

THE IMPACTS OF LIGNIN COVERAGE, RELATIVE BONDED AREA, AND FIBER PROPERTIES ON SHEET STRENGTH

Baoyu Wang,^a Rong Li,^a Beihai He,^b and Junrong Li^{b,*}

In order to determine the quantitative relationship between sheet strength and lignin coverage at the fiber surface, CTMP was blended with softwood bleached kraft pulp (BKP), refined softwood BKP, and hardwood BKP. The morphology of the fibers, fibers properties, fiber surface components and relative bonded area of sheets were investigated. Multi-linear regression equations of tensile strength index and internal bond strength were established. The results indicated that unbleached aspen CTMP fiber surfaces were covered by granules of lignin, and BKP fiber surfaces were predominated covered by microfibrils. Fiber properties have a significant impact on tensile strength index. RBA had a greater impact on IBS than lignin coverage. For the pulp samples tested, a 1% increase in lignin coverage at fiber surfaces would lead to a 0.48N·m/g decrease in tensile strength index and 5.32×10^{-3} J/m² decrease in internal bond strength.

Keywords: Lignin Coverage; CTMP; XPS; Tensile strength index; Internal bond strength

Contact information: a: Guangdong Industry Technical College, 510300, Guangzhou, China; b: State Key Laboratory of Pulp and Paper Engineering, South China University of Technology, 510640, Guangzhou, China; * Corresponding author: lljrr@scut.edu.cn

INTRODUCTION

Mechanical pulping converts wood chips into pulp by means of mechanical grinding. The production of mechanical pulp results in little removal of lignin content, and consequently produces paper that is not of as high in quality as chemical pulping. The advantages of mechanical pulping are its high pulp yield, low cost, and several desirable printing qualities of the paper it produces. These attributes contribute to commercial interest in mechanical pulping. However, the paper manufactured from mechanical pulp has relatively low strength, which limits its applications.

Tensile strength is the most commonly used parameter for describing the mechanical properties of the sheet. There are two factors contributing to the tensile strength of paper, sheet structure parameters and pulp fiber properties (Kärenlampi 1995). The Page theory (1969) explains tensile strength in terms of pulp fiber bonding properties and zero span tensile strength (ZSTS). Internal bond strength (IBS) refers to the energy required to peel one unit area of sheet; it plays an important role in paper processing, coating and printing. It can be evaluated in terms of specific bond strength (SBS) and relative bonded area (RBA) (Skowronski and Bichard 1987). The Scott Bond test is commonly used to test IBS. RBA refers to the ratio between the bonded surface area of the sheet and the surface area of dry pulp fibers in the sheet (William and Thode 1959; Swanson and Steber 1959).

Sheet strength originates from hydrogen bonding and Van der Waals interactions between fiber surfaces; therefore, chemical components at the fiber surface play a significant role in fiber bonding and sheet strength. With the development of surface analysis instruments such as Atomic Force Microscopy (AFM), X-Ray Photoelectron Spectroscopy (XPS), Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS), and Confocal Laser Scanning Microscope (CLSM), surface chemical components can be determined, making it possible to investigate the impacts of chemical components on sheet strength. The middle lamella (ML) of mechanical pulp is not fully removed during the pulping process, so hydrophobic lignin predominates on the fiber surface (Boras and Gatenholm 1999). However, the impacts of lignin coverage on tensile strength and IBS were not considered in the Page theory.

Chemithermomechanical pulp (CTMP) fibres are separated from each other either within ML or near the interface between ML and the P layer. For this reason the fiber surface is almost fully covered by granules that have been interpreted as lignin and extractives. Also it is known that lignin coverage at the surface of a mechanical pulp fiber is much higher than that in the bulk (Koljonen 2003). Compared with wood pulp, the surface of non-wood fiber (such as straw, weed, cane, bamboo and hemp) has enriched levels of lignin and extractives (Yu et al. 2002). Residual lignin, extractives, and metal ion precipitates at the fiber surface are unfavorable to fiber bonding and sheet strength (Li and Reeve 2004; Koljonen et al 2004; Shao and Li 2006; Wang et al 2010). Li et al. (2006) obtained CTMP with different kappa values by refining and carried out lignin absorption tests at fiber surfaces at different pH values. The results indicated that lignin present at the fiber surface would decrease sheet strength (Li et al. 2006), but the quantitative relationship between lignin coverage and sheet strength was not determined.

The present study investigated the impacts of lignin coverage, RBA, and fiber properties on tensile strength index and IBS. CTMP with higher surface lignin coverage was blended with bleached kraft pulp (BKP) having lower surface lignin coverage, and the properties of the mixed fibers including weighted length, width, and coarseness were tested. The RBA values of the resulting sheets were determined by nitrogen absorption, and surface lignin coverage was evaluated with XPS. The aim was to establish an equation between lignin coverage and sheet strength via multi-linear regression.

EXPRIMENTAL

Raw Material

The pulp used in this experiment included softwood bleached kraft pulp (SBKP), hardwood bleached kraft pulp (HBKP), and aspen chemithermomechanical pulp (CTMP). SBKP and HBKP were commercial pulpboard, and the aspen CTMP was obtained from the Shandong Huatai Group, Shandong, China.

Refining

SBKP was refined with a PFI refiner. Samples designated as SBKP5000 (5000 revolutions) and SBKP12000 (12000 revolutions) were obtained. The refining consistency was 10%.

Fiber Properties

The aspen CTMP was blended respectively with SBKP, SBKP5000, SBKP12000, and HBKP at furnish ratios of 0:100, 20:80, 40:60, 60:40, 80:20, and 100:0. The weighted length, width, and coarseness of the fiber blends were tested with an FS 300 Fiber Analyzer.

Surface Morphology by AFM

The testing mode of atomic force microscopy (AFM) includes contact mode, non-contact mode, and tapping mode. The tapping mode is usually applied to analyze pulp fiber surfaces. Height images, phase images, and amplified images can be acquired with the tapping mode. Since AFM is a height resolution imaging technique, it can be used to capture the image of a fiber surface either under atmospheric conditions or under water with an image size range from tens of micrometers to a few nanometers. Information such as fiber surface morphology, even or uneven phases, area of the granular phase, granular diameter, area of the microfibril phase, diameter of microfibers, and the microfibrils angle could be gathered. With this information, we can determine from which layer the fibers are separated (Koljonen et al. 2003; Fardim and Duran 2002).

The fiber morphology of SBKP, SBKP12000, and CTMP were captured with an AFM Nanoscope III with 3.2N/M elastic constant of the cantilever, 450 μm length of Si_3N_4 cantilever, and 5 to 10 nm curvature radius of the probe. Ten fibers were tested for each sample and three spots for each fiber. Representative height images, phase images, and amplified images were analyzed. The tapping mode was employed during the AFM scanning.

Handsheets Formation

Aspen CTMP was blended with SBKP, SBKP5000, SBKP12000, and HBKP with mass ratios of 0:100, 20:80, 40:60, 60:40, 80:20, and 100:0. Handsheets were prepared from these pulp blends with a basis weight of 60g/m^2 . The handsheets were formed under 0.9 bar of vacuum, dried at 95°C for 8 min, and then conditioned at 50% relative humidity (RH) and 23°C for at least 48 h prior to testing. Before the determination of lignin coverage at fiber surface with XPS, the handsheets were extracted with acetone at 70°C for 3h to removed the extractives.

XPS Analysis

X-ray photoelectron spectroscopy (XPS) is a sensitive surface analysis technique that can detect within depth ranges from 5 to 10nm (Kangas and Kleen 2004). The determination of chemical components at fiber surfaces is based on the area under the carbon peak and oxygen peak in an XPS spectrum. Lignin coverage can be determined by Equation 1 (Strom and Carlsson 1992). The prerequisite for using this formula is that lignin thickness at the fiber surface must be greater than the detection limit of the XPS method. Fortunately the thickness of lignin at fiber surfaces generally meets this requirement. Because the fiber is prone to absorb moisture, which causes unwanted oxygen enrichment at the fiber surface, significant errors can be associated with results calculated from Equation 1.

$$\text{lignin}\% = \frac{(O/C)_{\text{extractive-pulp}} - (O/C)_{\text{lignin}}}{(O/C)_{\text{cellulose}} - (O/C)_{\text{lignin}}} \quad (1)$$

The chemical shifts for carbon can be classified into four categories: unoxidized carbon, C_1 (C-C), carbon with one oxygen bond, C_2 (C-O), carbon with two oxygen bonds C_3 (O-C-O or C=O), and carbons with three oxygen bonds, C_4 (O=C-O). The quantities C_1 , C_2 , C_3 , and C_4 content at the fiber surface can be derived by Gaussian fitting of the C_1 s spectrum with higher resolutions. Lignin coverage could be also calculated with the Equation 2,

$$\text{lignin}\% = 100 \times (C_{1\text{extracted}} - \alpha) / 49 \quad (2)$$

where α represents the additional amount of C_1 due to surface pollution. Its value is 2%, which is determined by the C_1 content of fully bleached chemical pulp. An additional contribution to C_1 originates from fiber surface contamination and X ray treatment. The C_1 content of pure milled wood lignin (MWL) is 49% (Laine 1996), the result of lignin coverage determined by Eq. 2 has a good reproducibility (Koljonen and Österberg 2003).

In order to verify the reliability and repeatability of the XPS method, Johansson et al. (1999) analyzed 205 pulp samples. The results showed that the surface contamination can be avoided, and the XPS results were reliable and repeatable, even though the testing area of XPS was just 1 mm².

XPS measurements were performed with a Thermo ESCALAB 250- Multi-technique Surface Analysis using a monochromatic Al/K X-ray source ($h\nu = 1486.6$ eV). The used power was 150W, the area of X-ray measurement was 500×500μm, and the constant pass energy of the energy analyzer was 20 eV. The samples were outgassed overnight under a pressure of 1×10^{-9} Torr, each sample was measured at three different spots, and the results were averaged. Each measurement didn't exceed 30 min in order to avoid X-ray damage of the fiber surface.

Using a curve-fitting program, Gaussian curves were fitted for deconvolution of the carbon emission lines. It was assumed that the curves follow a shape of Gaussian to Lorentzian ratio (G/L) of 0.65, the oxygen bonding energy is 533eV, and the C1s bonding energy is 285eV. The chemical shifts relative to the C-C component used in the deconvolution were 1.7 ± 0.2 eV for C-O (C_2), 3.1 ± 0.3 eV for O-C-O or C=O (C_3), and the sensitivity factors for carbon and oxygen are 0.296 and 0.711 respectively. The constant full-width-half-maximum (FWHM) values were used in curve fitting of each spectrum. The contents of C_1 , C_2 , C_3 , and C_4 at the fiber surface were determined.

RBA Determination by Nitrogen Absorption

The size of a nitrogen molecule is about 4.3Å, and it is known that nitrogen absorption is an effective method for the determination of specific surface area (Stone and Scallan 1965). The calculation of RBA is presented as Equation 3,

$$\text{RBA} = 100\% \times (S_t - S_u) / S_t \quad (3)$$

where RBA is the relative bonded area (%), S_f is the specific surface area of dry fibers (g/m^2), and S_u is the specific surface area of the sheets (g/m^2).

Preparation of dry fiber

During the pulp dewatering, fibers and fibrils are drawn together by the Campbell effect. During the drying stage water is evaporated and hydrogen bonds are formed. The fibers hold onto each other tightly during this process, so it is impossible to obtain individual dry fibers in this way. Assaf et al. (1994) reported a method of displacing water from pulp with methanol and subsequently replacing the methanol with benzene before drying, which rendered the individual dry fibers and a large portion of the internal area of the fibers accessible to nitrogen. In this experiment the dry fibers were prepared by displacing the water in the pulp with acetone.

Determination of specific surface area of mixed dry fiber

When two kinds of fibers are mixed, the specific surface area of mixed dry fibers can be calculated by Equation 4,

$$A_o = A_1 \times c + A_2 \times (1 - c) \quad (4)$$

where A_o is the specific surface area of mixed fiber, A_1 is the specific surface area of the first kind of fiber, A_2 is the specific surface area of the second kind of fiber, and c is the fraction of the first kind of pulp.

Test of specific surface area

A Micromeritics ASAP nitrogen absorption instrument produced by American Micromeritics Company was used to test the specific surface area of dry fibers and sheets. The absorbate was high purity nitrogen, the temperature of liquid nitrogen was 77K, dry fibers and sheets were degassed completely at 90°C, and the absorption isotherm was determined. Two groups of data of each sample were tested, and the results were averaged.

Sheet Physical Properties

Sheet basis weight, thickness, tensile strength index, IBS and ZSTS were determined. An L&W TH-1 tensile strength tester was used to determine tensile strength index. A TMI 80-01-01-0002 Scott Bond tester was used for the IBS measurements.

RESULTS AND DISCUSSION

AFM Analysis

The morphological images of aspen CTMP are presented as Fig.1. Large amounts of a granular substance were presented at the fiber surface, with the granules almost covering the fiber surface completely. The diameter of these granules ranged from 50 nm to 109 nm, and fiber surfaces were rough. During the pulping of aspen CTMP, as the grinding temperature is increased up to the glass transition temperature of lignin, the

lignin is softened, and the fibers become easy to separate from each other within the ML. As a consequence, it is understandable that the aspen CTMP fiber surface was found to resemble the ML of fiber cell, and the granules were lignin (Gustafsson et al. 2003). The formation of hydrogen bonds between fibers was hindered by lignin at the fiber surface, which led to lower sheet strength.

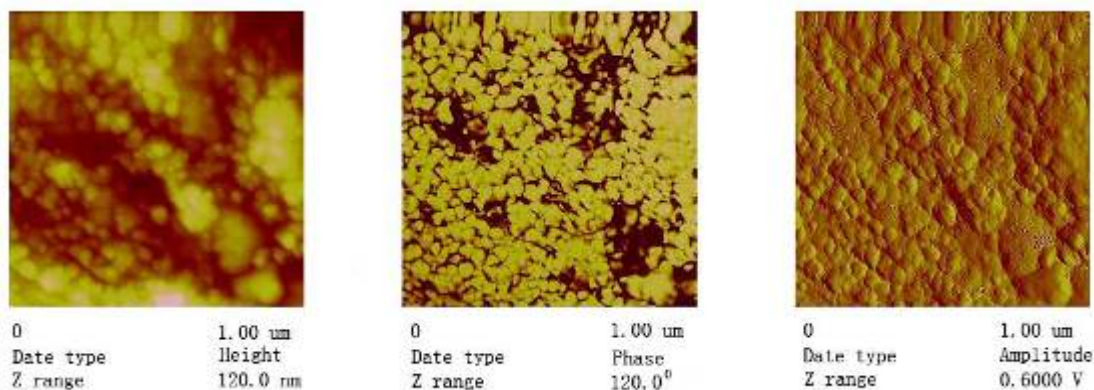


Fig. 1. CTMP surface AFM image (1um×1um). Left: height image; middle: phase image; right: amplitude image

Morphological images of SBKP are shown as Fig. 2. The direction of the fiber axis is vertical in the figure. Many microfibrils were presented at the fiber surface, and the diameters of these microfibrils ranged from 16 to 48 nm. The microfibril angles were $\pm 50^\circ$ to 60° . Based on these results, the fiber surface can be identified as the interface between the P layer and S₁ layer (Barnett and Bonham 2004). Compared with ML, the P and S₁ layers have a higher proportion of cellulose and hemicelluloses, which is favorable for sheet strength.

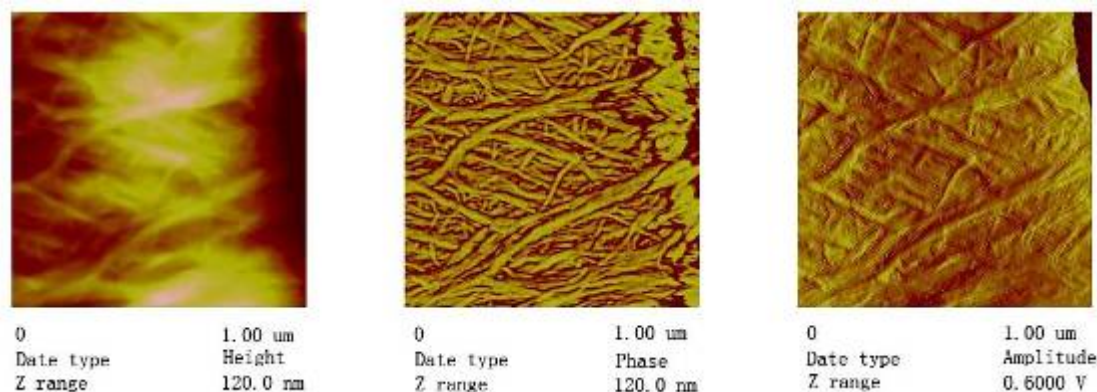


Fig. 2. SBKP surface AFM image (1um×1um) Left: height image; middle: phase image; right: amplitude image

Morphological images of SBKP12000 are given as Fig. 3. The images of SBKP12000 resembled those of SBKP; microfibrils were present at the fiber surface. However, the microfibrils angles were about 30° , and fiber surfaces were smooth, which is characteristic of the S₂ layer (Barnett and Bonham 2004). The SBKP pulp was refined

for 12000 revolutions at 10% pulp consistency and subjected to the action of mechanical friction and extrusion. During this process the P layers were removed, the S₁ and S₂ layers were exposed, fibers became more flexible, the formation of hydrogen bonds was promoted, and sheet strength increased.

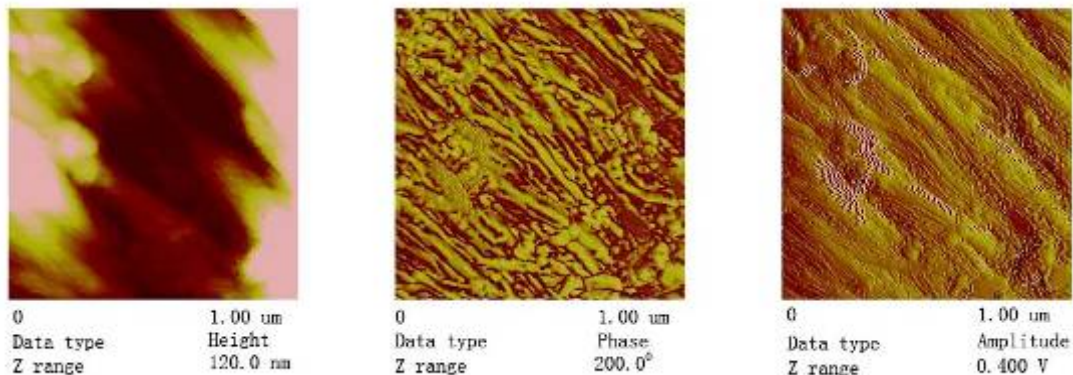


Fig. 3. SBKP12000 AFM image (1um × 1um) Left: height image; middle: phase image; right: amplitude image

3D AFM images of three kinds of pulp are presented in Fig. 4, where it can be seen that a significant number of granules were present at the rough surfaces of the CTMP fibers, and many microfibrils were present on the smoother surfaces of the SBKP and SBKP12000 fibers.

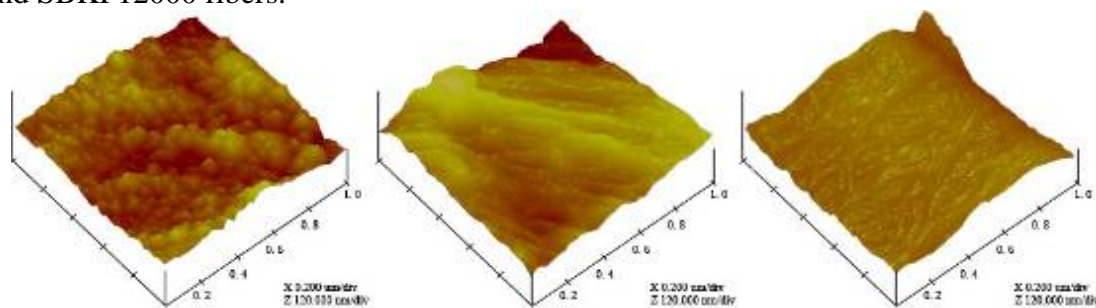


Fig. 4. 3D image of Fiber surface captured by AFM
Left: height image; middle: phase image; right: amplitude image

XPS

XPS scanning spectra of SBKP, SBKP5000, SBKP12000, HBKP, and CTMP are presented as Fig. 5, where it can be seen that oxygen, carbon, and a few sodium elements were present at the fiber surface. The sodium elements may have originated from chemicals used in the pulping process, such as sodium sulfide or sodium sulfite.

Impacts of the refining on lignin coverage at fiber surface were as follows: Johanna found a rough correlation between the amount of the fibrillar surface structure in AFM images and lignin coverage (Johanna et al. 2003). Here, the AFM results indicated that the CTMP fiber surface was essentially ML layer, the SBKP fiber surface consisted of the interface of P layer and S₁ layer, and the SBKP12000 fiber surface is within the S₂ sublayer.

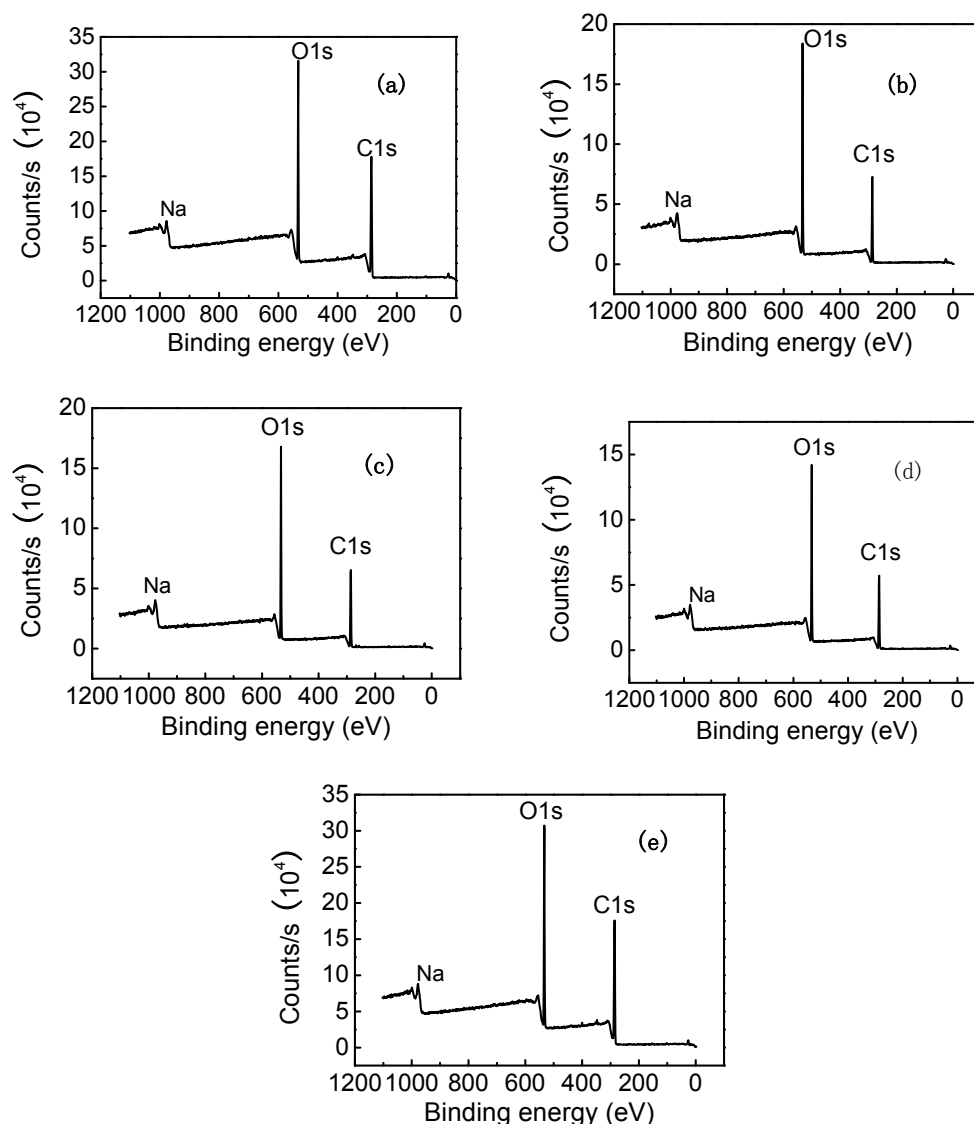


Fig. 5. XPS scan spectrum (0-1200eV) (a) SBKP, (b) SBKP5000, (c) SBKP12000, (d) HBKP, (e) CTMP

It is known that the sequence of lignin concentrations within the layers of a fiber cell are $ML > P > S_1, S_2$ (Chen et al. 1981), so the sequence of lignin coverage was $CTMP > SBKP > SBKP5000 > SBKP12000$ (see as Table 1). Lignin coverage would be reduced with refining.

Table 1. Lignin Coverage of the Pulp Fiber Surface

Pulp	SBKP	SBKP5000	SBKP12000	HBKP	CTMP
Lignin coverage (%)	10.1	9.5	5.8	13.4	48.7

Fiber Properties

Fiber length is an important property of a pulp. Longer fibers generally enhance the strength properties of pulp. Hardwood fibers have an average length around 1 mm,

whereas the average length of a softwood fiber is around 3 mm (Ek et al. 2009). Fiber coarseness is defined as weight per fiber length and is normally expressed in units of mg/m. Coarseness depends on fiber diameter, cell wall thickness, cell wall density and fiber cross section. Coarseness affects fiber failures, fiber strength, and fiber-bonding (Yu et al. 1999).

Fiber properties of the pulps are indicated in Table 2. SBKP had the longest fiber weighted length, SBKP5000 had the widest fibers, and CTMP had the largest fiber coarseness. Comparing the fiber properties of SBKP with SBKP5000 and SBKP12000, it can be concluded that refining could reduce fiber length, width, and coarseness.

Table 2. Fiber Properties

Pulp	Fiber weighted length (mm)	Fiber width (μm)	Fiber coarseness (mg/m)
SBKP	2.35	23.56	0.19
SBKP5000	1.90	24.13	0.19
SBKP12000	1.67	23.03	0.18
HBKP	0.79	14.06	0.08
CTMP	0.68	19.83	0.22

RBA Determined by N₂ Absorption Method

Results for the specific surface area (SSA) of dry fibers are listed in Table 3. The sequence of SSA was SBKP5000 > SBKP12000 > CTMP > HBKP > SBKP. It is interesting that the SSA of SBKP5000 was greater than that of SBKP12000; this is attributed to the fact that refining can cause fiber cell walls to collapse, resulting in the collapse of much smaller pores within the cell wall. Thus, nitrogen molecules were not able to be absorbed at the internal surface of the fiber cell. So SSA of dry fibers increased with the refining, and increased to the maximum value, then decreased with further refining.

Relative bond area (RBA) of sheets

The CTMP sheet had the highest SSA, followed by HBKP, SBKP5000, SBKP, and SBKP12000 in descending order. However, the RBA of CTMP sheet was the lowest, followed by SBKP, HBKP, SBKP12000, and SBKP5000 in ascending order. The fact that the RBA of the CTMP sheet was lowest was attributed to the fact that CTMP fibres were stiffer and had higher lignin coverage at the fiber surface. The higher RBA for SBKP 5000 and SBKP12000 was because their fibres were more flexible and they had a higher carbohydrate coverage at the fiber surface.

Table 3. SSA of Dry Fiber and Sheet, and Sheet RBA

Pulp	Dry fiber (m^2/g)	Sheet (m^2/g)	RBA (%)
SBKP	2.63	1.20	54.2
SBKP5000	4.91	1.21	75.3
SBKP12000	4.54	1.16	74.5
HBKP	3.05	1.39	54.4
CTMP	3.11	1.71	45.0

Sheet Strength

As shown in Table 4, tensile strength index and IBS of the five kinds of pulp had the same order: SBKP12000 > SBKP5000 > HBKP > SBKP > CTMP. However, the sequence of ZSTS was SBKP5000 > SBKP12000 > HBKP > SBKP > CTMP, and it could be concluded that sheet strength would be decreased with an increase in the CTMP ratio.

Table 4. Tensile Strength Index, ZSTS and IBS of Pulp

Pulp	Tensile strength index (N·m/g)	ZSTS (kN/15mm)	IBS (J/m ²)×10 ⁻³
SBKP	11.7	35.2	38.6
SBKP5000	66.0	49.1	432.0
SBKP12000	74.3	46.9	500.1
HBKP	16.3	40.0	46.6
CTMP	7.3	27.7	41.2

Properties of mixed fibers, sheet RBA, and strength are listed as Table 5. From this data as well as the preceding data, multi-linear regression was adopted to analyze the relationship between tensile strength index, IBS, and surface lignin coverage.

Table 5. Properties of Mixed Fibers, Sheet RBA and Strength

pulp	Ratio of CTMP	Weighted length (mm)	Width (um)	Coarseness (mg/m)	Lignin coverage (%)	RBA (%)	Tensile strength index (N.m/g)	ZSTS (kN/15m m)	IBS (J/m ²) ×10-3
SBKP	20	1.94	21.95	0.22	-	54.30	11.3	32.9	36.6
	40	1.53	20.98	0.23	30.16	54.64	11.0	32.2	37.5
	60	1.19	20.48	0.22	-	52.10	10.2	29.5	30.9
	80	0.94	20.11	0.21	37.32	49.36	9.0	28.0	37.0
SBKP5000	20	1.65	22.89	0.21	18.18	-	53.3	44.3	242.2
	40	1.32	21.63	0.2	30.16	65.60	35.4	36.5	154.0
	60	1.18	21.31	0.21	31.44	-	26.6	34.7	87.9
	80	0.94	20.78	0.21	37.32	47.87	14.5	29.5	54.2
SBKP12000	20	1.51	22.27	0.19	-	-	57.8	45.9	351.7
	40	1.31	21.6	0.19	20.18	58.72	41.1	37.5	215.5
	60	-	21.22	0.20	-	-	32.7	34.0	133.3
	80	0.87	20.71	0.21	32.35	43.11	17.2	29.8	84.4
HBKP	20	0.79	14.73	0.09	-	-	14.5	33.0	43.8
	40	0.77	15.54	0.11	27.1	44.88	13.0	32.6	61.9
	60	0.74	17.12	0.15	-	-	13.5	31.9	55.0
	80	0.75	17.39	0.15	32.73	36.90	10.0	28.6	49.2

Tensile strength index

Tensile strength is related to fiber width, length, coarseness, RBA, fiber strength, and shear bond strength per unit area (Page 1969). Here, lignin coverage was used as a substitute for shear bond strength. Multi-linear regression was performed for the tensile

strength index, and the dependent variable was tensile strength index. Independent variables were fiber weighted length, width, coarseness, *RBA*, fiber strength (expressed as *ZSTS*), and lignin coverage, respectively. Multi-linear regression was presented as Equation (5)

$$T = b_0 + b_1X_1 + b_2X_2 - b_3X_3 - b_4X_4 + b_5X_5 + b_6X_6 \quad (5)$$

where X_1 is the fiber weighted length (mm), X_2 is the fiber width (um), X_3 is fiber coarseness (mg/m), X_4 is lignin coverage (%), X_5 is relative bonded area (*RBA*), X_6 is *ZSTS* (kN/15 mm), b_0 is a constant, and $b_1, b_2, b_3, b_4, b_5,$ and b_6 are coefficients.

Results of the multi-linear regression are shown in Table 6. The correlation coefficient R value was 0.98, and the significance of the equation was 0.00, which indicated that this equation was significant. Significance of b_1, b_2 are less than 0.05 and significance of $b_3, b_4, b_5,$ and b_6 are more than 0.05 indicates that fiber length and width have significant effects and fiber coarseness, lignin coverage, *RBA* and zero span tensile strength have marginal effects.

Table 6. Multiple Regression of Tensile Index

Coefficient	Value	Std. Error	T	Sig.
b_0	-124.42	39.37	-3.16	0.02
b_1	-36.15	10.82	-3.34	0.02
b_2	7.26	2.65	2.74	0.03
b_3	-133.64	177.35	-0.75	0.48
b_4	-0.48	0.60	-0.80	0.45
b_5	0.50	0.61	0.82	0.44
b_6	1.61	1.40	1.15	0.30
R =0.98, R-Square=0.96, Significance of the equation=0.00				

The results of multi-linear regression can be expressed as Equation (6). Tensile strength index was positively proportional to fiber width, sheet *RBA*, and *ZSTS*. However, tensile strength index was negatively proportional to fiber weighted length, fiber coarseness and lignin coverage. The fact that tensile strength index was lowered with an increase in fiber length is an apparent contradiction with the theory of sheet strength; however this could be explained by noting that refining reduced fiber length, but it is also consistent with the higher degree of defibrillation, which can provide more interfiber bonding, causing the tensile strength index to increase. On the other hand, fines were helpful to bridge the fiber and to promote fiber bonding. Tensile strength index would be lowered by 0.48N·m/g with a 1 percent increase in lignin coverage at the fiber surface, that is to say that, for a sheet with basis weight of 100g/m², tensile strength index would increase 4800N·m if lignin coverage decreases from 100 percent to 0 percent, and the results were understandable to the test samples.

$$T = -124.42 + -36.15X_1 + 7.26X_2 - 133.64X_3 - 0.48X_4 + 0.50X_5 + 1.61X_6 \quad (6)$$

Internal bond strength

The sequence of *IBS* for the five kinds of pulps was SBKP12000 > SBKP5000 > HBKP > CTMP > SBKP. It is known that refining promotes fibrillation and fiber bonding. Therefore, sheet *IBS* was reduced with an increasing CTMP ratio.

IBS was positively correlated with *RBA* and negatively correlated with *SBS*. The *SBS* was affected by fiber surface components (Shao and Li 2006). Multi-linear regression was performed between *IBS*, *RBA* and lignin coverage. *IBS* was the dependent variable, whereas *RBA* and *LC* were independent variables. The results of multi-linear regression are shown as Equation 7,

$$IBS = b_1 \times RBA + b_2 \times LC \quad (7)$$

where *IBS* is internal bond strength (J/m^2), *RBA* is relative bond area (%), *LC* is lignin coverage (%), and b_1 and b_2 are coefficients.

The results of multi-linear regression are presented as Table 7 and Equation 8. It can be seen from the table that the significance of the equation and coefficients were less than 0.05. It was thus demonstrated that both lignin coverage and *RBA* had a significant effect on internal bond strength. Moreover, *RBA* played a more important role in the determination of *IBS* than lignin coverage did. A 1% increase in lignin coverage at the fiber surface would cause a $5.32 \times 10^{-3} J/m^2$ decrease in *IBS*. When increasing sheet internal bond strength, we should pay attention to the lignin coverage; however, more attention should be paid to the increase in *RBA*.

Table 7. Multiple Regression of Internal Bond Strength

coefficient	value	Std. Error	t	Sig.
b_1	5.11	1.40	5.90	.00
b_2	-5.32	-0.75	-3.18	.01
R = 0.89, R-Square = 0.80, Significance of the equation = 0.00				

$$IBS = 5.11 \times RBA - 5.32 \times 10^{-3} \times LC \quad (8)$$

CONCLUSIONS

Unbleached aspen CTMP exhibited enormous granules at the fiber surface, which could be interpreted as lignin. However, chemical pulps (BKP) were shown to be covered with a significant number of microfibrils at the fiber surface. When CTMP and BKP samples were blended, the lignin coverage of mixed fiber was proportional to the CTMP ratio in the mixture. Sheet relative bonded area (*RBA*) decreased with an increasing CTMP ratio. The order of sheet *RBA* was SBKP5000 > SBKP12000 > HBKP > SBKP > CTMP. With the increase of lignin coverage, sheet tensile strength index and *IBS* were reduced. For the test samples a 1% increase of lignin coverage would lead to a 0.48 N.m/g decrease in tensile strength index and a $5.32 \times 10^{-3} J/m^2$ decrease in *IBS*. *RBA* had a greater impact on *IBS* than lignin coverage. In order to improve sheet *IBS*, more attention should be paid to the increasing of sheet *RBA*.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the support of “the Fundamental Research Funds for the Central Universities, SCUT, 2009zm0086”.

REFERENCE CITED

- Assaf, A. G., Haas, R. H., and Puurves, C. B. (1944). “A new interpretation of the cellulose-water adsorption isotherm and data concerning the effect of swelling and drying on the colloidal surface of cellulose,” *J. Am. Chem. Soc.* 66, 66-73.
- Barnett, J. R., and Bonham, V. A. (2004). “Cellulose microfibril angle in the cell wall of wood fibres,” *Biol. Rev. Camb. Philos. Soc.* 79(2), 461-72.
- Boras, L., and Gatenholm, P. (1999). “Surface composition and morphology of CTMP fibres,” *Holzforschung* 53,188-194.
- Chen, J. X., Qiu, Y. G., and Yang, Z. Q. (1981), “Fibre morphology and microstructure of mason pine in south China,” *Chinese Pulp and Papermaking*. 5, 11-18.
- Ek, M., Gellerstedt, G., and Henriksson, G. (2009), *Pulp and Paper Chemistry and Technology: Pulping Chemistry and Technology*, 433-434.
- Fardim, P., and Duran, N. (2002). “Surface chemistry of eucalyptus wood pulp fibres: Effects of chemical pulping,” *Holzforschung* 56, 615-622.
- Gustafsson, J., Lehto, J. H., and Tienvieri, T. (2003). “Surface characteristics of thermomechanical pulps; The influence of defibration temperature and refining,” *Colloids and Surfaces A: Physic. and Eng. Aspects*. 225(1-3), 95-104.
- Johansson, L. S., Campbell, J. M., Koljonen, K., and Stenius, P. (1999). “Evaluation of surface lignin on cellulose fibres with XPS,” *Appl. Surf. Sci.* 145, 92-95.
- Johanna, G., Laura C., Jouko P., (2003). “The ultrastructure of spruce kraft pulps studied by atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS),” *Polymer* 44, 661-670.
- Kangas, H., and Kleen, M. (2004). “Surface chemical and morphological properties of mechanical pulp fines,” *Nordic Pulp and Paper Research Journal* 19(2), 191-199.
- Koljonen, K., and Österberg, M. (2003). “Surface Chemistry and morphology of different mechanical pulps determined by ESCA and AFM,” *Colloids and Surface A: Physicochem. Eng. Aspects*. 228, 143-158.
- Koljonen, K., Österberg, M., and Kleen, M. (2004). “Precipitation of lignin and extractives on kraft pulp: Effect on surface chemistry, surface morphology and paper strength,” *Cellulose* 11(2), 209-224.
- Laine, J. (1996). “The effect of cooking and bleaching on the surface chemistry and charge properties of kraft pulp fibres,” Doctoral thesis, Helsinki University of Technology,” Espoo, Finland.
- Li, K., and Reeve, D. E. (2004). “Determination of surface lignin of wood pulp fibres by X-ray photoelectron spectroscopy,” *Cellulose Chemi. Tech.* 38(3-4), 197-210.
- Li, K. Ch., Tan, X. Q., and Yan, D. B. (2006). “The middle lamella remainders on the surface of various mechanical pulp fibres,” *Surface Interface Analysis* 38, 1328-1335.

- Shao, Z. L., and Li, K. (2006). "The effect of fibre surface lignin on interfibre bonding," *Journal of Wood Chemistry and Technology* 26, 231-244.
- Skowronski, J., and Bichard, W. (1987). "Fibre to fibre bonds in paper. Part 1. Measurement of bond strength and specific bond strength," *Journal of Pulp and Paper Science* 13(5), 165-169.
- Stone, J. E., and Scallan, A.M. (1965). "Effect of component removal upon the porous structure of the cell wall of wood," *Journal of Polymer Science, Part C: Polymer Symposia*. 11(1), 13-25.
- Ström, G., and Carlsson, G. (1992). "Wettability of kraft pulps - Effect of surface composition and oxygen plasma treatment," *Journal of Adhesion Science Technology* 6(6), 745-761.
- Swanson, J. W. and Steber, A. J. (1959). "Fibre surface area and bonded area," *Tappi* 42(12), 986-994.
- Wang, B. Y., He, B. H., and Li, J. R. (2010). "Study on lignin coverage on Masson pine fibre," *BioResources* 5(3), 1799-1810.
- William, L. I., and Thode, E. F. (1959). "Factors contributing to the strength of a sheet of paper," *Tappi* 42(1), 83-93.
- Yu, Y., Kettunen, H., Hiltunen, E., and Niskanen, K. (1999). "Comparison of abaca and spruce as reinforcement," TAPPI International Paper Physics Conference, San Diego, U.S.A, 161-169.
- Yu, Y. Zh., Koljonen, K., and Paulapuro, H. (2002). "Surface chemical composition of some non-wood pulps," *Industrial Crops and Products* 15(2), 123-130.

Article submitted: June 26, 2011; Peer review completed: August 31, 2011; Revised version received and accepted: September 7, 2011; Published: September 10, 2011.