Refining and enzymatic treatment of secondary fibres for paperboard production: *Cyberflex* measurements of fibre flexibility

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Introduction

Recycling is generally affected by secondary fibre quality. High temperature and pressure during the drying stage causes irreversible changes in fibre morphology, which is the mainly responsible for the considerable reduction in the swelling and bonding ability (strength and number of bonds) [1, 2, 3]. Additionally, the reduced dewatering ability of these pulps is a major problem during paper manufacture as they decrease the speed on the paper machine and worsen sheet formation [4]. Secondary fibre upgrade is difficult and sometimes unpredictable, as the samples to be treated vary along with their history. Traditional upgrade methodologies have been used to improve secondary fibre properties, but the results are most of the times insufficient [1, 5]. Different reports suggest that treating pulps with enzymes and refining could overcome these problems [4, 6, 7, 8, 9]. More recently, Cellulose-Binding Domains (CBD's) usage has been shown as an interesting tool to modify recycled fibres properties [10].

Methods and Materials

A paper pulp, obtained after disintegration of old paperboard containers (mixture of 60% *Kraft* paper, 20% *fluting* and 20% *test liner*), was treated under different experimental conditions:

(i) refining, R, using a laboratory Valley beater (ISO 5264/1:1979);

(ii) enzymatic treatment, E, with a commercial cellulase (*Celluclast 1.5L*, Novo Nordisk);

(iii) cellulose-binding domains treatment, CBD, with a preparation obtained from the proteolytic digestion of *Celluclast 1.5L* [11];

(iv) refining + enzymatic treatment, RE;

(v) enzymatic treatment + refining, ER.

Enzymatic / CBD treatment of the samples: reactions took place in sodium citrate buffer 0.05 M, pH 5.0 (3% consistency, 50°C, continuous slow mixing) for 30 min, after a 10 min disintegration step. The enzymatic trials ended by boiling the suspension for 5 min. Both enzymatic and CBD treatments were evaluated by comparison with a control assay, which was made in the presence of heat-denatured enzyme ("Control E") or in the absence of CBD ("Control CBD"). Enzyme was used at 0.4 and 1.7 FPU/g pulp (dry basis) (0.7 and 2.8 mg protein) and CBD at 0.4, 1.4 and 2.8 mg protein/ g pulp (dry basis).

Pulp and Paper Testing: drainage rate (ISO 5267/1), burst (ISO 2758), tensile (ISO 1924/2), tear (ISO 1974), sheet density (ISO 534) and permeability to air flow (ISO 5636/3) were measured.

Flexibility measurements: after refining (0 – 30 min) and enzymatically treating (2.8 FPU/ g dry pulp, 15 min and 4 hours) the pulp, *Wet Fibre Flexibility Index* (% WFF) was measured using the *Cyberflex* analyser. The method involves fibres to bend over and wrap around a metallic wire representing a fibre of known dimensions, under specified experimental conditions. The more flexible the fibre, the more it will wrap around the wire. The overall pulp flexibility is expressed by an index ranging 0-100, which allows the direct comparison of different pulps [12, 13].

Results and Discussion

When fibres are refined, they randomly and repeatedly undergo tensile, compressive, shear and bending forces, which modify their properties [14]. Following this modification, fibres enlarge their surface area (due to increased fibrillation and swelling ability) and develop flexibility (Table 2), resulting in enhanced inter-fibre bounding. As a consequence, higher burst and tensile indexes are obtained (Table 1). Usually, both parameters increase to a maximum value and then decrease as a result of fibre breakage, when intensive refining occurs. At the same time, tear index is affected in the opposite way. This may be due to a decrease in inter-fibre bonding strength or fibre intrinsic strength and to the flexibility increase [15, 16].

However, the main inconvenient of refining is certainly the pulp drainage decrease. Drainability is essentially affected by the modification of fibre adsorptive capacities and fines release [7, 17]. Refining disrupts the fibre surface and increases the concentration of hydrophilic groups in the polysaccharide material, leading to further hydration [17]. Additionally, the hydrophilic groups may ionise in water, contributing to an osmotic effect which results directly in water entering into the fibre wall [18, 19]. The fibre surface erosion determines the swelling extension as it reduces the structure resistance. As well, it controls fines release into the pulp suspension. In secondary fibre, fines consist largely of microfibrils that strongly adhere to each other when they are originally dried on the paper machine. Their presence increases the specific surface area. They behave as fillers, with a small effect on strength but a large effect on drainage properties [7].

To improve the papermaking potential of secondary fibre it is important to establish a proper compromise between paper resistance and pulp drainage ability. Controlling fibre modification through the manipulation of several process variables (eg. rotational speed, residence time, temperature and plate design) is necessary [20], but refining may effectively upgrade secondary pulps [21].

Table 1: Pulp and paper physical properties after fibre modification

		Drainage (^{o}SR)	Tensile (Nm/g)	Burst (KPam^2/g)	Tear (mNm^2/g)
Refining	0 min	48	40.6	2.5	9.8
	15 min	70	54.3	3.5	8.5
	30 min	82	61.8	4.0	7.6
Enzymatic treatment	Control E	53	44.0	2.8	9.5
	0.7 mg protein	40	40.8	2.5	8.6
	2.8 mg protein	38	35.9	2.0	6.9
CBD's	Control CBD	50	36.5	2.3	9.2
	0.4 mg protein	50	40.0	2.4	9.4
	1.4 mg protein	43	39.0	2.5	9.0
	2.8 mg protein	44	37.9	2.4	8.4

According to some authors, refining may be improved by applying certain products (eg. starch, low-molecular-weight compounds) or treatments (eg. alkali, enzymes). Such refining aids are able to change the pulp characteristics during the process, accelerate the refining effects, or both [4, 6, 7, 8, 9, 17]. The use of enzymes was analysed in the present work by treating the fibres with a commercial cellulase, alone and combined with a refining-stage.

As it can be seen in Table 1 enzymes improved drainage and affected paper strength; although the results are not shown, the effect of enzymes before and after refining are identical. Cellulase activity effectively improves drainability of recycled fibres, but dramatically affects the paper strength [4, 9, 22]. The effect may be attributed to the enzymes action on the fibres surface, which is responsible for peeling away cellulose fibrils with high affinity for water, fines degradation, and modification of the interfacial properties. As we proposed in a previous study [10], the effect of °SR reduction by the enzymatic treatment can be interpreted as a consequence of fines stabilisation in the Shopper-Riegler apparatus. The strength properties maintenance depends on the fines and fibrils selective removal [4, 7, 22]. As in refining, the drainage/strength compromise is necessary; in this case, it is possible by controlling the enzyme dosage used (Table 1).

Refining improved sheet densification and decreased the paper permeability to air flow, while the enzymatic treatment increased both sheet density and permeability (data not shown). Sheet densification may arise from enhanced fibre flexibility and collapsibility. In fact, wet fibre flexibility (%WFF) measurements demonstrate this modification (Table 2). However, the generally accepted correlation between paper strength improvement and fibre flexibility gain (due to enhanced inter-fibre contact) is not always obvious in the present work [6, 23]. Although increased flexibility is always achieved, the strength indexes (tensile and burst) increase after refining, whereas they are considerably reduced after the enzymatic treatment.

%WFF increase after the enzymatic treatment may be related to the presence of adsorbed protein on the fibres surface [10]. Indeed, Nazhad and Paszner (1994) referred that the fibre-water interactions are very sensitive to the presence of external components [2]. In the enzymatically treated samples, protein adsorption increases the water affinity [10]. The effect can contribute to the disruption of the surface fibre arrangement in a mechanism similar to the one proposed by Milichovsky (1990), thus inducing higher flexibility. In addition, the enzymes action over the fibres seems to be able to develop modifications that are strong enough to damage the fibre intrinsic resistance and consequently paper strength is reduced.

Table 2: Wet fibre flexibility measurements (%WFF)

Refining			*Enzymatic treatment*			
R (0 min)	R (15 min)	R (30 min)	C (15 min)	E (15 min)	C (4 hours)	E (4 hours)
61.80	62.39	65.00	63.45	64.81	66.42	67.24

Cellulose-binding domains were also assayed for secondary fibre treatment (Table 1). Remarkably, the non-hydrolytic peptide was responsible for the simultaneous increase on drainage and strength, without modifying the sheet density or permeability. The CBD dosage seems to be critical to the process. As previously proposed, an excess of CBD may reduce the mechanical peeling of fines from the surface of fibres, thus worsening the final pulp characteristics [10].

How can the different non-hydrolytic CBD's and enzymatic effects be interpreted? In our opinion, both glycanases and CBD modify the fibres interfacial properties [10], and thereby the pulp and paper properties. Indeed, it has been recently shown [24] that CBD may lead to fibre disruption and crystallinity reduction, directly affecting the fibres hydration layers. The stabilisation of the fibres may allow a more homogeneous paper sheet, avoiding the formation of preferential draining channels. Upon drying, the interaction of the fibres is again possible [25]: apparently, the glycanolytic activity is detrimental to the paper strength, while a positive effect is obtained with CBD. The catalytic activity, and the much higher molecular weight of glycanases (versus CBD), may contribute for the different effects. More data on the use of CBD for pulp and paper modifications is necessary in order to support these assumptions.

Conclusions

Both refining and enzymatic treatment modify the secondary pulp and paper properties, by modifying the hydration properties of the fibres. Nevertheless, their successful application is related to a comprehensive control of the process. Refining is virtually associated to drainage and tear strength decrease and tensile and burst increase. The enzymatic treatment allows for an important increase in drainage but it is limited to the point that strength is not damaged. Cellulose Binding Domains probably share some of the good enzyme properties: hydration and slight surface disruption of the fibres (in a way similar to refining), without its drawbacks: fibre solubilisation or intrinsic fibre strength reduction. The hydration and stabilization of the fibres may lead to better paper sheet formation, resulting in improved paper resistance. Enzymes may have a similar effect, in some cases, but hydrolysis of the fibres surface is, probably, mainly detrimental.

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References

1. Marton, R., Brown, A., Granzow, S., Koeppicus, R. and Tomlinson, S., *Progress in Paper Recycling*, p.58 (1993).
2. Nazhad, M.M. and Paszner, L., *Tappi Journal* 77(9):171 (1994).
3. Weise, U. and Paulapuro, H., *J. Pulp and Paper Science* 25(5):163 (1999).
4. Pommier, J.-C., Fuentes, J.-L. and Goma, G. *Tappi Journal* 72(6):187 (1989).
5. Allen and Yaraskavitch, *Tappi Journal* 74(7):79 (1991).
6. Bobu, E., Moraru, T. and Popa, V.I., *7th Int. Conf. on Biotech. in the Pulp and Paper Ind.*, p. C143 (1998).
7. Bhat, G.R., Heitmann, J.A., and Joyce, T.W., *Tappi Journal* 74(9):151 (1991).
8. Stork, G. and Puls, J., *6th Int. Conf. on Biotech. in the Pulp and Paper Ind.*, p. 145 (1994).
9. Stork, G., Pereira, H. Wood, T.M., Dusterhoft, E.M., Toft, A. and Pulps, J., *Tappi Journal* 78(2):79 (1995).
10. Pala, H., Lemos, M.A., Mota, M. and Gama, F.M., *Enzyme and Microbial Technology* 29: 274 (2001).
11. Lemos, M.A., Teixeira, J.A., Mota, M. and Gama, F.M., *Biotechnol. Lett.* 22:703 (2000).
12. Cyberflex User Manual, CyberMetrics (1998).
13. Petit-Conil, M., Passas, R., Cleuet, J.C.., Fournier, R. and Voillot, C., *Paper Technology Symposium* (1999).
14. Seth, R.S., *Tappi Jou*rnal 82(3):147 (1999).
15. Seth and Page, *Tappi Journal* 71(2):103 (1988).
16. Page and MacLeod, *Tappi Journal* 75(1):172 (1992).
17. Milichovsky, M., *Tappi Journal* 73(10):221 (1990).
18. Lindström and Carlsson, Svensk Papperstidn 85(3):R14 (1982).
19. Scallan, *Tappi Journal* 66(11):73 (1983).
20. Kure, K.-A., Sabourin, M.J., Dahlqvist, G. and Ad Helle, T., *J. Pulp and Paper Science* 26(10):346 (2000).
21. Lumiainen, J.J., *Paper Technology* 40(2):29 (1998).
22. Jackson, L.S., Heitmann, J.A. and Joyce, T.W., *Tappi Journal* 76(3):147 (1993).
23. Abitz, P. and Luner, P., *Empire State Paper Res. Association Report #94*, Chapter V, p.67 (re-print 1995).
24. Xiao, Z., Gao, P., Wang, T., *Biotechnol. Lett.* 23:711 (2001).
25. Israelachvili, J., *Intermolecular and surface forces*, 2nd edition, Academic Press, p.399 (1992).