Fiber Characteristics and Bonding Strength of Poplar Refiner-Chemical Preconditioned Alkaline Peroxide Mechanical Pulp Fractions

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In China, alkaline peroxide mechanical pulping performed with refiner-chemical preconditioning (P-RC APMP) is well known to produce fiber with high bulk, opacity, and light scattering coefficient but weak bonding and strength properties. In this study, the characteristics of different P-RC APMP fiber fractions were investigated, and their effects on bonding strength properties were determined. The results showed that there was only 5.8% R30 fiber fraction and 14.1% P100/R200 fiber fraction, and the specific surface area increased from R30 to P100/R200. The tensile index increased by 51.85% and the bonding index increased by 15.35%, when the fibers were changed from the R30 fraction to the P100/R200 fraction. The short fiber fraction (P100/R200 fraction) had smaller fiber length and coarseness but larger specific surface area and greater surface charge density than the long fiber fraction (R30 fraction). The fiber specific surface area and surface charge density made significant contributions to the bonding capacity, whereas fiber coarseness and length were negatively correlated with the tensile index.

Keywords: Poplar P-RC APMP; Fiber fractions; Fiber characteristics; Bonding strength properties

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INTRODUCTION

High-yield pulp (HYP) is becoming more attractive for use in many paper and paperboard grades with high performance requirements since it has unique characteristics and can be flexibly produced by combining chemical and mechanical treatments (Liu *et al*. 2012). Typically, the properties of paper and paperboard products depend on the characteristics of the fiber they contain. There is much literature concerning the differences between chemical pulp fibers and preconditioning refiner chemical treatment alkaline peroxide mechanical pulp (P-RC APMP) fibers (Xu 1999; Zhou *et al.* 2005). Compared to chemical pulp, P-RC APMP has a relatively wide fiber length distribution, weak physical properties, and low brightness but also has a high bulk, opacity, and light scattering coefficient. Application of HYP in many grades not only decreases the production cost, but also improves the properties of the paper or paperboard products. However, excessive HYP usage can negatively affect interfiber bonding, resulting in poor bonding and strength properties (Xu 2001; Zhou *et al.* 2005).

The main strength properties of paper include the tensile strength, bursting strength, and tearing strength, which are attributed to interfiber bonding strength (fiber network or fiber matrix) and individual fiber strength. The fiber characteristics have a

significant effect on the strength properties of the products. There are many theories describing the relationship between fiber characteristics and the tensile strength of the sheet, perhaps the most widely used of which is the Page Equation (Page 1969), which illustrates that tensile strength is mainly affected by interfiber bonding strength and individual fiber strength. For sheets with weak interfiber bonding or low relative bonding area, translation of fiber strength to sheet strength happens primarily *via* long fibers. Otherwise, fibers with great bonding capacity may be broken, and the fiber network may disappear.

Fiber surfaces come into contact with one another to form a fiber matrix or sheet. The fiber surface properties have significant effects on the strength properties of the paper. P-RC APMP has high surface lignin content that inhibits hydrogen bonding because of the hydrophobic nature of lignin (Shao and Li 2006). The specific surface area and surface charge density play pivotal roles in determining the fiber-fiber bonding strength. The former contributes to the bonded area and the latter improves shear bonding strength (Kappel *et al*. 2009).

As mentioned above, there is a lot of lignin remaining on the HYP fiber surface, and a few fiber bonding points are exposed. P-RC APMP does, however, contain a large number of highly fibrillated fines. The disparity between the dimensions of different fiber fractions has important effects on the fiber characteristics and bonding properties (Lei *et al*. 2013; Li *et al.* 2014). In this study, the fiber characteristics of different P-RC APMP fiber fractions and their effects on interfiber bonding strength properties were investigated at the laboratory scale to evaluate the relationship between the HYP fiber fraction and the bonding strength; to provide more data for optimizing high-yield pulping technologies; and to determine how best to use this kind of HYP fibers rationally in many kinds of paper and paperboard grades.

EXPERIMENTAL

Materials

Poplar P-RC APMP, produced in a typical high-yield pulping line, was obtained from a mill in Shandong province in China. The pulp was classified by a Bauer-McNett classifier (TMI, USA) into different fiber fractions including R30, P30/R50, P50/R100, and P100/R200. Four fiber fractions were collected. R30 and P30/R50 were the long-fiber fractions, and P50/R100 and P100/R200 were the short-fiber fractions.

Methods

Handsheet making

Handsheets containing 100% P-RC APMP fiber fractions were made in a laboratory sheet former (Lab Tech, Canada). The sheet forming procedure and physical property measurements were conducted in accordance with their respective TAPPI standard methods, T205 sp-95 (1995) and T220 sp-96 (1996).

The dry zero-span tensile index, effective fiber length index (L), and fiber bonding index (B) were determined with a Z-span Tester (2400, PULMAC, USA) following TAPPI standard T220 sp-96 (1996). L and B were expressed according to Equations 1 and 2,

$$L = \frac{\text{wet short - span value}}{\text{wet zero - span value}} \quad (1)$$

$$B = \frac{\text{dry short - span value}}{\text{wet short - span value}} \quad (2)$$

where the measuring spacing of the short-span tensile strength was 0.40 mm and that of the zero-span tensile strength was 0.00 mm.

Confocal laser scanning microscopy images

A confocal laser scanning microscope (CLSM, EC-C1 NIKON, Japan) using a 40-x magnification, dry objective lens with a numerical aperture of 1.25 was employed. An argon ion laser with a wavelength of 488 nm was used as the illumination light. First, the different fiber fractions were dyed in an acridine orange solution. Then, two dyed fibers were mounted on a glass slide and covered by the other one. Finally, the fiber bonding model was fixed with some sealing agents and ready for CLSM scanning.

Fiber characteristics measurements

The morphologies of different P-RC APMP fiber fractions, including their fiber length, fiber width, and other properties, were measured using a fiber tester (Fiber Tester 912, L&W Inc., Sweden). Weighted average data were obtained from the fiber tester, an apparatus commonly used to evaluate fiber quality. The specific surface area and volume of the fiber were measured using a Specific Surface Area Tester (PULMAC, USA). Based on the fluid-permeability method, the specific surface area was calculated by measuring the resistance of liquid to travelling through a fiber filter cake (Xia *et al*. 1991). Two different methodologies, electrokinetic measurement and polyelectrolyte titration, were used to evaluate the charge density on the fiber surface. The electrokinetic character was evaluated using a Zeta Potential Tester (SZP-06, MUTEK, Germany) based on the theory of the electrical double layer, representing the potential difference between the positive and negative charges in the pulp suspension (Patton and Lee 1993). The polyelectrolyte titration was done with a Particle Charge Detector (PCD-04, MUTEK, Germany) to measure the carboxyl group contents in the different poplar P-RC APMP fiber fractions (Katz and Beatson 1984).

RESULTS AND DISCUSSION

Strength Properties of Handsheets Made from Different P-RC APMP Fiber Fractions

The strength properties of paper depend on a series of factors, mainly focused on two aspects: fiber characteristics and interfiber bonding activities. Usually, interfiber bonding strength is more important than individual fiber strength in determining the strength properties of sheets (Carlsson and Lindström 2005). Unlike conventional chemical pulp fibers, HYP fibers are partially covered by lignin, and the free hydroxyl groups exposed on the fiber surface are insufficient. Furthermore, the rigid and rough

nature of lignified fiber surface is not beneficial for good bonding strength, resulting in the unique characteristics and weak bonding capacity of HYP fibers.

As shown in Table 1, the tensile index increased by 48.55%, from 7.93 N·m/g in the R30 fraction to 11.78 N·m/g in the P100/R200 fraction, showing that the shorter fiber fraction had higher tensile strength. On the contrary, the tearing index decreased slightly, from 1.61 to 1.09 $mN \cdot m^2/g$, due to the decrease in fiber length (the length index decreased from 0.44 to 0.09) (Lei *et al*. 2013).

The zero-span tensile strength is a characterization of individual fiber strength. Table 1 shows that the short fiber fraction (P100/R200) had dramatically lower zero-span tensile strength than the long fiber fraction (*i.e.*, 133.57 N·m/g in the R30 fraction *versus* 80.89 N·m/g in the P100/R200 fraction).

Table 1. Properties of Handsheets Made from Different Poplar P-RC APMP Fiber Fractions

Fractions	R30	P30/R50	P50/R100	P100/R200
Tensile Index (N·m/g)	7.93	9.42	10.51	11.78
Tearing Index ($mN \cdot m^2/g$)	1.61	1.54	1.30	1.09
Zero-span Tensile Index (N·m/g)	133.57	123.64	115.69	80.89
Length Index	0.44	0.32	0.21	0.09
Air Permeability (s/100ml)	405	466	548	742
Z-directional Tensile Strength (kPa)	45.37	49.64	59.76	102.36
Bonding Index	2.03	2.13	2.29	2.41

The air permeability of handsheets is defined as the time it takes for 100 mL of air to pass through sheets and is a function of the amount of pores in fiber network. The Gurley porosity (air permeability) of handsheets increased remarkably, from 405 to 742 s/100 mL, when the fiber fraction was changed from R30 to P100/R200, indicating that there was relatively little porosity and good fiber-fiber bonding in the P100/R200 handsheets.

Z-directional tensile strength provides an indication of the bonding strength in the thickness direction of the sheets and depends mainly on the fiber bonding capacity. It is affected to a lesser extent by fiber length. As shown in Table 1, the Z-directional tensile strength dramatically improved, from 45.37 kPa in the R30 fraction to 102.36 kPa in the P100/R200 fraction. At the same time, the bonding index increased from 2.03 to 2.41, proving that the short fiber fraction had remarkable bonding capacity (Vainio and Paulapuro 2007).

The degree of interfiber bonding and fiber deformation of different fiber fractions can be observed in Fig. 1. Compared with the R30 fiber fraction (Fig. 1a), the P100/R200 fiber fraction (Fig. 1b) had a higher degree of collapse and became flatter, increasing the interfiber bonded area and resulting in strong bonding. The R30 fiber fraction had relatively more noncontact area (shadow area) and a thinner shape. Proper calendaring is therefore recommended for HYP-containing paper grades such as LWC or SC papers.

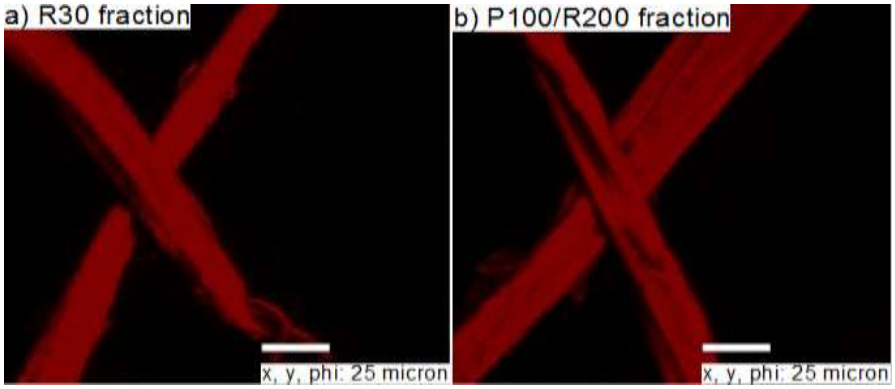

Fig. 1. CLSM images of different poplar P-RC APMP fiber fractions

Fiber Morphologies of Different P-RC APMP Fiber Fractions

The main fiber morphological properties include fiber length, width, curl index, kink index, and coarseness, each of which are significant indices for evaluating fiber quality and affect the properties of pulp and paper products. Seth (1995) pointed out that fiber length can have a significant influence on almost all strength properties including tearing strength, folding endurance, and tensile strength.

Table 2. Fiber Morphologies of Different Poplar P-RC APMP Fiber Fractions

Fiber fractions	R30	P30/R50	P50/R100	P100/R200
Content (%, on pulp)	5.8	23.7	32.5	14.1
Weighted Length (mm)	1.37	0.98	0.76	0.38
Weighted Width (μm)	39.1	32.5	29.8	28.1
Coarseness (μg/m)	264.8	187.2	149.4	116.2
Kink Index (mm^{-1})	0.891	1.007	1.021	1.079
Curl Index (%)	8.645	8.982	9.076	9.185

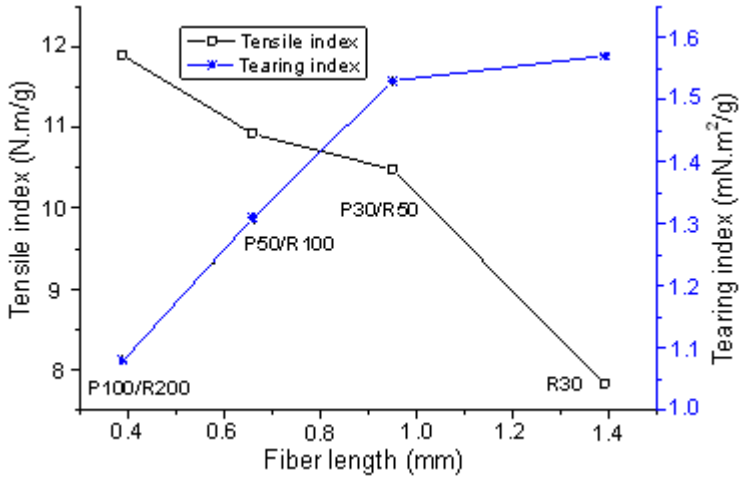

Fig. 2. Effects of fiber length on tensile index and tearing index of handsheets made from different poplar P-RC APMP fiber fractions

As shown in Table 2, the fiber length, width, and coarseness decreased with the increase of the mesh size from 30 to 200. The effect on coarseness was especially dramatic (decreased from 264.8 to 116.2 μg/m). The long fiber fractions (R30 and P30/R50) accounted for 29.5% (5.8 and 23.7%, respectively) of the total fiber and the short fiber fractions (P50/R100 and P100/R200) made up 46.6% (32.5 and 14.1%, respectively). However, the kink index and curl index clearly increased, indicating that the short fiber fractions were subject to bending or kinking due to the thermal or mechanical stresses applied during the refining process. As a result, they were more flexible (an attribute favorable to good bonding strength in sheets) than the long fiber fraction.

Fiber length was the key parameter determining the tearing strength. Decreases in the fiber length decreased the tearing strength. As shown in Fig. 2, the tearing index increased by approximately 50% when the fiber length changed from about 0.40 mm in the P100/R200 fraction to about 0.70 mm in the P50/R100 fraction. However, the tensile index exhibited a decreasing trend with increasing fiber length. There was a tremendous difference in the tearing and tensile strengths because of the huge difference in fiber length between the different HYP fiber fractions. Usually, the long fiber fraction contains lots of surface lignin, limiting sheet strength properties such as the specific bonding strength and tensile strength (Wang *et al*. 2010; 2011).

Specific Surface Area and Volume of Different P-RC APMP Fiber Fractions

The specific surface area is defined as the surface area per unit mass pulp and the specific volume is the volume per unit mass of pulp. Both are significant parameters with regard to pulp fiber quality. As for elastic materials, the same pulp fibers may respond differently under different pressures, and different fiber fractions may respond differently under the same pressure. As shown in Table 3, the long fiber fraction had a larger compressive coefficient (N), showing that the fiber network was more easily influenced by changes in the pressure. Therefore, the long fiber fraction may have better flexibility because it has greater compressibility (M) (Xia *et al.* 1991).

Table 3. Specific Surface Areas and Volumes of Different Poplar P-RC APMP Fiber Fractions

Fiber fractions	S_w (m^2/g)	V (cm^3/g)	N	M
R30	2.96	2.33	0.293	0.086
P30/R50	3.17	2.88	0.297	0.096
P50/R100	3.79	2.93	0.270	0.078
P100/R200	3.99	2.65	0.258	0.074

Note: S_w: specific surface area, V: specific volume, N: compressive coefficient, M: compressibility

Table 3 also shows that the specific surface area increased from 2.96 to 3.99 m^2/g when the fiber fraction was changed from R30 to P100/R200. However, the specific volume increased first and then decreased quickly. The specific volume was measured according to the fluid-permeability methodology (Clark 1978); the evaluation not only includes the cell wall but also the cell cavity. Because of its enormous level of fibrillation and strong swelling ability (Zhou *et al.* 2005), the short fiber fraction had a large specific

surface area. However, when the fiber length and coarseness were so small that the cells wall could burst, more of the cell cavities could be occupied (Xia 1991).

As shown in Fig. 3, the handsheets formed by fibers with larger specific surface area (short fiber fraction) had greater tensile and bonding indices. This is in agreement with the conclusions of Torgnysdotter *et al.* (2007) and Lindström (2005).

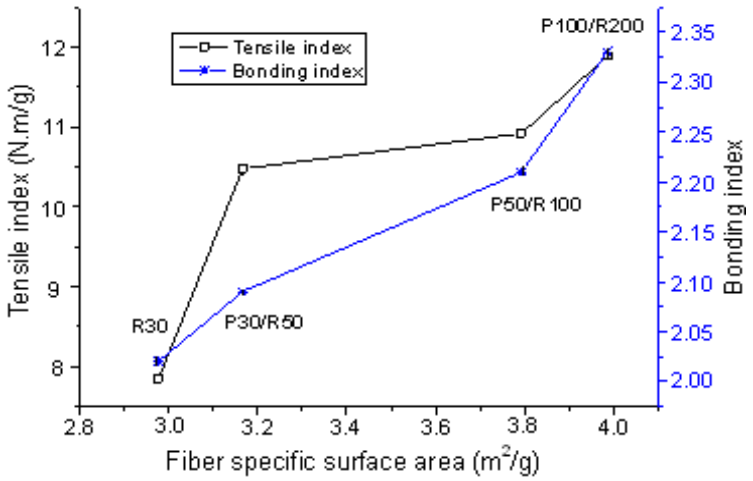

Fig. 3. Effects of fiber specific surface area on tensile and bonding indices of handsheets made from different poplar P-RC APMP fiber fractions

Surface Charge Density of Different P-RC APMP Fiber Fractions

Pulp fiber suspensions are known to hold a negative charge (Lindström 1992), and this phenomenon is attributed to the presence of acidic groups (mainly the carboxyl groups) in lignin and carbohydrates during the chemical pretreatment or fibrillation process. This is important to pulp properties such as fiber flexibility and bonding capacity. Acidic groups can improve the swelling capacity of fibers, increasing flexibility and the number of contact points between fibers.

Table 4 shows the charge densities of different poplar P-RC APMP fractions. The zeta potential is an indirect indication of the charge content and has been shown to be quantitatively related to the surface charge (Patton 1983). The absolute value of the zeta potential increased by 11.10 mV when the fiber fraction varied from R30 to P100/R200. The surface charge density also increased by 66.57% (from 47.93 to 79.84 μmol/g).

Table 4. Charge Density of Different Poplar P-RC APMP Fiber Fractions

Fiber fractions	R30	P30/R50	P50/R100	P100/R200
Zeta Potential (mV)	-46.80	-49.30	-52.00	-57.90
Surface Charge Density (μmol/g)	47.93	56.67	62.36	79.84
Carboxyl Group Content (meq/100 g)	15.34	23.18	27.45	33.29

Note: the pH was controlled at 5-6 and the electrical conductivity was adjusted to 0.3-0.5 ms/cm with KCl solution during the evaluation of zeta potential.

The short-fiber fraction had a relatively larger specific surface area (as shown in Table 3) such that there were more acidic groups exposed on the fiber surface to contribute to the surface charge density compared to the long-fiber fraction. As the main source for charge density on fibers, the carboxyl group exhibited a significant, increasing trend when the fiber fraction changed from R30 to P100/R200. The carboxyl group content in the P100/R200 fraction was approximately twice that of the R30 fraction, partially due to its large specific surface area.

The fiber surface charge had a great influence on the strength properties of the paper. As shown in Fig. 4, increases in the fiber surface charge density resulted in significant increases in the tensile index and the Z-directional tensile strength. The carboxyl groups present made the fibers more flexible and improved the relative bonded area. The P100/R200 fiber fraction, with higher fiber surface charge density, formed handsheets with better tensile and bonding strengths than other fiber fractions.

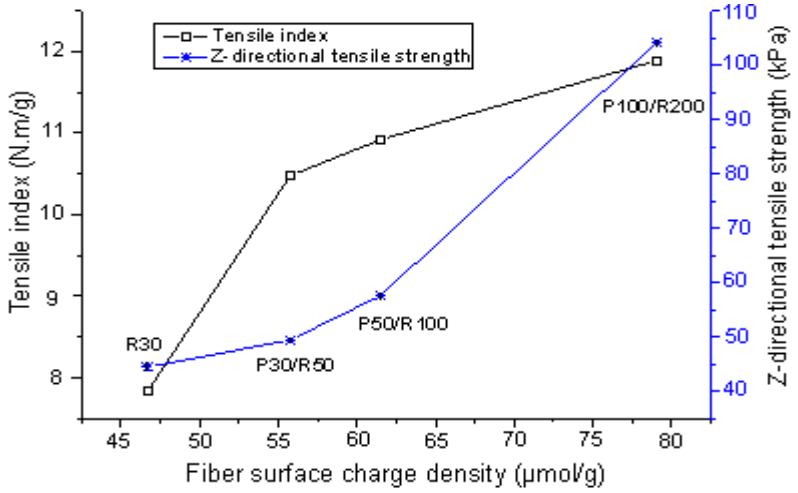

Fig. 4. Effects of fiber surface charge density on tensile index and Z-directional tensile strength of handsheets made from different poplar P-RC APMP fiber fractions

Correlation of Fiber Characteristics and Bonding Strength Properties

The Pearson correlation analysis was introduced to evaluate the response level between the fiber characteristics, tensile index, and bonding index, as shown in Table 5. The dependent variables were the tensile index and the bonding index and the independent variables were fiber length, coarseness, specific surface area, surface charge density, and carboxyl group content.

Table 5. Correlation Analysis among Fiber Characteristics and Both Tensile Index and Bonding Index

	Variables	Fiber Length	Coarseness	S_w	Surface Charge Density
Tensile Index	Pearson Correlation	-0.971*	-0.990**	0.865	0.893
	Significance	0.029	0.010	0.135	0.107
Bonding Index	Pearson Correlation	-0.972*	-0.940	0.977*	0.979*
	Significance	0.028	0.060	0.023	0.021

Note: * Correlation is significant at the 0.05 level; ** Correlation is significant at the 0.01 level.

Significance levels less than 0.05 in Table 5 indicated that the fiber length was correlated with both the tensile index and the bonding index. However, the Pearson correlation between the coarseness and tensile index was strongly negative. In practice, both refining and fines addition could promote interfiber bonding capacity and increase the tensile strength, though they decreased the average fiber length and coarseness (Lei *et al*. 2013). Wang (2011) obtained similar results using multi-linear regression analysis of the tensile index. The specific surface area and surface charge density exhibited positive correlations with the bonding index and nonlinear relationships with the tensile index.

Based on the significance levels shown in Table 5, the bonding capacity of HYP fibers could be improved by increasing their specific surface area and surface charge density during the pulping process. The tensile strength could be controlled by the fiber length and coarseness, which may be achieved by adjusting the refining intensity and related parameters in practice. The HYP fibers with good bonding capacity could be accepted by relatively more paper or paperboard grades.

CONCLUSIONS

1. The fiber characteristics of the various P-RC APMP fractions were quite different. There was only 5.8% R30 fiber fraction and 14.1% P100/R200 fiber fraction. The short fiber fraction (P100/R200) had smaller fiber length (0.38mm) and coarseness (116.2μg/m), but larger specific surface area (3.99 m^2/g) and greater surface charge density (79.84 μmol/g) than the long fiber fraction (R30 fraction).
2. The tensile index increased by 51.85% and the bonding index increased by 15.35%, when the P-RC APMP fiber fractions were changed from R30 to P100/R200.
3. According to the correlation analysis, the P-RC APMP fiber specific surface area and surface charge density were strongly related to the bonding capacity, whereas the fiber coarseness and length were negatively correlated with the tensile index.

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