Impact of Drying on the Quality of Bamboo Kraft Pulps

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This study investigates how drying affects the quality of bamboo kraft pulps. Two bamboo pulps, cooked to different kappa numbers (*i.e.* 10 and 26) and D(EOP)D bleached to approximately the same brightness, were used to examine the relationship between cooking, drying, refining, and pulp/fiber properties. Drying of the two pulps caused, as expected, a loss in tensile and burst strength while the tear index was improved. The bleached high kappa pulp required less energy to reach a certain Schopper Riegler value and exhibited greater strength properties than the low kappa number pulp. These differences were also maintained after drying. Results showed that the properties of the pulp before drying determined the final strength potential of the pulp after drying. Thus, kraft cooking of bamboo to high kappa number prior to bleaching gave pulps with improved response to refining and pulp strength properties, which in turn influenced the properties of the dried pulps.

Keywords: Bamboo; Dislocation; Drying; Fiber dimensions; Hornification; Kinks; Kraft cooking; Strength properties; Xylan

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INTRODUCTION

Hornification is a term used to describe structural changes in chemical pulp fibers caused by water removal during drying and/or pulp fiber recycling. In general, hornification is defined as the relative reduction in water holding capacity, *i.e.* water retention value (WRV), which also contributes to a lower swelling ability of pulp fibers after drying. A review of what happens to cellulosic fibers during papermaking and recycling has recently been published by Hubbe *et al.* (2007). The loss in swelling ability of "once dried fibers" is well known and is thought to depend on an increase in inter-fibrillar bonding through the cross-linking between cellulose fibrils when the fiber wall collapses during drying. This indirectly effects the pore size distribution, reduces the specific fiber surface area (Stone and Scallan 1965; Wang *et al.* 2003), reduces fiber surface fibrillation (Klungness and Caufield 1982), and decreases the elasticity of the fiber wall (Scallan and Tigerström 1992). In general, the hornification phenomenon is associated with the formation of irreversible or partially reversible hydrogen bonding in pulp fibers upon drying. However, Diniz *et al.* (2004) proposed that hornification is due to lactone bridge formation in lignocellulosic materials upon drying.

A consequence of drying-induced structural changes is the formation of a stiff fiber with a collapsed outer surface, resulting in lower bonding potential and thus also paper strength properties. The most common and commercial approach to restore the swelling ability of dried pulp fibers is refining. Refining causes some of the initial bonds between the cellulose microfibrils within the cell wall to rupture, thus allowing osmotic and entropic forces to produce increased fiber swelling. Wang *et al.* (2003) showed that even though the pore volume of previously dried pulps could be recovered by refining, normal levels of refining did not reopen some small pores closed during drying, *i.e.* refining does not completely reverse hornification. Several investigations have shown that the magnitude of hornification is related to the content of hemicelluloses in the pulp, with high hemicellulose content reducing the tendency of fibers to undergo drying induced property changes of hornification (Spiegelberg 1966; Oksanen *et al.* 1997; Cao *et al.* 1998; Hult *et al.* 2001; Rebuzzi and Evtuguin 2006; Moss and Pere 2006).

Prevention of hornification can be done by introducing steric and electrostatic groups into pulp fibers by means of chemical modification of the cellulose hydroxyl groups. Introducing anionic charge by means of carboxymethylation or TEMPO-oxidation has been shown to be a promising approach to reduce the effect of hornification during drying (Lindström and Carlsson 1982; Laivins and Scallan 1993; Saito *et al.* 2006; Lasseuguette 2008). Carboxyl groups increase pulp fiber accessibility and affinity to water. Furthermore, Köhnke (2010) showed recently that modification of fibers by adsorption of xylan on the fibers before drying preserved a considerable part of fiber swelling, wall porosity, specific fiber surface area, and wet fibre flexibility observed in the never dried state. This in turn provided “once dried” pulp fibers with increased tensile strength and beatability. Other proposed technologies to reduce the effect on fiber hornification are adsorption of polyelectrolytes or CMC on the pulp fibers (Aarne *et al.* 2010) and addition of sucrose (Bracato and Banerjee 2010). The effect of drying *i.e.* drying procedure, temperature, and time have also been studied recently (Brancato and Banerjee 2010; Luo and Zhu 2011).

Several publications discuss the effect of hornification of chemical pulps from a fiber and paper point of view as well as different ways to restore pulp properties by means of refining and chemical means, while process-related issues have seldom been discussed. The objective of this study was therefore to examine the correlation between bamboo kraft cooking procedures and the pulp/fiber properties before and after drying.

EXPERIMENTAL

Cooking and Bleaching

Bamboo (3-5 years old, mixed southern species) was supplied by the Guangdong Shaoneng Group Co. Ltd., Zhuji Paper Industry Branch, Shaoguan city, Guangdong Province, China. The bamboo chips were sorted by hand to remove pin and oversized chips and knots. The accepted bamboo chips had a thickness of 5 mm (max) and length of ca. 35 mm. Technical grade NaOH and Na_2S were used in the pulping process, in which the liquor-to-wood ratio was 4:1. After cooking, the pulp was thoroughly washed, defibrated, and screened on a flat screen with 0.2 mm slots. Accepted pulp was dewatered in a centrifuge and homogenized. The unbleached bamboo pulps were then D_0(EOP)D_1 bleached to a final brightness of 88% ISO or above. Conditions used in kraft cooking and subsequent D_0(EOP)D_1 bleaching are shown in Tables 1 and 2 together with the pulp properties obtained.

Table 1. Kraft Conditions of Bamboo and the Resulting Kraft Pulp Properties

Sample	Effective alkali (%)	Sulfidity (%)	Cooking temp. (°C)	Cooking time (min)	Yield (%)	Kappa number	Brightness (%ISO)	Viscosity (mL/g)
KP10	23	25	155	180	46.4	9.6	41.0	1060
KP26	20	25	145	75	52.1	24.6	35.1	1197

Table 2. Details of Bleaching Conditions and Basic Properties of the Bleached Bamboo Pulps

Stage	Issues	KP10	KP26
D_0	Temp.(ºC)	65	70
	Time (min)	45	45
	Act. Cl (kg/t)	20	50
	NaOH (kg/t)	1.3	6.5
	Final pH	2.8	2.1
EOP	Temp.(ºC)	75	80
	Time (min)	60	60
	NaOH (kg/t)	9.5	17.0
	H_2O_2 (kg/t)	5	7
	Mg^{2+} (kg/t)	0.15	0.30
	O_2 press., Mpa	0.3	0.3
	Final pH	11.0	10.6
D_1	Temp.(ºC)	75	75
	Time (min)	240	240
	Act. Cl (kg/t)	10	20
	NaOH (kg/t)	1.5	5.0
	Final pH	4.1	4.4
Pulp properties	Kappa number	0.9	1.4
	Brightness (%ISO)	87.9	89.3
	Viscosity (mL/g)	956	1204
	Brightness reversion (%)	0.69	0.73

Method for Simulation of Sheet Drying

Handmade sheets with a grammage of 100g/m^2 for simulation of sheet drying were performed by disintegrating the never-dried pulps for 15000 revolutions at 3% pulp consistency in a disintegrator and sheet forming in a Finnish sheet former. Sheets were then pressed in a hydraulic press at a pressure of 14 to 15 kg/cm^2 for 5 min. The second pressing was performed in a roll press between blotters until a dryness of 45% was reached. The sheets were thereafter dried between blotters in a drum heater at 58ºC for ca. 2 h, or until a dryness of 85 to 88% was reached (checked by weighing). Sheets were then cooled for 5 minutes and placed in plastic bags until use.

Refining and Storage

The dried and never dried bleached bamboo pulps were beaten in a laboratory PFI-mill at AkzoNobel, Bohus, Sweden, according to ISO 5264-2: 2002. Handmade sheets (60 g/m^2) were prepared immediately after refining according to the ISO standard method 3688 with white water circulation where six circulations were done prior to the final preparation.

Analysis of Pulp and Paper Properties

All pulp samples, unbleached and bleached, were analyzed for kappa number, viscosity, and brightness according to ISO standard 302, 5351, and 2470, respectively. The refined pulps were immediately after refining characterized for SR-number (ISO 5267-1:99), fiber dimensions and fiber defects (*i.e.* shape factor and number of kinks) using a Fibre tester® at AkzoNobel, Bohus, Sweden. Fiber dislocations were determined using HCL-treatment (Ander *et al.* 2008). The content of carbohydrates was determined according to Dahlman (2000). The CyberMetrics analyzer at CTP (France) was used to determine the wet fiber flexibility. The mechanical strength properties (*i.e.* tensile, burst, and tear) were determined according to ISO 1924-3, 2758, 1974:1900, respectively.

Scanning Electron Microscopy (SEM)

Paper sheets made from the never dried and dried unrefined and refined (2000 revs) pulps were examined using a SEM at 10 kV. Paper samples (*ca.* 1 cm^2) were cut from the sheets, mounted on stubs, and examined in the environmental mode at 0.9 Torr using a LFD detector.

RESULTS AND DISCUSSION

Effect of Hornification on Pulp/Fibre and Paper Sheet Properties

Two bamboo pulps, cooked to different kappa numbers and then D(EOP)D bleached to similar levels of ISO brightness, were used to investigate the relationship between the refining of never-dried and dried pulps and pulp/fiber properties. It should be pointed out that PFI milling used in this study differs somewhat in refining effect compared to industrial refiners. According to Kerekes (2002), PFI-milling gives higher internal fibrillation and lower external fibrillation and fiber shortening compared to industrial refiners. However, even though PFI-milling does not reflect industrial refining totally, it is a valuable tool for comparing pulps in laboratory scale.

An overview of the results for the pulp and sheet properties is presented in Table 3. The high kappa number pulp (KP26) required less energy to reach a certain SR value and also exhibited higher strength properties, especially tensile, burst, and tear indexes at any given degree of refining (*i.e.* number of revolutions in the PFI mill) in comparison with the low kappa pulp (KP10). The initial strength properties of the high kappa pulp (KP26) were about 78% higher than the low kappa pulp (KP10), and this difference remained almost constant throughout refining; *i.e.* the strength properties of the unrefined pulp characterized the pulp to be refined. These results are in good agreement with previous studies (Heijnesson-Hultén *et al.* 2010).

As expected, drying resulted in pulps which were more difficult to refine and had lower strength properties compared with the never dried pulps at all degrees of refining (Table 3, Figs. 1 and 2). The strength properties could, however, be restored to some extent by refining, although much more energy was required in the refining procedure to reach a certain SR and/or strength value (Figs. 1 and 2).

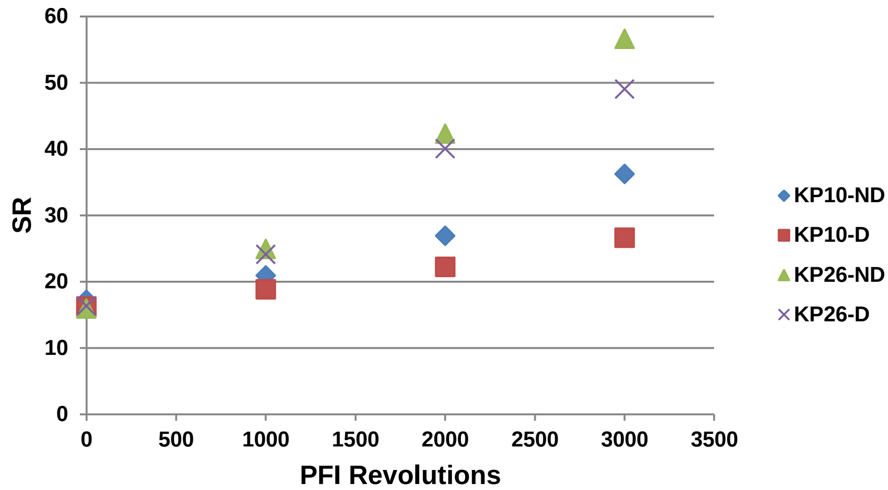

Fig. 1. Effect of refining on the Schopper Riegler of never dried (ND) and dried (D) bamboo pulps

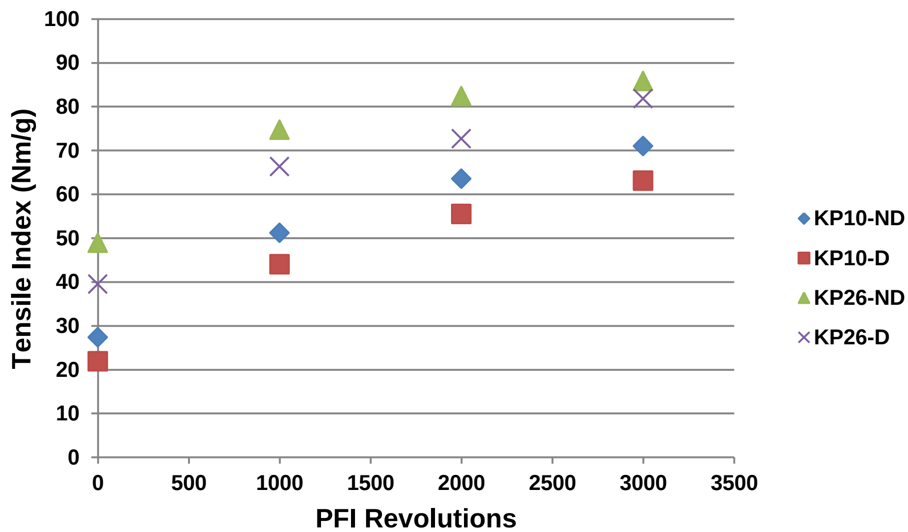

Fig. 2. Effect of refining on the tensile index of the never dried (ND) and dried (D) bamboo pulps

Several investigations have shown that the content of hemicelluloses in a pulp is an important factor when it comes to restoring the strength properties of pulp fibers (Spiegelberg 1966; Oksanen *et al.* 1997; Cao *et al.* 1998; Hult *et al.* 2001; Rebuzzi and Evtuguin 2006; Moss and Pere 2006). However, even though the content of hemicelluloses of the bleached high kappa pulp was *ca*. 1 % higher (Table 4) than in the low kappa pulp, no difference in restoration was noted between the two pulps. It is possible that the difference in content of hemicelluloses between the pulps was too low to show any beneficial effect on refining and strength restoration. The more severe bleaching of the high kappa number pulp used to reach the same brightness as the pulp with low kappa number did not influence the hornification and strength restoration. In fact, the difference in tensile index between the never dried and dried pulps remained almost constant throughout refining. Furthermore, KP26-ND and KP26-D (high kappa pulps), even after drying, were easier to refine resulting in paper sheets with higher tensile index and burst strength compared with KP10-ND (never dried low kappa pulp) at all degrees of refining. This indicates that the initial properties of the pulp before drying and refining are of major importance for final pulp quality. Thus, kraft cooking of bamboo pulps to high kappa number prior to bleaching gives pulps with improved response to refining and pulp strength properties which in turn influences the properties of the dried pulps.

Table 3. Refining and Mechanical Strength Properties of Bleached Bamboo Paper Sheets Prepared from Never Dried (ND) and Dried (D) Pulps

Sample	PFI (revs.)	SR	WRV (g/g)	Density (kg/m^3)	Tear (mNm^2/g)	Burst (kPam^2/g)	Tensile (Nm/g)	TEA (J/g)	Tens. stiff. (mNm/kg)
KP10-ND	0	17.2	1.34	501	7.3	1.3	27.4	0.38	5.0
	1000	20.9	1.45	577	8.8	3.0	51.2	1.06	6.7
	2000	26.9	1.52	622	8.4	4.0	63.6	1.44	7.4
	3000	36.2	1.60	654	7.9	4.5	71.0	1.70	7.8
KP10-D	0	16.2	1.03	463	7.5	1.0	21.9	0.25	4.2
	1000	18.8	1.30	535	10.1	2.5	44.1	0.74	6.4
	2000	22.2	1.41	578	9.5	3.5	55.5	1-25	6.7
	3000	26.6	1.47	604	9.1	4.0	63.1	1.54	7.2
KP26-ND	0	15.9	1.51	524	10.1	2.7	48.9	0.69	6.6
	1000	24.9	1.67	604	8.5	4.7	74.8	1.44	7.8
	2000	42.3	1.79	653	8.2	5.3	82.4	1.69	8.2
	3000	56.6	1.89	678	7.5	5.8	85.8	2.01	8.2
KP26-D	0	16.3	1.16	504	10.5	1.9	39.5	0.52	5.9
	1000	24.1	1.49	578	9.6	3.9	66.4	1.24	7.5
	2000	40.0	1.62	617	9.3	4.7	72.7	1.49	7.6
	3000	49.0	1.76	647	8.7	5.0	81.8	1.89	8.1

Table 4. Carbohydrate Composition of the Bleached Bamboo Pulps

Sample	Glucan (%)	Mannan (%)	Xylan (%)	Galactan (%)	Arabinan (%)	Total (%)
KP10	81.0±2.11	<0.1	17.4±0.53	<0.1	0.67±0.02	99.6
KP26	80.2±0.23	<0.1	18.2±0.10	<0.1	0.97±0.02	99.6

It is well known that differences in fiber dimensions are important for influencing the response to refining as well as strength properties. In our study, the length-weighted fiber length was lower for the low kappa pulp (KP10) than high kappa pulp (KP26) but decreased for both pulps upon drying (Table 5). This will certainly influence the final pulp strength properties. Fiber defects (*i.e.* kinks and dislocations) are also closely related to strength properties and are introduced when pulp fibers are subjected to compression and/or mechanical stresses, for example, during pulping, bleaching, and refining. The number of dislocations per mm fiber of the high and low kappa number pulp was 0.50

and 1.22, respectively. Therefore cooking to high kappa number introduces fewer dislocations in the fiber wall, and the fibers also show less sensitivity towards mechanical stresses and/or compression compared with the low kappa pulp.

Table 5. Fiber Properties of Refined Never Dried (ND) and Dried (D) Bleached Bamboo Fibers

Sample	PFI (revs.)	Fiber length (mm)	Fiber width (µm)	Shape Factor (%)	Kinks per mm	Kinks per fiber	WRV (g/g)
KP10-ND	0	1.52	17.9	81.3	0.87	1.08	1.34
	1000	1.48	18.2	85.1	0.70	0.84	1.45
	2000	1.50	18.7	85.5	0.65	0.80	1.52
	3000	1.47	18.7	85.8	0.62	0.75	1.60
KP10-D	0	1.48	17.7	81.7	0.89	1.07	1.03
	1000	1.48	18.0	85.0	0.69	0.84	1.30
	2000	1.51	18.5	85.7	0.64	0.77	1.41
	3000	1.44	18.8	85.6	0.67	0.79	1.47
KP26-ND	0	1.60	18.0	86.2	0.51	0.65	1.51
	1000	1.59	18.5	86.9	0.43	0.55	1.67
	2000	1.58	18.5	86.4	0.49	0.62	1.79
	3000	1.54	18.7	86.3	0.52	0.64	1.89
KP26-D	0	1.57	17.7	86.0	0.53	0.66	1.16
	1000	1.55	18.2	86.5	0.49	0.62	1.49
	2000	1.57	18.5	86.3	0.48	0.60	1.62
	3000	1.55	18.6	86.1	0.55	0.68	1.76

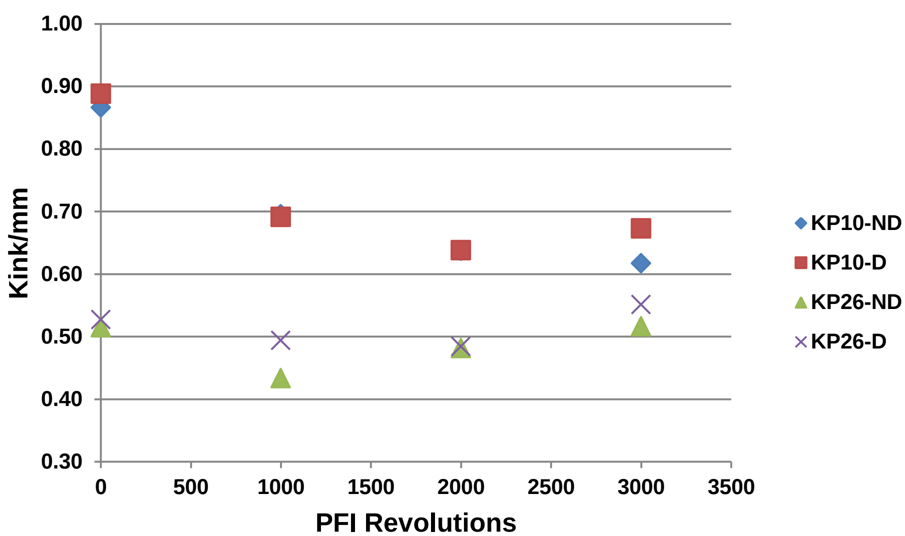

Fig. 3. Effect of refining on the number of kinks per mm fiber of the never dried (ND) and dried (D) bamboo pulps

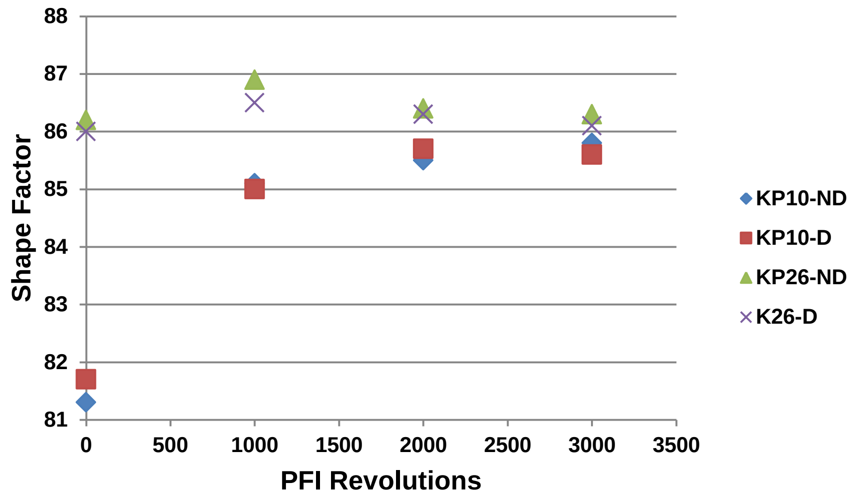

Fig. 4. Effect of refining on the shape factor of the never dried (ND) and dried (D) bamboo pulps

Recently, Kunnari *et al.* (2007) concluded that shape factor is one of the main parameters determining wet and dry paper strength and runnability and that the amount of curl should be minimized by changing parameters in the refining and stock preparation. As seen in Table 5, the shape factor was almost 5 units lower for unrefined KP10 compared to KP26. However, after refining the difference between the pulps was only *ca.* 1 unit. The trend in the results regarding the number of kinks per mm fiber (a measure of fiber defects) was similar (Table 5). However, even though the difference in shape factor and number of kinks between KP26 and KP10 was greatest for the unrefined pulps and diminished during refining, this was not reflected in the pulp strength development (*cf.* Figs. 2, 3, and 4). Furthermore, no major differences were noted in the number of fiber defects between the never dried and dried pulps (Figs. 3 and 4). The differences in strength properties between the dried and never dried pulps are therefore most probably dependent on other parameters such as formation of stiffer fibers due to cross-linking between cellulose fibrils in the fiber wall and collapsed fiber surfaces during drying, which results in a lower ability of the fibers to form strong fiber-fiber joints.

In contrast, the tear index values for the dried pulps were higher than the never dried pulps (Fig. 5) and on refining, the dried low kappa pulp showed the highest tear index values at any given number of PFI revolutions. However, the tear index as a function of the tensile index was highest for the dried high kappa pulp at any given tensile index, while the dried low kappa pulp showed similar results as the never dried high kappa number pulp (Fig. 6).

The apparent density of a given pulp is a crude measure of the relative bonded area (RBA). As shown in Fig. 7, cooking to high kappa number gave a pulp with lower density (*i.e.* higher bulk) than the low kappa pulp at any given tensile index value which is in good agreement with previous results (Heijnesson-Hultén *et al.* 2010). Furthermore, even after drying, KP26 showed higher bulk compared to KP10 at any given tensile index value. The higher bulk of the never dried and dried high kappa pulps may be explained by the straighter fibers (Table 4). The wet fiber flexibility of never dried KP10 and KP26 was determined to be $4.2*10^{11}$ and $1.2*10^{11}$ $N^{-1}m^{-2}$, respectively. The lower flexibility of the high kappa number pulp probably also influenced the bulk. Thus, the initial properties of the pulp appear to determine the final pulp quality to a large extent.

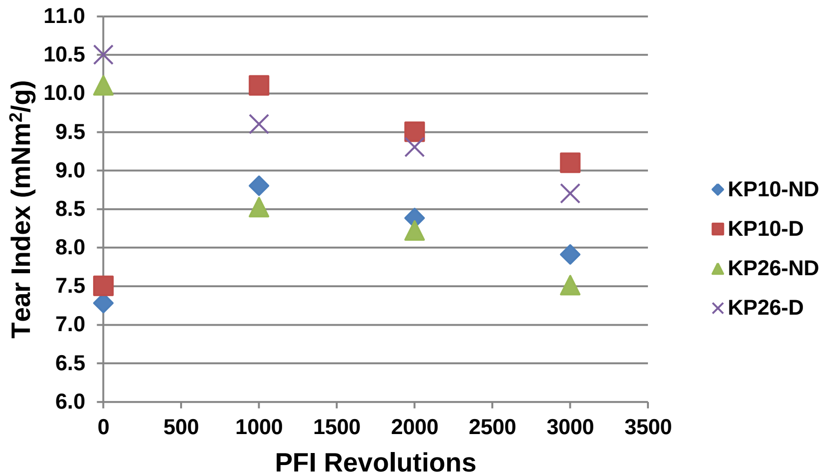

Fig. 5. Effect of refining on the tear index of the never dried (ND) and dried (D) bamboo pulps

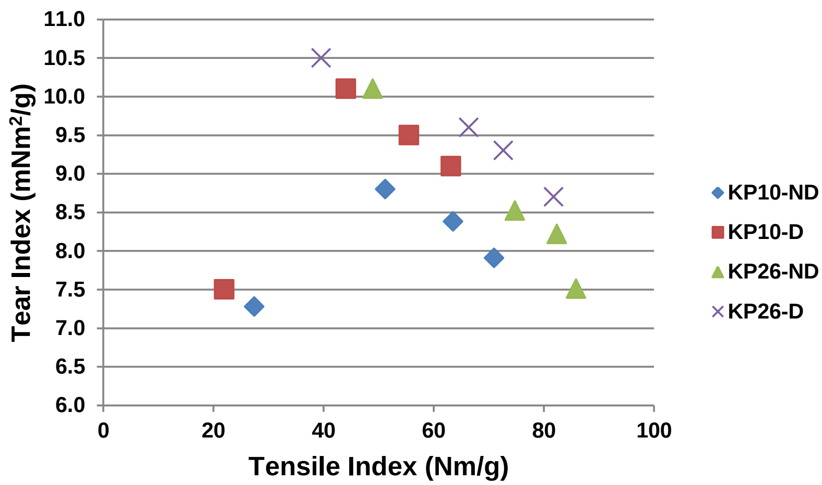

Fig. 6. Tear index *vs*. tensile index of the never dried (ND) and dried (D) bamboo pulps

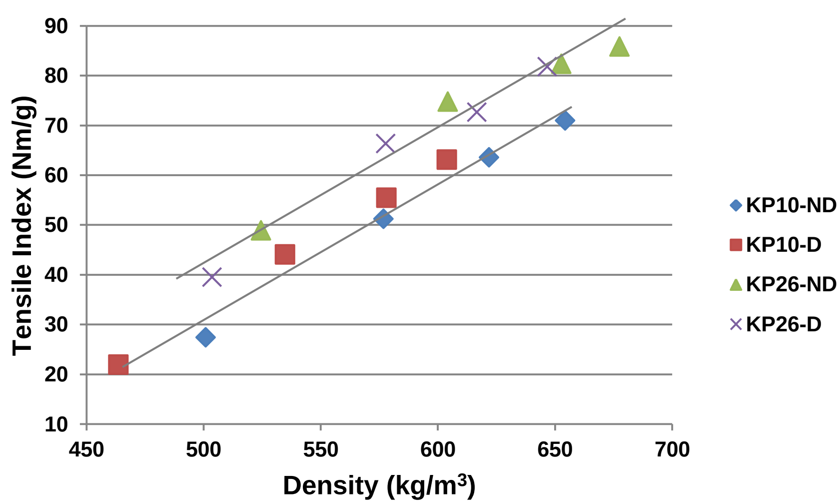

Fig. 7. Tensile index *vs.* the apparent density of the never dried (ND) and dried (D) bamboo pulps

SEM micrographs of the fiber surface of pulp samples from the unrefined (0 revs) and refined (2000 revs) paper sheets prepared from the never dried and dried low and high kappa pulps are shown in Figs. 8 through 11.

From the observations it was only possible to suggest a number of trends including: *i*) That it was difficult to see any real differences between the dried- and never dried pulp samples, although possibly the never-dried pulps showed a tendency to have a more open paper sheet structure (*i.e.* KP10 and KP26); *ii*) Refining produced a more compact paper sheet surface, with flatter fibers and broad fiber-fiber contacts in contrast to the unrefined samples; and *iii*) The high kappa pulp (KP26) showed less kinks/dislocations and straighter fibers.

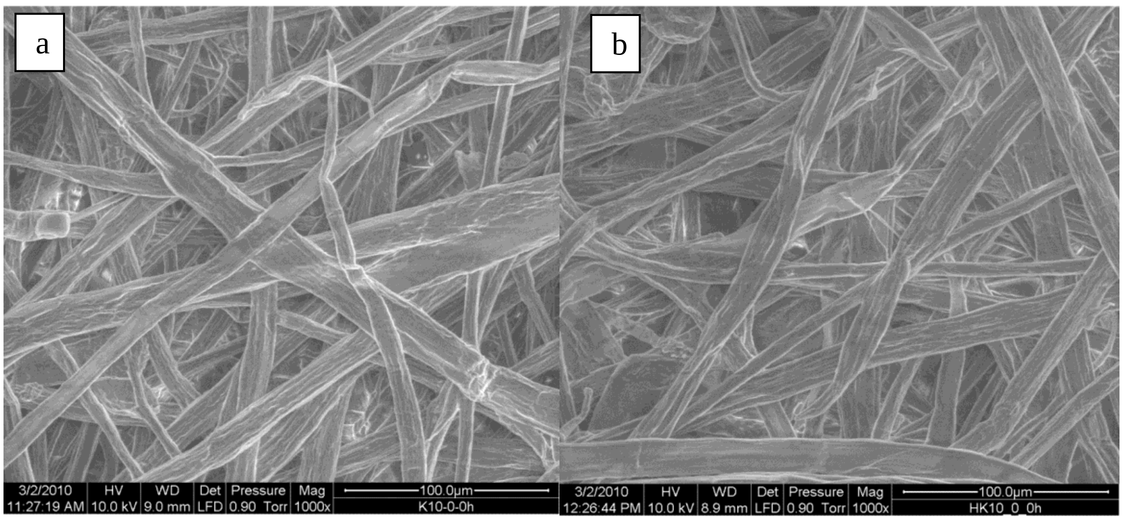

Fig. 8. SEM micrographs of the surface of paper sheets made from unrefined a) never dried and b) dried bamboo kraft pulp with kappa number 10

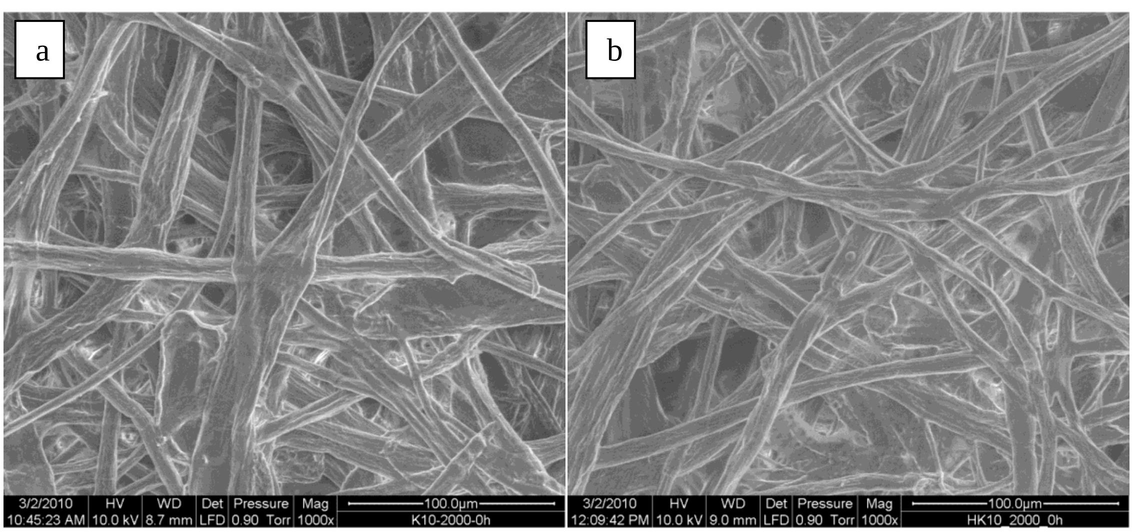

Fig. 9. SEM micrographs of the surface of paper sheets made from refined (2000 revs) a) never dried and b) dried bamboo kraft pulp with kappa number 10

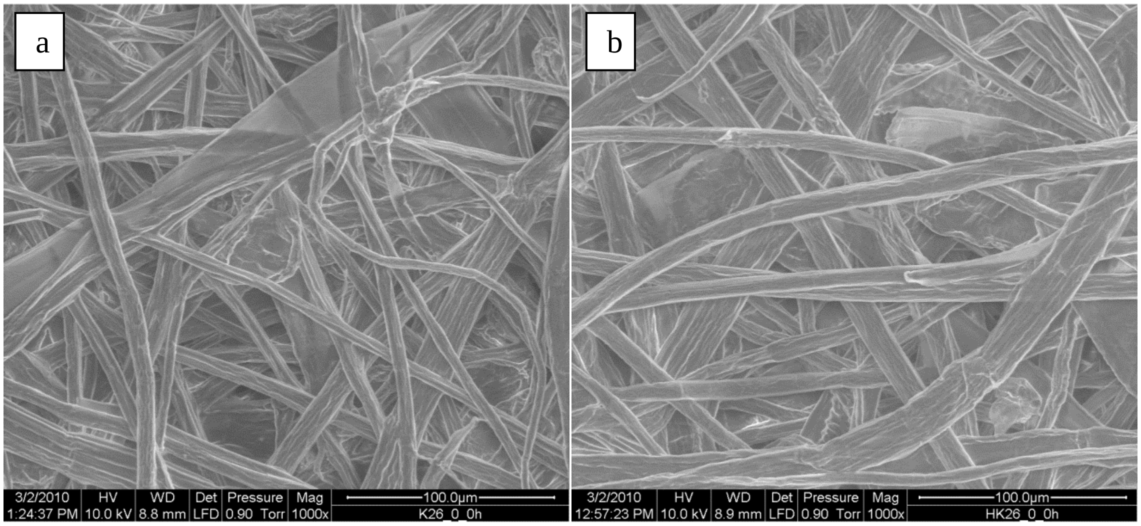

Fig. 10. SEM micrographs of the surface of paper sheets made from unrefined a) never dried and b) dried bamboo kraft pulp with kappa number 26

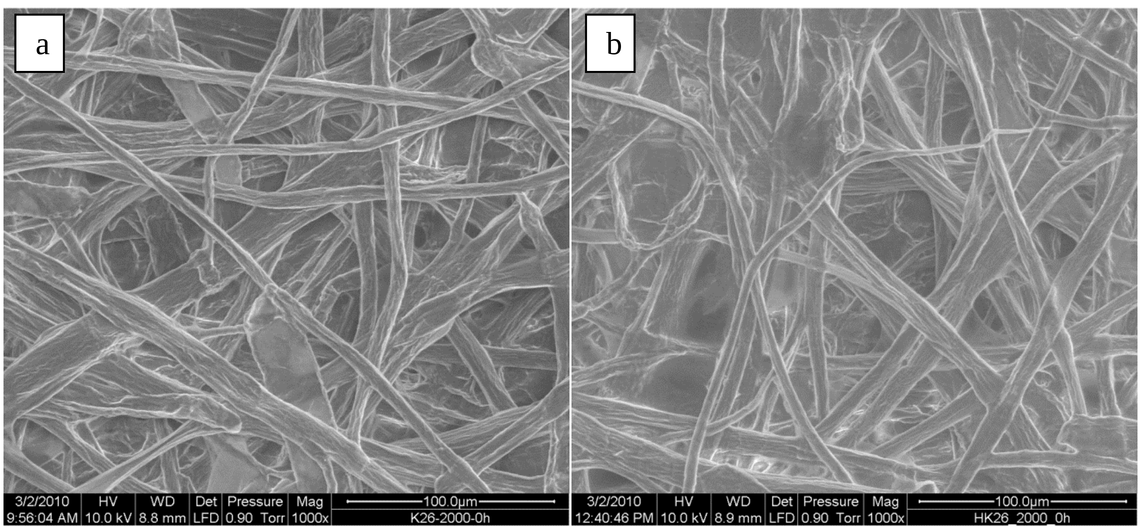

Fig. 11. SEM micrographs of the surface of paper sheets made from refined (2000 revs) a) never dried and b) dried bamboo kraft pulp with kappa number 26

CONCLUSIONS

1. Drying of two bamboo pulps with kappa number 10 and 26 resulted in a loss in tensile and burst strength while the tear index value was improved. The effect of drying induced property changes could be restored by refining. However, more energy was required to reach a certain Schopper Riegler and/or strength value.

2. The difference in strength properties between the never dried and dried pulps of kappa number 10 and 26, respectively, was similar and remained almost constant throughout refining.

3. The bleached high kappa number pulp required less energy to reach a certain Schopper Riegler value and exhibited much higher strength properties than the low kappa number pulp, differences that were maintained after drying.

4. The results indicated that the native properties of the bamboo pulps studied determined the strength potential of the pulps after drying. Kraft cooking of bamboo to high kappa number prior to bleaching gave pulps with higher pulp strength and improved response to refining both before and after drying of the pulps.

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