EFFECT OF RECYCLING ON FUNDAMENTAL PROPERTIES OF HARDWOOD AND WHEAT STRAW PULP FIBERS, AND OF HANDSHEETS MADE THEREOF

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The effect of recycling on the fundamental properties of hardwood and wheat straw pulp fibers and of the handsheets made thereof was investigated. Recycling tended to decrease the tensile strength and burst strength of both types of paper sheets, while increasing their tear strength. It clearly had no impact on the fiber length and fiber strength (zero-span tensile strength) of either wheat straw or hardwood pulps, however, the content of fines gradually decreased. The content of fines of hardwood pulp was larger than that of wheat straw pulp both initially and after recycling. The degree of polymerization (DP) of wheat straw and hardwood pulps significantly decreased at early recycling stages. Recycling also led to a decrease of the water retention value (WRV) and loss of hemicelluloses, which resulted in the decrease of recycled paper strength. Consequently, the strength loss of papers made from wheat straw and hardwood pulps depended on the decrease in fiber swelling (hornification) and in hemicelluloses content during recycling.

Keywords: recycling, properties, strength loss, water retention value, hornification, hemicelluloses

INTRODUCTION

Recycling can turn waste paper into treasure by reducing papermaking costs, deforestation, environmental pollution and by protecting ecological balance. The rapid increase in the use of waste paper by the international papermaking industry is a sign, on the one hand, of environmental awareness and, on the other, of the viability of turning waste of profit.

Cellulosic fiber is well-known for its ability to be used repeatedly for papermaking. In spite of this, researchers have shown that recycling usually causes strength loss, especially in mechanical pulps.[1-3] Therefore, many mechanisms have been proposed to explain the strength loss of paper, such as changes in fiber dimensions, fiber strength, chemical compositions of the fiber, inter- and intra-fiber bonding, degree of polymerization (DP) of cellulose molecules, surface conditions of the fiber and so on.[4-5] Nevertheless, this remains a matter for discussion.[6-13] Repeated recycling of paper is a complex process, which generally includes disintegration, soaking, deinking, papermaking, pressing and drying stages, and the behavior of different pulps to recycling has been investigated.

A large number of studies have been focused on the evaluation of the recycling potential of wood pulp fibers.[9-10,14-21] To our knowledge, little research has involved straw pulp, especially wheat straw pulp. Wheat straw is the main raw material for pulp and paper in China and it is widely distributed, in both southern and northern China. Wheat straw pulp accounts for one third of the pulp yield in China.[22]

Therefore, hardwood and wheat straw pulps were selected to investigate their fundamental properties and the reasons of strength loss during recycling. This work had two specific objectives: the first one was to study the difference in the recycling behavior of hardwood and wheat straw fibers, and the other was to explore the true reason of strength loss of paper made from recycled fibers.

EXPERIMENTAL

Materials

Commercial never-dried bleached hardwood (aspen) kraft pulp was obtained from a papermaking company in Dongguan city, China. The cellulose, hemicellulose and lignin contents of the bleached hardwood pulp were of 80.5%, 18.3% and 2.1%, respectively.

Wheat straw was laboratory cooked in an 18-liter digester using a conventional soda-anthraquinone process. Cooking was carried out under the following conditions: 800 g o.d. wheat straw, maximum temperature of 158 ^{o}C, time to reach maximum temperature of 90 min, time at the temperature of 30 min, 14% NaOH, 0.05% anthraquinone, and liquor-to-straw ratio of 4/1. The eventual moisture contents of unbleached wheat straw pulp and bleached hardwood pulp were of 82% and 80% by weight in never-dried state. The use of never-dried pulps was considered important, since a high water content is known to protect cellulose crystallites from mechanical damage.[23] The cellulose, hemicellulose and lignin contents of the unbleached wheat straw pulp were of 67.5%, 22.1% and 10.9%, respectively.

Paper recycling

Handsheets were made on a British handsheet machine according to Tappi standards.[24] The basis weight of unbleached wheat straw pulp paperboard and bleached hardwood pulp paper was of 200 and 60 g/m^2, respectively. Repetitive recycling was carried out on handsheets made from hardwood and wheat straw pulps. Some handsheets were placed in a humidity-controlled room according to TAPPI T 402 and their physical properties were assessed 24 h later. The rest of the handsheets were soaked in deionized water for at least 8 h. The rewetted handsheets were disintegrated at 30,000 revolutions in a disintegrator. Most of the recycled pulp was remade into handsheets and dried according to the described procedure. The recycling procedure was repeated for a total of five cycles.

Determination of Water Retention Value

The water retention value (WRV) was determined by the centrifugal method on 1.5 g samples (o.d.). The pulp was centrifuged at 3000 × g for 15 minutes and then weighed before and after drying. WRV is calculated as follows:[22]

$$WRV = \frac{m_1 - m_2}{m_2} \times 100\% \quad (1)$$

where m_1 is the weight of wet pulp after centrifugation, m_2 is the weight of dry pulp.

Determination of cellulose crystallinity by X-ray diffraction

The X-ray diffraction (XRD) scattering pattern of the pulp was analyzed on a Philipps X'Pert MPD diffractometer using a Cu-Kα source (λ=0.154 nm) in the 2θ ranging between 4-40° and a scanning step width of 0.02°/scan. Each analysis was carried out in triplicate. The background scattering was subtracted from the pulp diffraction diagram. The crystalline reflections and the amorphous halo were defined according to previously described recommendations.[25] The degree of cellulose crystallinity (CrI) and the average width of crystallite in the 002 lattice plane (L_{002}) were calculated as follows:[22]

$$\text{CrI, \%} = \frac{I_{cr}}{I_{cr} + I_{am}} \times 100 \quad (2)$$

$$L_{002} = \frac{K\lambda}{\beta_\theta \cos\theta} \quad (3)$$

where I_{cr} and I_{am} are the scattering intensities from the crystalline and amorphous regions of cellulose, respectively. β is the width of the middle height of the 002 reflection, in radians; θ is the corresponding Bragg scattering angle of the 002 reflection, in radians; λ is the wavelength of the X-ray source (0.154 nm); and K is the Scherer constant (0.9).

Test methods

Fiber length (weight-weighted) and the content of fines (weight-weighted) were measured using a KAJAANI FS-200 fiber analyzer. The beating degree (^{0}SR), degree of polymerization (DP), zero span tensile strength and pentosan content were determined according to Tappi standard methods. Handsheets and laboratory testing were performed according to ISO standards methods.

RESULTS AND DISCUSSION

Effect of recycling on physical properties of handsheets

The results obtained for the physical properties of the paper sheets (tensile, burst and tear indexes, stretch and tightness) made from recycled wheat straw and hardwood pulps are shown in Table 1. A decrease in the tensile and burst indexes, as well as in stretch and tightness, was noted after recycling. Wheat straw paper displayed a single increase in the tear index after recycling. Conversely, there was an initial increase followed by a decrease in the tear index of the handsheets made from hardwood pulp after recycling, which was in good agreement with previous results reported by Howard.[1]

In addition, in order to observe in detail the effect of repeated recycling on the tensile and burst indexes of the handsheets, the percentage decreases in these properties, defined as 100 × (property value before recycling – the value at N_{th} recycling) divided by the value before recycling, were plotted against the number of recycling rounds in Figure 1. Generally, the decreases in the tensile and burst indexes of the handsheets from hardwood pulp were greater than those for the handsheets from wheat straw pulp. Also, it was noted that the tensile and burst indexes of the handsheets made from hardwood and wheat straw pulps dramatically decreased during the early rounds of recycling (especially in the first and the second cycles).

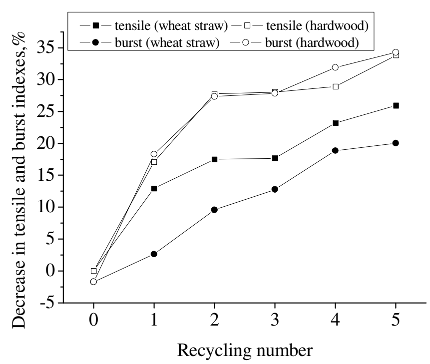

Figure 1: Decrease in tensile and burst indexes as a function of recycling number for handsheets made from recycled wheat straw pulp and hardwood pulp

Table 1
Evolution of physical properties of handsheets during recycling

Pulp	Number of recycling	Tensile index, N·m/g	Burst index, kPa·m^2/g	Tear index, mN·m^2/g	Stretch, %	Tightness, g/cm^3
Wheat straw	0	61.7	3.76	5.61	3.81	0.90
	1	53.7	3.61	5.87	3.10	0.89
	2	50.9	3.37	6.13	3.06	0.85
	3	50.8	3.26	6.27	3.05	0.82
	4	47.4	3.05	7.31	3.10	0.80
	5	45.7	3.01	7.66	2.77	0.78
Hard-wood	0	69.5	4.57	3.24	3.85	0.65
	1	57.6	3.73	3.27	3.70	0.62
	2	50.2	3.35	3.66	2.89	0.60
	3	50	3.33	3.48	2.84	0.57
	4	49.4	3.16	3.32	2.93	0.49
	5	46	3.03	3.24	2.91	0.34

Table 2
Effect of recycling on fundamental properties of fibers

Pulp	Number of recycling	Fiber length (weight-weighted), mm	Fines (weight-weighted), %	WRV, %	^{0}SR	DP	Zero-span tensile strength, N·m/g
Wheat straw	0	1.42	3.98	191.2	46	564	167
	1	1.35	3.91	180.5	40	543	152
	2	1.36	3.82	170.2	38	532	165
	3	1.35	3.24	168.8	36	518	160
	4	1.40	2.81	165.1	35	557	156
	5	1.38	2.31	160.2	32	560	161
Hard-wood	0	1.09	6.07	154.5	33	895	158
	1	1.24	5.23	136.8	32	884	143
	2	1.23	5.01	127.6	30	862	144
	3	1.21	4.87	119.1	28	851	146
	4	1.23	4.13	108.2	25	868	140
	5	1.06	3.90	106.3	22	875	142

Effect of recycling on fundamental properties of pulp fibers

The data listed in Table 2 reveal the changes that occurred in the fundamental properties of wheat straw and hardwood pulps during recycling. Clearly, recycling did not affect the fiber length of either wheat straw pulp or hardwood pulp. However, the content of fines gradually decreased with an increase of recycling times, which contributed to a stable fiber length of the pulps. On the other hand, the content of fines of the hardwood pulp was larger than that of the wheat straw pulp.

The molecular weight of cellulose and the content of fines are acknowledged as the two main factors affecting the DP of pulp.[5] The DP of wheat straw and hardwood pulps significantly decreased at the early recycling stages. This suggests that cellulose degradation and/or cellulose chain scission occurred during the recycling of fibers. However, at late recycling stages, the DP of wheat straw and hardwood pulps presented an increasing trend due to the loss of fines. On the other hand, the DP of wheat straw and hardwood pulps decreased by 8.2% and 4.9%, respectively, after three rounds of recycling. The behavior of the pulps regarding their DP was significantly distinctive. This could be explained by the fact that the molecular weight of cellulose of hardwood pulp is much higher than that of wheat straw pulp cellulose. Therefore, hardwood pulp was less sensitive to the mechanical treatment during recycling.

As regards fiber strength, which was determined by the zero-span tensile index, the first recycling resulted in a slight decrease in zero-span tensile strength. However, no distinctive changes were observed on further recycling for either wheat straw or hardwood pulp handsheets. The nearly constant zero-span tensile strength during further recycling suggests that either fiber strength slightly decreases upon recycling or the effect of the fiber straightening is relatively small.

The decrease in the degree of beating (SR) in these experiments, with an increase in the recycling number up to five times is shown in Figure 2. The content of fines is the main factor that affects the SR of pulp, so the loss of fines during recycling results in freeness increases, and finally causes the decrease of SR, as reported earlier by Yamagishi and Oye.[17] Their research results demonstrated that freeness increased with an increase of the recycling number at least up to five times, although the rate of increase and other details could differ because of variation in samples and recycling conditions. For the wheat straw pulp, the decrease in SR was the sharpest after the first recycling and then slowed down with an increase in the number of recycling. On the other hand, the SR of hardwood pulp decreased more proportionally to the recycling number for up to 5 cycles.

Changes in internal (fiber wall) fibrillation upon recycling are commonly referred to as hornification and WRV is used as a fiber hornification index.[26] The percentage decrease in WRV for wheat straw pulp and hardwood pulp with recycling number is shown in Figure 3. WRV decreased rapidly with an increase in the recycling number, but, for wheat straw pulp, it leveled off remarkably after the second recycling round. On the other hand, WRV decreased significantly at all recycling stages for hardwood pulp, and the decrease was noticeably larger than that for wheat straw pulp.

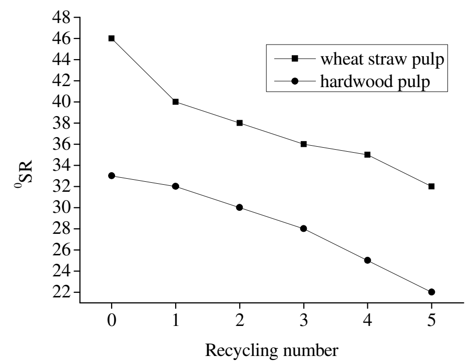

Figure 2: Evolution of SR as a function of recycling number

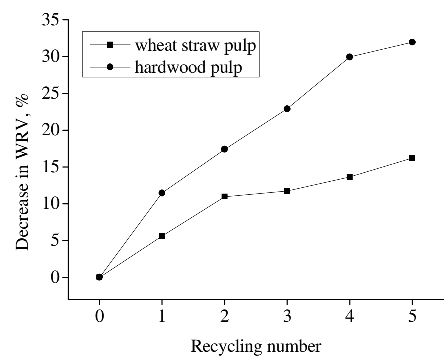

Figure 3: Evolution of WRV as a function of recycling number

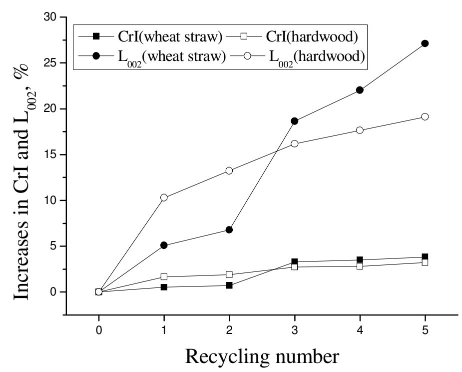

Figure 4: Evolution of CrI and L_{002} as a function of recycling number for handsheets made from recycled wheat straw pulp and hardwood pulp

Reasons of strength loss during recycling

The strength loss of the pulp upon recycling has been attributed to several factors, such as changes in fiber dimensions, in chemical composition of the fiber, loss in fiber strength, degradation of cellulose, and loss in fiber bonding because of hornification.[4-5]

Fiber strength loss, as indicated by the data revealing the reduction of zero-span tensile strength (Table 2), could be one of the mechanisms for the strength reduction.[4-5] However, the loss of zero-span tensile strength was small and no correlation with the number of recycling rounds was observed for the handsheets made from the two pulps. Thus, the fiber strength loss cannot be regarded as a mechanism to explain strength reduction.

From the comparison of SR and WRV data obtained in this study, it can be concluded that the beating effect was slightly higher on hardwood pulp than on wheat straw pulp. The decrease in WRV upon recycling was more significant for hardwood pulp than for wheat straw pulp. In addition, the decrease in tensile and burst indexes was also greater for the handsheets made from hardwood pulp than for those from wheat straw pulp. These results demonstrate that hornification, indicated by a decrease in WRV, could be regarded as one of the mechanisms of tensile and burst strength reduction during recycling, and WRV could be a measure of hornification. However, our findings are not in agreement with the results achieved by Yamauchi and Yamamoto.[13]

Figure 4 shows the percent increase in CrI and L_{002} with an increasing recycling number for the handsheets from recycled wheat straw pulp and hardwood pulp, which led to a swelling restriction of the fibers (which represented the decrease in WRV), resulting in strength loss. As illustrated in Figure 4, the increase in CrI and L_{002} was more significant for hardwood pulp handsheets than for the wheat straw pulp ones at the early recycling stages, however, it was smaller than that occurring in wheat straw pulp handsheets during further recycling.

Table 3
Evolution of cellulose crystallinity, width of crystallites and hemicelluloses content during recycling

Pulp	Number of recycling	0	1	2	3	4	5
Wheat straw	CrI, %	78.0	78.4	78.6	80.6	80.8	81.0
	L_{002}, nm	5.9	6.2	6.3	7.0	7.2	7.5
	Hemicelluloses,%	24.1	22.2	21.5	20.6	20.2	20.0
Pulp	Number of recycling	0	1	2	3	4	5
Hardwood	CrI, %	80.6	81.9	82.1	82.8	82.8	83.2
	L_{002}, nm	6.8	7.5	7.7	7.9	8.0	8.1
	Hemicelluloses, %	8.23	7.76	7.44	6.03	5.82	4.42

Some authors attributed paper strength loss to the loss of hemicelluloses upon recycling.[6,25] As shown in Table 3, the hemicelluloses (pentosan) content of wheat straw and hardwood pulps decreased with an increasing recycling number, which is in accord with previous research results.[6,25,27] The hemicelluloses content of wheat straw and hardwood pulps decreased by 17% and 46% after five recycling rounds, respectively, compared to the virgin pulps. The percent rate of hemicelluloses loss of hardwood pulp was significantly larger than that of wheat straw pulp, since the hemicelluloses content of wheat straw pulp is much larger than that of hardwood pulp. Hemicelluloses play a protective role in preventing hornification. The hemicelluloses are mainly strongly hydrophilic low-molecular pentosans, which play an important role in preserving fiber swelling after drying or recycling.[28] The swelling capacity of fibers with high hydrophilic low-molecular pentosan content is largely restored after drying. However, the swelling of fibers with low hydrophilic low-molecular pentosan content significantly decreases after drying. The hydrophilic hemicellulose layers existing on the fibril surface can promote better swelling of dried fibers, facilitating water attraction and preventing strong interaction between the crystalline regions of adjacent fibrils. The concentration of hemicelluloses on the fiber surface of pulps with high hemicellulose content is usually higher than on the surface of pulps with low hemicellulose content. This may also contribute to better swelling of dried pulps with high hemicelllulose content than that of pulps with low hemicelluloses content due to easier fiber separation in suspension and higher contact area with water.

In summary, the strength loss of papers from wheat straw and hardwood pulps mainly depended on the decrease in the fiber swelling (hornification) and the loss of hemicelluloses during recycling.

CONCLUSION

The SR of hardwood and wheat straw pulp fibers decreased upon recycling, while the SR of hardwood pulp decreased more proportionally to the increasing recycling number for up to 5 recycling rounds. The DP of wheat straw and hardwood pulps decreased by 8.2% and 4.9%, respectively, after five rounds of recycling. Cellulose degradation and/or cellulose chain scission occurred during the recycling process of fibers. The crystallinity of cellulose and the average width of crystallites increased with an increase of the recycling number, which led to a swelling restriction of the fibers (*i.e.* a decrease in WRV), resulting in strength loss. Also, the decrease in the hemicelluloses content with an increasing recycling number might be one of the reasons for the strength loss of the handsheets made from hardwood and wheat straw pulps.

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REFERENCES

[1] R. C. Howard and W. Bichared, *J. Pulp Paper Sci*., **18**, 151 (1992).
[2] R. L. Ellis and K. Sedlchek, *Tappi J*., **76**, 143 (1993).
[3] J. Bouchard and M. J. Douek, *Pulp Paper Sci*., **20**, 131 (1994).
[4] M. M. Nazhad and L. Paszner, *Tappi J*., **77**, 171 (1994).
[5] M. Garg and S. P. Singh, *Appita J*., **59**, 274 (2006).
[6] B. Cao, U. Tschirner and S. Ramaswamy, *Tappi J*., **81**, 119 (1998).
[7] K. N. Law, J. L. Valade and J. Y. Quan, *Tappi J*., **79**, 167 (1996).
[8] H. F. Jang, R. C. Howard and R. S. Seth, *Tappi J*., **78**, 131 (1995).
[9] N. Wistara and R. A. Yong, *Cellulose*, **6**, 291 (1999).
[10] N. Wistara, X. J. Zhang and R. A. Yong, *Cellulose*, **6**, 325 (1999).
[11] A. Torgnysdotter and L. Wågberg, *Nordic Pulp Paper Res*. *J*., **18**, 455 (2003).
[12] N. K. Bhradwaj and V. Rajan, *Appita J*., **57**, 305 (2004).
[13] T. Yamauchi and M. Yamamoto, *Appita J*., **61**, 396 (2008).
[14] R. C. Mckee, *Paper Trade J*., **155**, 34 (1971).
[15] A. Bovin, N. Hartler and A. Teder, *Paper Tech*., **5**, 261 (1972).
[16] R. A. Horn, *Paper Trade J*., **159**, 78 (1975).
[17] Y. Yamagishi and R. Oye, *Japan Tappi J*., **35**, 33 (1981).
[18] J. H. Klungness and D. F. Caulfield, *Tappi J*., **65**, 94 (1982).
[19] J. F. Bobalek and M. Chaturvedi, *Tappi J*., **72**, 146 (1989).
[20] L. N. Law, J. L. Valade and J. Quan, *Tappi J*., **79**, 167 (1996).
[21] L. N. Law, J. L. Valade and Z. Li, *Tappi J*., **79**, 181 (1996).
[22] Y. M. Chen, Y. Wang, J. Q. Wan and Y. W. Ma, *Cellulose*, **17**, 329 (2010).
[23] C. F. Wijnman, *Tappi J*., **37**, 96 (1954).
[24] Tappi Test Methods, Tappi Press, Atlanta, GA, 2000-2001 (2002).
[25] F. D. Rebuzzi and V. Evtuguin, *Macromol*. *Symp*., **232**, 121 (2006).
[26] G. Jame, *Tappi J*., **41**, 180 (1958).
[27] T. Oksanen, J. Buchert and L. Viikari, *Holzforschung*, **51**, 355 (1997).
[28] S. Y. Shao, *Hubei Paper*, **4**, 11 (2001).