Enzymatic Refining and Cellulose Nanofiber Addition in Papermaking Processes from Recycled and Deinked Slurries

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Recycling and deinking processes cause fiber damage because of hornification phenomena and increased external fibrillation. Mechanical refining has been used for many years to enhance the mechanical properties of paper. Biorefining of pulp using enzymes is receiving increasing interest for energy reduction at the refining step of the paper-making process. Moreover, enzymes have also been used for the enhancement of mechanical properties without affecting the drainage rate. As an alternative to mechanical refining treatment, a combination of an enzymatic treatment and cellulose nanofibril (CNF) addition was explored to enhance the mechanical properties of paper. The tests were carried out on a deinked pulp (DIP) suspension made of 50% old newspapers (ONP) and 50% old magazines (OMG). Various enzyme charges and CNF amounts were added to the mixture of ONP and OMG. All pulps (treated and untreated) were characterized from a morphological point of view, and the paper sheets made thereof were mechanically characterized. The combination of the enzymatic treatment with the addition of 3% CNF provided sufficient tensile strength for the paper to be used in high-performance applications.

Keywords: Recycled paper; Biorefining; Endoglucanases; Nanofibrillated cellulose; Mechanical properties; Papermaking

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INTRODUCTION

Europe is one of the global leaders in paper recycling. The paper recycling rate in Europe reached 71.7% in 2013 (CEPI 2013), representing an increase of 45% in the last 15 years. To further extend the limits of paper recycling, the quality of the recovered paper is a crucial issue (Miranda Carreño *et al*. 2010), and a huge effort is required to maintain the quality of the final paper products (Miranda *et al*. 2011) or even to improve it to achieve higher performance applications. Moreover, better quality fibers could allow the use of lower basis weights or fillers, such as precipitated calcium carbonate. In this sense, the papermaking industry is forced to implement several concurrent strategies, as recycling is expected to be a central part of its activities (Hubbe 2014).

Paper fiber is now recycled an average of 3.5 times in Europe, far exceeding the world-wide average of 2.4 (CEPI 2013). As is well known, with each recycle, the quality of the raw materials deteriorates because of the undesirable changes in fiber properties and the higher drainage resistance of the pulps. The first is due to hornification and it affects interfiber bonding and consequently paper strength. The second process makes sheet formation difficult, decreases paper machine runnability, and increases drying energy consumption (Rashmi and Nishi 2010; Hubbe 2014).

Currently, the proportion of recovered fibers used for paper production (utilization rate) has reached approximately 52% (Pöyry 2011) and is much higher for cases like newsprint (96.9%). In this case, the upgrading of the fiber quality is a key issue in maintaining the sustainability and competitiveness of the process. Nevertheless, the whole market share of the recovered fibers is still low because of the decrease in the mechanical properties of papers produced from recycled fibers. It is also well known that one of the problems with recycled papers is the hornification phenomena. This phenomena, together with loss of molecular weight, presence of contaminants, or debonding effects of fillers, have become topics of concern because they cause loss of properties and fiber degradation (Hubbe 2014). A large number of studies have focused on the recovery of fibers (Howard 1995; Ackermann et *al.* 2000; Hubbe and Heitmann 2007). Specifically, deinked fibers are of particular interest, and many efforts have been made to exploit them, even using enzymes (Carrasco *et al.* 1997, 1999; Pelach *et al.* 2001; Pèlach *et al.* 2002; Pelach *et al.* 2003a; Pèlach *et al.* 2003b; Vilaseca *et al.* 2005).

Mechanical refining has the objective of enhancing the mechanical properties of paper, increasing the specific surface and, consequently, enhancing the number of bonds per volume. It has been demonstrated that mechanical refining causes fiber shortening, fines production, and an increase in the specific surface area and relative bonding area (RBA) (Dasgupta 1994). Moreover, this increase in the number of bonds per volume has a negative effect on the drainage rate of pulp slurries (Norell *et al.* 1999). On the other hand, biorefining has received growing interest (Torres *et al.* 2012) because fiber modification with enzymes (*e.g.*, endo-β-1,4-glucanases) can result in a substantial increase in pulp freeness with only a slight or even no loss of physical properties. If the treatment applied is limited, enzymes will remove elements having a great affinity for water. If the treatment is extended, fibrillation becomes pronounced, strength increases, and drainage decreases (Garcia *et al.* 2002; Kim *et al.* 2006; Gil *et al.* 2009; Torres *et al.* 2012; González *et al.* 2013; Pelletier *et al.* 2013).

In recent years, several authors have investigated alternative treatments of pulp slurries with the purpose of enhancing mechanical properties without harming fibers drastically. One of the promising options is the addition of cellulose nanofibers (CNFs) as a strength-reinforcing additive to improve the physical and mechanical properties of paper (Ahola *et al.* 2008; Taipale *et al.* 2010; González *et al.* 2012; Delgado-Aguilar *et al.* 2014). However, in most of the cases, a decrease in the drainage rate was also noted because of the ability of CNF to hold huge amounts of water (González *et al.* 2012, Delgado-Aguilar *et al.* 2015a,b). Specifically, Delgado-Aguilar *et al.* (2015a) explored the addition of CNFs in bulk in deinked pulp (DIP) suspensions, achieving a maximum increase of 82% in breaking length with a Schopper–Riegler degree of 87 °SR when 4.5 wt% CNF was added.

To alleviate this shortcoming, the aim of the present work is to enhance the mechanical properties of recycled and deinked paper using enzymatic treatment. Moreover, the combination of this enzymatic treatment (biorefining) and CNF addition will be studied to further improve the physical and mechanical properties to reach the mechanical requirements of newsprint or papers for high-performance applications such as packaging or envelopes.

EXPERIMENTAL

Materials

Old newspapers (ONP), supplied by Diari de Girona S.L. (Girona, Spain), and old magazines (OMG), kindly supplied by Drim S.A. (Girona, Spain), were characterized before proceeding with laboratory disintegration and flotation for deinking. Both ONP and OMG were stored for one week before starting the experiments. A mixture of 50% ONP: 50% OMG was disintegrated in a laboratory pulper equipped with a helico rotor at a consistency of 10% and in basic medium (0.6% NaOH, expressed on dry pulp). Disintegration was carried out at 50 °C and 1100 rpm during 15 min. Next, the pulp was diluted to 2% consistency, adding 0.4% surfactant (Sulfopon 101SPZ, Henkel, Spain) and floated in the same pulper provided with air bubbling from the bottom of the container. The yield of this operation was 84% (w/w). Biorefining was performed with endo-β-1,4-glucanase (Serzym 50), supplied by SERTEC-20 S.L. (Spain), with an activity of 84,000 CMU/g at 60 °C and at a pH of 4.8 over a carboxymethylcellulose (CMC) substrate. All the chemical reagents for the enzymatic treatment were provided by Sigma Aldrich (Spain).

Experimental Procedure of This Work

Figure 1 reflects the whole experimental procedure of the present work.

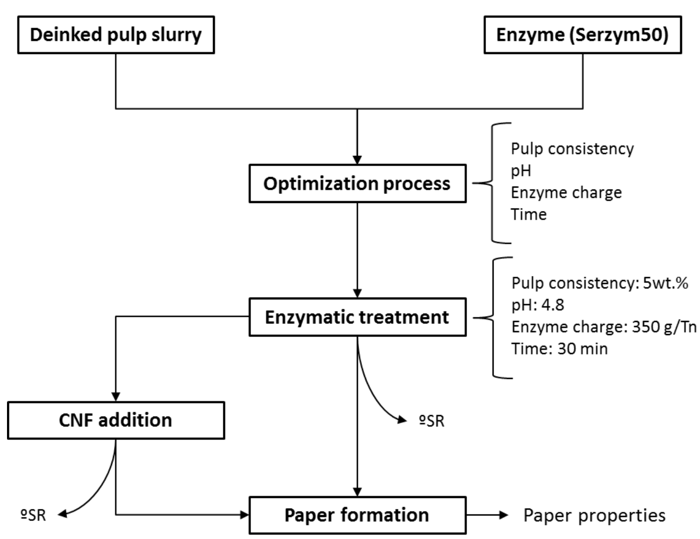

Fig. 1. Experimental procedure of the present work

Optimization of Enzymatic Treatment

The optimization of the enzymatic treatment was carried out by varying the parameters involved in the biorefining process, which are (i) enzyme charge, (ii) time, (iii) pulp consistency, (iv) pH, and (v) temperature. First, the enzyme charge was varied from 0 to 400 g/Tn (grams of Serzym 50 per dry tonne of pulp). Next, the effect of pH was studied, from 4.5 to 7.5. The pulp consistency was varied from 1 to 10 wt%. Finally, the treatment time was also varied, from 0 to 90 min. The temperature was set at 65 °C, as reported by González *et al.* (2013).

The optimization of the enzymatic treatment of the DIP suspension is reflected in the Results and Discussion section.

Enzymatic Treatment

Enzymatic treatment was carried out according to González *et al.* (2013). For enzymatic treatment, 75 dry g of ONP/OMG pulp was suspended in 1,500 mL (5 wt%) of distilled water. The formed slurry was then stirred and heated at 65 °C. The pH was set at 4.8 by the addition of diluted HCl (3%) solution. At this point, enzymes (350 g per Tn of dried pulp) were added to the slurry, and stirring was continued for 30 min. The enzymatic reaction was stopped by increasing pH by adding NaOH solution (10%). The resulting enzyme-treated pulp was finally washed with distilled water to eliminate the remaining enzyme and the reagents. These conditions were chosen based on the experiments described in the Results and Discussion section of the present paper.

Preparation of Cellulose Nanofibers

CNFs were obtained through the chemical modification of fibers based on 2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) mediated oxidation of commercial bleached eucalyptus pulp, followed by high-pressure homogenization. The reaction was performed under alkaline pH conditions, following the methodology reported elsewhere (Saito *et al.* 2007). In a typical experiment, 15 g of cellulose fibers was dispersed in distilled water containing TEMPO (0.016 g per g of fibers) and NaBr (0.1 g per g of fibers). The mixture was stirred for 15 min to assure a good dispersion. After this, a 15% sodium hypochlorite (NaClO) solution was added drop by drop to the slurry. The volume of NaClO was calculated to add 5 mmol per gram of cellulose. The pH was kept at 10 by adding drops from a 0.5 M NaOH solution. The oxidation was considered finished when the pH was constant at 10. The oxidized fibers were then filtered and washed with distilled water five times. Finally, the fiber suspension was cooled at room temperature before going through mechanical treatment. Fibrillation of oxidized fibers was performed by pumping a 1 to 2 wt% fiber suspension through a high-pressure homogenizer (NS1001L PANDA 2K-GEA Niro Soavi, Italy). Operation conditions were set at 600 bar pressure. This operation was carried out up to seven times until a transparent gel-like product was produced. These CNF were the same used in a previous work (Delgado-Aguilar 2015a).

Incorporation of CNFs into the Pulp Suspensions

CNFs were added to a 1.5% consistency ONP/OMG pulp furnish, prepared with tap water (289 μS/cm), and mixed in a pulp disintegrator for 60 min at 3,000 rpm. This methodology has been used in previous works (González *et al.* 2012; Alcalá *et al.* 2013) and has proven to be effective in improving the dispersion of CNF in papermaking pulps. After this step, cationic starch and colloidal silica were added at corresponding doses of 0.5% and 0.8 %, respectively, expressed on dry pulp. The application of these retention agents was done at gentle agitation of the suspension at 1% consistency for 20 min. This step is necessary to avoid the loss of CNF during the dewatering process because filters at the bottom of the stock container in the Rapid-Köthen equipment are not able to retain nanometric material. The amount of CNFs added was calculated to obtain paper sheets with various percentages of CNFs. Paper sheets with an average basis weight of 75 g/m^2 were prepared.

Physical Characterization

Pulp suspensions were characterized by means of: Schopper-Riegler freeness (ºSR) following the ISO 5267-1 standard, and morphological analysis, carried out by using a MorFi Compact analyzer (TechPap, Grenoble, France), which is able to calculate, among other parameters, average length weighted in average (L_w), diameter (d), fines percentage (%), and ratio of microfibrils (RoM) (Huber *et al.* 2008). The conductivity of the background and the slurry was measured using a conductometer CRISON BASIC 30 (L'Hospitalet de Llobregat, Spain).

Characterization of handsheets obtained from the different fibrous suspensions was performed by determining mechanical properties as breaking length and Young's modulus (ISO 1924), Mullen index (ISO 2758), and Scott Bond (TAPPI T569 (2000)). Void volume was determined according to Delgado-Aguilar *et al.* (2015a) to assist in the discussion.

RESULTS AND DISCUSSION

In the first part of the work, the optimum conditions for the biorefining process were investigated. In the second part of the work, the synergic action between biorefined pulp and CNF addition was studied.

Determination of Optimal Conditions for Enzymatic Treatment

The main parameters to be considered when a paper slurry is treated with endo-β-1,4-glucanase are the following: (i) enzyme charge, (ii) time, (iii) pulp consistency, (iv) pH, and (v) temperature.

In this work, biorefining process was applied to recycled and deinked pulp made of old newspapers (50 wt%), and old magazines (50 wt%), instead of the traditional mechanical refining, avoiding fiber deterioration.

To determine the optimal activity of the enzymes, parameters were varied with the purpose of studying their effect on the final mechanical properties. Figure 2 shows the changes in breaking length and the ratio of macrofibrils (RoM) while enzyme charge was varied.

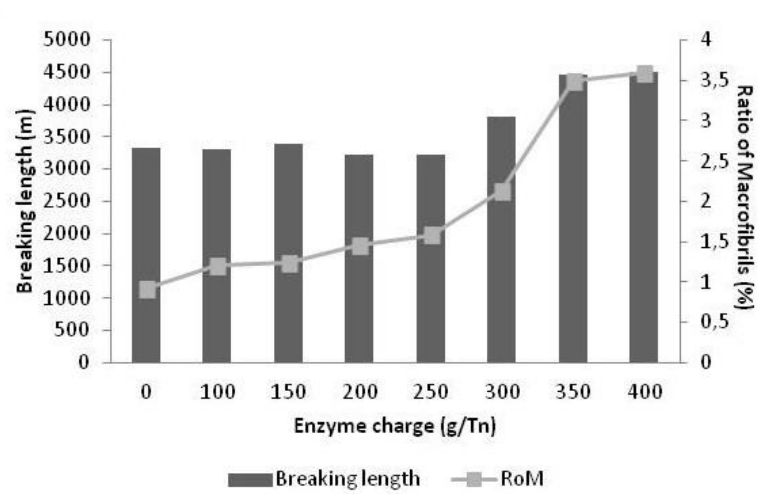

Fig. 2. Effect of enzyme charge on paper breaking length and RoM

Regarding the rest of the parameters, pH was set at 4.8, where the enzyme has its maximum activity, as reflected in the data sheet. Time and pulp consistency were set according to González *et al.* (2013) at 30 min and 5 wt%, respectively. Paper sheets made of DIP suspension without any enzymatic treatment have 3326 m of breaking length (32.61 N·m/g). Using this value as a reference, Fig. 2 shows that from 0 to 250 g/Tn of enzyme charge, the change in the breaking length was marginal. However, between 250 g/Tn and 350g/Tn, a steady enhancement in the breaking length (38%) is noted to level off over a charge of approximately 350 g/Tn. It is likely that charges less than 250 g/Tn are not sufficient to reach the critical charge (volume per volume) able to notably enhance the tensile resistance. The value of breaking length reached with 350 g/Tn of enzyme charge is higher than the breaking length possible through more than 2000 revolutions of a PFI refiner (Delgado-Aguilar *et al.* 2015a).

The evolution in ratio of macrofibrils (RoM) is also included in Fig. 2. In the first domain between enzyme charges of 0 and 250 g/Tn, RoM increased from 0.919 to 1.585 (72% increase). However, this enhancement was not sufficient to bring about an improvement in the breaking length. Between 250 g/Tn and 350g/Tn, a similar trend (as in breaking length) was noted with steady enhancement (120%) up to 350 g/Tn, followed by a plateau at values greater than this charge.

Endoglucanases can decrease the degree of polymerization of cellulosic chains drastically because of their operating principle (Ek *et al.* 2009) and, consequently, decrease the intrinsic tensile strength of fibers. This type of enzyme usually acts on the amorphous part of the cellulose chain, cutting the β-1-4 bonds, generating external fibrillation and/or fibrils in the paper slurry, and, consequently, increasing the crystallinity of cellulose.

Additionally, Momeni (2014) illustrated a possible mechanism of interaction between fibers and endoglucanases, as shown in Fig. 3.

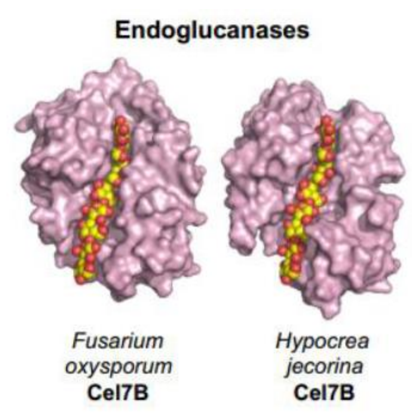

Fig. 3. Molecular surface of endoglucanases ant their interaction with fibers (from Momeni 2014)

Endoglucanases envelop individual cellulose chains, at appropriate enzyme charges (Fig. 3), to access the amorphous part thereof. If the fiber to be enzymatically treated has a pronounced external fibrillation (recycled pulps), this surrounding will become more difficult than in the case of virgin pulps without any refining. This fact could explain the differences in the increase in breaking length between DIP papers and bleached eucalyptus pulp ones (González *et al.* 2013), a part of the hornification phenomena that recycled fibers experience with successive recycling processes. For instance, an application of 300 g/Tn provided to DIP papers resulted in a 15% increase, while for bleached eucalyptus pulp, there was a 64% increase.

The effect of pH on the enzyme activity was also investigated at three levels of enzyme charge (300, 350, and 400 g/Tn) using an enzymatic treatment time of 30 min and a pulp consistency of 5 wt%. Results shown in Fig. 4 indicated that the highest pH for enzyme activity was located from 4.8 to 6.5, with an optimum close to 4.8, as per the supplier specifications.

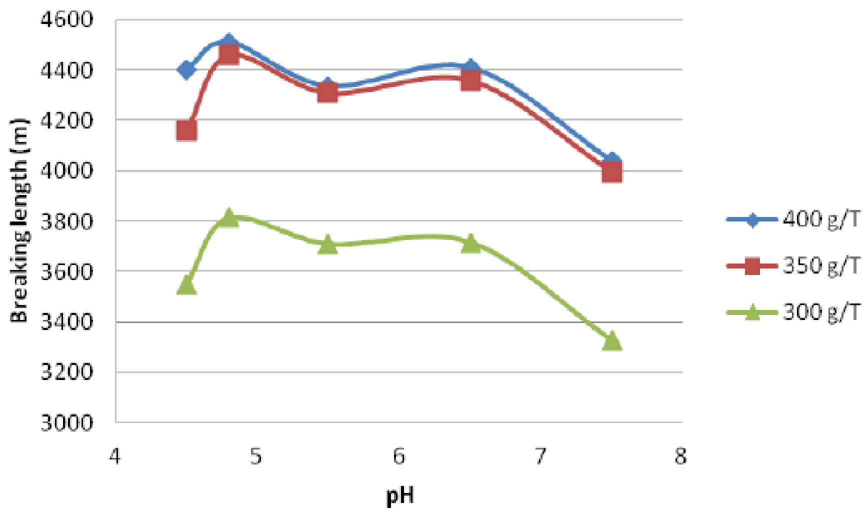

Fig. 4. Effect of pH in biorefining treatments

The effect of consistency was also studied at a pH 4.8 with an enzyme dosage of 350 g/Tn for 30 min. Results shown in Fig. 5 indicated that 5 wt% consistency was the optimum working level.

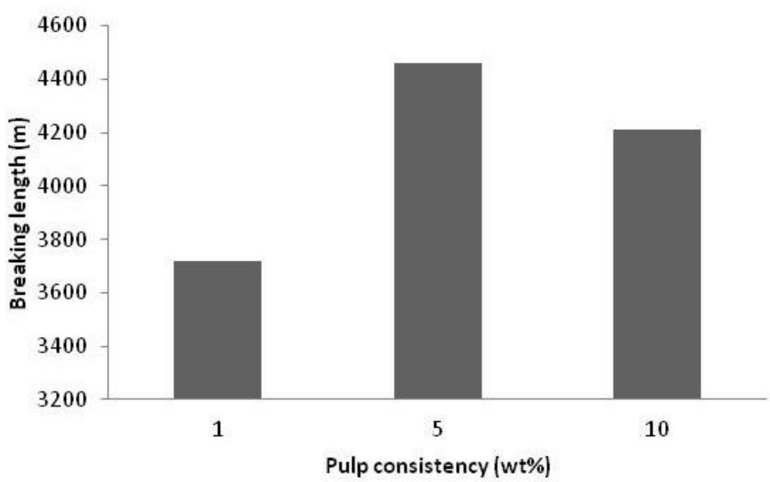

Fig. 5. Effect of pulp consistency on paper breaking length

The enzyme charge with regard to the total volume became higher as the pulp consistency increased. This may be the main reason for the increase in the efficiency from 1 to 5 wt%, where charge is increased and the total volume of the suspension decreased. The enzyme concentration at 10 wt% consistency probably was too high for the suitable performance of enzymes, decreasing the breaking length slightly (6%).

The time of enzyme treatment was also investigated over a domain from 0 to 90 min at a pH 4.8, 5 wt% consistency, and a temperature of 65 °C. Data shown in Fig. 6 reveal an improvement in the breaking length with treatment time up to 45 min. Over this time, the breaking length remained nearly constant up to 60 min, after which it decreased. This behavior is similar to the effect of time on virgin pulps (González *et al.* 2013).

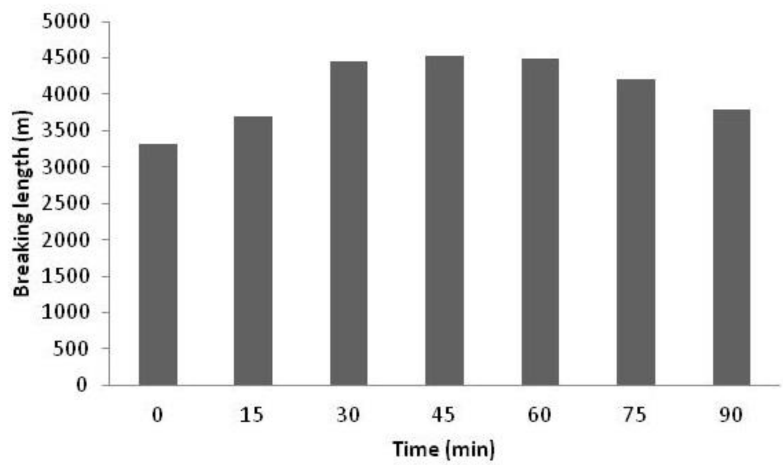

Fig. 6. Effect of reaction time on paper breaking length

The breaking length with 45 min of treatment time did not experience any noticeable improvement, so 30 min was established as the treatment time for energy-saving reasons.

Having determined the different roles of each parameter over the breaking length, the final treatment conditions were the following: (i) 350 g/Tn enzyme charge, (ii) 30 min, (iii) 5 wt% pulp consistency, (iv) pH 4.8, and (v) 65 °C. This treatment provided the recycled and deinked paper sheets with a 34% increase in breaking length (from 3326 to 4460 m). The breaking length, 4460 m, would represent about 6000 m in the machine direction (assuming an anisotropy ratio of 1.35), a value notably higher than ONP in the machine direction (Delgado-Aguilar *et al.* 2015a).

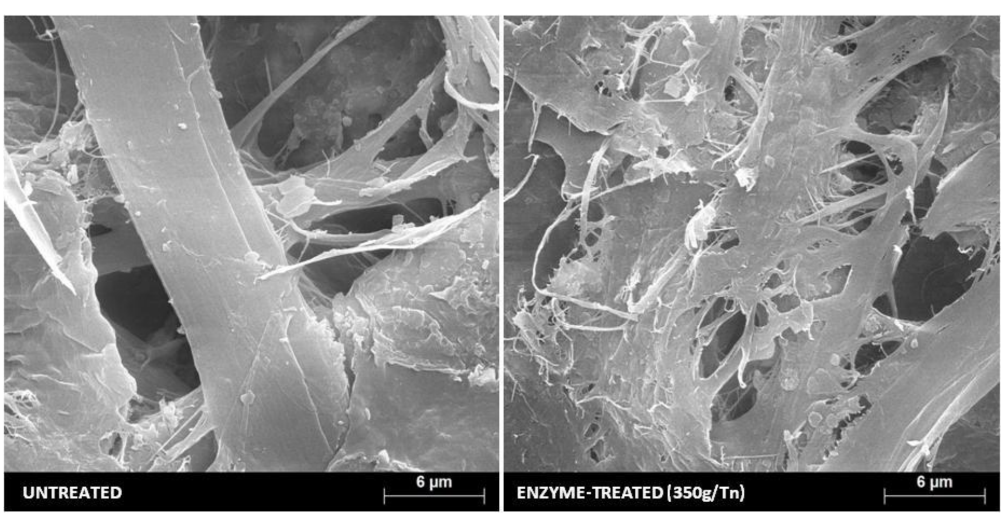

Fig. 7. SEM images of untreated and enzyme-treated paper sheets

Another important parameter in papermaking is the drainage rate, because it affects the runnability in the paper machine. Schopper–Riegler degree (°SR) and Canadian standard freeness are useful parameters to evaluate the drainage capacity of a pulp. Considering the increase in the RoM and the external fibrillation observed in SEM images (Fig. 7), a decrease in the drainage rate was expected. In this sense, surprisingly, the Schopper–Riegler degree only increased from 64 to 66 °SR.

Table 1 shows that the fiber macro-morphology (length, width, and fines) was not affected by the enzymatic treatment. The morphological analysis indicates that the increase on the RoM probably was the main cause of the improvement in the mechanical properties. The RoM enhanced inter-fiber bonds and fiber shrinkage.

Table 1. Morphology of Untreated and Enzyme-Treated Pulps

Pulp type	Length (μm)	Width (μm)	Fines (%)	RoM (%)
Untreated	843 (11)	18.6 (0.2)	40.38 (0.12)	0.919 (0.032)
Enzyme-treated	841 (9)	18.3 (0.1)	40.43 (0.14)	3.487 (0.087)

Synergic Action between Enzymatic Treatment and CNFs

To further improve the mechanical properties, the synergic action between CNFs and enzymatic treatment was studied. The suitability of CNFs as a paper additive has been studied by several authors in recent years (Ahola *et al.* 2008; Eriksen *et al.* 2008; Sehaqui *et al.* 2011; González *et al.* 2012). The level of CNF addition ranged between 0 and 3 wt% to avoid excessive loss of the drainability of the pulp suspension. Data collected in Table 2 clearly indicate an improvement in all the mechanical properties of paper with increasing CNF content. For instance, in the presence of 3 wt% CNF, the enhancements in the breaking length, the Young's modulus, and the Scott Bond were approximately 21%, 55%, and 55%, respectively.

Table 2. Pulp and Paper Properties of DIP Suspensions, Untreated and Enzyme-Treated

Pulp type	CNF (%)	°SR	Breaking length (m)	Y. Modulus (GPa)	Mullen Index (kPa·m^2/g)	Scott Bond (J/m^2)
Untreated	0	64	3326 (69)	3.26 (0.11)	2.14 (0.09)	301.50 (29.31)
Enzyme-treated	0	66	4460 (93)	4.22 (0.18)	2.42 (0.11)	315.80 (23.39)
	1.5	77	5015 (101)	4.82 (0.16)	2.73 (0.07)	361.20 (33.09)
	3	80	5421 (116)	5.07 (0.23)	2.92 (0.19)	411.50 (43.01)

As can be seen in Table 2, the addition of a 3 wt% CNFs to the biorefined DIP pulp increased the breaking length to 5421 m (isotropic formation). Considering this value, and applying again an anisotropy ratio of 1.35, this would represent approximately 7500 m of breaking length in the machine direction, which is a value 1.5 times higher than the original newspaper (Delgado-Aguilar *et al.* 2015a).

However, in terms of mechanical property improvement, enzyme-treated pulps were found to be less sensitive to the enhancements associated with the addition of CNFs.

Comparing the breaking length results of the present study with untreated DIP suspensions, a 3 wt% of CNF addition resulted in an increase in the biorefined paper of 21% of breaking length besides the 52% increase that untreated DIP papers experienced, for the same CNF addition, in the work developed by Delgado-Aguilar *et al.* (2015a). This difference may be due to the differences in RBA between reference papers (Lindström *et al.* 2014).

Breaking length, like some other mechanical properties, depends on many factors: (i) number of bonds per volume unit, (ii) quality of bonds, and (iii) intrinsic tensile strength of the fibers (Marais and Wågberg 2012). When RBA increases, the number of bonds per volume unit also increases. Moreover, as the quality of this bonds increases, the mechanical properties also tend to increase. When the maximum number of bonds and their quality are achieved, the breaking length of the paper will approach the intrinsic breaking length of fibers. Taking into account this hypothesis based on Page's equation (Page 1969), the differences observed in the CNF performance on each substrate are understandable. Another demonstration of this fact is that CNFs demonstrate better behavior when they are applied over bleached kraft pulps (González *et al.* 2012, 2013) rather than in recycled and DIP suspensions (Delgado-Aguilar *et al.* 2015a).

Regarding the rest of the mechanical properties, it was observed that their evolution was in concordance with breaking length, *i.e.*, each property could be linearly correlated with tensile resistance.

Another property shown in Table 2 is °SR. The drainage rate was characterized using the °SR technique, and pulp showed a clear loss in the drainability. This increase in °SR was due to the porosity decrease as CNF percentage was increased because of their ability to fill the void spaces between fibers; moreover, shrinkage of CNFs draws the larger fibers together because of surface tension forces.

A way to mitigate the effect on the drainage rate could be the addition of drainage aids, such as polyethyleneimine. Although it is true that drainage aids limit and even decrease the mechanical properties of paper, a 0.2 wt% addition over dried pulp of polyethyleneimine decreased, for instance, the drainage rate from 80 to 61 °SR and the breaking length by 13% in the case of enzyme-treated DIP suspensions with a 3 wt% of CNF addition.

CONCLUSIONS

In the present work, paper sheets of DIP suspensions were made to study the effect of biorefining processes and to understand if the combination between enzymatic treatment and CNF addition provides a competitive performance to the paper.

1. With regard to the treatment with endoglucanases, it was demonstrated that it can be applied to recycled and deinked pulp suspensions. Moreover, the optimal conditions of biorefining were determined. This technique allows improving mechanical properties without drastically decreasing the drainage rate. Through the use of biorefining it was shown that it is possible to achieve the mechanical requirements for newsprint without mechanically refining the fibers or adding CNFs. The increase in breaking length (more than 30%) is an achievement, especially taking into account the small decrease in the drainage rate.

2. Through the combination of biorefining and CNF addition, it has been found that CNFs have a worse performance when they are added to an enzyme-treated pulp. Still, using the synergic action of both techniques, it is possible to produce papers able to be used for high-performance applications. Adding 3% CNFs to the enzyme-treated pulp, paper sheets with 5421 m of breaking length (isotropic sheet former) can be produced, representing more than 7500 m in the machine direction.
3. The combination of biorefining processes and CNF addition seems to be a promising alternative to conventional processes, based on mechanical refining by applying energy.
4. The results obtained in the present work clearly show that it could be possible to decrease the basis weight of papers, as they have better mechanical performance, or even to add fillers to decrease production costs, considering the influence of these changes in optical properties for their final application.

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