proteins in wood adhesive formulations (Pizzi and Mittal 2003; Rowell 2005). Because of its higher nitrogen content, TMP SS is the best candidate for panel manufacturing, and kraft sludge is the worst.

Because of its average fiber length and fines proportion (Fig 3), kraft sludge is the best candidate for MDF manufacturing. Chemical pulping produces fewer fines and longer fibers. As reported previously (Ochoa de Alda 2008), sludge has high fines proportion and short average fiber length.

Effect of Secondary Sludge:Primary Sludge Ratio on Panels

IB strength of panels increased with increasing SS proportion (or SS:PS ratio) (Fig 4). As found by the polynomial contrast presented in Table 3, IB increased partly linearly with a nonlinear effect (Table 3). The nonlinear effect was caused by a leveling off above 20% SS content. For the CTMP sludge source, maximum strength was

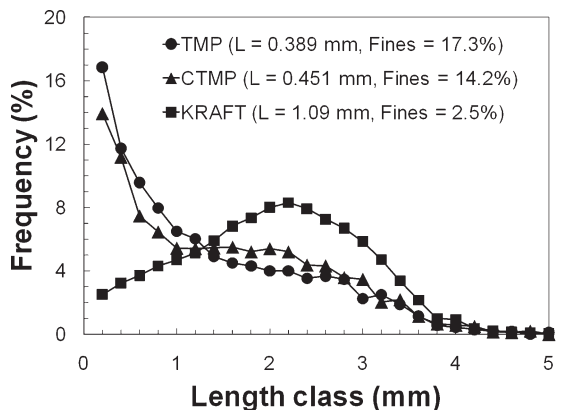


Figure 3. Fiber length distributions of sludge from the three pulping processes.

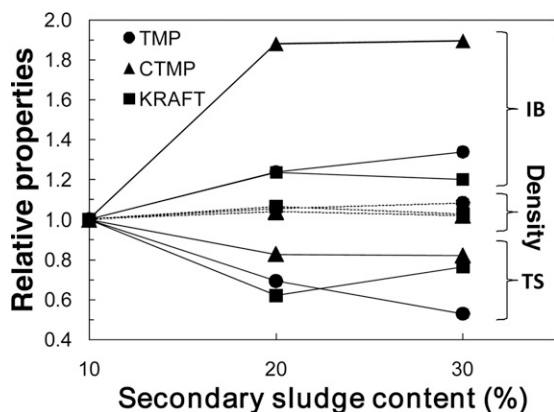


Figure 4. Relative variation in internal bond strength (IB) and sludge from thickness swell (TS) of binderless sludge panels made with the three pulping processes with increasing secondary sludge (SS) content.

Table 3. Analysis of variance results and selected contrasts (F values) on sludge panel properties.

Source of variation	IB	MOE	MOR	TS
SS content	36**	<1 ^{NS}	<1 ^{NS}	279**
Linear effect	45**	<1 ^{NS}	<1 ^{NS}	302**
Residual effects	9.8**	<1 ^{NS}	<1 ^{NS}	255**
Pulping process	283**	140**	73**	5175**
TMP vs CTMP	19**	16**	11**	2.8 ^{NS}
TMP vs Kraft	360**	162**	79**	8144**
CTMP vs Kraft	522**	267**	141**	8413**
SS content × pulping process	11**	7.8**	3.8*	117**

* Significant at 0.05 probability level.

** Significant at 0.01 probability level.

^{NS} Not significant at 0.05 probability level.

IB, internal bond strength; MOE, modulus of elasticity; MOR, modulus of rupture; TS, thickness swell; SS, secondary sludge; TMP, thermomechanical pulping; CTMP, chemithermomechanical pulping.

reached at the middle SS level. For the TMP sludge source, IB increased up to 30% SS content. This suggests that optimum SS level varies with pulping process. IB increased by 90% for the CTMP source and 34% for the TMP source with increasing SS content from 10-30% of panel mass. Because no adhesive was used, this result was attributed to the adhesive properties of SS. The positive correlation between nitrogen content and panel IB (Fig 5a; Table 4) suggests that proteins were involved in the bonding process. Lignin content also correlated positively with IB (Fig 5b; Table 4). Pressing temperature of 210°C

is within the typical range for wood welding (Ganne-Chédeville et al 2006) and well above the glass transition temperature of lignin (Rowell 2005). Thus, lignin and hemicellulose bonding by softening and crosslinking may have occurred. For the specific case of kraft lignin, this hypothesis was addressed in a previous report (Westin et al 2001). It was found that addition of kraft lignin in wood-based panels decreased IB strength. The nonfibrous proportion of sludge may have interfered with interfiber bonding, thereby decreasing bonding strength. Accordingly, a negative correlation between ash content and IB was found (Fig 5c; Table 4). However, as shown in Fig 5c, extreme kraft sludge contents strongly influenced the correlation coefficient, and therefore, this result should be interpreted with caution. Adhesion caused by microbial extracellular polysaccharides was also reported (Haag et al 2006).

Bending modulus of elasticity (MOE) and modulus of rupture (MOR) were not significantly affected by SS:PS ratio (Table 3) because bending properties are less affected by adhesive performance than IB or thickness swell (TS) (Maloney 1993). Panel TS decreased by up to 92% with increasing SS content (Table 2; Fig 4). This can be explained partially by the adhesive effect of SS. Because of a strong correlation between IB and TS (Table 4), most significant correlations between IB and sludge chemical components were also found with TS. As in other natural adhesives (Pizzi 1989; Rowell 2005), SS adhesive bonds may not be water-resistant. However, our results showed that these bonds were sufficient to increase dimensional stability.

Effect of Pulping Process on Panel Properties

Pulping process significantly affected all measured panel properties (Table 3). Use of CTMP sludge resulted in the highest mechanical properties, and TMP and CTMP gave similar TS, whereas kraft sludge resulted in the lowest properties (Tables 2 and 3). Because no adhesive was used, these differences can be explained by

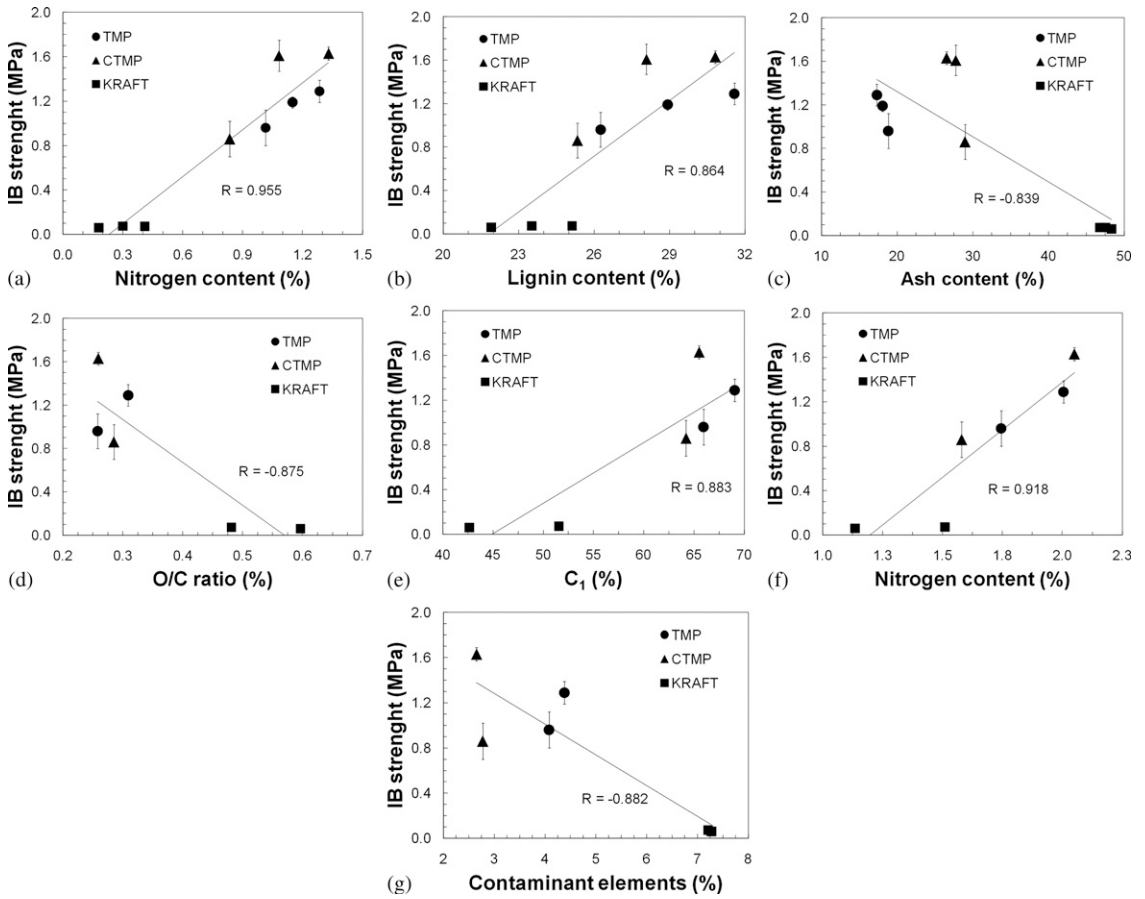


Figure 5. Internal bond strength (IB) of binderless sludge panels as a function of (a) nitrogen content from elemental analysis, (b) lignin content, (c) ash content, (d) oxygen-to-carbon (O/C) ratio from XPS results, (e) C_1 component, (f) nitrogen content from XPS results, and (g) contaminant elements (elements other than O, C, and N) obtained by XPS (error bars represent ± 1 standard deviation, error bars for kraft series are smaller than marker size). O, oxygen; C, carbon; N, nitrogen; XPS, X-ray photoelectron spectroscopy.

chemical composition of the sludge (Table 1). Kraft sludge had high ash content, which most probably affected adhesion efficiency (Fig 5c). It also contained low proportions of nitrogen and lignin, substances that correlate with IB. Accordingly, the greatest IB was expected in panels made with TMP sludge, because it contained more nitrogen and lignin and less ash, although CTMP panels were stronger (Table 2). High extractive content of TMP sludge (Table 1) would be one plausible explanation, but no significant correlation was found between extractives and IB (Table 4). CTMP panels showed the best bending properties, whereas panels

made with kraft again showed the worst. However, panels made with kraft sludge performed better in bending properties than in IB and TS compared with other pulping processes. This result is explained by the greater length of kraft sludge fibers (Fig 3), which builds bending strength and compensates for its low adhesive properties. Accordingly, the greater MOE and MOR of CTMP sludge compared with TMP (Tables 2 and 3) can be explained by its greater average fiber length (Fig 3) and better cohesiveness. The significant interaction between pulping process and SS:PS ratio indicated that effect of SS content varies with pulping process.

Table 4. Correlation coefficients between internal bond (IB) strength and thickness swell (TS) of panels and selected chemical characteristics.

	IB	TS
IB	1	-0.923**
TS	-0.923**	1
Bulk chemical composition (sludge)		
Ash (%)	-0.839**	0.932**
Cellulose (%)	0.053 ^{NS}	0.036 ^{NS}
Pentosans (%)	-0.802**	0.882**
Lignin (%)	0.864**	-0.825**
Extractives (%)	0.374 ^{NS}	-0.530 ^{NS}
Nitrogen (%)	0.955**	-0.956**
Surface chemistry (XPS)		
O/C	Sludge	-0.867*
	Panels	0.979**
N _{1s}	Sludge	-0.874*
	Panels	0.978**
Other elements	Sludge	0.834*
	Panels	-0.924**
C ₁	Sludge	0.918**
	Panels	-0.869*
C ₂	Sludge	-0.928**
	Panels	0.992**
C ₃	Sludge	-0.882*
	Panels	0.925**
C ₁	Sludge	0.275 ^{NS}
	Panels	-0.611 ^{NS}
C ₂	Sludge	0.883*
	Panels	-0.988**
C ₃	Sludge	0.028 ^{NS}
	Panels	0.335 ^{NS}
C ₃	Sludge	-0.869*
	Panels	0.974**
C ₃	Sludge	-0.707 ^{NS}
	Panels	0.927**
C ₃	Sludge	-0.887*
	Panels	0.992**

* Significant at 0.05 probability level.

** Significant at 0.01 probability level.

^{NS} Not significant at 0.05 probability level.

XPS, X-ray photoelectron spectroscopy; O/C, oxygen-to-carbon ratio.

Pulping process significantly affected TS (Table 3). Kraft panels were unstable compared with TMP and CTMP panels (Table 2). This low performance was attributed to the high hydrophilic nature and low self-bonding ability of kraft sludge, as discussed previously. Based on pulping process, kraft sludge fibers were superior in terms of fiber quality. However, with the exception of the fiber length effect on bending properties, properties of sludge panels did not increase with increasing fiber quality.

Sludge panels were graded according to the American National Standard (ANSI 2004) for basic hardboard for TS, MOR, and IB (Table 5). This standard suggests threshold properties for North American hardboard products. The TMP panel with 30% SS met all ANSI requirements, but none of the other panels met the minimum requirement because of insufficient bending properties or dimensional instability. This sug-

Table 5. Threshold values for classification of basic hardboards according to the American National Standard Institute (ANSI 2004).

ANSI class	IB (MPa)	MOR (MPa)	TS (%)
Class 1 (best)	0.90	41.1	15
Class 5 (lowest)	0.17	13.8	30

IB, internal bond strength; MOR, modulus of rupture; TS, thickness swell.

gests that pulp and paper sludge could be recycled in a commercial product but that sludge source (pulp process) and type (PS, SS) must be properly selected. To recycle sludge and produce satisfactory quality panels, using wood fibers in addition to sludge and synthetic resin should be considered.

Bonding Properties of Sludge

FTIR and XPS analyses were performed to better understand adhesive properties of sludge. Pulp spectra are given for comparison. Typical IR vibration bands were identified according to literature on wood and pulp (Pandey and Theagarajan 1997; Pandey 1999; Bouafif et al 2008). These bands occurred in all spectra (Fig 6). The broad band centered at 3344 cm⁻¹ was assigned to O-H and N-H bond-stretching vibrations. The methyl/methylene pure stretching vibration of C-H bonds appeared at 2900 cm⁻¹. The absorption band at 1734 cm⁻¹ emanated from the stretching vibration of unconjugated carbonyl groups (C=O) of wood lignin and extractives. The band at 1510 cm⁻¹ was assigned to aromatic skeleton vibrations in lignin, and the band at 1607 cm⁻¹ was a contribution from both aromatic skeleton and C=O group vibrations in lignin. The band at 1454 cm⁻¹ was associated with both C-H asymmetric deformation and aromatic skeleton vibrations in lignin. The band at 1653 cm⁻¹ emanated from H-O-H bond angle vibration (Olsson and Salmén 2004). The 1500-1000-cm⁻¹ region of IR spectra is called the "fingerprint" (Pavia et al 1979), and bands in this region were assigned to various complex vibration modes in wood carbohydrates and lignin. In good agreement with chemical compositions in Table 1, lignin peaks (1734, 1607, 1510, 1454, and 1267 cm⁻¹) were seen in TMP pulp and

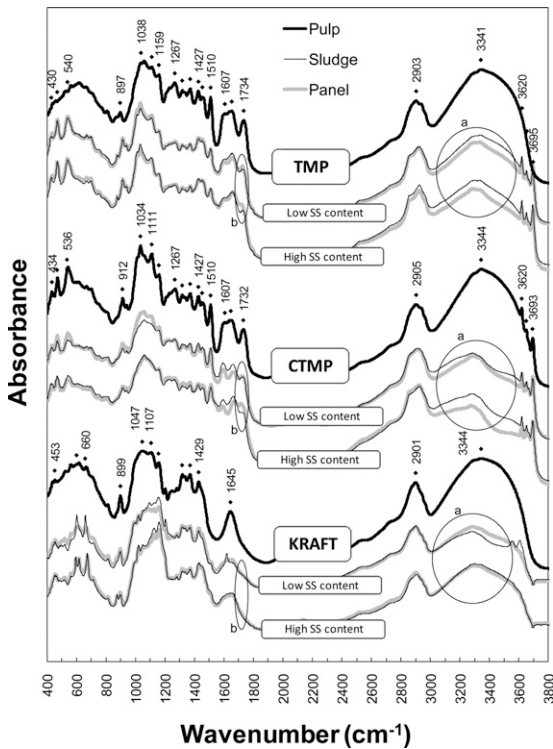


Figure 6. FTIR-DRIFTS spectra of pulp, sludge, and binderless sludge panels made with the three pulping processes and two secondary sludge (SS) contents. FTIR-DRIFT, diffuse reflectance IR Fourier transform spectroscopy.

CTMP paper spectra and are weak or absent in kraft pulp spectra. However, no lignin peaks were seen in kraft sludge spectra, although 20-36% of Klason lignin was measured. As previously reported (Jackson and Line 1997) and discussed, acid extraction methods may overestimate lignin content in sludge.

TMP and CTMP sludge spectra and CTMP pulp spectra showed six additional peaks not assigned to wood (three peaks below 700 cm^{-1} and three above 3500 cm^{-1}). These bands were reported for kaolinitic clay (Saikia et al 2003), a common filler in paper formulation. Low SS content kraft sludge spectra showed a sharp doublet at 660 and 600 cm^{-1} and another sharp band at 1618 cm^{-1} . These bands were reported for calcium sulfate (Wightman et al 2004), a common filler in pulp and paper production. Another dif-

ference between pulp and sludge spectra was the $3600\text{-}3000\text{ cm}^{-1}$ band intensity and shape. This region of IR spectra strongly depends on sorbed water, which typically appears as a strong band centered at 3400 cm^{-1} (Chen et al 1998). Although SS contains proteins (Cetin and Erdinciler 2004), typical bond vibration bands for protein were not identified in sludge spectra. The main reported bands for the protein peptide bond are 3300 , 3100 , $1690\text{-}1600$, $1575\text{-}1480$, $1301\text{-}1229$, $767\text{-}625$, $800\text{-}640$, $606\text{-}537$, and 200 cm^{-1} (Haris and Chapman 1994). One problem is that these absorption bands overlap with those of wood.

Spectra of sludge (before hot-pressing) and panels (after hot-pressing) were compared with provide information on chemical changes with hot-pressing. Differences were seen in two zones: $3000\text{-}3600\text{ cm}^{-1}$ (noted a on Fig 6) and $1735\text{-}1710\text{ cm}^{-1}$ (noted b on Fig 6). These differences were seen at low SS content in TMP and CTMP samples, were greater at high SS content, and were not seen in kraft samples. In good agreement with panel IB, this result suggests that some chemical bonds were formed in low SS content TMP and CTMP panels, that more bonds were formed at high SS content, and that very few bonds were formed in kraft panels. Intensity and shape variations in the $3600\text{-}3000\text{-cm}^{-1}$ region suggest changes in water content or hydrogen bond pattern (Chen et al 1998). However, hydrogen bond bands are always overlapped by the broad band associated with water centered at 3400 cm^{-1} (Chen et al 1998). Nevertheless, intensity of the $3000\text{-}3600\text{-cm}^{-1}$ band decreases as panel IB strength increases and TS decreases. Probably, hydrogen bonds were formed within material during hot-pressing, decreasing polar groups available for water molecules to bond with. Changes at $1735\text{-}1710\text{ cm}^{-1}$ may have resulted from a frequency shift in carbonyl (C=O) bond vibrations that lengthen when engaged in hydrogen bonding (Pavia et al 1979). Because the 210°C pressing temperature was above the softening point for amorphous wood polymers, changes in the $1735\text{-}1710\text{-cm}^{-1}$ region may also be related to

hemicelluloses and lignin. FTIR detected some chemical bond changes but was unable to provide more information about SS bonding.

FTIR provided little information, and that information was qualitative only. In contrast, most XPS values correlated with IB and TS of panels (Table 4). The oxygen-to-carbon (O/C) ratio was used to compare the proportion of lignin, carbohydrates, and extractives on the fiber surface. The theoretical O/C ratio of pure cellulose is 0.83 (five oxygen atoms per six carbon atoms) (Rowell 2005; Bouafif et al 2008). O/C ratio ranges from 0.3-0.4 for lignin and is about 0.1 for extractives (Rowell 2005; Bouafif et al 2008). Accordingly, the lignin-free, cellulose-rich, and low-extractive-content kraft pulp had the highest O/C ratio among the three pulps at 0.71 (Tables 1 and 6). Very similar O/C ratio of 0.72 was reported for comparable pulp (Bouafif et al 2008). Conversely, the high-lignin, high-extractive content TMP pulp had the lowest O/C ratio, at 0.30, which was slightly lower than the 0.38 reported for comparable pulp (Koljonen et al 2003). However, 0.28-0.35 was reported for softwood particles (Bouafif et al 2008). CTMP pulp O/C ratio was between those of TMP and kraft pulp at 0.49. A similar value of 0.51 was reported by Koljonen et al (2003).

Negative correlation between O/C ratio and IB strength (Fig 5d) suggested that the proportion of lignin, carbohydrates, and functional groups on the fiber surface affected bonding properties. Low O/C ratio indicated high lignin or extractives content on the fiber surface. High O/C ratio indicated high cellulose content on the fiber surface with many polar groups available for bonding such as hydroxyls (OH). Negative coefficient of correlation between IB and O/C ratio indicated that this effect cannot explain the adhesion mechanism in sludge panels. However, as discussed previously, extreme values for kraft sludge influenced the correlation coefficient, and therefore, this result should be interpreted with caution. The C_{1s} peak was deconvoluted into three components according to degree of oxidation: C₁ refers to unoxidized carbon (ie C-C, C-H), C₂ corresponds to carbon with

Table 6. Apparent concentration (atomic percentage) of selected elements and carbon peak analysis (percentage of peak area) in pulp, sludge, and binderless sludge panels with two SS:PS ratio obtained using XPS.

	Pulping process	TMP			CTMP			Kraft		
		SS content (SS:PS ratio)		Low (1:9)	High (3:7)	Paper		Low (1:9)	High (3:7)	High (3:7)
O/C	Sludge Panels	0.30 (0.01)	0.27 (0.01)	0.26 (0.02)	0.25 (0.00)	0.49 (0.00)	0.31 (0.00)	0.71 (0.04)	0.71 (0.03)	0.50 (0.02)
N _{1s} (at.%)	Sludge Panels	0.3 (0.0)	2.6 (0.0)	1.7 (0.1)	3.0 (0.2)	0.3 (0.0)	0.29 (0.02)	—	0.60 (0.05)	0.48 (0.02)
	Other elements ^a (at. %)	0.1 (0.0)	2.5 (0.2)	2.0 (0.1)	2.0 (0.1)	—	1.6 (0.2)	0.18 (0.1)	1.0 (0.0)	1.9 (0.1)
C ₁ (% area)	Sludge Panels	—	4.1 (0.7)	4.4 (0.3)	4.4 (0.3)	3.1 (0.6)	2.4 (0.0)	1.8 (0.0)	1.1 (0.0)	1.5 (0.4)
	Sludge Panels	40.2 (0.8)	57.0 (1.3)	66.0 (3.0)	51.2 (2.6)	42.7 (0.4)	51.1 (2.8)	9.4 (5.6)	7.6 (0.5)	6.7 (0.3)
C ₂ (% area)	Sludge Panels	—	33.6 (0.7)	27.3 (2.8)	39.4 (1.2)	—	2.8 (0.3)	—	7.3 (0.3)	7.2 (0.1)
	Sludge Panels	44.6 (1.1)	33.6 (0.7)	27.3 (2.8)	69.1 (0.6)	45.9 (0.4)	64.2 (0.9)	—	35.4 (0.6)	46.8 (0.4)
C ₃ (% area)	Sludge Panels	9.9 (0.5)	6.5 (0.4)	7.1 (0.5)	24.4 (0.7)	—	38.6 (1.6)	64.4 (6.2)	42.7 (3.2)	51.6 (1.9)
	Sludge Panels	—	3.9 (0.1)	4.0 (0.1)	4.0 (0.1)	8.3 (0.1)	28.8 (0.5)	—	46.8 (5.2)	38.4 (4.6)
							7.2 (1.0)	24.7 (1.1)	42.0 (2.4)	35.5 (1.9)
							4.4 (0.3)	—	14.8 (5.2)	11.9 (3.0)
							—	—	12.3 (0.9)	10.6 (0.1)

Standard deviations in parentheses.
^a Elements other than oxygen, carbon, and nitrogen. May include silicone, aluminum, magnesium, calcium, iron, sulfur, sodium, and phosphorus.
SS:PS, secondary sludge:primary sludge; XPS, X-ray photoelectron spectroscopy; TMP, thermomechanical pulping; CTMP, chemithermomechanical pulping; O/C, oxygen-to-carbon ratio.

one bonded oxygen (ie C-O), and C₃ is assigned to carbon with two bonds to oxygen (ie O-C-O and C=O) (Rowell 2005; Bouafif et al 2008). Accordingly, the C₁ component arises mainly from lignin and extractives and C₂ and C₃ mainly from carbohydrates (Rowell 2005; Bouafif et al 2008). According to reported values (Bouafif et al 2008), lignin-free, cellulose-rich kraft pulp has the lowest C₁ component and the highest C₂ and C₃ components among the three pulps (Table 6). Carbon peak proportions of TMP and CTMP pulps are similar, according to their similar carbohydrate and lignin contents (Tables 1 and 6). The C₁ component, assigned to lignin and extractives, was the lowest for kraft sludge because it had the lowest extractive content among sludge samples (Tables 1 and 6).

For all panel formulations, the C₁ component increased and C₂ and C₃ components decreased after hot-pressing (Table 6). This suggests that lignin content on the fiber surface increased after hot-pressing, whereas carbohydrate content decreased. The glass transition temperature for lignin is largely exceeded at the pressing temperature used (210°C) (Rowell 2005). Consequently, lignin passes from a glassy to a rubbery state, allowing it to flow and possibly increasing its presence on the fiber surface. None of the C_{1s} components of sludge correlated with panel IB, whereas all components of panels were significantly correlated (Fig 5e; Table 4). This indicates that changes in lignin content on the fiber surface during hot-pressing affected IB and TS.

Nitrogen is the third most abundant element on most sludge and panel sample surfaces. Nitrogen is found in proteins but not in wood and is about ten times more abundant on the sludge surface than on the pulp surface (Table 6). Nitrogen levels obtained with XPS and by the nitrogen analyzer confirmed that nitrogen content was higher in SS than in PS and that TMP had the highest nitrogen level and kraft the lowest. Nitrogen content values from XPS were systematically higher and suggest that proteins were present on the fiber surface. In good agree-

ment with nitrogen concentrations obtained with the nitrogen analyzer (Fig 5a), nitrogen content on the fiber surface correlates positively with IB and negatively with TS (Fig 5f; Table 4).

Other nonorganic elements were detected on the fiber surface (Table 6), suggesting surface contamination. Surface concentrations of these elements are in good agreement with ash content (Tables 1 and 6). The most common were silicone, aluminum, magnesium, calcium, and iron. Concentrations of these nonorganic elements correlate negatively with IB (Fig 5g) and positively with TS. As for ash content, contaminants on the fiber surface interfered with interfiber bonding and decreased panel performance.

Chemical characterization of sludge and XPS provided similar clues to explain adhesive properties of sludge. Proteins played an important role as well as increased lignin content on the fiber surface, whereas fiber surface contamination decreased bonding efficiency. FTIR detected some chemical changes but was less useful than XPS.

CONCLUSIONS

This study presents a comparative evaluation of binderless panels made from common sludge sources generated by the pulp and paper industry. Sludge ratio (SS:PS) and pulping process (TMP, CTMP, and kraft) were investigated. Increasing SS proportion positively affected panel IB and TS but did not affect bending properties. IB increased by 90% for CTMP panels, and TS improved by 92% for TMP panels with increasing SS content from 10-30%. Significant correlation coefficients were found between nitrogen content and IB, between lignin content and IB, and between ash content and IB. TS also correlated with nitrogen, lignin, and ash contents. FTIR and XPS results suggested that bonding could be attributed to increased protein and lignin content on sludge fiber surface, whereas sludge fiber surface contamination decreased bonding efficiency. Significant variations in panel properties were measured across pulping processes. CTMP panels had the highest

mechanical properties and kraft the lowest. TMP and CTMP panels were not significantly different in terms of TS, and kraft panels ranked last. Only the TMP panel formulation at SS:PS ratio of 3:7 met ANSI requirements for basic hardboard. All other formulations were not dimensionally stable enough to meet the standard.

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