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The Role of Absorbed Hemicelluloses on Final Paper Properties and Printability

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Abstract: Hemicelluloses isolated from eucalyptus wood were adsorbed onto both bleached eucalyptus kraft pulp and pine kraft pulp as part of a general strategy to investigate their role on final sheet mechanics and physical properties. The tensile indices increased upon hemicelluloses addition and respectively reached a maximum at 9 mg/g and 10 mg/g hemicelluloses adsorption for bleached eucalyptus kraft pulp and pine kraft pulp, whereas the tear index increased depending on the pulp type. The air permeability and surface roughness of the bleached eucalyptus kraft pulp slightly decreased, however, brightness and opacity did not changed. SEM analysis shows that hemicelluloses adsorption increases bleached eucalyptus kraft pulp fibers interaction, whereas the effect of hemicelluloses addition on the beaten pine kraft pulp is unclear. The hemicelluloses adsorption also affected printability. It was found that print through for the bleached eucalyptus kraft pulp hand sheet slightly decreased, but for the bleached pine kraft pulp hand sheet it was unaffected. Print densities were not influenced.

Keywords: Bleached eucalyptus kraft pulp, Bleached pine kraft pulp, Eucalyptus hemicelluloses, Paper properties, Printability

Introduction

Wood is the major global resource used for manufacturing pulp generally by the kraft process. However, although a magnificent industrial process grand in scope, a significant portion of the wood hemicelluloses are removed with lignin and accumulate into the black liquor for minimal energy recovery in the boiler. Lignin has a relatively high heating value of 27 MJ/kg, whereas the heating value of hemicelluloses is just about one half [1]. Moreover, hemicelluloses are not best used for fuel, but have the potential to be used for manufacturing liquid energy and chemicals, such as ethanol, acetone, butanol, and diesel [2,3]. Yet, dissolved hemicelluloses are difficult to separate from black liquor. Recently, many efforts have investigated extracting hemicelluloses before kraft pulping, the so-called VPP or Value Prior to Pulping process [4-6]. Hemicelluloses pre-extraction can decrease chemical usage in the pulping and bleaching process [5-8]. However, to the detriment of VPP, it has impact on the final strength properties of the product from the hemicelluloses loss [9,10]. Particular attention has been cast on this problem from studies looking at adsorption of isolated hemicelluloses onto paper-grade pulps [11-13].

In general, hemicelluloses have a significant influence on many physical properties of paper-grade paper and pulp. Because of a richness in end groups and low molecular weight and hydrodynamic radius of gyration, hemicelluloses can serve as inter-fiber bonding agents to increase inter-fiber bonding area [14] and consequently, strength properties, such as tensile index, burst index and tear index, can be improved [11,12,15]. Hemicelluloses can diminish fibrillar aggregation, increase the accessibility of amorphous cellulose regions to water, and improve water retention [16]. Thus, pulp beatability is promoted and hornification is reduced with hemicelluloses addition [13,17,18]. These latter findings are a consequence of hemicelluloses inclusion on the pulp surface rather than inside fibers for strength development [19].

Although several studies on the effect of hemicelluloses addition on pulp and paper strength properties have been published, comprehensive studies on paper properties of the hemicelluloses addition are lacking [11,12,15]. Hemicelluloses can improve the flexibility and conformability of fibers which strongly affected the structure and properties of paper. In addition, the printability mainly depends on the structure and properties of paper. In our previous work, we investigated the effect of hemicelluloses loss on paper printability and found that print density and print through affected by the structure and properties of paper [20]. To the best of our knowledge, the effects of hemicelluloses adsorption on the structure and printability of paper have not yet been published. The objective here was to develop a more comprehensive understanding of how the addition of hemicelluloses affects final paper properties, especially the paper structure, and printability.

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Experimental

Materials

Dried industrial elemental chlorine free (ECF) bleached eucalyptus kraft pulp (BHKP) and pine (*Pinus radiate*) kraft pulp (BSKP) were provided by Yongkai Paper Group (Nanning, China). The pulps used came by disintegrating kraft bleached paperboards in a laboratory disintegrator at 10,000 revs at RT. The BSKP was beaten at 3,000 revs with a PFI. The beating degree of BSKP and BHKP is 23.7 °SR and 22 °SR, respectively.

Isolation of Eucalyptus Hemicelluloses

Air dried eucalyptus chips were ground using a laboratory mill and screened to a size between 80 mesh and 40 mesh. The powder was stored in sealed packets. The powder was delignified using sodium chlorite under acidic conditions at 75 °C for 3 h. The residue (holocellulose) was extracted with 10 % NaOH at a solid-to-liquor ratio of 1:20 (g/m*l*) for 10 h at 30 °C. The filtrate was acidified with glacial acetic acid until pH 5.5-6.0. The product was mixed with 3 volumes ethanol, centrifugated, washed with 95 % ethanol, and dried under vacuum. The yield of hemicelluloses is roughly 10 % based on raw materials, but was not determined in detail.

The carbohydrate content of the pulps was analyzed by a Dionex HPLC system (ICS-3000) equipped with an electro-chemical detector and a PA20 column following a two-step hydrolysis with 72 % and 4 % sulfuric acid, respectively.

Adsorption of Eucalyptus Hemicelluloses on the Kraft Pulps

Eucalyptus hemicelluloses were dissolved in 10 mM NaCl. A sample of pulp was dispersed in 10 mM NaCl solution and preheated to 80 °C. The hemicelluloses solution was added, the suspension was diluted to 2.5 % consistency, and the mixture was incubated at 80 °C.

The amount of adsorbed hemicelluloses was calculated from the hemicelluloses content in solution before and after adsorption. A separated liquid (0.5 m*l*) was mixed with 4 m*l* $CaCl_2$ solution (4.62 M) and 0.5 m*l* I_2 (0.5 %)/KI solution (2.1 %). Hemicelluloses form colored iodine-complexes in $CaCl_2$ solution. The amount of hemicelluloses in separated liquid was calculated from the absorbance of the colored iodine-complexes at 610 nm using the method of Kohnke [21].

SEM Analysis of Hand Sheets

The surface morphology of the hand sheets was determined using a scanning electron microscope (SEM). The surfaces were coated with gold for analysis and observed using a LEO 530V operating at 10 kV.

Hand Sheets Preparation and Testing

The pulps were made into 60 g/m^2 hand sheets on a Rapid-köthen sheet forming machine (RK-2A KWT, PTI, Austria) according to ISO Standard Method 5269-2.

Structural properties (bulk, air permeability, and PPS roughness), strength properties (tensile, tear, and burst), and optical properties (brightness and opacity) were measured at 23±1 °C and 50±2 % relative humidity following the corresponding ISO standard methods. In addition, the air permeability of paper was measured with an L&W Air Permeance tester (Type 166, Sweden).

Hand sheets were printed on using an IGT printability tester (Model AIC2-5T2000). The paper received standard magenta offset ink with 0.2 m/s printing speed and 625N printing force. The printed paper strips were kept in a standard test room for at least 6 h after printing. The print density was measured with an X-rite 530 Spectrodensitometer (X-Rite Color Management, USA), according to SCAN-P 36:02. Print through testing was carried out with a Color Touch PC (Technidyne, USA) and calculated according to SCAN-P 36:02.

Results and Discussion

Adsorption of Eucalyptus Hemicelluloses on BHKP and BSKP

The time-dependent adsorption of eucalyptus hemicelluloses on BHKP and BSKP is shown in Figure 1. The hemicelluloses adsorption on BHKP was rapid during the first 60 min after which a steady state was reached in approximately 180 min. Hemicelluloses adsorption onto BSKP had a similar trend but the adsorption amount was slightly higher. BHKP and BSKP have similar beating degree, but BSKP was beaten before hemicelluloses adsorption and BHKP was not. So BSKP has more flakes and filaments detached from the fiber surface than BHKP, as shown in Figure 2. This may lead to the high hemicelluloses adsorption amount on BSKP. In

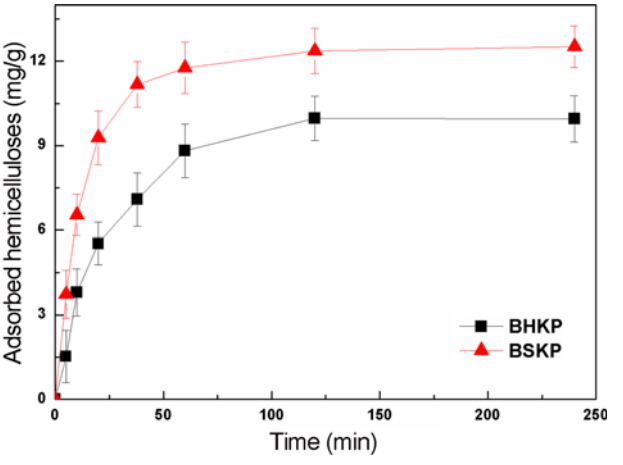

Figure 1. Adsorption amount of eucalyptus hemicelluloses on BHKP and BSKP as a function of time. The initial concentration of eucalyptus hemicelluloses was 40 mg/g pulp fiber.

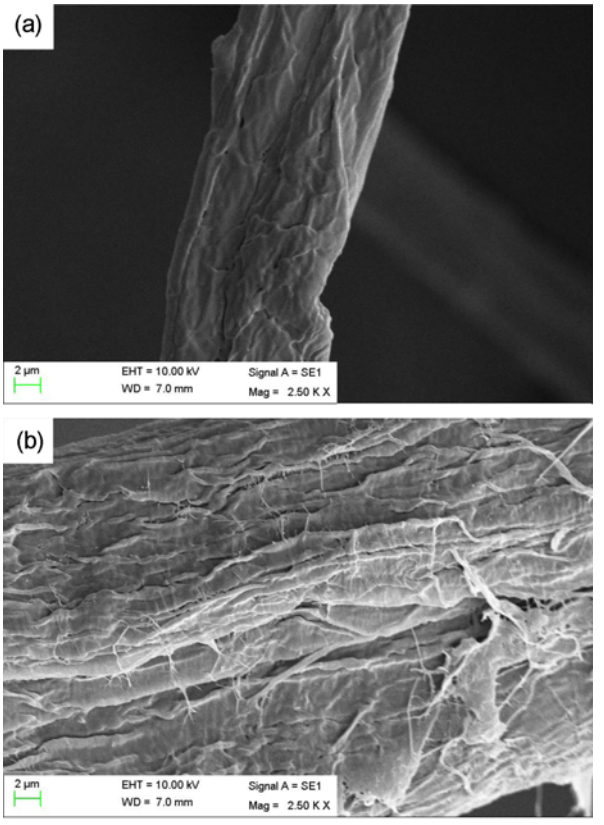

Figure 2. SEM of BHKP fiber (a) and BSKP fiber (b).

addition, xylan tends to strongly interact with hardwood pulp, but weakly interact with softwood pulp [22,23].

In order to study the mechanism of eucalyptus hemicelluloses adsorption onto kraft pulps, two kinetic models [24,25], Pseudo first-order and Pseudo second-order were used to analyze the experimental data. Linear plots of $\log(q_e-q_t)$ against time (t) and t/q_t versus time (t) are plotted (Figure 3) in order to understand the applicability of Pseudo first-order and Pseudo second-order for eucalyptus hemicelluloses adsorption onto BSKP and BHKP. The correlation coefficient values and the calculated q_e are shown in Table 1. The linearity of the plots (R^2) (Table 1) and the linear fit (Figure 3) indicate that the pseudo-second order is more qualified than the pseudo-second order for the eucalyptus hemicelluloses adsorption onto kraft pulp fibers. In addition, the equilibrium adsorption amount (Table 1) predicted by the pseudo second-order is very close to the measured value. The results show that the adsorption of hemicelluloses on BHKP and BSKP follow Pseudo second-order kinetics. Hemicelluloses function occurred after shear adsorption onto the pulp fiber. The xylan-type hemicelluloses adsorption formed a junction zone on the fiber surface and unsubstituted linear sections presented themselves as loops and/or tails. The unsubstituted linear sections likely interacted with other unsubstituted

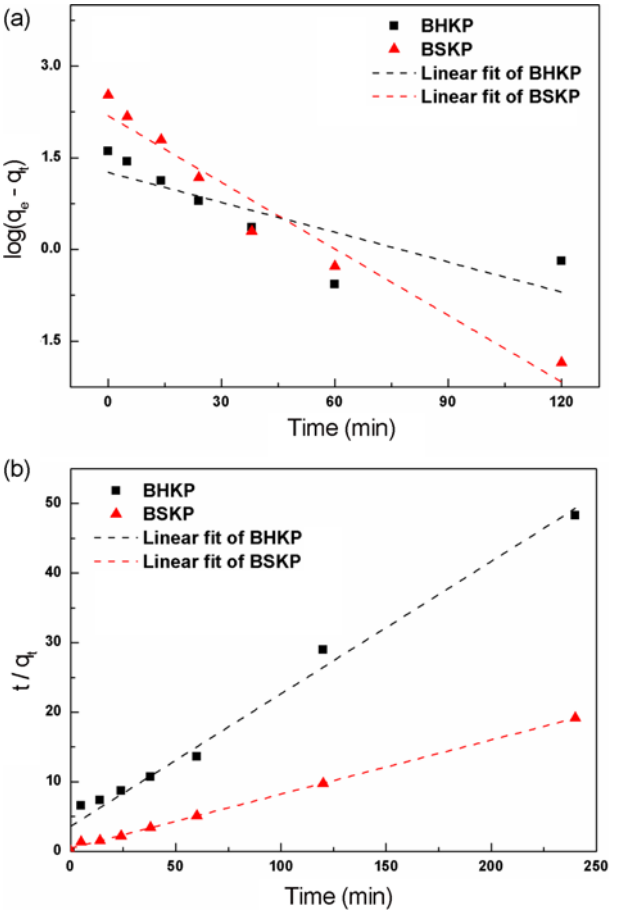

Figure 3. Pseudo-first order kinetics (a) and Pseudo-second order kinetics (b) of eucalyptus hemicelluloses adsorption on the BHKP and BSKP fibers.

Table 1. Kinetic parameters for eucalyptus hemicellulose on BHKP and BSKP

	Kinetic models	k	q_e	R^2	q_e, exp[a]
BHKP	Pseudo first-order	0.038	10.7	0.978	10.0
	Pseudo second-order	0.010	10.2	0.988	
BSKP	Pseudo first-order	0.0356	8.4	0.968	12.5
	Pseudo second-order	0.011	12.9	0.998	

[a]Experimental data.

linear sections of the free xylan [23,26,27].

The amount of hemicelluloses adsorbed (mg hemicelluloses per g pulp) as a function of dosage is shown in Figure 4. The adsorption amount on the BHKP and BSKP increased with increasing hemicelluloses dosage. When the hemicelluloses dosage was 4 %, the amount of hemicelluloses adsorption on BHKP and BSKP, respectively, reached 1.01 wt-% and 1.15 wt-% of the pulp fiber, while above this point the amount of hemicelluloses adsorption plateaued.

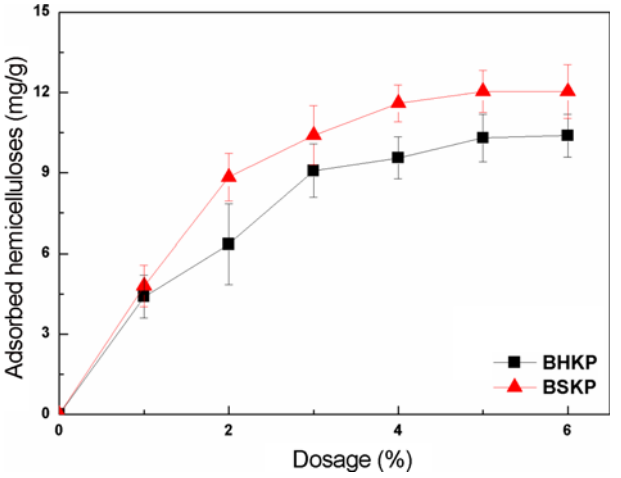

Figure 4. The adsorbed amount of eucalyptus hemicelluloses on BHKP and BSKP.

Influence of Eucalyptus Hemicelluloses on Properties of Hand Sheets

Influence of Eucalyptus Hemicelluloses Adsorption on Structural and Optical Properties

Hemicelluloses are polysaccharides that have an amorphous structure and variegated chain chemical composition. Hemicelluloses adsorption onto a pulp fiber can change fibrillar aggregation and absorption capacity of the amorphous cellulose region [16]. However, does hemicelluloses adsorption also result in different structural properties such as bulk, surface roughness, and air permeability? Such changes after eucalyptus hemicelluloses addition are shown in Table 2 and Figure 5. For both pulps, it did not affect hand sheet bulk. The amount of hemicelluloses adsorption affected the air permeability of BHKP and the air permeability increased with hemicelluloses adsorption BHKP, as shown in Figure 5. For BSKP, the air permeability was not improved with hemicelluloses adsorption. From Figure 5, the PPS roughness of BHKP had a very small decrease with hemicelluloses adsorption at about 10 mg/g, whereas the PPS roughness of BSKP was not changed with hemicelluloses adsorption. It can be hypothesized that the BSKP pulps formed a compact paper structure, as seen in the Figure 8(a), then the eucalyptus hemicelluloses addition had no effect on air permeability and PPS roughness.

The optical properties of BHKP and BSKP hand sheets indicated (as shown in Table 2) that eucalyptus hemicelluloses adsorption had no influence on ISO brightness and opacity.

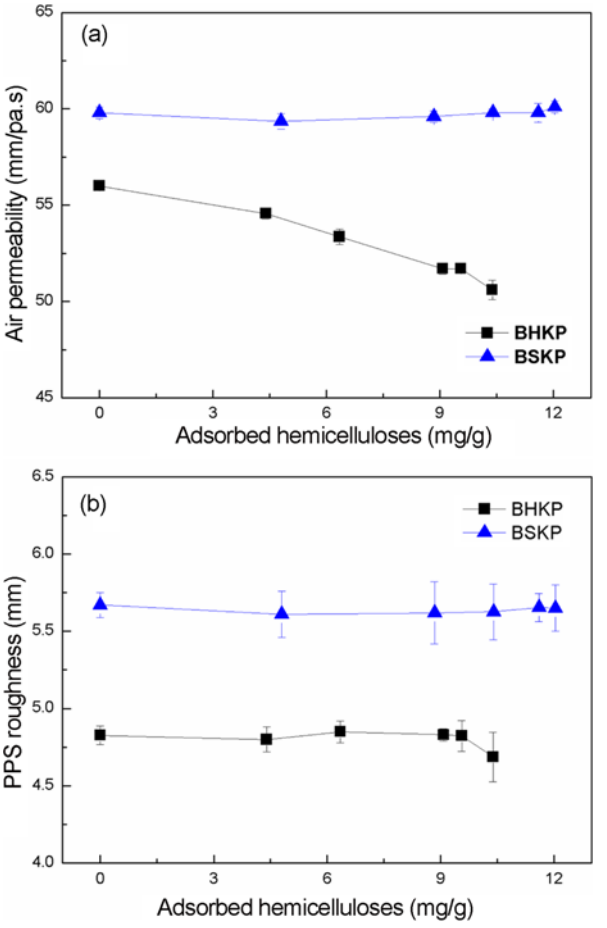

Figure 5. Influence of eucalyptus hemicelluloses adsorption on air permeability (a) and PPS roughness (b).

Influence of Eucalyptus Hemicelluloses Adsorption on Strength Properties

The effect of eucalyptus hemicelluloses adsorption on the strength properties of BHKP and BSKP were also evaluated. The results for tensile index are shown in Figure 6(a). For BHKP, the tensile indices all increased to reach a plateau of 28 % relative to the BHKP control sample at 9 mg/g hemicelluloses adsorption (about 4 % hemicelluloses dosage). For BSKP, the tensile indices show a relatively small degree of improvement at eucalyptus hemicelluloses adsorption below 10 mg/g (about 4 % hemicelluloses dosage) and then the change of tensile index did not become clear as the

Table 2. Influence of eucalyptus hemicelluloses adsorption on bulk and optical properties

Sample	BHKP				BSKP			
	0	3	4	6	0	3	4	6
Bulk (cm^3/g)	2.04	1.97	1.97	1.97	1.61	1.63	1.60	1.65
Brightness (%)	87.1	86.4	86.5	87.2	85.9	87.7	86.9	86.7
Opacity (%)	85.5	85.6	86.1	85.7	67.1	67.1	67.7	67.6

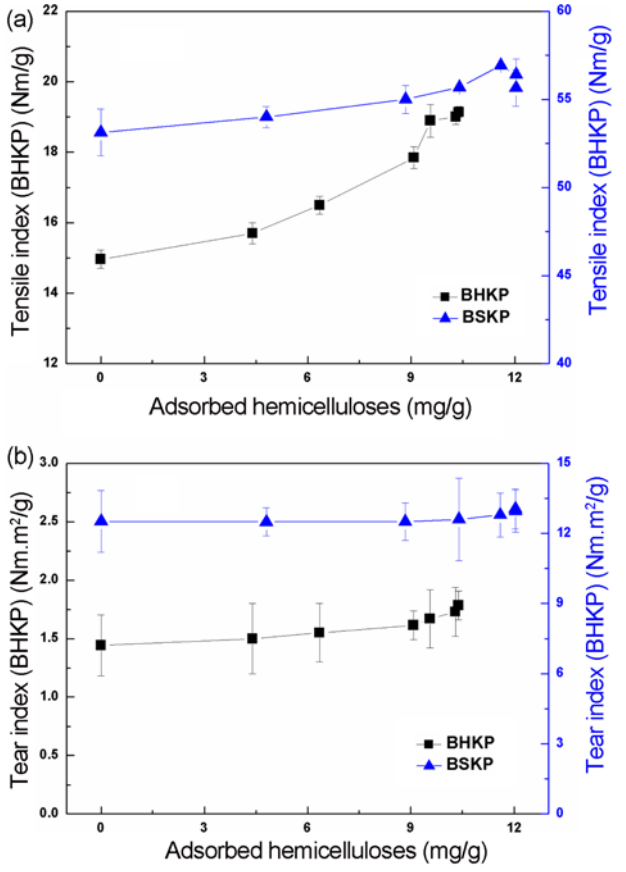

Figure 6. Influence of eucalyptus hemicelluloses adsorption on the tensile (a) and tear (b) indices.

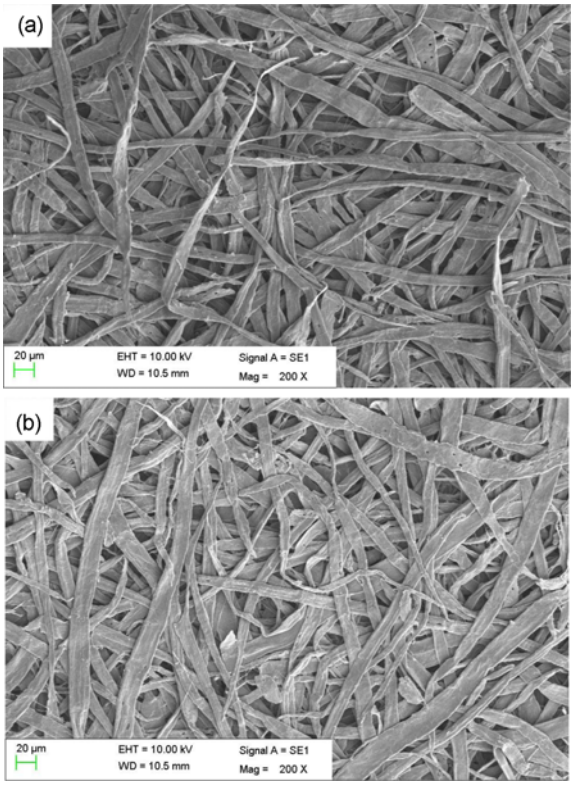

Figure 7. SEM of BHKP hand sheets with or without eucalyptus hemicelluloses adsorption; (a) BHKP and (b) BHKP with 4 % hemicelluloses dosage.

dosage increased beyond 10 mg/g. Maximum increases in tensile indices with hemicelluloses addition were 7 % compared to the BSKP control sample, much lower than that of adsorbed BHKP. According to Figure 6(b), the tear index changes depending on the type of pulp. For example, the tear index of the BHKP increased by 24 % when adding hemicelluloses, but the eucalyptus hemicelluloses addition in BSKP did not affect tear index.

The hemicelluloses used in this study were isolated from eucalyptus wood with NaOH and precipitated from ethanol. According to carbohydrate analyses, xylan is the main polysaccharide component displaying 82 % of the dry mass. There are only low concentrations of araban and glucan accounting for 3 % and 0.8 %, respectively. The eucalyptus hemicelluloses are xylan-type polysaccharides and have more side chains compared to cellulose. Hemicelluloses adsorption on pulp can provide a higher degree of hydrogen bond between polysaccharides and increase inter-fiber bonding to significantly enhance mechanical and structural properties of the final paper [11,29].

SEM

Figures 7 and 8 show SEM images of fiber interactions with and without eucalyptus hemicelluloses addition. BHKP with 4 % hemicelluloses dosage had more compact interactions among fibers than BHKP without hemicelluloses adsorption. Eucalyptus hemicelluloses adsorption increases inter-fiber bonding. From Figure 8(a), BSKP without hemicelluloses adsorption already had a compact interaction, whereas hemicelluloses adsorption had no clear effect on the fiber interactions in BSKP.

The Effect of Eucalyptus Hemicelluloses Adsorption on Printability

Print density and print through are important factors for final products. Print density influences the appearance of a range of colors in the print products. Print through reflects visible prints on the reverse side, an undesirable result in manufactured printing products [29]. Our previous work showed that removal of hemicelluloses from bleached eucalyptus kraft pulps affects printability, while extensive removal of hemicelluloses can result in decreased print density and print through [20]. Hemicelluloses are the important component in the pulp fiber; the removal of hemicelluloses can change the surface energy of fiber and increase surface roughness and the porosity of the paper. The changes of paper and/or fiber lead to change the ink

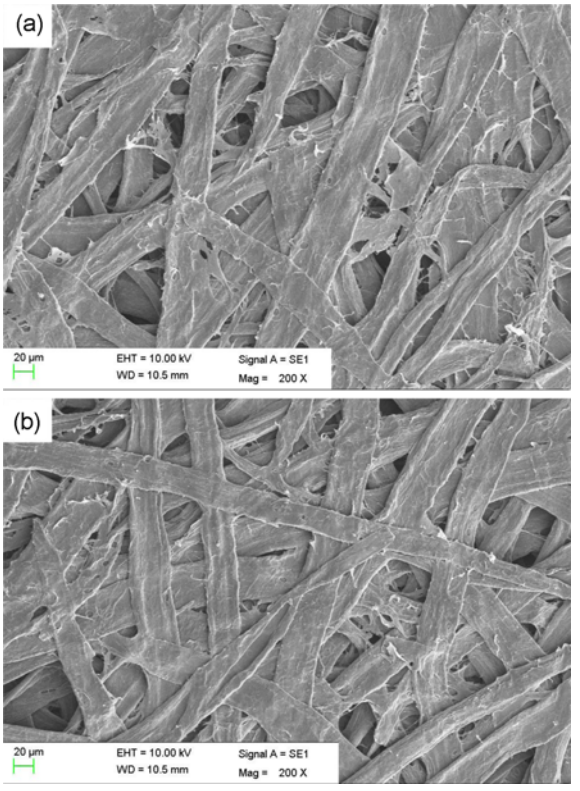

Figure 8. SEM of BSKP hand sheets with or without eucalyptus hemicelluloses adsorption; (a) BSKP and (b) BSKP with 4 % hemicelluloses dosage.

penetration which influences printability.

The adsorption amount of hemicelluloses on BHKP and BSKP reached a plateau after 4 % hemicelluloses dosage. So, we compared the original BHKP and BSKP papers and the BHKP and BSKP papers with 4 % hemicelluloses dosage. Figure 9 shows the variation of print density and print through with the amount of ink. According to Figure 9(a) and (b), hemicelluloses addition had no obvious effect on the print density of the BHKP and BSKP hand sheets. A similar phenomenon was observed in our previous work, where a slight removal of hemicelluloses from kraft pulp did not decrease print density [20].

According to Figure 9(c), print through slightly decreased with eucalyptus hemicelluloses adsorption onto BHKP for high amount of ink. During the drying process of the printed products, part of the ink penetrates into the inter-fiber spaces by capillary action and then wick into the intra-fiber and fiber cell wall pores or spread along the fiber surface [29]. As mentioned previously, hemicelluloses adsorption changed the porosity of the paper leading to reduced ink penetration. In addition, the hemicelluloses adsorption changes the fiber surface energy which was affected by the component of fiber [30]. The fiber surface free energy affects the penetration and spreading of ink [31]. When the amount of ink on paper is below 4 g/m^2, print through was not affected by the hemicelluloses addition. The possible explanation is that the amount of ink on the paper only covers the paper surface and

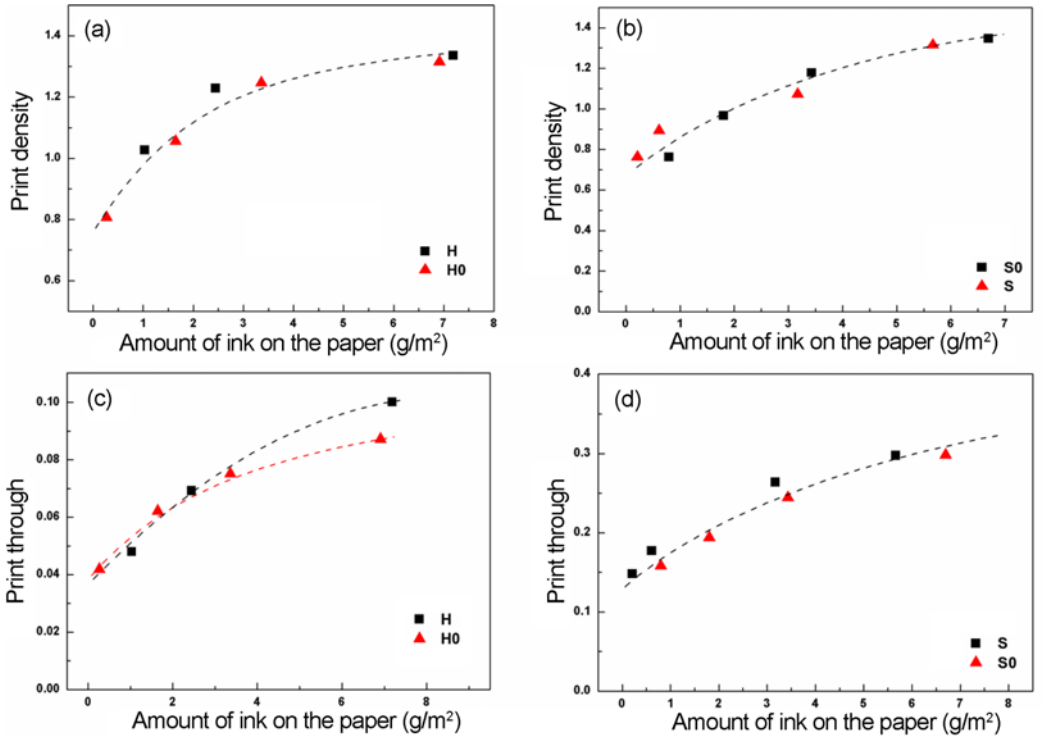

Figure 9. Print density and print through as a function of ink on hand sheets; H: BHKP hand sheet, H0: BHKP hand sheet with hemicelluloses adsorption, S: BSKP hand sheet, S0: BSKP hand sheet with hemicelluloses adsorption.

ink penetration is low and hardly leads to print through. Print through in the BSKP hand sheet was not affected by hemicelluloses adsorption (Figure 9(d)).

Conclusion

1. Eucalyptus hemicelluloses adsorbed onto ECF bleached eucalyptus kraft pulp and pine kraft pulp follow pseudo second-order kinetics. The adsorption q_e on BSKP was slightly higher than that of BHKP.
2. Bulk of BHKP and BSKP were not affected by hemicelluloses adsorption. Air permeability and surface roughness of BHKP slightly decreased, whereas air permeability and surface roughness of BSKP was unaffected. The optical properties for both pulps were not changed.
3. For BHKP and BSKP, the tensile indices increased with hemicelluloses addition and respectively reached a maximum at 9 mg/g and 10 mg/g hemicelluloses adsorption. The tear index of BHKP after hemicelluloses addition slightly increased, whereas the tear index of BSKP was unaffected.
4. SEM analysis shows that the fibers of BHKP with hemicelluloses addition had more compact interactions than unmodified fibers.
5. Print through of BHKP slightly decreased with hemicelluloses addition, whereas print through of BSKP was unaffected by the hemicelluloses addition. The effects of hemicelluloses addition on print density for both pulps were not obvious.

Acknowledgments

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