Correlation Analysis for Fiber Characteristics and Strength Properties of Softwood Kraft Pulps from Different Stages of a Bleaching Fiber Line

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During sequential bleaching operations, pulp fiber properties are gradually changed due to mechanical and chemical treatments. In this study, the correlations between pulp or fiber properties such as kappa number, viscosity, total charge, fiber length, and zero-span tensile strength as well as Scott bond of elemental chlorine free (ECF) bleached softwood kraft pulps was investigated. The influence of zero-span tensile strength and Scott bond on tensile and tear strength was also discussed. The Scott bond and zero-span tensile strength showed a strong logarithmic correlation with pulp kappa number and pulp viscosity, while the regression coefficient for Scott bond was negative. An overall deterioration of paper tensile and tear strength from pulps whether beaten or not were observed along the multi-stage ECF bleaching operations. Changing contributions to sheet tensile or tear strength could be mostly attributed to changes in zero-span tensile strength rather than Scott bond during ECF bleaching.

Keywords: Softwood kraft pulp; Bleaching; Scott bond; Fiber properties; Zero-span tensile strength

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INTRODUCTION

Fibers are the basic structural elements of paper. The characteristics of pulp fibers are of critical importance, and they naturally influence the mechanical properties of the final paper. For paper and paperboard, strength, that is the ability to tolerate applied stresses, is one of the most relevant properties. Single fiber strength is very important to paper and paperboard. Also fibers' abilities to form fiber-to-fiber bonds are important for the strength of paper and paperboard.

Much research effort has been devoted to explore the relationships between chemical and physical properties of the pulp fiber and their inherent papermaking strength properties. The contribution of hemicelluloses to fiber strength has been widely discussed and is not entirely clear (Spiegelberg 1966; Schonberg *et al.* 2001). The effect of lignin on tensile strength and tensile stiffness of paper sheets has been reported (Risen *et al.* 2004; Neagu *et al.* 2006). The correlation between the cellulose degradation and fiber strength has also been discussed (Gurnagul *et al.* 1992; Joutsimo *et al.* 2005).

Cellulosic fibers are normally negatively charged when suspended in water due to the presence and ionization of acidic groups such as carboxyl, sulphonic acid, and phenolic hydroxyl groups. The fiber charge is a dominating factor in affecting the fiber hydrophility, swelling capacity and also in controlling the wet end chemistry of paper making processes.

The population of ionized groups is highly dependent on the origin of fiber cell wall constituents and on the chemical treatments during pulping and bleaching of fibers. Previous studies have indicated that the carbohydrate losses and concomitant dissolution of lignin generally decreased the charge on bleached kraft fibers. Different bleaching agents used in kraft pulp bleaching react with residual lignin in different ways. Ozone and chlorine dioxide reduce the amount of charge considerably. An exception of a slight total charge increase after oxygen delignification was also reported (Laine and Stenius 1997; Yang *et al.* 2003; Risen *et al.* 2004; Zhang *et al.* 2007).

Fiber morphological aspects such as length, width, curl, and fines, have been considered as a dominating influence on pulp quality. The fundamentals of improving interfiber bonding and the related mechanisms with paper strength properties have been recognized and explained extensively in the literature (Richard 1974; Paavilainen 1994; Moral *et al.* 2010). In the course of sequential bleaching operations, the morphology of wood fibers is inevitably changed along with the dissolution and removal of acidic polysaccharides particularly xylans and degraded lignin. It is possible that the effect of bleaching on fiber morphology might be no significant than that of a beating or refining process.

Some mathematical models for sheet strength had been proposed (Page 1969; Shallhorn and Karnis 1979; Johnston 1997). However, it was hard to build a predictive model of paper strength directly from fiber characteristics. Bleaching processes are commonly designed to achieve high pulp brightness. But they also affect the physical and chemical properties of pulp fibers. The fiber quality cannot be fully comprehended merely through a few test methods. However, evaluation of the effects of such parameters is instructive in understanding the relationships between fiber properties and sheet strength. Meanwhile, a more detailed understanding of the bleaching process and fiber quality is also globally relevant. In this study, the changes of pulp fiber parameters along the bleaching fiber line such as kappa number, viscosity, total charge, fiber length and so on were determined. The sheet strength properties including zero-span tensile, internal bond, tensile strength, and tear strength were measured. The objective of the study was to establish relationships between these fiber parameters and sheet strength properties. Correlation analysis was made based on the same kind or batch of kraft fibers.

EXPERIMENTAL

Materials

Pulp samples from one softwood kraft pulp line were used for the studies in this investigation. The pulps were obtained from Juntai Pulp and Paper Co., Ltd. in Hunan Province, China. The pulps were oxygen delignified and ECF bleached according to the following sequence: $DE_{OP}DP_{O}$. Six pulp samples collected including unbleached stock were washed, dewatered, and stored in the cold room at 4 ^{o}C for further tests.

Analyses for Pulp Fibers

The pulp kappa number was determined according to TAPPI test method T236 om-02. The pulp viscosity was determined according to ISO 5351:2004 and brightness according to ISO 2470:1999. The water retention value was measured using a centrifuge method and calculated according to TAPPI um-256. The fiber morphology such as length, width, and curl was tested using a fiber morphology analyser (Morfi-Compact, Techpap Co. Ltd, France). The total and surface charge of pulp samples were determined by conductometric titration and polyelectrolyte titration according to Lloyd and Horne (1993), and Wagberg *et al.* (1989), respectively. The conductometric and polyelectrolyte titrations were performed using a conductivity meter and a particle charge detector (Mutek PCD-06).

Strength Testing of Handsheets

Paper handsheets of pulp samples of 80 g/m^2 were prepared using a standard handsheet former as described in TAPPI test method T205 sp-02. The physical strength properties of handsheets – zero-span tensile index, Scott bond, tensile, and tear strength index – were determined according to TAPPI test methods T273, T569 om-03, T494, and T414, respectively.

RESULTS AND DISCUSSION

Changes in Pulp Fiber Properties during ECF Bleaching

A summary of basic pulp properties of softwood pulp during ECF bleaching is listed in Table 1. The unbleached pulp with a higher kappa number of 33.7 contained proportionally more residual lignin available for reaction in the first oxygen delignification stage. The oxygen delignification stage comprises two oxygen reactors in series which allow for about 60% kappa reduction. After the ECF bleaching, a high pulp brightness of 85%ISO was achieved along with the kappa number decreasing to only 1.7. The pulp viscosity, which represents the degree of degradation of the cellulose and hemicelluloses, was gradually decreased with the multi-stage bleaching operations. The drainage velocity of pulps was measured by a dynamic drainage jar at 0.1% pulp consistency. The seconds were recorded with a stopwatch when 100 mL of filtrate was collected. It showed a little increase after bleaching.

Table 1. Basic Pulp Properties 0f Softwood Pulp during ECF Bleaching

Bleaching stage	Kappa number	Viscosity (mL/g)	Brightness (%ISO)	Dynamic drainage (s/100mL)	Water retention value (g/g)
Unbleached	33.7	1046	23.4	37.5	126.2
O	12.6	865	37.3	36.0	131.5
OD_0	5.6	822	53.0	35.0	126.8
OD_0E_{OP}	3.5	774	73.8	36.0	128.5
$OD_0E_{OP}D_1$	1.8	740	84.2	35.5	120.6
$OD_0E_{OP}D_1P_O$	1.7	731	85.0	36.9	121.1

The water retention value of pulps exhibited no significant change during the ECF bleaching. But the bleaching stage under acidic conditions exhibited a lower water retention value than those samples subjected to alkaline conditions.

The results of measured fiber morphology and charge properties of pulp samples are presented in Table 2. It can be noted that a slight decrease of fiber length and width occurred during bleaching. And they can be seen as constant in the two final bleaching stages. Bleaching also caused an overall increase of the proportion of kinked and curled fibers which, in general, represent the fiber flexibility. The fiber cell wall of the softwood pulp was proposed to be softened, loosened, and shrunk in axial and radial directions when lignin and carbohydrates were removed sequentially by chemicals. The total and surface charge for the investigated pulps decreased gradually as bleaching proceeded. A decrease in lignin content will lead to a decrease in total and surface charge, as carboxylic groups are removed with the lignin. The 28% drop for the total charge took place in the second stage of chlorine dioxide bleaching, while 13% drop in the first stage of oxygen delignification. Chlorine dioxide reduced the amount of total charge considerably. The result of the D_0 bleaching stage was consistent with Laine and Risen (Laine and Stenius 1997; Risen *et al.* 2004). Not any increase but a decrease in total charge was found for oxygen delignification. This might be due to the different pulping conditions or plant materials. A biggest drop of 22% for the surface charge occurred in the first stage of oxygen delignification. The lignin on the outer surface of fibers was removed prior to removal of lignin from internal layers of the cell wall.

Table 2. Morphology and Charge Properties of Softwood Pulp Fibers during ECF Bleaching

Bleaching stage	Weighted fiber length (mm)	Weighted fiber width (μm)	Kinked fibers (%)	Curl (%)	Total charge (mmol/kg)	Surface charge (mmol/kg)
Unbleached	2.27	35.4	61.8	15.1	104.42	23.49
O	2.16	33.8	63.4	14.2	90.75	18.40
OD_0	2.11	33.5	68.6	17.5	65.54	17.77
OD_0E_{OP}	2.07	31.8	69.6	18.5	63.43	16.76
$OD_0E_{OP}D_1$	2.05	31.4	68.0	17.8	62.93	15.07
$OD_0E_{OP}D_1P_O$	2.06	31.5	69.7	19.2	58.16	15.00

Correlation Analysis for Fiber Parameters and Strength Properties

The evaluation of pulp strength properties by conventional methods is not suitable for detailed specifications of pulps or fiber line, as the measured tensile strength is a combination of tensile strength of fibers and fiber-to-fiber bond strength. So the single fiber strength and internal bonding strength were determined separately by the zero-span tensile test and Scott bond test. The traditional strength properties such as tensile and tear index were also considered.

The zero-span tensile test is a widely used method for evaluating the average strength of individual fiber rather than the strength of the paper itself. In the zero-span test, the tested sheet strips and, consequently, a given fiber is clamped at zero span of the tester jaws. The test was already described and analyzed by several authors (Mohlin *et al.* 1996; Seth 2001; Hakansson *et al.* 2004; Wathen *et al.* 2006; Zeng *et al.* 2012). In Fig. 1, zero-span tensile was represented as a function of pulp kappa number. The results showed a strong logarithmical correlation with regression coefficient, R^2 of about 0.99, between the pulp kappa number and the zero-span tensile index. The regression model was as follows: y = 6.76 Ln(x) + 92.57, where y = zero-span tensile index and x = kappa number of pulps. The relationships between zero-span tensile strength and other pulp fiber parameters are presented in Table 3.

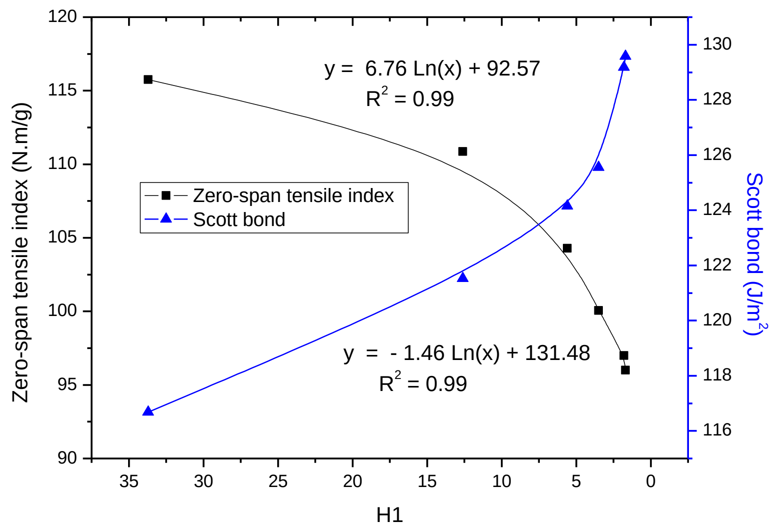

Fig. 1. Zero-span tensile index and Scott bond as the function of pulp kappa number

Table 3. Regression Analysis for Measured Fiber Properties and Individual Fiber Strength, as well as Internal Bond Strength

Strength properties*	Fiber Parameters	Regression equations	Regression coefficients, R^2
Zero-span tensile strength	Kappa number	y = 6.76 Ln(x) + 92.57	0.99
	Viscosity	y = 57.15 Ln(x) - 279.64	0.93
	Length	y = 89.15 x - 84.85	0.93
	Width	y = 4.81 x - 54.19	0.95
	Curl	y = -3.63 x + 165.87	0.82
	Total charge	y = 0.41 x + 73.86	0.93
	Surface charge	y = 2.37 x + 61.86	0.88
Scott bond energy	Kappa number	y = -4.16 Ln(x) + 131.48	0.99
	Viscosity	y = -35.77 Ln(x) + 364.59	0.96
	Length	y = -55.09 x + 241.15	0.94
	Width	y = -2.94 x + 221.12	0.93
	Curl	y = 2.04 x + 89.72	0.68
	Total charge	y = -0.24 x + 142.47	0.87
	Surface charge	y = -1.51 x + 151.33	0.95
*The pulps used for handsheet preparing were not beaten here.			

A logarithmical correlation with regression coefficient R^2 = 0.93 was also found for pulp viscosity to zero-span tensile strength. The loss in zero-span tensile strength of bleached pulps has been attributed to weakening or deterioration of the fiber matrix by the removal of lignin and the degradation of carbohydrates. An accelerating drop in zero-span tensile index indicates more intensive individual fiber damage. A linear relationships to zero-span tensile strength, with regression coefficient greater than 0.90, was obtained for total charge, as well as fiber length and width. The correlation between total charge and zero-span tensile strength was greater than that of surface charge.

The internal bond strength is conventionally defined as the energy or strength required for breaking bonds per unit area of paper sheet in the Z direction, *i.e.* at a 90^o angle to the plane of the fiber mat composite. The Scott bond tester, expressed as breaking energy per unit area with J/m^2, is a most common apparatus for measuring internal bond strength. A negative logarithmical correlation between the pulp kappa number and the internal bond strength of papersheet was found in Fig. 1. The Scott bond energy increased logarithmically with the decline of kappa number. The regression model for internal bond strength was as follows: y = -1.46 lnx + 131.48, where y = Scott bond energy and x = kappa number of pulps. The regression coefficient R^2 was 0.99.

Table 3 also presents the relationships between internal bond strength and other pulp or fiber parameters. There was a negative logarithmical correlation with regression coefficient R^2 = 0.96 for pulp viscosity to internal bond strength. The internal bond strength of paper sheet was mainly determined by two factors. One was the interfiber or fiber-to-fiber bonds in adhesive joints between fibers. The other was the numbers or contact area of fiber bonds generally described as the relative bonded area. An interfiber bond can be defined as the zone where fibers are so close to each other that the intermolecular hydrogen bonds as well as Van der Waals forces or molecular entanglement can occur (Retulainen *et al.* 1998). Therefore the chemical composition of the fiber, especially on the fiber surface, may play an important role in inter-fiber bonding. Due to the hydrophobic nature, the presence of lignin in the bonded area may constitute a barrier to the formation of hydrogen bonds between cellulose molecules.

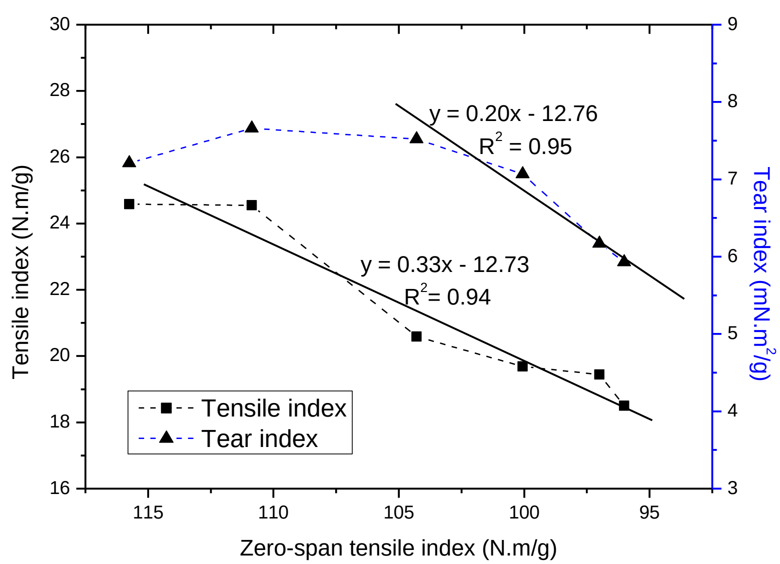

Fig. 2. Tensile and tear strength as the function of Zero-span tensile strength

During the bleaching, the removal of lignin and the exposure of cellulose would result in more generation of hydrogen bonds between adjacent fibers in paper sheet. In addition, negative linear relationships to internal bond strength, with regression coefficient greater than 0.90, were obtained for fiber length, width, and surface charge. The correlation for surface charge to internal bond strength greater than that of total charge indicated that the surface charge of fibers was more important for internal bond strength.

The tensile and tear strength of pulps across the fiber line of ECF bleaching are shown in Figs. 2 and 3. The unbleached pulp with the highest zero-span tensile value did not present higher tensile and tear strength compared with pulp fibers after oxygen delignification. This might be due to the fact that sheets made from unbleached pulp had a lower sheet internal bond strength measured by Scot bond test. The tensile index of pulps was decreased along the ECF bleaching line. The turning point for decline of tear strength was located in the D_0 stage. The decline section of tensile and tear strength may depend on the loss of the average strength of individual fibers determined by the zero-span tensile test.

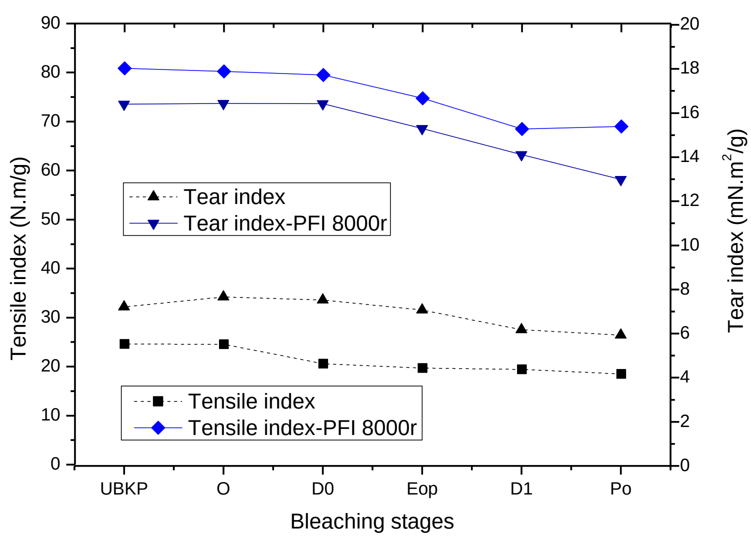

Fig. 3. Tensile and tear strength index of handsheets made from different pulps without beaten and beaten with PFI in 8000 revolutions

It was observed in Fig. 3 that the value of tensile and tear strength of pulps after being beaten increased 2 to 3 times compared to the original pulps. But the overall decline tendency of tensile or tear strength during bleaching was the same. The turning point for a large strength drop across the D_0 stage was indicated. Linear correlations greater than 0.94 were found for all decline sections between zero-span tensile strength and tensile strength, as well as tear strength, as shown in Fig. 2. Meanwhile, previous studies had found that Scott bond energy is greatly improved by beating treatment, as shown as Fig. 4. For instance, the Scott bond of unbleached kraft pulp was 116.7J/m^2 without beating and reached to 340.0J/m^2 after being beaten with a degree of 30 ^{o}SR. According to strength theories, paper strength is considered to be governed by the gradual failure of the interfiber bonds, or in well-bonded papers also by fiber rupture. The two failure modes are difficult to control separately because pulping and papermaking operations affect the strength of fibers, their bonding, and variation in the structure of paper (Niskanen and Kärenlampi 1998). However, no positive relationships of Scott bond to tensile or tear strength was found for bleached pulps, even though the tear strength of oxygen delignified pulp was somewhat higher than that of unbleached pulp. Perhaps the increase of Scott bond by bleaching was mostly derived from the enhancement of intermolecular hydrogen bonds inside the contact points rather than the numbers or area of contact points between adjacent fibers in specific paper sheet, expressed as the relative bonded area. On the contrary, the sharp increase of Scott bond by beating for kraft pulps was probably contributed by relative bonded area. Higher relative bonded area means that more fibers bond to each other and thereby engage in fiber rupture in across section of sheet strips during the tensile strength test. In Fig. 3 it was reasonable to deduce that the tensile strength of softwood kraft pulps along the bleaching line was governed mostly by the individual fiber strength and the numbers of fibers engaged in rupture. With an infinite Scott bond, the tensile strength of paper would be equal to the zero-span tensile strength, while all fibers in specific broken transaction of the test strip would engage in rupture ideally. A further study on relative boned area of paper sheet from bleached pulps should be done to confirm this view. On the other hand, it can be concluded that the increase of Scott bond generating from the fiber modification by chemical agents during bleaching was limited compared to beating treatment.

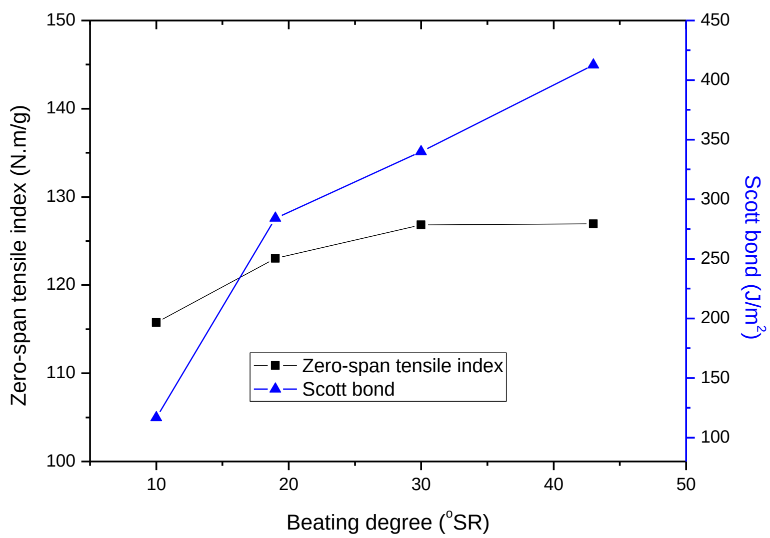

Fig. 4. Influence of beating on Zero-span tensile index and Scott bond of unbleached pulp

CONCLUSIONS

1. A rapidly rising brightness of pulps with a gradually decrease of kappa number and viscosity was obtained along the fiber bleaching line. In general, the effects of multi-stage bleaching processes on the morphological characteristics were limited to a mild

extent with a slight decrease of fiber length and width. The total and surface charge of softwood pulps decreased to a large extent in the course of carbohydrate losses and the removal of lignin during the ECF bleaching.

2. The Scott bond and zero-span tensile strength showed a strong logarithmical correlation with pulp kappa number, as well as pulp viscosity. The Scott bond increased with the decline of the kappa number, while on the contrary the zero-span tensile strength decreased.
3. An overall deterioration of paper tensile and tear strength from pulps whether beaten or not were observed along the ECF bleaching fiber line. The contribution of Scott bond to tensile or tear strength was relatively small due to the fact that the amplification itself caused by bleaching chemicals was limited compared to beating treatment. During the ECF bleaching, the tensile and tear strength were mostly governed by the average of individual fiber strength.

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