IMPROVING PAPERMAKING WITH CELLULOSE-BINDING DOMAINS

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RESUMO
A influência dos domínios de ligação à celulose (CBDs) nas propriedades das fibras celulósicas foi estudada em diferentes amostras de pasta, nomeadamente em pastas recicladas (de papéis kraft e de escritório) e químicas (Eucalipto e Pinho). Foi observado que as fibras tratadas com CBDs exibiam melhorias na drenabilidade da pasta, com redução do °SR até 15% e um aumento da permeabilidade ao ar das folhas de pasta, enquanto as propriedades de resistência não eram significativamente afectadas. A carga iónica de superfície das fibras diminuiu com este tratamento, mas o efeito da adição de um polímero catiónico (amido catiónico) não foi afectado pelo tratamento com CBD, pelo menos na amostra de pasta estudada. Foi também observado que o comportamento das diferentes fibras estudadas, no que respeita às propriedades avaliadas, era dependente da sua origem e morfologia.

PALAVRAS CHAVE: Domínios de ligação à celulose; fibras recicladas; pasta química branqueada; drenabilidade da pasta; propriedades da pasta

ABSTRACT
The influence of cellulose-binding domains (CBDs) on cellulosic fibres properties was studied in different pulp samples, namely recycled (from kraft and office waste papers) and chemical (Eucalypt and Pine) pulps. It was observed that the fibres treated with CBDs exhibited an improvement in pulp drainability with reduction of the °SR by up to 15% and an increase in air permeability of pulp handsheets, while the strength properties were not significantly affected. The surface charge of the fibres was decreased with this treatment, but the effect of the addition of a cationic polymer (cationic starch) was not affected by the CBD treatment, at least in the studied pulp sample. It was also remarked that the behaviour of the different studied fibres concerning the tested properties was dependent of the fibre morphology and origin.

KEY WORDS: Cellulose binding domains; recycled fibres; bleached chemical pulp; pulp drainability; pulp properties

MELHORAMENTO DA FABRICAÇÃO DE PAPEL USANDO DOMÍNIOS DE LIGAÇÃO À CELULOSE

INTRODUCTION

Polymeric additives are widely used in paper manufacturing to improve paper quality, which allows the use of low quality fibres (like fibres from waste papers) to produce paper with good properties. Usually, the use of recycled fibres in papermaking results in a decrease in paper strength properties. In general, it is assumed that the poor properties of recycled paper are mainly due to structural changes in the fibre caused by drying. Moreover, the paper machine runnability is deteriorated by the bad drainability of recycled pulp. Cellulases and hemicellulases are a class of additives, which may be used with the objective of to modify the fibre properties in order to improve or to change paper properties. The use of enzymes to modify or restore fibre properties in the recycling paper industry has become a useful method.

Recycled fibres can be upgraded through treatments with cellulases. In fact, the enzymes modify the interfacial properties of fibres, increasing the water affinity, which in turn change the technical properties of pulp and paper, such as drainability and strength (Pala *et al.*, 2002). According to other investigations, fibres treatment with different cellulases or hemicellulases lead to energy savings in beating and refining by reducing the beating time to achieve the same beating level, without affecting the pulp strength properties (Bhardwaj *et al.*, 1996)

Most cellulases have two different structural domains: a catalitic domain (CD) and a cellulose-binding domain (CBD). The binding domains are involved in the adsorption of enzyme to the cellulosic substrates, having no catalytic activity. Since they have a high affinity to cellulose (Tomme *et al.*, 1998; Xiao *et al.*, 2001), they offer quite a number of possibilities as additives for papermaking.

Relative bonded area (RBA), flexibility and fibrillation can be modified with endoglucanase V with CBD as well as without CBD in order to improve fibre properties (López-Lorenzo *et al.*, 2003). The better beatability of the bleached chemical pulp treated with intact endoglucanases than that treated with the corresponding core proteins suggests that the presence of CBD in endoglucanases could, however, result in beneficial effects on pulp properties (Suurnäkki *et al.*, 2000). Other authors had also observed that the existence or absence of enzyme CBD might play a determinative role on the effects of enzymatic treatments on pulp and paper properties (Dienes *et al.*, 2004).

It has been suggested that CBDs disrupts the structure of cellulose fibres surface but has no detectable hydrolytic activity (Din *et al.*, 1991; Xiao *et al.*, 2001). The binding of cellulose-binding domains to cellulose, under a wide range of environmental conditions, without the need for chemical reactions, makes them attractive molecules for the design of a new class of paper modifying agents that are environmentally friendly (Levy *et al.* 2002; Shoseyov *et al.*, 2003).

Treatment of secondary paper fibres with cellulose-binding domains allows for improvements of pulp drainability and of paper mechanical properties (Pala *et al.*, 2001; Pala *et al.*, 2003). The interface system fibre-water-fibre, and after drying, fibre-air-fibre, may be affected by the CBD treatment, influencing the pulp and paper technical properties (Pala *et al.*, 2003). Similarly, Levy and coworkers showed that a CBD from *Clostridium cellulovorans* improve the mechanical properties of Whatman paper sheets, as well as transform it into a more water-repellent paper, effects that were even more significant when a double CBD was used (Levy *et al.* 2002).

In this work, the influence of CBDs was studied on the pulps drainability (Schopper-Riegler index, °SR), on the fibres surface charge (zeta potential determinations) and on the paper handsheets properties (air permeability, density and tensile and tear strengths, at different beating degrees in a PFI mill). These studies were done in different type of fibres, recycled fibres from waste kraft papers (corresponding to long fibres, Rlf) and from waste office papers (corresponding to short fibres, Rsf). The behaviour of fibres from chemical pulps was also studied, using Eucalypt and Pine bleached pulps. The effect of the simultaneous use of CBDs and an usual chemical additive for papermaking (cationic starch) was also studied for one type of fibres (recycled fibres from waste office papers).

EXPERIMENTAL

CBDs were obtained using the method described in Lemos *et al.* The fibres used as primary fibres were bleached chemical pulps from Eucalypt and Pine woods and as secondary fibres were recycled kraft paper from old paperboard containers (kindly supplied by *Portucel Viana* company, actually *Gescartão*) and recycled office paper (kindly supplied by *Nisa* company).

The treatment was performed by mixing the CBDs (2 mg per gram of dried fibres) with 30 g (dried weight) of fibres (after PFI beating at 0, 1000 and 3000 revolutions) in acetate buffer (50 mM, pH 5,0) to a final volume of 2 L for 30 minutes at 22-25°C. Afterwards, the fibres were filtered. The pulp handsheet properties were analysed using ISO standard procedures.

The Zeta potential determinations were performed by a method using the streaming potential principle in a Mutek SZP 06 equipment. The consistency of the pulp suspensions was 1,5% and its conductivity was adjusted with KCl to 0,25 mS/cm. The value of each essay were the result of four determinations.

RESULTS AND DISCUSSION

The CBDs adsorption to cellulose fibres led to a reduction of the Schopper-Riegler degree by up to 15% (fig.1), indicating a stabilisation of the fines and a better distribution of the fibres in the mixture, which is probably due to the modification of surface properties of fibres with changes of the interfacial system fibre-water-fibre as described in previous studies (Pinto *et al.*, 2004; Pala *et al.*, 2003). The effect of CBDs were more noticeable in the case of short fibres (Rsf and Eucalypt) and at higher degrees of beating (3000 PFI revolutions). Regarding the long fibres, the Pine ones showed no variation, but the recycled pulp (Rlf) presented a decrease in °SR (fig.1**a**), which could be attributed to the shortening of the fibres by the recycling steps.

The air permeability of the pulp handsheets (fig. 2) increased with this treatment. This feature is more emphasised in recycled pulps (fig. 2**a**), which have shorter fibres, more fines and lower air permeability than the chemical ones. This increase is in agreement with the modification of fibre surface properties induced by the CBDs treatment as referred above, which probably gives rise to changes in the interfacial system fibre-air-fibre after drying (Pala *et al.*, 2003). This behaviour suggests a stabilisation of fibres and fines that allows a better passing through of the air in the paper structure.

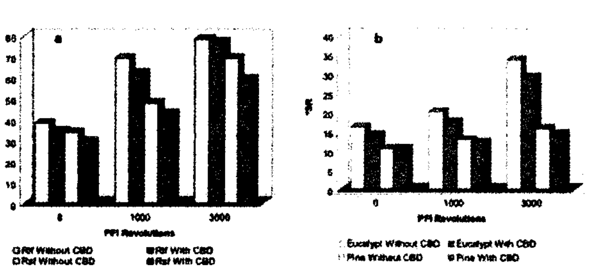

Figure 1: Schopper Riegler degree at different beating levels for the recycled (a) and the chemical (b) pulps treated with CBDs and without treatment.

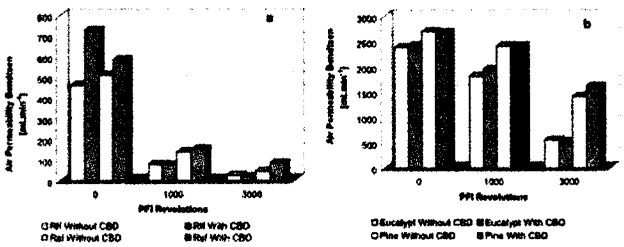

Figure 2: Air permeability of pulp hansheets at different beating levels for the recycled (a) and the chemical (b) pulps treated with CBDs and without treatment.

The density of the pulp handsheets (fig. 3), which could be considered indicative of the conformability of individual fibres, reflecting the fibres bonding potential, was only slightly increased by CBD treatment, in particular in the case of recycled fibres (fig. 3**a**).

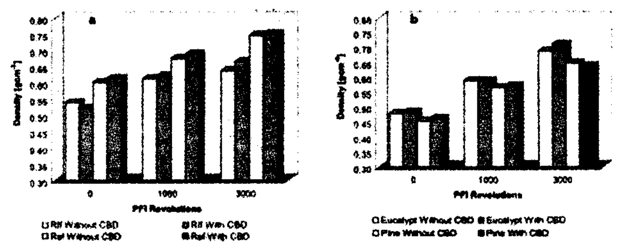

Figure 3: Density of pulp hansheets at different beating levels for the recycled (a) and the chemical (b) pulps treated with CBDs and without treatment.

The strength properties (fig. 4 and 5) were not significantly affected, with the exception of tear index for the recycled pulps (fig. 5**a**) in general and the short fibres in particular, which decreased by up to 12%. This feature could be attributed to the fact that the recycled fibres are already more damaged than the chemical ones, and its tear index is already lower than the others, so the effect of CBDs is more pronounced. This behaviour is probably also due to the structural changes undergone by cellulose, namely the decrease of crystalline index (Xiao *et al.*, 2001), even if no soluble sugars were detected with these treatments (Pala *et al.*, 2003).

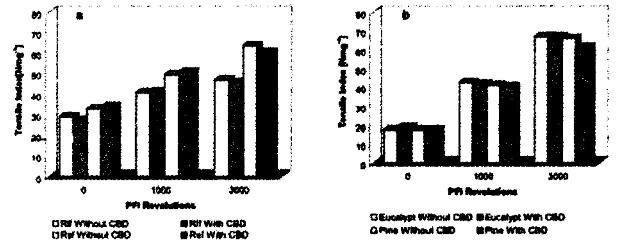

Figure 4: Tensile index of pulp hansheets at different beating levels for the recycled (a) and the chemical (b) pulps treated with CBDs and without treatment.

The surface charge of the fibres was determined as Zeta potential for a chemical pulp (Eucalypt) and for a recycled one (Rlf). As shown in Figure 6, the adsorbed CBDs reduced the Zeta potential,

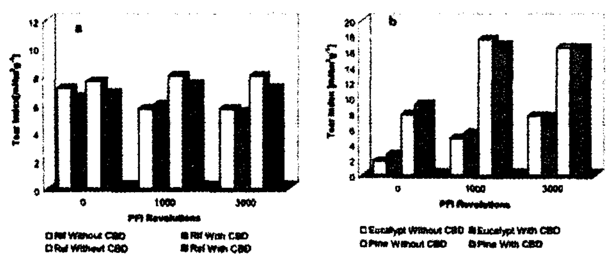

Figure 5: Tear index of pulp hansheets at different beating levels for the recycled (a) and the chemical (b) pulps treated with CBDs and without treatment.

particularly in the case of Eucalypt pulp. The hardwood fibres have more anionic surface charge than the softwood ones due to the presence of more glucuronic acids in the former, which is observed in the obtained results, since the Rlf fibres were mostly proceeding from softwood pulps. Thus the effect of CBDs treatment is more notorious in the case of the more charged fibres. Moreover, the presence of contaminants (like glues or paint) in the recycled fibres can mask the effect of the CBDs adsorption.

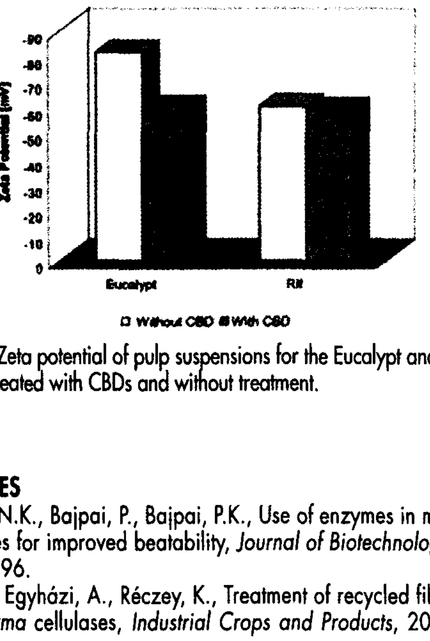

Figure 6: Zeta potential of pulp suspensions for the Eucalypt and recycled (Rlf) fibres treated with CBDs and without treatment.

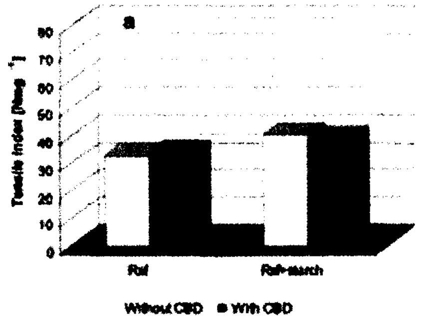

Figure 7: Tensile index (a) and density (b) of pulp hansheets refined at 30-35 °SR for the recycled pulp from waste office papers (Rsf) alone and with cationic starch treated with CBDs and without treatment.

Although the CBDs treatment decreases the cellulose surface charge, probably by blocking up the anionic sites of fibres, the effect of a cationic polymer used as dry strength additive in paper-making, cationic starch, was not affected, as it can be observed in Figure 7 **a** and **b**.

CONCLUSIONS

The present work showed the effect of a treatment with cellulose-binding domains on different types of fibres. The effect of this treatment was found to be dependent on the fibre origin, namely morphology and cellulose structure. The fibres from recycled pulps in general, and the short ones in particular, exhibited effects more noticeable than the others.

The results obtained showed that the fibres can be modified by the CBDs adsorption in order to improve some of its properties, specially the drainability and in some cases the strength. The increase in drainage rate could lead to energy savings in papermaking, and improve the runnability of recycled papermaking.

Other possibility for further studies is to use the CBDs in association with other molecules that could benefit paper properties but that don't have a natural adsorption to cellulose, by means of the high affinity that CBDs have to cellulose.

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