IMPROVING BAGASSE PULP PAPER SHEET PROPERTIES WITH MICROFIBRILLATED CELLULOSE ISOLATED FROM XYLANASE-TREATED BAGASSE

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Abstract. To improve the properties of paper sheets, microfibrillated cellulose (MFC) was isolated from bleached bagasse pulp pretreated with xylanase enzymes and returned to the pulp in varying amounts. The standard hand sheet paper-making method was used. The effect of adding different amounts of MFC on tensile strength (wet and dry), tear resistance, burst strength, opacity, and porosity of paper sheets was studied. Adding MFC to bagasse pulp improved wet and dry tensile strength, but tear resistance and burst strength decreased with increasing amounts of MFC. Also, adding MFC to bagasse pulp did not significantly affect opacity, slightly decreased porosity, and tightened the texture of the paper sheets as observed from scanning electron microscopy images. The strength properties of paper sheets made from bagasse and MFC were compared with those of paper sheets made from bagasse and softwood fibers. Paper sheets containing MFC had higher tensile strength (wet and dry) than those containing softwood fibers, but the later had higher tear resistance and burst strength.

Keywords: Bagasse, microfibrillated cellulose, strength properties, paper sheets.

INTRODUCTION

Microfibrillated cellulose (MFC) isolated from lignocellulosic materials has been recognized as a promising future natural polymer. Nanopaper sheets prepared from MFC tend to have very high tensile strength, low water absorption, high wet tensile strength, and transparency when hot-pressed during drying (Hassan et al 2010a, 2010b). Despite the many published studies on the properties of sheets made of MFC (nanopaper sheets) and the use of MFC as a reinforcing element for different polymer matrices (Siró and Plackett 2010), no studies have been published on the effect of substituting MFC for paper pulp fibers on the properties of paper sheets prepared by the standard method for paper sheet making. Bagasse is used in several countries as a pulp source for paper manufacturing. Bagasse fibers are short and similar to hardwood pulp (Rials and Wolcott 1997). For this reason, usually softwood fibers, ie long fibers, are added to bagasse

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to improve its properties such as tensile strength and tear resistance. In addition, using a dry and wet strength agent is common practice in the paper industry.

In a previous study, Hassan et al (2010a) found that nanopaper sheets made from MFC isolated from bagasse pulp had high wet and dry tensile strength and also high transparency. In addition, pretreating bagasse pulp with xylanase and dilute alkali resulted in MFC paper sheets with higher wet and dry tensile strength compared with those from untreated bagasse (Hassan et al 2010b). In the current study, MFC isolated from bagasse pulp that was pretreated with xylanase enzymes was used to improve the properties of paper sheets made from bagasse pulp.

MATERIALS AND METHODS

Materials

The bleached pulp raw materials were kraft bagasse and a softwood (southern pine, *Pinus* spp). Chemical composition of bagasse pulp was 70.6% α-cellulose, 29.7% pentosans, 0.82% ash, and a degree of polymerization (DP) of 1135. Chemical composition of softwood pulp was 83.6% α-cellulose, 14.2% pentosans, and 0.42% ash. For hand sheet paper making, bagasse and softwood pulps were beaten separately in a Valley beater at 2% consistency up to a degree of freeness of about 42.

Pretreatment of Bagasse Pulp

For xylanase treatment, *Trichoderma reesei* NRRL 6156 fungus was used for production of crude xylanase enzymes using a minimal medium (Medeiros et al 2002) supplemented with 5% corn cobs as an inducer carbon source for xylanase. Xylanase activity was determined as described earlier (Bastawde 1992). Enzymatic treatment of bagasse pulp with xylanase enzymes was carried out as follows: 20 g of bleached bagasse pulp was treated with crude xylanase enzymes in citrate buffer (pH 5.3) in a 500-mL conical flask at 10% consistency. The loading of xylanase enzymes was 60 IU/g, and the hydrolysis reaction mixture was kept under shaking condition (200 rpm) at 50°C for 4 h. At the end of the reaction period, the pulp was filtered and washed thoroughly with distilled water.

Isolation and Characterization of Microfibrillated Cellulose

Bagasse pulp was first disintegrated by a high-shear mixer using pulp suspensions of 2% consistency. The fibers were refined with a high-shear ultrafine friction grinder, a supermasscolloider (MKCA6-2; Masuko Sangyo Co Ltd, Masuko, Sanguo, Japan), and passed through the instrument up to 30 times. The gap between the discs was set to 9 μm. The refined fibers were homogenized using a two-chamber high-pressure homogenizer (APV-2000; APV Systems, Alberstlund, Denmark) after being diluted with water to 1% consistency and passed through the instrument once. The pressure was kept at 4 MPa in one chamber and 40 MPa in the other. The MFC was centrifuged at 10,000 rpm to reduce its water content and kept wet in a refrigerator. Chemical composition of isolated MFC was 73.5% α-cellulose, 23.2% pentosans, and 1248 DP.

Transmission electron microscopy was performed with a Jeol 1230 transmission electron microscope (Jeol Instruments, Tokyo, Japan) with an acceleration voltage of 100 kV. A drop of fiber suspension was used on a copper grid bearing a carbon film. Scanning electron microscopy (SEM) was performed with a Jeol JXA 840A system running at 5-10 keV. Before scanning, samples were coated with gold using a sputter coater system (Edwards Sputter Coater; BOC Edwards, Sussex, UK). Figure 1 shows MFC isolated from bagasse pulp pretreated with xylanase enzymes. The diameter of the microfibrils ranged 9-25 nm, whereas the diameter of the microfibrillar bands was as much as 90 nm (Hassan et al 2010b).

Hand Sheet Paper Making and Testing

MFC was added to bagasse pulp in ratios of 10-90% (by weight), the mixture was disintegrated

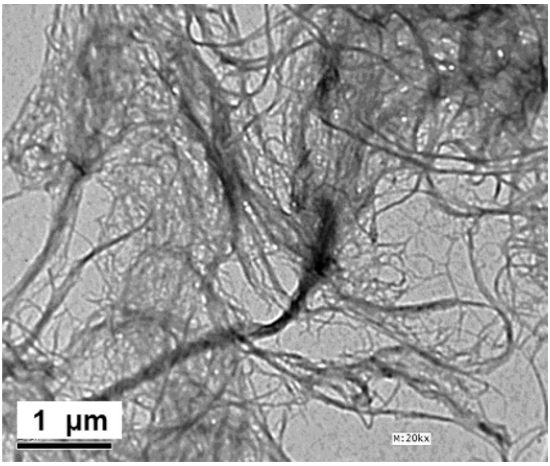

Figure 1. Microfibrillated cellulose isolated from xylanase-pretreated bagasse pulp.

with a high-shear mixer at 3000 rpm for 5 min, and kept at 1000 rpm for 30 min to ensure homogenous distribution of MFC and bagasse fibers. In another study, softwood pulp was added to bagasse pulp at a ratio of 30% softwood fibers. In both studies, hand sheets were made according to the SCAN standard method (SCAN 1976). The target basis weight was 80 g/m^2. The paper sheets were conditioned at 50% RH for 48 h before testing.

Tensile strength testing was carried out according to TAPPI T494 (TAPPI 2006) using a universal testing machine (LR10K; Lloyd Instruments, Fareham, UK) with a 100-N load cell at a constant crosshead speed of 62.5 mm/min. Wet tensile strength testing was carried out using a the testing machine with a 100-N load cell according to TAPPI T456 (TAPPI 2003). Tear resistance was measured with an Elmendorf-type tear tester (Thiwing-Albert Instrument Co, Philadelphia, PA) using TAPPI T414 (TAPPI 2004). Burst strength was measured by a Mullen tester (BF Perkins, Chicopee, MA) using TAPPI T403 (TAPPI 2002a). Opacity was measured according to TAPPI T519 (TAPPI 2002b) using a D25-2 color/difference meter (Hunter Associates Laboratory, Inc, Fairfax, VA). Porosity was measured according to ASTM D726-58 (ASTM 1971) using a Model 4110 densometer (W. & L.E. Gurley, Troy, NY). The results are an average of at least six specimens.

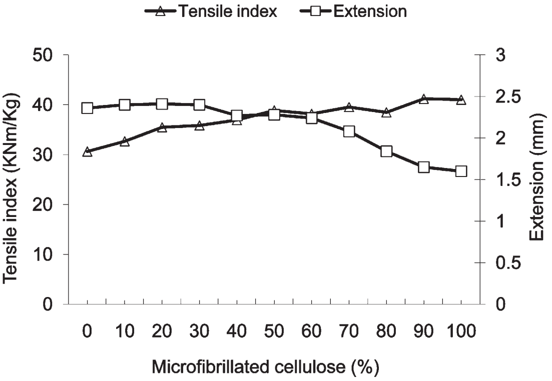

Figure 2. Effect of microfibrillated cellulose (MFC) addition on tensile strength and extension of paper sheets prepared from mixtures of MFC and bagasse pulp.

RESULTS AND DISCUSSION

Effect of Microfibrillated Cellulose Addition on Paper Sheet Properties

In standard hand sheet paper making, a 150-mesh (≈100 µm) screen is used to form a wet mat of fibers. The diameter and length of bagasse fibers were about 25 µm and several hundreds micrometers, respectively, while the diameter of isolated MFC was <0.1 µm and the length was several micrometers. However, forming a paper sheet from 100% MFC on the screen of the paper machine was possible. Of course, loss of MFC was probable during filtration, but the MFC nanofibers appeared to form an interlocked network during filtration. The same should occur when MFC is mixed with pulp fibers.

Strength. Figure 2 shows the effect of adding MFC on tensile strength and the extension of paper sheets. The amount and quality of fiber bonding is the most important factor affecting tensile strength of paper sheets. As expected, paper sheets made from MFC had higher tensile strength than those made from bagasse pulp. This could be caused by the greater hydrogen bonding between the MFC, because of their nano-sized diameter, and the much greater surface area compared with the pulp fibers.

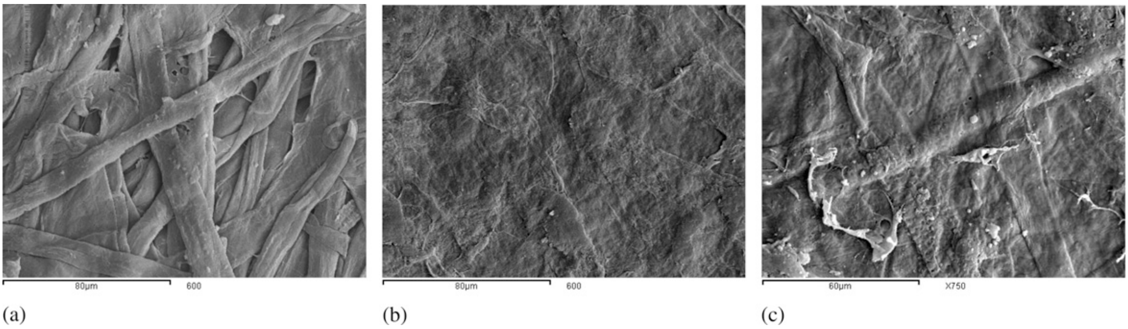

Figure 3. Scanning electron micrographs of paper sheets made from (a) bagasse pulp, (b) microfibrillated cellulose (MFC) isolated from bagasse, and (c) bagasse pulp and MFC (70/30).

In addition, the fine web-like network structure of MFC films (Henriksson et al 2008) can increase the load failure during the test.

Gradual increase in tensile strength occurred with increasing MFC content up to 50%. This improvement of tensile strength could have been caused by the greater extent of hydrogen bonding upon substitution of MFC for pulp fibers, which in turn was caused by the greater surface area of MFC and also possibly by the formation of a network of MFC linked to the pulp fibers (Fig 3). Tensile strength increased 7-27% as a result of adding MFC from 10-50%, respectively. At MFC content higher than 50% and up to 80%, there was no substantive change in tensile strength. A slight increase in tensile strength occurred at greater than 80% MFC. In the previous work of Hassan et al (2010a, 2010b), nanopaper sheets were prepared by drying the wet-formed sheets under pressure, ie hot pressing, whereas in this study, the paper sheets made from 100% MFC were prepared and dried according to the standard method of hand sheet making. Therefore, tensile strength of paper sheets prepared in this study was lower than that of nanopaper sheets prepared by hot-pressing. In addition, nanopaper sheets prepared by hot-pressing had high transparency, whereas those prepared in this study had a similar appearance to regular paper sheets (Fig 4). This could be attributed to less possibility of microfibril aggregation in nanopaper sheets prepared by hot-pressing and thus lower light scattering than those prepared by the standard method. Adding MFC to bagasse pulp at ratios more than 30% resulted in a decrease in extension at break. The decrease in extension was remarkable at high MFC ratios (>60%), which could be attributed to the low extension at break of the MFC caused by their nano size.

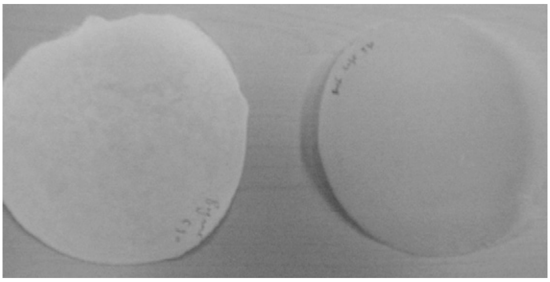

Figure 4. Paper sheets made from microfibrillated cellulose by hot pressing (right) and by standard hand sheet making method (left).

Wet tensile strength is an important property in paper products, especially those used in wet conditions. Henriksson et al (2007) and Hassan et al (2010a, 2010b) have reported on the high tensile strength of MFC sheets in the wet state. In addition, MFC can improve the wet tensile strength in nanocomposites (Hosokawa et al 1991; Taniguchi and Okamura 1998; Gällstedt and Hedenqvist 2006; Nordqvist et al 2007; Hassan et al 2010c). Although the mechanical properties of MFC films were decreased when immersed in water, their structure was retained. This property was attributed to the strong interaction between adjacent nanofibers after drying, most likely dominated by hydrogen bonding.

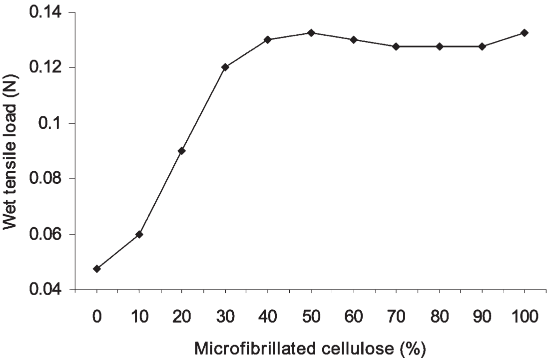

Figure 5. Effect of microfibrillated cellulose (MFC) addition on wet tensile strength of paper sheets prepared from mixtures of MFC and bagasse pulp.

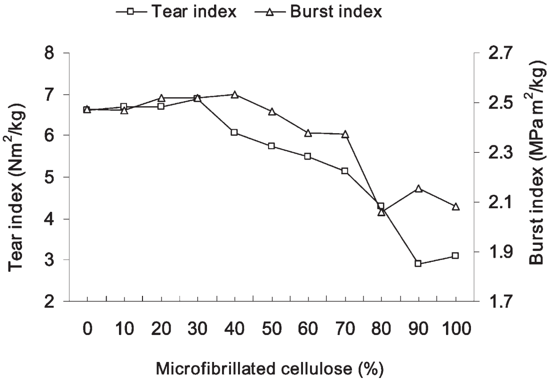

Figure 6. Effect of microfibrillated cellulose (MFC) addition on tear index and burst index of paper sheets prepared from mixtures of MFC and bagasse pulp.

The effect of adding MFC on wet tensile strength of paper sheets made from bagasse pulp is shown in Fig 5. Even at low ratios, adding MFC remarkably improved the wet tensile strength of paper sheets. With addition of 40% MFC, improvement in wet tensile strength was about 188%. No further improvement of wet tensile strength occurred with increasing MFC. The remarkable effect of MFC on wet tensile strength at low percentages could be related to their nano size and high surface area as well as the higher wet tensile strength of MFC compared with bagasse fibers. In addition, the remarkable increase in wet tensile strength at low MFC ratio could have been caused by the formation of a network and the strong hydrogen bonding between MFC and bagasse fibers in the dried paper sheets. The strong bonding between MFC and the fibers resisted water penetration into the web of the paper sheets and thus reduced the negative effect of water on tensile strength.

All previously published studies on the properties of MFC sheets prepared by solution casting or hot pressing focused on the high tensile strength properties of the prepared sheet, but none reported on the tear resistance of these sheets. This study looked at the effect of adding MFC on tear resistance of paper sheets made from bagasse pulp (Fig 6). In sheets made from neat MFC, tear resistance was 55% lower than for those made from neat bagasse fibers because propagation of a tear through an MFC sheet was much easier than in paper sheets made from bagasse. Tear resistance of paper sheets depends on the total number of fibers participating in the sheet rupture, the length of the fibers, and the number and strength of the fiber-to-fiber bonds (Brandon 1981). The work involved in tearing consists of two components: pulling fibers out of the paper sheet and rupturing the fibers, the latter occurring much less than the former. The number of fibers participating in the sheet rupture is determined by the grammage of the sheet and its flexibility. In a rigid sheet, the force is concentrated on a few fibers in a small area, whereas in a flexible sheet, the force is distributed across a much larger area and therefore a larger number of fibers.

The lower tear resistance of sheets made from MFC compared with those made from bagasse could be attributed to the higher cohesion of MFC sheets, and therefore much energy is consumed in rupturing the fibrils rather than pulling them out of the sheet. Rupturing MFC fibrils is much easier than the fibers because of the small diameter of the fibrils. In addition, the higher cohesion of MFC sheets may tend to concentrate the tearing force into a smaller area. Adding up to 30% MFC to bagasse pulp did not deteriorate tear resistance of paper sheets. Further increase in MFC resulted in a decrease in tear resistance of the paper sheets.

The effect of adding MFC on burst strength of paper sheets made from bagasse pulp is shown in Fig 6. Paper sheet burst strength depends on fiber length, interfiber bonding, and stretch of the sheet (Brandon 1981). Burst strength of paper sheets made from MFC is about 16% lower than those made from bagasse pulp fibers. This could be attributed to the lower stretch of MFC paper sheets compared with that of bagasse pulp. Adding MFC to bagasse pulp did not substantively affect the burst strength of paper sheets up to about 50% MFC. This means that the expected decrease in burst strength as a result of adding MFC was compensated by the formation of a network between bagasse fibers and MFC. At higher MFC content, the burst strength decreased, and the decrease was remarkable at MFC content greater than 70%.

Opacity. No significant change in opacity of paper sheets was found with addition of MFC. Paper sheets made from both bagasse fiber and MFC had opacity of about 90%. The unexpected high opacity of paper sheets made from 100% MFC was attributed to the method of sheet formation. The method used led to aggregation of MFC upon drying and consequently increased light scattering. Therefore, the opacity was similar to that of paper sheets made from bagasse pulp.

Porosity. Paper porosity is an important property, and its desired value depends on the application for which the paper is produced. The porosity of paper sheets made from MFC and bagasse fibers was measured according to the ASTM D378 method, which measures the time required for passage of 0.1 m^3 of air through a diameter of 6.45 mm under constant pressure. The recorded time for paper sheets made from bagasse was 25 s. Substituting MFC for bagasse resulted in a slight decrease in porosity, and at the different MFC ratios, the time recorded ranged 25-28 s. This means that despite the smoother and tighter texture of the MFC, as is clear from the SEM of paper sheet samples (Fig 3), the maximum decrease in porosity is not more than $\approx$12%. These results indicate that paper sheets with considerable porosity can be obtained with addition of MFC to bagasse pulp and pores within MFC networks allow passage of air without significant resistance. A previous study on MFC sheets using FE-SEM and porosity measurement showed highly porous structure with fine pores (Henriksson et al 2008).

Comparing Softwood Fibers with Microfibrillated Cellulose

In paper mills that use short fibers such as bagasse, about 20-30% of long softwood fibers are added to improve the strength properties of paper sheets. In this study, 30% softwood fiber was added to bagasse fiber and the properties of paper sheets made from that mixture were measured and compared with those made from 30% MFC added to bagasse fibers (Table 1).

MFC isolated from bagasse can improve dry tensile strength of paper sheets made from bagasse pulp slightly more than those from softwood fibers. In addition, MFC can improve the wet tensile strength of the paper sheets by about 150%, whereas the softwood fibers have no significant effect on wet tensile strength. Adding softwood fibers improved tear resistance and burst strength of the paper sheet, whereas adding MFC did not significantly affect these properties at the ratios studied.

Table 1. Strength properties of paper sheets made from variations of bagasse, microfibrillated cellulose, and softwood pulp.

Paper sheet sample	Tensile index (KN·m/Kg)	Extension at break (mm)	Burst index (MPa·m^2/kg)	Tear index (N·m^2/kg)	Maximum wet-tensile load (N)
100% bagasse fiber	30.6 (3.4)	2.36 (0.39)	2.48 (0.16)	6.62 (0.26)	0.048 (0.012)
Bagasse fibers/MFC (70/30)	36.8 (6.4)	2.34 (0.30)	2.52 (0.26)	6.89 (0.34)	0.120 (0.017)
Bagasse fibers/softwood fibers (70/30)	34.3 (5.4)	2.40 (0.36)	3.34 (0.22)	8.83 (0.49)	0.056 (0.013)
100% softwood fibers	55.7 (3.9)	2.56 (0.47)	4.96 (0.26)	10.45 (0.37)	0.069 (0.011)

Values in parentheses are the standard deviations.

CONCLUSIONS

MFC isolated from xylanase-treated bagasse can act as a dry and wet strength agent in paper sheets made from bagasse fibers when added in ratios up to 30%. Higher MFC ratios improve tensile strength of paper sheets but decrease tear and burst strength. Adding MFC improves tensile strength, especially wet tensile strength, of paper sheets made from bagasse pulp more than from adding softwood fibers, whereas softwood fibers are better for improving tear resistance and burst strength.

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