KRAFT PULP OXIDATION AND ITS INFLUENCE ON RECYCLING CHARACTERISTICS OF FIBRES

XIANLIANG SONG and KWEI-NAM LAW*

College of Material Science and Technology, Beijing Forestry University, Engineering Research Centre of Forestry Biomass Materials and Bioenergy, Ministry of Education, Beijing, China 100083

**Centre Intégré en Pâtes et Papiers, Université du Québec à Trois-Rivières, Trois-Rivières, Québec, Canada*

Received July 23, 2009

The work examines the effects of TEMPO-mediated 2,2,6,6-tetramethyl-1-piperidinyloxy (4-acetmido-TEMPO) oxidation on the characteristics of fibres and the recycling behaviour of oxidized fibres. Oxidation had a significant impact on fibre and paper properties, being dependent on the degree of oxidation. Generally, high-level oxidation had a negative effect on the beating degree of pulp, sheet density, folding endurance of paper and fibre bonding. However, pre-oxidation of once-dried fibres prior to secondary recycling could minimize the adverse influence of hornification.

Keywords: carboxylic acid, hornification, oxidation, recycling

INTRODUCTION

The hornification of recycled fibres is a stiffening effect on the cell wall, as a result of drying in papermaking.[1-3] The effects of recycling on paper quality have been thoroughly studied, particularly for chemical pulps.[4-16] In fact, the hornification level of the cell wall is associated with the chemical nature and fibre history.[17,18] According to Laivins and Scallan,[1] the presence of lignin plays an important role in the hornification phenomenon; the lignin interferes with the bonding between the cellulose chains, influencing the hornification effect. As a result, low-yield pulps suffer a higher hornification than the high-yield counterparts. Additionally, kraft fibres behave differently from the way the sulfite counterparts do during recycling.[6] Adversely, the lignin-rich mechanical fibres can actually benefit from recycling[9] by acquiring improved mechanical properties, as repeated recycling might increase the flexibility of the cell wall structure in mechanical fibres. Further on, beating of chemical fibres tends to enhance the effect of hornification.[10] Pulp bleaching[11] and freezing[15] could also induce hornification. Although the effects of recycling on the paper quality are well known, the recyclability loss of the secondary fibres is not fully understood. Different methods have been used, such as refining,[19-21] physical fractionation,[22,23] blending[8] and treatment with chemical additives. [24-26]

It has been shown that the inter-fibre bonding strength of fibres is related to the carboxyl content on the fibre surface.[27-34] Consequently, studies on oxidation mediated by a free radical, 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO), suggest that the process is relatively simple and that it has been utilized to convert the primary alcohol groups into carboxylic acid groups.[35-39] TEMPO-mediated oxidation has been recently applied to improve the properties of chemical[40,41] and mechanical [42,43] pulps. A scheme of TEMPO-mediated oxidation of the primary alcohol groups of cellulose in bleached hardwood kraft pulp is provided in literature.[40] Despite the extensive work done on the creation of carboxyl content on the fibre surface, only few investigations have been devoted to the influence of carboxylic acid generation on the recycling behaviour of fibres. In the present study, TEMPO-mediated oxidation was applied to generate carboxylic acid on aspen kraft fibres and to evaluate the oxidation impact on properties of paper prepared from once- and twice-dried fibres.

EXPERIMENTAL

Materials

The aspen kraft pulp used in the study, purchased from the Shandong Huatai Paper Group (China), came in a dry-lap form and had a beating degree of 15 °SR and a brightness of about 80%. The sample lap was soaked in water at room temperature, for 12 h, prior to its beating in a Valley beater at 2% consistency and room temperature (ISO standard 5264-1-1992). The final beating degree was of 45 °SR. In the paper, virgin pulp was used.

Oxidation

Oxidation was conducted using four main components: 4-acetamido TEMPO, sodium bromide (NaBr), sodium hypochlorite (NaOCl) and water. TEMPO acted as a catalyst, NaOCl/NaBr as a regenerating oxidant and water as a solvent. A part of the virgin pulp was oxidized before being recycled once, another part was first recycled and then oxidized. The oxidation procedure employed was similar to that described in literature.[43] The pH of the system was maintained at 10.5, using a NaOH or HCl solution, as depending on the situation. The specific conditions employed were the following: 4-acetamido TEMPO – 0.25%, NaClO – 92.59 mmol/15 g, NaBr – 92.59 mmol/15 g, pH – 10.5, temperature – 21 °C, reaction time – 20, 30, 40 and 50 min.

Determination of carboxylic acid content

The carboxylic acid content of the treated and untreated pulp samples was determined by a conductiometric titration technique.[44]

Handsheet formation

The beaten pulp was divided into two groups; one was oxidized, the other – not. Standard 60 g/m^2 handsheets were prepared from each group. Half of the handsheets in each group was used for characterization, while the other half was recycled once by soaking in water overnight and disintegrated before being transformed into standard handsheets and tested by the ISO standard method 5270-1998. A part of the untreated recycled pulp was oxidized and then processed into standard handsheets.

Determination of surface charge

Surface charge density (SCD) of fibres was determined by the back titration method. In fact, it was measured by colloidal titration with polyvinyl sulfonic acid potassium salt (PVSK) and poly-diallyl-dimethyl ammonium chloride (polyDADMAC). During the process, the sample was first diluted to an about 1% consistency and its pH was adjusted to 7.8. Further on, the water was filtered out using a G3 glass filter and the pulp was then placed in a 250 mL conical flask. An excess of PVSK solution and deionized water was added to the pulp slurry until a total volume of 150 mL was reached. The suspension was stirred for 30 min, after which the water was filtered out and the unreacted portion of PVSK present in water was back-titrated using polyDADMAC. The amount of PVSK that reacted with the fibres is a measure of surface charge.[45]

Measurement of water retention value (WRV)

The WRV value of the samples was determined with a LD4-2-A centrifuge (Beijing Medical Factory, China). The speed used was 2500 rev/min, for 15 min. In the process, 1 g sample pulp (o.d. basis) was diluted in 60 mL deionized water. Other details were given in a previous work of ours.[46]

RESULTS AND DISCUSSION

Effect of oxidation on fibre properties

Under the oxidation conditions here applied, gradual increases were recorded in the carboxyl content, as a function of reaction time (Fig. 1). However, the highest increase in the carboxyl content was obtained at a 50 min reaction time. As a result, the anionic surface charge density (SCD) of fibre augmented correspondingly. Some gradual increases in water retention value (WRV) were also observed, which might be attributed, in part, to the alkalinity (pH 10.5) applied in the oxidation process, or to the increased SCD or carboxyl content, which can form hydrogen bonds with water. As to the fibre beating degree (°SR), which is a physical effect, it did not show any definite significant changes.

As seen in Figure 2, the effect of recycled fibre oxidation was dependent on the history of the recycled fibres. When the fibres were oxidized prior to recycling (O-R-1), the WRV of the sample changed significantly following additional oxidation. A low oxidation level of the virgin fibre, for 20 min, gave the highest WRV. This peak value gradually decreased with increasing the oxidation time, which is a result of fibre surface damaging through additional oxidation.[47] In contrast, when the fibres were first recycled and then oxidated (R-1-O), the WRV remained relatively unchanged. This observation suggests that pre-oxidation could minimize the hornification effect on aspen kraft pulp fibres, and also that post-oxidation of the recycled fibres could bring about undesirable changes in the cell wall structure and sheet properties, as further discussed in the study.

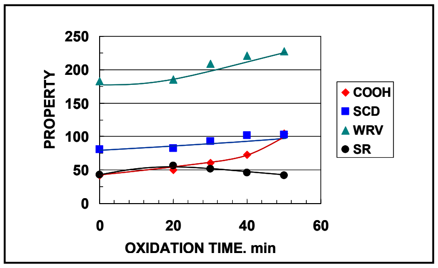

Figure 1: Oxidation of virgin fibre. Carboxyl content (COOH, mmol/kg); anionic surface charge density (SCD, mmol/kg); water retention value (WRV, g water/100 g fibre); beating degree (°SR)

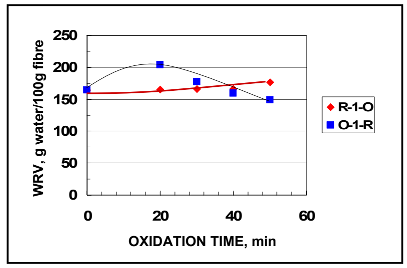

Figure 2: Water retention value of recycled fibres
R-1-O – The fibres were first recycled and then oxidated
O-1-R – The fibres were oxidized prior to recycling

Effect of oxidation on sheet properties

Beating degree

As shown in Figure 3, the level of oxidation has a definite influence on the fibre beating degree (or freeness). Interestingly, a low oxidation level of the virgin fibre, obtained in 20 min, gave the highest beating degree (°SR), or the lowest freeness. This peak value decreased gradually with increasing the carboxyl content. In fact, the beating degree dropped slightly below the value of the untreated virgin pulp when oxidation was carried out for 50 min, which suggests that further oxidation is undesirable. A similar tendency was also observed for the first oxidized and then recycled pulp (O-R-1). The oxidation of once-recycled (R-1-O) pulp could not significantly reduce the drop in the beating degree (or the increase in freeness), meaning that, once hornification is set, oxidation is ineffective in reversing the situation. However, a low degree of oxidation of the virgin fibre prior to recycling could help minimize the influence of hornification. Nevertheless, a high level of oxidation, attained, for example, in 50 min, or a carboxyl content higher than 100 mmol/kg aggravated the nature of hornification. This characteristic may be associated with the erosion of the fibre surface during further oxidation.[47]

Sheet density

The density of handsheets made of virgin fibres decreased gradually with increasing the reaction time or the carboxyl content (Fig. 4), which seems to be related to the drop in beating degree (or increased freeness), as illustrated in Figure 3. This observation indicates that oxidation changed both the chemical and physical nature of fibres. It is believed that, in the oxidation process, some chemical components – such as hemicelluloses – might have been dissolved, making the cellulose structure denser upon drying. The densified cellulose structure would render the individual fibre stiffer and thus make the sheet bulkier. However, when oxidation was conducted prior to recycling (O-R-1), sheet density increased, in contrast to the post-oxidation of the recycled fibre (R-1-O). In fact, the levels of oxidation had little influence on the density of the sheet made from R-1-O fibres. These characteristics reveal that the impact of oxidation on sheet density is associated with the history of the fibres used.

Tensile and burst indices

The influence of oxidation on tensile and burst indices is illustrated in Figures 5 and 6, respectively. Despite the different oxidation responses of the various fibre types (*i.e.* virgin, O-R-1 and R-1-O), a direct and relatively close relationship may be generally observed between sheet density, and tensile and burst indices. As shown in Figure 4, the oxidation of the virgin fibres decreased sheet density and, as a result, it reduced the tensile and burst indices. This reveals that the increase in carboxylic acid content, assumed to improve the inter-fibre bonding potential, is overshadowed by the changes occurring in the physical nature of the treated fibres. Additionally, the drop in these strength properties might be attributed to the increase in the repulsive force between fibres, as the carboxyl content increases.[48] On the other hand, it is, however noteworthy that the oxidation of virgin pulp before recycling (O-R-1) could significantly minimize the adverse effect of hornification on tensile and burst strengths; the reason is still unclear at this point. However, the oxidation of previously recycled fibres yielded no such benefits. Moreover, the influence of the physical defects that could be introduced during pulping, bleaching and subsequent laboratory recycling, on the mechanical properties of handsheet is unknown and, hence, unaccounted for in the discussion.

Tear index

Usually, a normal beating curve for chemical pulp has two parts. First, the tearing resistance of paper increases with increasing tensile strength or sheet density, or with decreasing freeness. Secondly, the increase in tear index usually reaches a peak value before falling off gradually, with further increases in tensile strength or density. The first part may be attributed to the increase in inter-fibre bonding, which reduces the number of fibres pulled out of the fibrous network, while the second part is due to the loss in fibre strength, thus increasing the possible fibre failure during the tearing test. Figure 7 shows that the tear index decreases with increasing sheet density (Fig. 7A) or tensile index (Fig. 7B). If our previous knowledge on beating of chemical pulps is valid, Figure 7 reveals that oxidation had degraded the intrinsic fibre strength, since the tear index fell with increasing sheet density or tensile index (indicator of inter-fibre bonding capacity). Note that, at a given sheet density or tensile index, the O-R-1 pulps exhibit higher tear index than their virgin counterparts. This might suggest that the recycled fibres have higher fibre strength due to their hornified cell wall, which remains to be verified by future measurements of the zero-span tensile test.

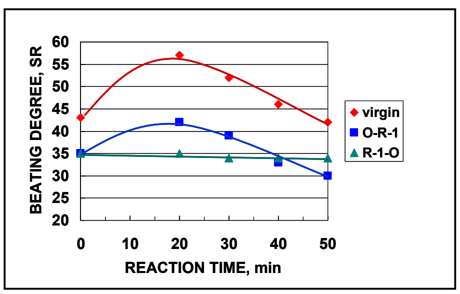

Figure 3: Effect of oxidation on fibre beating

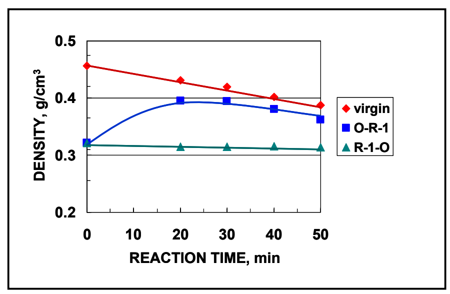

Figure 4: Effect of oxidation on sheet density

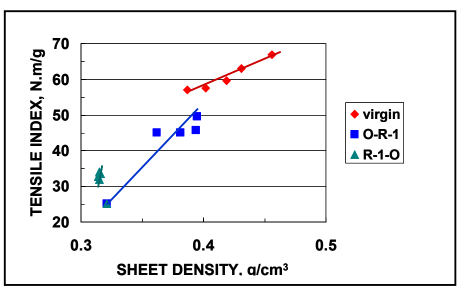

Figure 5: Tensile index *vs*. sheet density

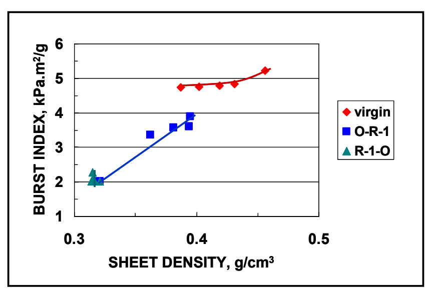

Figure 6: Burst index *vs*. sheet density

Folding endurance

Fibre hornification, a consequence of cell wall stiffening, increases fibre stiffness and gives bulky sheets. Figure 4 reveals that not only the recycling process, but also oxidation can induce fibre stiffening. Increased stiffness (or decreased flexibility) is accompanied by an increase in fibre brittleness or loss in folding endurance (Fig. 8). Consequently, the oxidation of the virgin fibre reduced remarkably sheet folding endurance. The rewetting-drying process (*e.g.* O-R-1 and R-1-O) had considerably aggravated its adverse effect on folding endurance (Fig. 8).

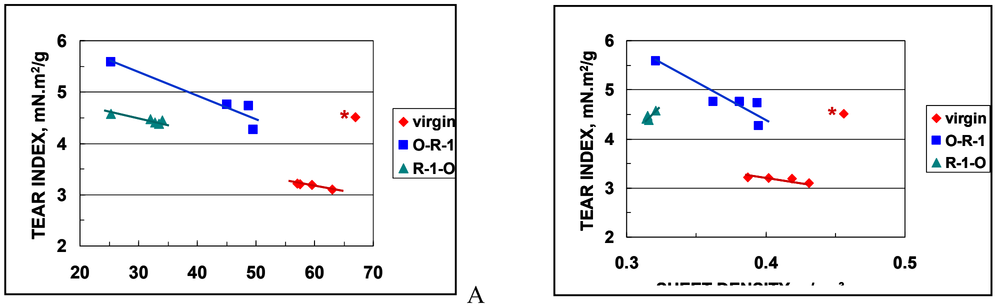

Figure 7: A – Tear index *vs*. sheet density; B – Tear index *vs*. tensile index (asterisks indicate the untreated virgin pulp)

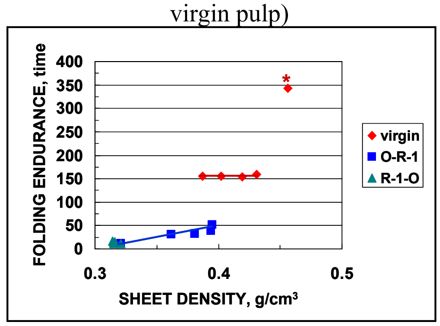

Figure 8: Folding endurance of handsheet *vs*. density (asterisk indicates untreated virgin pulp)

CONCLUSIONS

The beating degree increases when the pulp is oxidized to a low carboxyl content (≈ 50 mmol/kg), but it gradually decreases with increasing the carboxyl content or reaction time.

Fibre oxidation causes a remarkable reduction in pulp beating degree.

Fibre oxidation decreases sheet density. However, the oxidation of virgin fibre prior to recycling minimizes the loss in WRV and sheet density.

Fibre oxidation decreases the tensile and burst indices to some extent. However, fibre oxidation prior to recycling minimizes the loss in these properties.

Fibre oxidation influences negatively the tear index of paper.

The oxidation of virgin fibre reduces substantially handsheet folding endurance.

ACKNOWLEDGEMENTS: The project was sponsored by the Scientific Research Foundation for the Returned Overseas Chinese Scholars, Ministry of Education of the People's Republic of China.

REFERENCES

[1] G. V. Laivins and A. M. Scallan., *Procs. 10th Fundamental Research Symposium*, Oxford, U.K., 1993, p. 1235.

[2] M. M. Nazhad and L. Paszner, *TAPPI J*., **77**, 171 (1994).

[3] J. M. B. Fernandes Diniz, M. H. Gil and J. A. A. M. Castro, *Wood Sci. Technol*., **37**, 489 (2004).

[4] U. Weise, *Pap. Puu*, **80**, 110 (1998).

[5] R. C. Howard, *Pap. Technol*., **32**, 20 (1991).

[6] R. C. Howard and W. Bichard, *J. Pulp Pap. Sci*., **18**, J151 (1992).

[7] A. M. Scallan and J. Grgnon, *Svensk Papperstidn*., **82**, 40 (1979).

[8] J. L. Valade, K. N. Law and Y. X. Peng, *Progr. Paper Recycl.,* **3**, 60 (1994).

[9] K. N. Law, J. L. Valade and Z. J. Li, *Tappi J.,* **79**, 181 (1996).

[10] G. V. Laivins and A. M. Scallan, *J. Pulp Paper Sci*., **22**, J178 (1997).

[11] W. D. Wan Rosli, S. Amran and K. N. Law, *Prog. Paper Recycl*., **11**, 10 (2001).

[12] K. N. Law, X. L. Song and C. Daneault, *Cellulose Chem. Technol*., **40**, 335 (2006).

[13] F. Rebuzzi and D. V. Evtuguin, *Macromol. Symp*., **232**, 121 (2006).

[14] M. Garg and S. P. Singh, *Appita J*., **59**, 274 (2006).

[15] X. L. Song, K. N. Law, C. Daneault and N. Ying, *Beijing Linye Daxue Xuebao*, **29**, 128 (2007).

[16] Z. Dang, T. Elder, J. Hsieh and A. J. Ragauskas, *Holzforschung*, **61**, 451 (2007).

[17] B. Cao, U. Tschirner and S. Ramaswamy, *Tappi J*., **81**, 119 (1998).

[18] X. Song, K. N. Law, C. Daneault and N. Yin, *Trans. China Pulp Pap*., **22**, 12 (2007).

[19] J. Lumiainen, *Pap. Technol*., **35**, 41 (1994).

[20] K. Taegeun and H. Paulapuro, *Prog. Paper Recycl*., **15**, 11 (2006).

[21] C. Le Ny and M. Messmer, *Pulp Pap.-Can.*, **10**, 38 (2007).
[22] M. Kohrs, *Pap. Technol.*, **33**, 10 (1992).
[23] H. Selder, *Pap. Technol.*, **33**, 13 (1992).
[24] M. A. Hubbe and M. Zhang, *Procs. TAPPI Practical Papermaking Conference*, Milwaukee, WI, USA, 2005, p. 1213.
[25] M. Zhang, M. A. Hubbe, R. A. Venditti and J. A. Heitmann, *Procs. TAPPI Papermakers Conference*, Cincinnati, OH, USA, 2001, p. 801.
[26] M. Zhang, M. A. Hubbe, R. A. Venditti and J. A. Heitmann, *Prog. Paper Recycl.*, **13**, 5 (2004).
[27] T. Lindström and G. Carlsson, *Svensk Papperstidn.*, **85**, R14 (1982).
[28] T. Lindström and M. Kolman, *Svensk Papperstidn.*, **85**, R140 (1982).
[29] A. M. Scallan, *Tappi J.*, **66**, 73 (1983).
[30] C. Heitner and D. Atack, *Pulp Pap.-Can.*, **84**, 59 (1983).
[31] P. Engstrand, B. Sjogren, K. Olander and M. Htun, *Procs. Appita 6th SWPC*, Melbourne, Australia, 1991, **1**, p. 75.
[32] L. Wågberg and M. Björklund, *Nordic Pulp Pap. Res. J.*, **1**, 53 (1993).
[33] Z. Zhang, B. Sjogren, P. Engstrand and M. Htun, *J. Wood Chem. Technol.*, **14**, 83 (1994).
[34] D. Barzyk, D. H. Page and A. Ragauskas, *J. Pulp Pap. Sci.*, **23**, J59 (1997).
[35] J. M. Bobbitt, *J. Org. Chem.*, **63**, 9367 (1998).
[36] N. J. Davis and S. L. Flitsch, *Tetrahedron Letters*, **34**, 1181 (1993).
[37] A. E. J. de Nooy, A. C. Besemer and H. van Bekkum, *Carbohydr. Res.*, **269**, 89 (1995).
[38] A. E. J. de Nooy, A. C. Besemer, H. van Bekkum, J. A. P. P. van Dijk and J. A. M. Smit, *Macromolecules*, **29**, 6541 (1996).
[39] C. Tahiri and M. R. Vignon, *Cellulose*, **7**, 177 (2000).
[40] T. Itaoka, A. Isogai and F. Onabe, *Nordic Pulp Pap. Res. J.*, **14**, 279 (1999).
[41] T. Kitaoka, A. Isogai and F. Onabe, *Nordic Pulp Pap. Res. J.*, **15**, 177 (2000).
[42] J. Le Roux, D. Daneault and B. Chabot, *Pulp Pap.-Can.*, **107**, 39 (2006).
[43] K. N. Law, C. Daneault and R. Guimond, *J. Pulp Pap. Sci.*, **33**, 138 (2007).
[44] S. Katz, R. P. Beatson and A. M. Scallan, *Svensk Papperstidn.*, **6**, R48 (1984).
[45] S. Chen, X. Lin and D. Chen, *J. Cellulose Sci. Technol.*, **10**, 27 (2002).
[46] K. N. Law, C. Daneault and X. Song, *Cellulose Chem. Technol.*, **40**, 439 (2006).
[47] B. Sun, C. Gu, J. Ma and B. Liang, *Journal of Donghua University*, **29**, 98 (2003).
[48] X. Jin and C. Cao, *China Pulp Paper*, **22**, 44 (2003).