NEW STRATEGY FOR THE PRODUCTION OF PACKAGING FROM RECYCLED FIBERS

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The paper industry needs to implement several concurrent strategies. In particular, the industry can be expected to view recycling as a central part of its activities. These activities will be focused on the intense demand of chemical and biochemical strategies to enhance bonding within paper and paperboard. Nowadays, on average, 55% of fibrous compositions for papermaking are made of recycled fibers. In this field, about 65-70% are fibrous compositions intended to be used for packaging papermaking. Corrugated cardboard is one of the most significant examples, since it is made of fluting (internal part) and test liner (external part). In test liner mills, fibrous compositions are made of 50% paper cuts from the cardboard industry and the rest of other types of paper and cardboard. Some test liner papers have low content of mineral fillers. While recycling, fibers get damaged due to the hornification phenomena and mechanical refining of the pulp (with the purpose of enhancing the mechanical properties). The producer does not have many alternatives to address this situation: to increase the quality of the pulp, to slightly refine the pulp or to add some chemical additives that enhance mechanical properties. One strategy or alternative to this situation could be biorefining processes of the pulp. The present work aims to biorefine a pulp made of recycled fibers with the purpose of restoring the mechanical properties of the industrial test liner or improving them and making possible the addition of mineral fillers in order to decrease the production costs. It was observed that, at best, the tensile strength improved by 55% with regard to the original breaking length of the industrial test liner.

Keywords: recycled fibers, fluting, biorefining, hornification

INTRODUCTION

The paper industry needs to implement several concurrent strategies. In particular, the industry can be expected to view recycling as a central part of its activities. These activities will be focused on the intense demand of chemical and biochemical strategies to enhance bonding within paper and paperboard.[1] Nowadays, on average, more than 50% of fibrous compositions for papermaking are made of recycled fibers.[2] In this field, about 65-70% belongs to fibrous compositions supposed to be used for packaging. Corrugated cardboard is one of the most significant examples, since it is made of fluting (internal part) and test liner (external part).

In test liner paper mills, the fibrous compositions are made of 50% paper cuts from the cardboard industry and the rest of other types of paper and cardboard. Some test liner papers have low content of mineral fillers. Generally, industrial test liner is made from 100% recycled fibers and is characterized as having a breaking length close to 5300 m and a Young modulus of 4.8 GPa.

The recycling process normally decreases the mechanical properties by 30-35%, mainly due to the hornification phenomena and fiber damage.

In this situation, there are different strategies to adopt for the achievement of the initial mechanical properties: (i) modification of the fibrous composition adding fibers with higher quality, (ii) submission of the recycled fibers to a soft mechanical refining, assuming the impact of

the successive refining processes, (iii) addition of CNF to the suspension, (iv) addition of dry strength agents and, finally, (v) biorefining processes by means of enzyme addition to the pulp slurry. These strategies can be applied individually or taking advantage of their synergies.

In the present work, biorefining was selected as a way to improve the mechanical properties through the addition of endo-β-1,4-glucanases. There are just a few articles reporting on the use of endo-β-1,4-glucanases to enhance the properties of paper (some of them without any success)[3-8] and even fewer in recycled paper. These enzymes act randomly on the amorphous areas of fibers, reducing the length of cellulose chains, since they degrade the β-1,4 bonds. Moreover, as it was reported by Skals *et al.*,[9] the use of enzymes is supposed to be environmentally efficient in terms of CO_2 emissions. Not only that, enzymes are supposed to reduce the refining intensity by 33%, with the consequent reduction of energy, and to raise the breaking length to values higher than the ones obtained by full mechanical refining.

García *et al.*[10] analyzed SEM micro-photographs of enzyme treated and untreated beaten pulp. He observed the morphological changes on the fibres, such as flake formation and peeling due to the enzymatic treatment. Such modifications helped to improve the bonding ability between fibres, thus leading to increased fibre strength. Kim *et al.*[11] used the term "biobeating" to refer to the use of enzymes in beating as a way of saving energy.

The final objective was to obtain superior or similar properties to those of industrial test liner through the application of endo-β-1,4-glucanases.

EXPERIMENTAL

Test liner of 180 g/m^2 was used as reference material and it was provided by SAICA (LECTA group, Zaragoza, Spain).

The recycled pulp slurry for the present study was composed of 10% old newspapers, 10% magazines, 48% scrap cardboard (test liner and fluting) and 32% other recovered cardboards. All paper was pulped in alkaline medium (1wt% of NaOH with regard to the amount of fiber) for 10 minutes at 50 ºC.

Enzymatic treatment

For the enzymatic treatment, 75 g of dried recycled paper pulp were suspended in 1500 mL (5 wt%) of distilled water. The formed slurry was then stirred and heated at 60 ºC. The pH was set at different levels (4.5, 4.8, 5.5, 6.5 and 7.5) by the addition of diluted HCl (3%). At this point, enzymes (0.3 g per kg of dried pulp) were added to the slurry followed by stirring during 30 minutes. The enzymatic reaction was stopped by increasing the pH by adding a NaOH solution of at least pH 10. The resulting enzyme-treated pulp was used to make handsheets.

Preparation of paper handsheets for mechanical testing

In order to establish the laboratory conditions, paper sheets were produced according to standard TAPPI T-205 sp-02.

Physical properties were determined, such as Schopper-Riegler degree (UNE-EN ISO 5267-1), as well as fiber morphology using a MorFi equipment (Techpap, France).

Paper sheets with an average basis weight of 75 g/m^2 were produced in a sheet former (ISP mod. 786FH) according to ISO standard 5269-2 and conditioned in a weather chamber at 25 ºC and 50% of relative humidity for 48 hours before mechanical tests were performed.

Paper sheets were characterized as reported elsewhere[8] as to their tensile strength, burst index, tear index, Scott Bond, Gurley permeability and porosity.

RESULTS AND DISCUSSION

It is well known that paper produced on an industrial scale is anisotropic. This means that the tensile strength tested in machine direction is higher than that in cross direction. Moreover, industrial paper is usually subjected to a starch bath in order to smooth the surface and provide even more tensile resistance by an increase of about 7.5%. Table 1 shows the differences between testing the paper in machine direction and in cross direction.

Discounting the input provided by the starch, the breaking length before the size-press would be 4915 m, and taking into account an anisotropy rate of 1.33 (at minimum) – 3695 m in an isotropic sheet former. In this sense, the Young Modulus would be decreased to 3.35 GPa. On the other hand, the burst index does not depend on the orientation of fibers, since it represents a perpendicular strength on paper. In contrast, the internal bond is slightly affected by this fiber orientation. Thus, the objectives to be achieved through the enzymatic refining are those reflected in Table 1, or even higher.

With these considerations, the present paper explored the possibility of using enzymes with the purpose of enhancing the mechanical properties of recycled paper. The enzymatic treatment was carried out at 5 wt% of pulp consistency, 60 ºC of

operating temperature, five different pH levels during 30 minutes with an enzyme charge of 0.3 g/kg of fiber. Table 2 shows the effect of the enzymatic refining at five different pH levels.

Table 1
Machine and cross direction properties of commercial test liner

	B.I. ($KPam^2/g$)	sd	T.I. $N \cdot m/g$	sd	B.L. m.	sd	Y.M. Mpa	sd	S.B. J/m^2	sd
Liner MD	2.29	0.04	52.09	1.71	5313	175	4822.57	66.76	244.90	18.60
Liner CD	2.29	0.04	20.35	0.74	2076	76	2056.23	57.22	255.00	20.10

Machine direction (MD), cross direction (CD), burst index (B.I.), breaking length (B.L.), tensile index (T.I.), Young's Modulus (Y.M.), Scott bond (S.B.)

Table 2
Mechanical properties recycled paper biorefined at different pH

pH	°SR	T.I. $N \cdot m^2/g$	sd	B.L. m.	sd	Y.M. Mpa	sd	S.B. J/m^2	sd
Untreated	41	29.75	2.42	3034	97	3106.30	284.43	153.10	9.71
4.5	56	43.71	6.97	4456	710	4134.80	259.36	239.95	16.91
4.8	60	46.31	3.29	4720	335	4088.31	319.20	319.05	16.03
5.5	63	44.51	7.24	4537	738	3655.82	388.70	271.45	21.30
6.5	62	42.91	9.13	4213	287	3611.73	411.39	263.36	18.13
7.5	61	41.95	6.28	4108	531	3598.26	303.14	255.55	16.71

Breaking length (B.L.), tensile index (T.I.), Young's Modulus (Y.M.), Scott bond (S.B.)

As it is reflected in Table 2, the breaking length increases in all cases with regard to the original breaking length (untreated pulp), reaching a maximum at pH 4.8. The increase at this point is 56%. Comparatively with virgin pulps (i.e. bleached kraft hardwood pulp), this breaking length increase is not so much higher, since it is possible to reach a breaking length increase of about 68% for this pulp.[12] On the other hand, and in greater consonance with the pulp used in the present study, a 34% increase in breaking length was achieved by treating enzymatically a pulp made of 50% old newspapers and 50% old magazines.[13] Thus, it seems that recycled pulps are less sensitive to biorefining, while virgin pulps can achieve greater mechanical properties through enzymatic treatment. Breaking length, as well as some other mechanical properties of paper, depends on many factors: (i) number of bonds per volume unit, (ii) quality of bonds, and (iii) intrinsic tensile strength of the fibers.[14] When the relative bonded area (RBA) increases, the number of bonds per volume unit also increases. Moreover, as the quality of these 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 tensile strength of fibers. Taking into account this hypothesis based on Page's equation,[15] the differences observed in the enzyme performance on each substrate are understandable. Schematically, and in order to bear out this situation, Figure 1 shows the morphological differences between virgin and recycled pulps, fibrillation and fine elements being more pronounced in the latter.

Endoglucanases can decrease the degree of polymerization of cellulosic chains drastically because of their operating principle[16] and, consequently, they decrease the intrinsic tensile strength of the fibers. This type of enzyme usually acts on the amorphous part of the cellulose chain,[17] cutting the β-1-4 bonds, generating external fibrillation and/or fibrils in the paper slurry, and, consequently, increasing the crystallinity of cellulose. Additionally, Figure 2 shows a possible mechanism of interaction between fibers and endoglucanases.

Endoglucanases envelop individual cellulose chains, at appropriate enzyme charges, to access the amorphous part thereof. If the fiber to be enzymatically treated has a pronounced external fibrillation (such is the case of recycled pulps), this surrounding will become more difficult than in the case of virgin pulps without any refining, as it has been stated before.

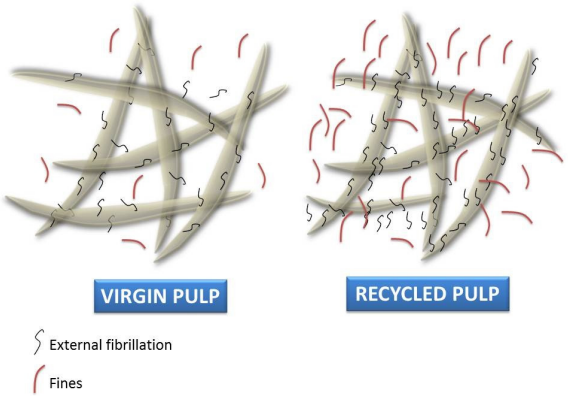

Figure 1: Virgin and recycled pulp scheme

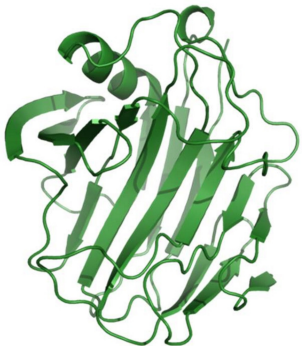

Figure 2: Molecular surface of endoglucanases and their interaction with fibers

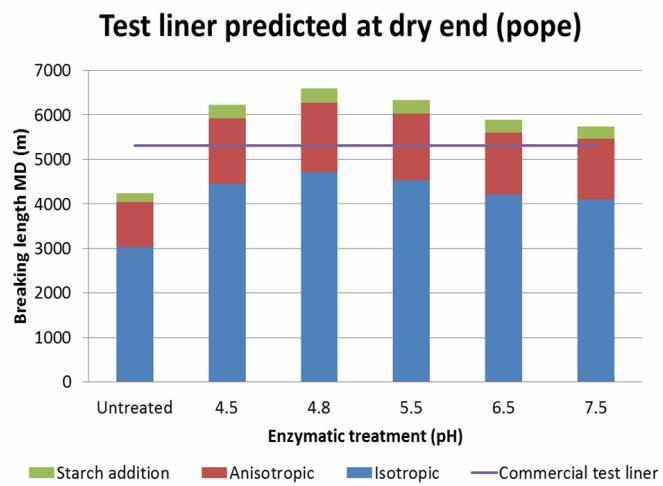

Figure 3: Prediction of the properties at the pope

This better performance of the enzymes is in agreement with the data sheet of the supplier, where an activity of 84000 CMU/g under these conditions is reported over a CMC substrate.

From this point, while pH increases, the breaking length decreases until 4108 m at pH 7.5. In order to compare all the obtained breaking lengths and to compare them with the commercial test liner, Figure 3 shows the breaking length increase that would represent the production on an industrial scale of biorefined pulps.

As can be remarked, the breaking length is exceeded in all cases, even discounting the effect of the starch bath. As it has been stated, a higher value is found at pH 4.8 with a final breaking length (predicted) of 6750 m. This optimum pH was also found by Delgado-Aguilar *et al.*,[12] for recycled pulp made of old newspapers and old magazines. Comparatively, the breaking length that paper would reach if the pulp was treated at 7.5 of pH would be approximately 5873 m. This value is higher than the one reported in Table 1 (5313 m for commercial test liner). In this sense, it is well known that paper is produced at neutral pH and, thus, this could be an interesting treatment to take into consideration.

Regarding the Young modulus, it is possible to see an increase in all cases but, the highest value is found at a pH of 4.5, which decreases as the pH is increased.

The enzymatic treatment modifies fiber morphology, increasing the microfibrillation and the specific surface and, then, increasing the surface density of OH groups capable to bond the adjacent fibers. Figure 4 shows two SEM images of untreated and enzyme-treated pulp (pH 4.8).

As may be noted in the SEM images, enzyme-treated pulp has a smoother surface due to this increase in the specific surface and microfibrillation. Moreover, the porosity was also reduced by the action of the enzymes (Table 3). The increase in smoothness, as well as its effect

on porosity, is mainly due to the increase of the ratio of microfibrils, which indicates an increase in the external fibrillation of fibers and, consequently, will favor an increase on mechanical properties, as it has been mentioned above.

Another interesting point to be remarked in Table 3 is the reduction in the density of the untreated papers with regard to the original commercial test liner. This is mainly due to the hornification phenomena, which cause a reduction of fiber conformability.

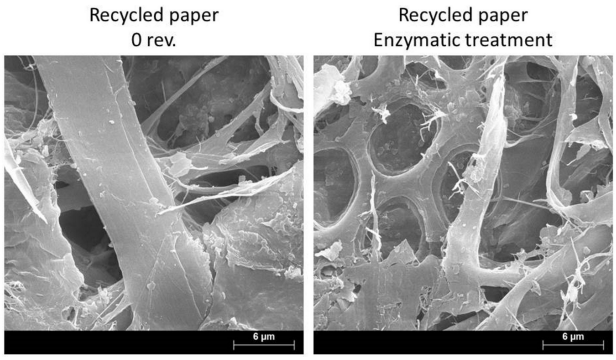

Figure 4: SEM images of untreated and enzyme-treated pulps

Table 3
Physical properties of commercial test liner, untreated and enzyme-treated pulps

Paper	Density (g/cm^3)	Bulk (cm^3/g)	Void volume (%)
Commercial test liner	0.644	1.55	57.07
Untreated	0.599	1.67	60.07
Enzyme-treated (pH = 4.8)	0.622	1.61	58.53

Commercial test liner papers are denser than the original recycled pulp made of the composition described in the experimental section. Density is usually a parameter strongly related to the tensile strength that papers can achieve. As papers are denser, breaking length usually becomes higher. In this sense, comparing the density of the untreated pulp with that of the commercial test liner, the differences in breaking length between them are understandable. Thus, when pulp is enzyme-treated, it is possible to see that its density, as well as breaking length, is closer to that of test liner (Figure 3), which is supposed to be higher than that of a commercial one.

CONCLUSION

The present work aims to find an alternative to the conventional recycling and mechanical refining of fibers in order to recover the mechanical properties. For that, a mixture of scrap cardboard, old newspapers, magazines and other cardboards was achieved.

Biorefining or enzymatic refining allows to further exceed the mechanical requirements, which means that the obtained paper could be used for high performance applications or, which would be more sustainable, to reduce basis weights in order to save fiber and to produce lighter products for the same application.

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