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Changes in the microstructure and properties of aspen chemithermomechanical pulp fibres during recycling

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ABSTRACT

The effects of recycling on the microstructure and properties of bleached aspen chemithermomechanical pulp (CTMP) fibres were systematically investigated. The low-temperature nitrogen adsorption and atomic force microscopy results showed that a substantial amount of large pores and most of the very small pores in the fibre wall closed and the fibre surface became less coarse and porous during recycling. The partial cocrystallisation of cellulose microfibrils took place, as reflected in the increment of the cellulose crystallinity and the width of the crystallite in the 0 0 2 lattice plane. These irreversible structural changes caused significant hornification of the recycled fibres, leading to the loss of swelling and bonding capability. The decrease of the tensile index, burst index, and tear index further demonstrated the deterioration of the fibre properties. However, the single-fibre strength considerably increased after recycling, which was mainly due to the enlarged cellulose aggregates in the fibre wall.

1. Introduction

The production and consumption of paper and paperboard have increased considerably all over the world, and the pulp and paper industry has become an important player in the utilisation and consumption of fibrous raw materials. As the demand for papermaking raw materials continues to grow and the supply of virgin fibres continues to dwindle, recycled fibre as a renewable resource is becoming increasingly important to ensure sustainability. The use of recycled fibre can reduce the consumption of biomass resources, reduce unnecessary landfilling, and ultimately protect the environment. Currently, recycled pulp is an important component of paper products of various grades and a potential biomass feedstock for the future biobased economy (Luo & Zhu, 2011). However, some irreversible changes in the bulk and surface properties of fibres are unavoidable during conventional papermaking practices (Letková, Letko, & Vrška, 2011). Numerous studies have been conducted on the effect of recycling on the physical properties of the fibres, concluding that recycling causes a significant reduction in breaking length, burst, and fold and a less severe reduction in apparent density and stretch (Howard, 1990; Wistara & Young, 1999).

It is generally accepted that the loss of strength during recycling is caused by hornification, surface deactivation, and reductions in the wet flexibility and bonding properties of the fibres (Tschirner, Barsness, & Keeler, 2007). Many attempts have been made to explain the exact causes and mechanisms involved in hornification. Multiple hypotheses were proposed for chemical pulps, but many are contradictory. The most prevalent hypothesis is the formation of irreversible intra-fibre hydrogen bonds among the cellulose microfibrils, which restrict cellulose swelling and decrease its absorption capacity (Diniz, Gil, & Castro, 2004). According to Brancato (2008), the free microfibrils of the fibre surface drew together during cycles of wetting and drying, forming intra-fibre hydrogen bonds, laminating, and presenting a more uniform fibre surface.

One mechanism proposed to explain hornification was the reorganisation of the fibre cell wall structure, resulting in the creation of additional crystalline zones. Tschirner et al. (2007) found that recycling caused only small changes in the chemical composition but considerably increased the crystallinity index. Based on

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the results of wide-angle X-ray diffraction measurements, Toba, Yamamoto, and Yoshida (2013) presumed that noncrystalline cellulose formed hydrogen bonds with the cellulose at the surface of the crystalline region, thus enlarging the crystal size. According to Newman (2004), the growth of crystalline domains involved cocrystallisation rather than accretion of cellulose from noncrystalline domains, suggesting that the cocrystallisation of cellulose might provide a mechanism for hornification. The more hydrophobic surfaces of the crystalline elements in cellulose fibrils had an increased preference for aggregation (Idström, Brelid, Nydén, & Nordstierna, 2013).

Some studies found evidence to suggest that the formation of lactone bridges in fibres was the primary cause of hornification (Fernandes Diniz et al., 2004). Chen et al. (2011) found that the lactone content of unbleached wheat straw pulp increased with increasing drying temperature and drying time. Some of the existent carboxylic acid groups in the lignocellulosic structure would interact with hydroxyl groups in neighbouring polymeric chains and establish covalent lactone bridges (Fernandes Diniz et al., 2004). Lindström and Carlsson (1982) reported that when in their hydrogen or acidic form, the carboxyl groups promoted increased hornification of cellulose fibres.

Hornification was also thought to be caused by pore closure and fibre collapse, which failed to reverse when the fibres were rewet. The irreversible closure of pores and cracks could lead to less fibre–fibre bonded area in the recycled fibres, reducing the interfibre bonding capability during papermaking. Haggkvist, Li, & Odberg (1998) investigated the influence of drying and pressing on the pore size and pore size distribution in the cellulose fibre wall by a ^{1}H and ^{2}H NMR relaxation method. The results indicated that the pore shrinkage in cellulose fibres during pressing or drying was a process in which the cell wall pores of a wet cellulose fibre successively shrank as the moisture content decreased. Maloney and Paulapuro (1999) showed that hornification primarily affected the volume of macropores, with relatively little effect on micropores. However, according to the results reported by Stone and Scallan (1968), the large and intermediate-sized pores were reduced upon drying. Because of the lack of re-opening of recycled fibre lumens in the wet state, the amount of bound water adsorbed to fibre wall substantially influenced the re-swelling capability of recycled fibres (Khantayanuwong, Toshiharu, Akira, & Fumihiko, 2002).

As low-yield chemical pulps undergo hornification to a greater degree than mechanical pulps, some studies have reported that hemicelluloses and possibly lignin inhibit any hornification effects. Cao, Tschirner, and Ramaswamy (1998) demonstrated that the content of pulp hemicelluloses, principally pentosans and especially xylan, governed the strength and optical properties of recycled pulps. Lignin content did not significantly affect the recycling potential of these pulps. The retention of a certain amount of hemicelluloses might effectively inhibit the irreversible pore closure of fibres after the papermaking process (Chen, Wan, & Ma, 2009). The greater hornification of acid sulphite *Eucalyptus globulus* pulp relative to bleached kraft pulp was attributed to the lower 4-*O*-methylglucuronoxylan content in the former and the unfavourable rearrangement of cellulose molecules in the crystalline and amorphous regions during acid sulphite pulping (Rebuzzi & Evtuguin, 2005).

High-yield pulps, which lead to the more efficient utilisation of wood resources, have been widely used in the manufacturing of newsprint and coated printing grades and as a replacement for chemical pulp in producing lightweight and supercalendered printing paper. Most of these paper grades are short-life products with a life span of only a few days (*e.g.*, newsprint) or a few weeks (*e.g.*, packaging). With the rapidly growing use of recycled fibres, it is not surprising that these fibres may be recycled several times in a short period. Therefore, the potentially deleterious effect of repeated recycling upon the fibre properties should be quantified.

The main method of producing bleached high-yield pulps is chemithermomechanical pulp (CTMP) processing and subsequent bleaching with peroxide under alkaline conditions. It is known that fibre fracture of the CTMP takes place in the lignin-rich middle lamella or primary wall, resulting in surface properties that differ from those of chemical pulps and other high-yield pulps, such as stone-ground wood pulp (SGW), refiner mechanical pulp (RMP), and thermomechanical pulp (TMP). Many studies have shown that the fibres of CTMP differ from those of chemical pulp in their properties, such as size, shape, surface chemistry, flexibility, and bonding. Moreover, CTMP retains a considerable fraction of the original lignin, and only a small fraction of hemicelluloses may be removed. Therefore, it is expected to exhibit different behaviour during recycling. However, there is limited information on the behaviour of CTMP fibres during recycling. The aim of this work is to gain fundamental knowledge about which parameters result in the changes in the microstructure and properties of CTMP fibres.

Table 1
Characteristics of the bleached aspen CTMP.

	Cellulose (%)	Pentosan (%)	Carboxyl groups (mmol kg^{-1})	Lignin (%)	Extractives (%)
Wood	46.06	19.21	–	28.79	3.82
BCTMP	56.87	13.83	124.92	24.22	0.86

2. Materials and methods

2.1. Materials

Never-dried bleached aspen CTMP manufactured using hydrogen peroxide in both the chemical pretreatment and the bleaching stage was obtained from Huatai Group Corp., Ltd. (Shandong, China). The pulp was supplied in a wet state with a moisture content of approximately 72% by weight. The basic characteristics of the pulp are shown in Table 1.

2.2. Methods

2.2.1. Drying-rewetting treatment of pulp

Handsheets of approximately 60 g m^{-2} for bleached aspen CTMP were made in a standard handsheet-making apparatus (Blattbildner-Sheet Former, RK-3A, Austria PTI Company). A certain number of handsheets were retained for testing. The remaining handsheets were soaked in deionised water for 24 h and disintegrated for 20,000 revolutions using a standard pulp disintegrator (H158, Messmer Instruments Ltd). The redisintegrated pulp was then used to prepare handsheets once again. The recycling procedure was repeated until six drying-rewetting cycles were achieved (Howard & Bichard, 1992). These resulting pulps were named R_0, R_1, and so on according to the number of drying-rewetting cycles.

2.2.2. Fibre morphological parameters

The morphological properties of the never-recycled and the recycled fibres, such as the mean fibre length and fines content, were analysed with a fibre quality analyser (FQA, OpTest Equipment Inc., Canada) according to Brancato (2008).

2.2.3. Analysis of the pore structure of the fibre wall

The pore sizes and the pore size distributions of the fibres were measured by low-temperature nitrogen adsorption (Chen et al., 2011). The vacuum freeze-dried pulps were reduced to small pieces, and a surface area and porosimetry analyser (V-Sorb 2800P, Beijing APP Technology Co. Ltd.) was used for the structural

analyses of the fibre pores. High-purity N_2 was used as the absorbate, and the adsorption-desorption of high-purity N_2 was determined at 77 K in a liquid-nitrogen trap using a static volumetric method. Calculations based on the Brunauer–Emmett–Teller (BET) equation, Barrett–Joyner–Halenda (BHJ) model, Horvath–Kawazoe (H–K) model, and *T*-plot approach, among others, were used to analyse the BET surface area, the total pore volume, and the average pore size of the fibre samples.

2.2.4. Analysis of fibre surface topography

The fibres were dispersed into deionised water for 2 h and dropped onto mica plates. The specimens were then air-dried at ambient temperature in an atmosphere free of dust. The surface ultrastructure of the fibres was analysed using atomic force microscopy (AFM). A Multimode 8 AFM instrument (Bruker Company) equipped with a NanoScope V controller and NanoScope version 8.10 software (Veeco/Digital Instruments) was used. The specimens were scanned under a standard mode (ScanAsyst) using a tip with a radius of approximately 2 nm at ambient temperature and humidity. Image processing software (NanoScope 8.10) was used for the analysis of the AFM images.

2.2.5. Determination of the cellulose crystallinity

The X-ray diffraction profiles of the fibre samples were recorded using an X-ray diffractometer (D8-Advance, Germany Bruker AXS Corporation) (Chen et al., 2011). Ni-filtered Cu *K*α radiation ($\lambda = 0.1542$ nm) generated at a voltage of 40 kV and a current of 40 mA was utilised, and a scan speed of 1–2° min^{-1} from 5° to 50° was used. The degree of crystallinity was estimated by Segal's method using the following equation:

$$\text{Crystallinity,} \quad \% = \left[\frac{I_{002}}{I_{002}} + I_{\text{am}}\right] \times 100\%$$

where I_{002} is the intensity of the 0 0 2 peak when 2θ is approximately 22.5° and represents the diffraction intensity of the crystallising area. I_{am} is the intensity of the 0 0 2 and 1 0 1 peaks when 2θ is approximately 18° and represents the diffraction intensity of the amorphous area.

The crystallite size was calculated using the Scherrer equation with the method based on the width of the diffraction patterns (Toba et al., 2013):

$$D = \frac{k\lambda}{B\cos\theta}$$

where *D* is the average width of the crystallite in the 0 0 2 lattice plane, *k* is the Scherrer constant (0.9), λ is the wavelength of the X-ray source (0.1542 nm), B is the half-band width in radians, and 2θ is the Bragg angle.

2.2.6. Determination of the water retention value (WRV)

The WRV of the pulp was determined by the centrifugal method (Chen et al., 2009). Approximately 1.5 g (o.d.) of pulp was placed in a centrifuge at 3000 rpm for 15 min to remove all free water. The wet pulp was weighed immediately in a pre-weighted weighing bottle and dried in an oven at 105 ± 2 °C for 24 h. Next, the dry pulp was weighed again to determine the amount of bound water. The WRV was calculated as the weight of bound water per unit of dry pulp using the following equation:

$$\text{WRV,} \quad \% = \left[\frac{(m_1 - m_2)}{m_2}\right] \times 100\%.$$

where m_1 is the weight of the wet pulp after centrifugation and m_2 is the weight of the dry pulp (in grams).

The degree of hornification was calculated by determining the percentage decrease in the WRV of the recycled pulps (WRV_{RX}) relative to the virgin pulp (WRV_{R0}) using the following equation (Rebuzzi & Evtuguin, 2005):

$$\text{Degree of hornification,\%} = \left[\frac{(WRV_{RO} - WRV_{RX})}{WRV_{RO}}\right] \times 100\%$$

2.2.7. Determination of paper sheet properties

The fibre strength and fibre bonding number were assessed using a Pulmac instrument (Z-Span 2400). The interfibre bonding strength was measured using an internal bond strength tester (TMI 80-20). The tensile index, burst index, and tear index of the paper sheets were analysed according to GB/T12914-2008, GB/T 454-2002, and GB/T 455-2002, respectively. The light-scattering coefficient and whiteness of the paper sheets were measured according to GB/T10339-2007 and GB/T 7974-2002, respectively.

Table 2
Morphological aspects of recycled bleached aspen CTMP fibres.

Fibre sample	Ln (mm)	Width (μm)	Fines content (%)	Kink index	Curl index
R_0	0.605	22.3	8.51	0.67	0.045
R_1	0.609	22.1	8.43	0.48	0.033
R_2	0.615	22.5	8.27	0.36	0.032
R_3	0.635	21.8	7.99	0.36	0.030
R_4	0.624	21.9	7.76	0.30	0.027
R_5	0.632	21.6	7.59	0.27	0.030

3. Results and discussion

Cellulose fibres will undergo irreversible degradation when exposed to the cycles of rewetting, formation, and drying. The recycling behaviour of fibres is related to the physical and chemical nature of the virgin fibres. The bleached CTMP produced from aspen retains approximately 72.0% and 84.1% of the virgin hemicellulose and lignin contents, respectively, as shown in Table 1. This is very different from chemical pulps, for which the lignin component is almost completely removed, and mechanical pulps, such as SGW and RMP, which contain nearly all of the chemical components originally present in the wood (Law, Valade, & Li, 1996).

3.1. Changes in the fibre morphology properties

Table 2 demonstrates the changes in the morphological aspects of bleached aspen CTMP fibres induced by recycling treatment. After five drying-rewetting cycles, the fine content of the recycled pulp decreased by 10.8%, indicating some loss of fines during the recycling process. The average length of the recycled fibres increases slightly with the recycling times. However, no significant change in the fibre width can be observed in Table 2. This indicates that the recycling procedure does not cause fibre fragmentation.

As shown in Table 2, the kink index and the curl index of the virgin fibre are 0.67 and 0.045, respectively, indicating that the bleached aspen CTMP fibres are much stiffer than other pulp grades (Seth, 2006). During the recycling process, both the kink index and the curl index of the recycled pulp decrease slightly with recycling time, with the main decrease being observed after the first recycling. The recycling process consists of re-slushing, paper sheet formation, pressing, and drying. Shrinkage stresses in the fibre wall during paper sheet drying probably straighten the fibres and reduce the crimps and kinks in the fibres.

3.2. Changes in the pore structure of the fibre wall

The characterisation of the specific surface area, pore volume, pore size, and pore size distribution is important for understanding the fibre properties, such as the swelling ability and flexibility

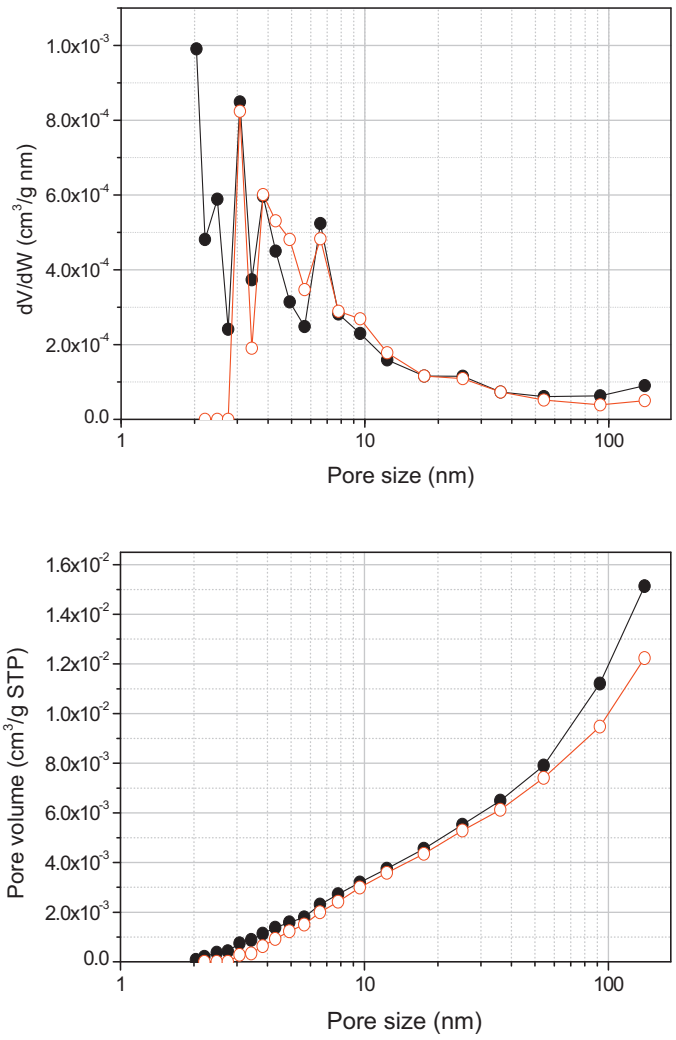

Fig. 1. Differential distribution curve (a) and integral distribution curve (b) of the BJH adsorption pore size of aspen bleached CTMP fibres (-●- virgin fibres, -○- singly recycled fibres).

(Haggkvist et al., 1998). The results in Fig. 1 show that the mean diameter of the fibre pores is in the range of 2–150 nm, which is much less than that of the chemical pulp reported by Chen et al. (2011). According to Maloney and Paulapuro (1999), only micropores are present in wood, and macropores are formed by the dissolution of lignin and hemicelluloses in chemical pulping. During chemithermomechanical pulping, only 15.9% and 28.0% of the lignin and hemicellulose contents, respectively, are removed (Table 1), leaving a small space between lamellae, which forms relatively small pores and cracks. The presence of macropores in fibre wall is attributed to the mechanical refining during the CTMP pulping.

As seen in Table 3, the BET surface area, cumulative pore volume, and average pore size of the fibre wall in the recycled fibres decrease with the number of recycling repetitions, indicating that the cell wall pores of the fibre may shrink or even close irreversibly. Furthermore, although the average pore size of the recycled fibre wall is not significantly different from that of the virgin fibre, the BET surface area and the BJH adsorption cumulative volume of the recycled fibres decrease significantly. Compared with virgin fibre, the BET specific surface area of the recycled fibre wall is 27.4% lower and the cumulative pore volume is 13.2% lower after the first recycling.

According to Fig. 1, the pore size distribution of the fibre wall becomes narrower after the first recycling. The difference in the

Table 3
Change in pore properties of bleached aspen CTMP fibre after recycling.

Fibre sample	BET surface area ($m^2\ g^{-1}$)	BJH adsorption cumulative volume ($cm^3\ g^{-1}$)	BJH adsorption average pore size (nm)
R_0	2.63	0.0151	15.86
R_1	1.91	0.0131	15.11
R_2	1.67	0.0130	14.91
R_3	1.45	0.0122	14.88
R_4	1.32	0.0116	14.46
R_5	1.20	0.0090	14.22
R_6	0.83	0.0077	13.91

pore characteristics between the virgin fibre and the recycled fibre seems to primarily result from the large pores. The number of large pores (larger than 55 nm) and the number of very small pores (smaller than 3 nm) decrease when the fibres are first recycled, indicating that recycling closes a substantial amount of the large pores and most of the very small pores. This is in agreement with previous results indicating that drying primarily closes macropores and has only a small effect on micropores (Maloney & Paulapuro, 1999). The reduction of the number of macropores seems to result from the decrease in the internal fibre volume during the sheet formation and drying. In addition, irreversible hydrogen bonding and possibly Van der Waals bonding occur between microfibrils, resulting in the irreversible closure of the very small pores in the fibre cell wall.

3.3. Changes in the fibre surface topography

Atomic force microscopy (AFM) is employed to observe the changes in the surface topography of the fibre during recycling (Fig. 2). Compared to the virgin fibre (Fig. 2a), the surface structure of the recycled fibre is less coarse and porous, as observed in Fig. 2b. This decrease in porosity and coarseness results from an irreversible collapse of the fibre wall structure during recycling (Östlund, Köhnke, Nordstierna, & Nydén, 2010). Furthermore, compared with the virgin fibre, the recycled fibre has larger cellulose aggregates, as shown in Fig. 2. This may be mainly related to the thermally induced lateral aggregation of adjacent cellulose microfibrils (cocrystallisation) (Figueiredo, Evtuguin, & Saraiva, 2010).

3.4. Crystal structure and single-fibre strength

The degree of crystallinity and the crystallite size are important parameters of the cellulose fibre, affecting the physical and mechanical properties (Sheikhi, Talaeipour, Hemasi, Eslam, & Gumuskaya, 2010). The bleached aspen CTMP initially has a crystallinity of 53.47%, and the crystallite size of cellulose in the 002 lattice plane (L_{002}) is 4.21 nm, as shown in Table 4. An increase of approximately 5% in crystallinity after the first recycling is followed by a slight increase in crystallinity for the successive recycling treatments. Meanwhile, the crystallite size of the fibre slightly increases with the number of recycling rounds. Because the crystalline region of cellulose is quite stable and almost unaffected

Table 4
Effect of recycling on crystallinity, crystallite size, and fibre strength of bleached aspen CTMP fibres.

Fibre sample	R_0	R_1	R_2	R_3	R_4	R_5	R_6
Crystallinity (%)	53.47	56.36	57.29	58.02	58.91	59.18	59.40
Crystallite size (nm)	4.21	4.43	4.45	4.62	4.71	4.73	4.80
Fibre strength ($N\,cm^{-1}$)	36.50	37.76	38.51	40.63	41.69	42.05	–

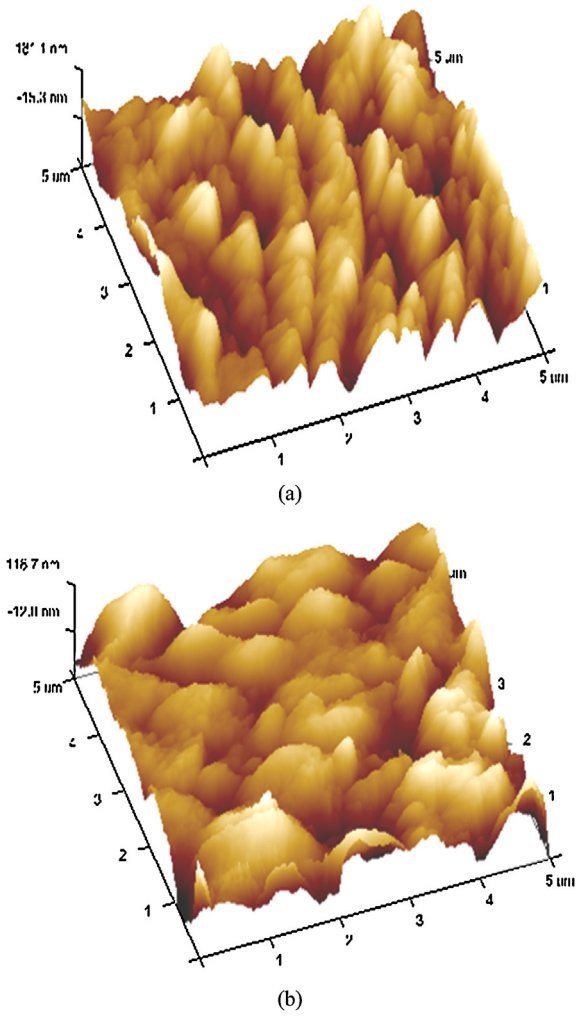

Fig. 2. Three-dimensional reconstructed atomic force microscopy images of virgin CTMP fibre (a) and singly recycled CTMP fibre (b).

by the recycling treatment (Khantayanuwong et al., 2002), it can be assumed that the growth of crystalline domains stems from the cocrystallisation of the adjacent cellulose microfibrils and the accretion of cellulose from noncrystalline domains (recrystallisation) (Figueiredo et al., 2010).

As the cellulose microfibrils are the load-bearing component of the fibres (Forsström, Torgnysdotter, & Wågberg, 2005b), the increment of the average crystallite width and the degree of crystallinity enhances the single-fibre strength (Table 4). The single-fibre strength increases by approximately 15% after five recycling treatments. This finding is not in agreement with the results reported by Howard and Bichard (1992), who observed no significant change in fibre strength during recycling for TMP and CTMP. It can be concluded that the reorientation of microfibrils and the better alignment of carbohydrate chains lead to more intense hydrogen bonding (Lundberg, 1978), increasing the strength of the individual fibres of the recycled pulp.

3.5. Fibre swelling capability and bonding properties

The water retention value (WRV) is used as a measure of the internal fibre swelling capacity of the pulp. As seen in Table 5, the WRV of the fibre continuously decreases as the number of recycling repetitions increases, implying that the re-swelling capability of the recycled fibres decreases and the degree of hornification increases. The most rapid decrease in the WRV of fibres occurs after the first recycling, and subsequent recycling further exacerbates the swelling capacity of the fibres. After five recycling treatments, the degree of hornification increased by 28.7%. This trend agrees with that for chemical pulp as reported by Wistara and Young (1999), although the hornification increment of CTMP is lower than that of the chemical pulp. During recycling, some of the amorphous region of cellulose can experience an increase in crystallinity and a decrease in water accessibility as a result of forming irreversible hydrogen bonds (Isogai, Akishima, Onabe, & Usuda, 1991), resulting in an irreversible reduction in the swelling ability of the fibres. Additionally, the shrinkage of the fibre wall and the irreversible closure of some pores is another important cause of the reduced uptake of water and reducing swelling of the fibre upon rewetting (Östlund et al., 2010).

Table 5
Changes in the WRV, hornification, and bonding capability of bleached aspen CTMP fibres during recycling.

Fibre sample	R_0	R_1	R_2	R_3	R_4	R_5
WRV (%)	150	132	128	119	110	107
Degree of hornification (%)	0	12.0	14.7	20.7	26.7	28.7
Fibre bonding number	1.82	1.64	1.59	1.51	1.50	1.42
Internal bond strength ($J\,m^{-2}$)	103.6	115.6	108.0	98.3	92.0	80.8
Light-scattering coefficient ($m^2\,kg^{-1}$)	29.27	30.96	34.07	37.90	43.32	45.58

The reductions in WRV indicate a decrease in the accessible hydroxyl groups in the fibre cell wall, leading to a decrease in the bonding capability of the recycled fibres, as shown in Table 5. It can be noticed that the fibre bonding number of the recycled pulp continuously decreases as the number of recycling treatments increases. It must be mentioned that the internal bond strength of the recycled fibres increases slightly after the first and second recycling treatments. In the CTMP process, the fibres are separated within the middle lamellar zone by synergic chemical, temperature, and mechanical action. The fibres produced by this process are heavily coated with lignin, which can block the formation of hydrogen bonds and prevent interfibre bonding (Lien, Kolehmainen, Hiltunen, & Nazhad, 2004). During repeated recycling, the lignin and extractives on the surface of fibre are partly washed away, and the interfibre bonding slightly increases. However, the internal bond strength of the recycled fibres begins to decrease in the third recycling treatment due to a reduction in interfibre bonding capability. After five recycling treatments, only 88% of the internal bond strength is retained.

The specific strength of the interfibre bonding and the interfibre bonding area are two major factors influencing the fibre–fibre joint strength. As the specific strength of interfibre bonding is not affected by the recycling treatment, the decrease in the fibre–fibre joint strength of recycled fibres is mainly due to the reduction of the interfibre bonding area (Cao, Tschirner, & Ramaswamy, 1999). As shown in Table 5, the light scattering coefficient of the recycled paper sheets, which is an indicator of the non-bonded area of the fibres, increases markedly with the number of recycling treatments. This finding indicates that the relative bonded area (RBA) between fibres is significantly decreased by recycling (Seth, 2006), leading to a marked reduction in the internal bond strength of the recycled fibre. Because the fibres with larger pores allow for a larger molecular contact area (Forsström, Andreasson, & Wågberg, 2005a), the closure of pores and the decrease of the special surface (Table 3) are the main causes of the reduction of RBA. On the other hand, it is generally accepted that the molecular contact zone depends on the softness of the fibre. The rearrangement of cellulose molecules in fibrils and interfibril aggregation in recycled fibres lead to fibre stiffening, surface collapse, and shrinkage, which

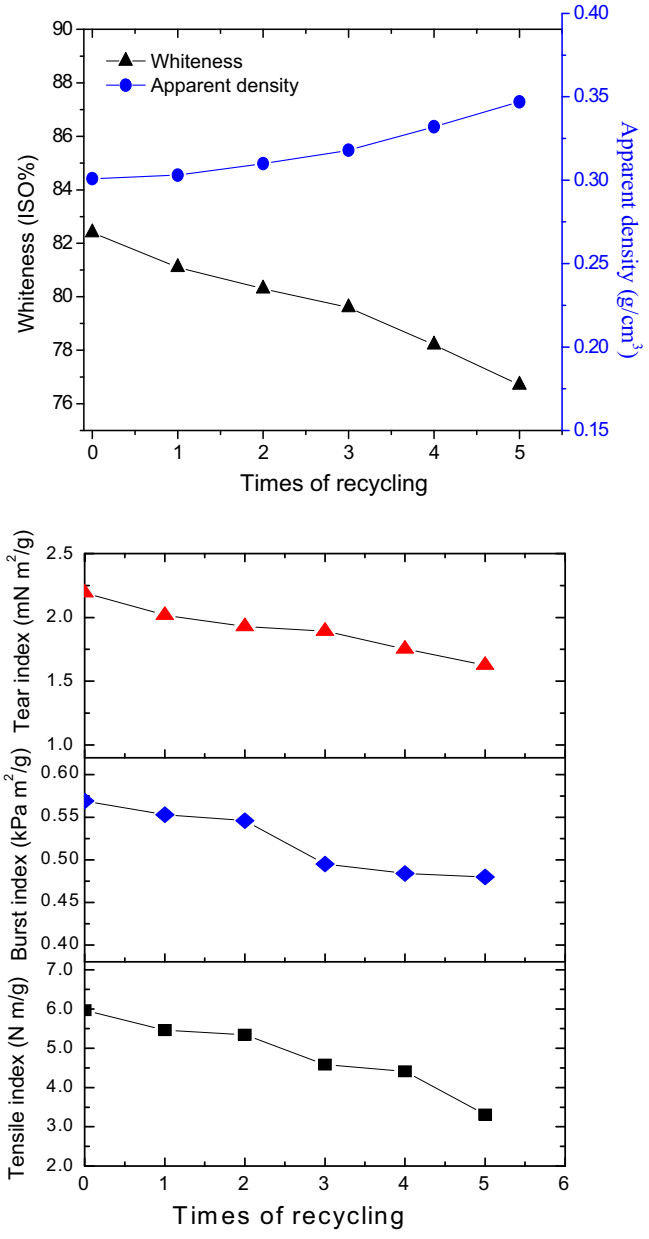

Fig. 3. Changes in the whiteness and apparent density (a) and strength properties (b) of paper sheets during recycling.

consequently decrease the interfibre contacts during paper sheet formation.

The loss of the conformability and bonding capability of recycled fibre can also be observed in inferior strength properties of the paper sheets in Fig. 3. As can be seen in Fig. 3(a), the recycled paper sheets have lower whiteness and higher apparent density than paper sheets from virgin fibres. The whiteness of the bleached aspen CTMP retains 93.1% of its original value after five recycling treatments, indicating that chromophore groups, such as lactone bridges, are formed during the recycling treatment. The slight increase in the apparent density of the recycled paper sheets may be attributed to the low curl index and kink index of the recycled fibres (Page, Seth, Jordan, & Barbe, 1985) (Table 2). The apparent density may also be benefit from the cocrystallisation of the cellulose microfibrils. The increase in the crystallinity increases the modulus of elasticity of the cellulose, which increases the apparent density of the resulting paper sheets (Scallan & Tigerström, 1992). The decrease in the pore sizes in the fibre wall and the collapse of the fibre lumens also promote hornification and result in a more compact structure, leading to denser paper sheets.

Fig. 3(b) shows that the tensile index and burst index of the paper sheet decreased by 44.6% and 15.7%, respectively, after five recycling treatments. The strength of the paper sheets depends on the strength of the individual fibres and the joint strength between the fibres. Because the recycling treatment improved the single-fibre strength (Table 4), the decrease in the tensile indices and burst indices of the recycled paper sheets are due to the decrease in the interfibre bonding strength. Furthermore, the tear index of bleached aspen CTMP retains only 74.1% of its original value after five cycles. The tear strength is mainly related to the fibre length, the strength of each fibre, and the bonding ability of fibres. The distinct reduction in the tear strength of the recycled fibre with a noticeable increase of fibre individual strength (Table 4) and a small increase in fibre length (Table 2) indicates that the inferior strength quality of recycled papers is caused by a loss in the potential bonding of fibres.

4. Conclusions

The bleached aspen CTMP, as a representative chemimechanical pulp, behaved as a chemical pulp rather than a mechanical pulp in many aspects during recycling, although it retained a large amount of hemicellulose and lignin. Repeated recycling has promoted the shrinkage and collapse of the fibre wall and the irreversible closure of some pores, resulting in a decrease in the relative bonded area between the fibres. The degree of crystallinity and the crystallite size of the cellulose increased with the number of recycling treatments, demonstrating that the cellulose microfibrils suffered partial cocrystallisation. This caused a significant increase in the hornification of the recycled fibres, deteriorating their swelling and bonding capability. The tensile strength, bursting strength, tear strength, and whiteness of the recycled paper sheets decreased with number of recycling treatments. However, the single-fibre strength increased considerably and the apparent densities of the fibres increased somewhat during recycling.

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