NOVEL BLEACHING OF THERMOMECHANICAL PULP FOR IMPROVED PAPER PROPERTIES

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ABSTRACT

Production of mechanical pulp is expected to increase significantly to meet the growing global demand for paper. Mechanical pulping uses wood resources more efficiently with less negative impact on the environment than does chemical pulping. However, several problems related to mechanical pulping need to be resolved: high energy consumption, low paper strength properties, problems with pitch, and color reversion. Biopulping, an alternative pulping method, resolves the energy, strength, and pitch limitations but does not address brightness or color reversion. Optical properties can be improved and stabilized by incorporating calcium carbonate into pulp by fiber loading. The objective of this work was to investigate the technical feasibility of combining biopulping with fiber loading. We expected the combined technologies would save energy, improve paper properties, and reduce the production costs compared with current technology. This paper summarizes results obtained from a laboratory-scale handsheet investigation using a typical mill furnish for producing lightweight coated paper. Our results identified synergy between the complementary biopulping and fiber loading technologies enabling a substitution of up to 10% kraft with mechanical fiber without compromising paper properties. Simultaneous peroxide bleaching during fiber loading, an attractive alternative to a separate bleach stage, also was explored. These are the first results of combining these technologies.

INTRODUCTION AND BACKGROUND

Mechanical pulps comprise approximately 25% of the world's wood pulp production. This volume is expected to grow considerably for two reasons: growing global demand for paper and a sharp increase in coated groundwood paper applications (1). Mechanical pulping is an attractive option for meeting increased fiber demand efficiently with minimal environmental impact (2). However, the greatest challenge to expanding mechanical pulping is finding ways to dramatically decrease electrical energy consumption, increase strength properties, and reduce color reversion, which are classical disadvantages of mechanical pulp that impact production cost and limit its inclusion in wood-free furnishes (3).

Biopulping, a technology developed at the USDA Forest Service, Forest Products Laboratory (FPL), resolves two of these drawbacks through significant electrical energy savings and increased pulp strength (4). During biopulping, inoculated white-rot fungus colonizes on the surface and interior of the wood chips and secretes lignin-degrading enzymes that soften the wood. Resulting fibers are longer and more porous and highly fibrillated than fibers from untreated chips. Increased fiber length and fibrillation improves interfiber bonding and corresponding paper strength. However, lignin-degrading enzymes produced by the fungi oxidize lignin, forming quinones (colored compounds) that darken the wood chips (5). The advantages of biotreatment are offset by the considerable loss of pulp brightness critical to the production of high quality paper.

High temperature and pressure used during thermomechanical pulping (TMP) introduces additional chromophores that adversely affect pulp brightness. Refiner speed, pulp consistency, energy input, and retention time also influence the ultimate brightness of the refined pulp (6). Because bleachability is inextricably linked to the initial

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[1]The use of trade or firm names in this publication is for reader information and does not imply endorsement by the U.S. Department of Agriculture of any product or service.

brightness after pulping, any changes in process variables that contribute to a higher brightness pulp are reflected in the final bleached brightness (7).

In the case of bio-treated chips, the additive chromophores introduced during fungal incubation and TMP processing cause a loss of approximately 10 to 15 brightness points (depending upon wood species) compared with pulp produced from the untreated control chips (8,9). Unfortunately, this brightness loss has been a major barrier to commercializing biopulping. The cost of additional bleaching chemicals required to recover this brightness loss offsets much of the savings in energy costs (Horn, E., Akhtar, M., Mann, D., unpublished data, 2000).

High brightness and opacity are essential properties of quality paper, particularly with the paper industry's efforts to produce lightweight papers. A cost-effective method was needed to increase the optical properties of bio-treated pulp and capitalize on the energy savings and strength improvements that biopulping offers.

Alkaline-sized paper dominates the industry, in part a result of increased levels of filler used in papermaking (10). Because alkaline conditions enhance paper strength, more filler can be incorporated into the sheet. High brightness calcium carbonate is a logical choice for a filler because it is inexpensive to manufacture, improves the permanence of lignin-containing paper, and contributes excellent optical properties and sheet formation (11). The amount of filler that can be added is limited, because fillers disrupt interfiber bonding and reduce paper strength (Tables I and II).

Table I. Effect of increased filler content on 60 g/m^2 paper properties by direct-loaded furnish containing control TMP, GW, and 50% SWBK[a]

Amount of filler (%)	Burst index (kN/g)	Tearing index (mN-m^2/g)	Tensile index (Nm/g)	Breaking length (m)	ISO-brightness (%)	Printing opacity (%)	Scatt. coeff. (m^2/kg)	Density (kg/m^3)	Specific volume (cm^3/g)	$CaCO^3$ content in sheet (%)
0	1.94	9.80	27.6	2,812	64	93	53	491	2.04	0
10	1.37	7.87	20.1	2,048	65	97	75	486	2.06	9.2
20	0.88	6.22	13.6	1,414	69	97	83	486	2.06	19.7
30	0.63	4.32	9.7	993	73	98	85	500	2.00	28.3

[a]TMP, thermomechanical pulp; GW, groundwood; SWBK, bleached mixed softwood kraft.

Table II. Effect of increased filler content on 60 g/m^2 paper properties by direct-loaded furnish containing bio-TMP, GW, and 50% SWBK[a]

Amount of filler (%)	Burst index (kN/g)	Tearing index (mN-m^2/g)	Tensile index (Nm/g)	Breaking length (m)	ISO-brightness (%)	Printing opacity (%)	Scatt. coeff. (m^2/kg)	Density (kg/m^3)	Specific volume (cm^3/g)	$CaCO^3$ content in sheet (%)
0	2.05	10.15	28	2,869	55	95	49	491	2.04	0
10	1.47	9.78	24	2,436	57	97	56	475	2.10	3.1
20	0.93	7.01	16	1,668	61	98	74	510	1.96	15.2
30	0.65	5.04	12	1,183	64	98	86	497	2.01	25.5

[a]TMP, thermomechanical pulp; GW, groundwood; SWBK, bleached mixed softwood kraft.

Fiber loading, another technology developed at FPL, is carried out at high consistency and high alkalinity. Calcium hydroxide mixed into moist pulp fibers reacts with carbon dioxide under pressure, converting the calcium hydroxide to calcium carbonate ($CaCO_3$). Substantial $CaCO_3$ is incorporated within the lumen and cell walls of fibers without significantly compromising the strength properties of paper formed from these pulps (12, 13, 14). Because this process has no by-products and saves energy during paper drying, it is also environmentally sound. However, fiber loading pulp to high carbonate levels reduces sheet bulk, a problem unacceptable for producing lightweight paper. Because mechanical pulps, such as TMP, produce a bulkier sheet, it could be advantageous to include more TMP in a paper furnish that includes fiber-loaded pulp. Increasing the amount of conventional TMP is not possible due to decreased paper strength; however, a stronger pulp, such as bio-TMP, does permit a higher fraction of high bulk TMP to be included in the furnish while maintaining paper strength (15**).**

Since bio-TMP fibers are more porous and highly fibrillated than control TMP fibers, we anticipated that bio-TMP fibers could retain more $CaCO_3$ during processing than was possible with control pulps, resulting in increased brightness and opacity. We also found that hydrogen peroxide bleaching could substitute Ca $(OH)_2$ for NaOH for the source of alkalinity, as others had suggested previously (16, 17, 18). We predicted that it should be possible to consolidate peroxide bleaching with fiber loading using calcium hydroxide required for fiber loading as the source of alkalinity for bleaching. Were this possible, a substantial advantage could be achieved using bio-treated fibers.

Bleaching

Implicit with bio-treatment is the loss of ~10 brightness points compared with the control pulp. Previous experiments on this furnish established that 60% more H_2O_2 was required to bleach the bio-treated TMP to the brightness of the bleached untreated control (Horn, E., Akhtar, M., Mann, D., unpublished data, 2000). Fortunately, early research established that biopulps are more responsive to bleaching chemicals than were the untreated pulps, probably because of the removal of pitch that normally would consume bleaching chemicals (8). Others also have observed that pitch content of wood chips is reduced significantly during the fungal incubation stage of biopulping, saving refining energy and making subsequent processing less problematic (19, 20, 21).

Because Ca $(OH)_2$ can serve as the source of alkalinity for peroxide bleaching, we speculated it would be possible to simultaneously achieve bleaching and fiber loading. Fiber loading is done at ~40°C, which is substantially below the temperature for optimum peroxide bleaching. Assuming that the peroxide contained within the fiber-loaded pulp remains relatively latent during $CaCO_3$ formation, a bleach stage could be added following fiber loading comparable to conventional bleach tower retention.

The work summarized in this paper presents results of the combined technologies, biopulping and simultaneous fiber loading–bleaching, for the preparation of a typical mill furnish for coated base stock. This is the first time results of these combined technologies are being reported.

EXPERIMENTAL METHODS

Pulp Furnish

We used a mixture of aspen groundwood (GW) pulp, spruce TMP, and bleached mixed softwood kraft (SWBK) pulp in a typical furnish for producing light-weight coated paper in a ratio of 22.5%, 27.5%, 50%, respectively. The spruce TMP is the variable component of this furnish. TMP was produced from both the control chips and the bio-treated (inoculated with *Ceriporiopsis subvermispora* SS-3) chips at FPL. Kraft wetlap pulp was refined to 420 Canadian standard freeness (CSF) using a 305-mm-diameter Sprout–Waldren (Springfield, OH) atmospheric refiner; TMP was prepared on a 305-mm-diameter Sprout Bauer (Springfield, OH) pressurized refiner. Initial brightness levels (International Organization for Standardization (ISO)) of the separate pulps were as follows: GW—62% to 64%, TMP control—50% to 55%, bio-TMP—40%, and SWBK—80%. The brightness target for the blend was 72% to 74% ISO.

Materials for Fiber Loading

It is possible to fiber load all types of fibers, but because the spruce TMP portion of this furnish requires substantial bleaching to meet the brightness target, the mechanical pulp components GW and TMP were selected for simultaneous fiber loading and bleaching.

Dry calcium hydroxide used for fiber loading was an industrial grade Mississippi Codex hydrated lime (Mississippi Lime Co, Alton, IL). Comparative direct loading was done with papermakers grade (HO) precipitated calcium carbonate (PCC) obtained from Specialty Minerals, Inc. (Bethlehem, PA).

Methods

For fiber loading, 1.5-kg batches of GW–TMP blends prepared by adding dry calcium hydroxide (20% based on o.d. pulp) into moist pulp, mixing thoroughly in the Hobart laboratory mixer (Troy, NY) at 20% consistency for 15 min. The pulp was added into the chamber of a Sprout Bauer refiner and reacted with carbon dioxide at 207 kPa for 10 min retention before passing through the refiner at a wide plate gap. In instances where peroxide was included, 2% H_2O_2 and typical stabilizers (3% sodium silicate, 0.05% magnesium sulfate) were mixed into the mechanical pulp blend at 20% consistency prior to adding the calcium hydroxide into the Hobart mixer. The pulp was reacted with CO_2 as previously described and passed through the refiner. Exit temperature of the pulp was approximately 40°C to 45°C. Fiber-loaded pulp (containing peroxide) was transferred into a plastic bag and held for 1 h at 60°C. After bleaching, the fiber-loaded pulp was blended 50:50 with SWBK for handsheet preparation and testing following TAPPI methods.

Handsheets (60 g/m^3) for direct loading were made (TAPPI T-205) by first mixing equal portions of the GW–TMP blend with the SWBK. Papermaker's PCC was then added directly into the doler tank to the approximate ash level of the fiber-loaded handsheets. Considerable excess of PCC was required to retain a target ash level in handsheets. Handsheets were made and evaluated for physical and optical properties according to TAPPI standard test method T-220. Ash content was measured at 400°C according to T211.

DISCUSSION OF RESULTS

The effect of added filler on handsheet properties made from the blended furnish, GW (22.5%), control TMP (27.5%), and SWBKP (50%), are summarized in Table I. For direct loading, papermakers PCC was added during handsheet making. Sheet properties of direct loading a comparable blend, with bio-treated TMP substituted for the control, are shown in Table II. As expected, the initial strength properties (no filler added) of the blends made from bio-treated TMP are somewhat higher than those made from the unfilled blend including the control TMP. However, when PCC was added to varying paper ash levels, strength properties of all the blends decreased as the filler load increased. While it is difficult to reach a specific ash level retained in handsheets for exact comparison of the direct- and fiber-loaded blends, the trend of decreasing strength with increasing filler is clear. The initial brightness of the control TMP blend is 64% ISO, which is 9% brightness points higher than the initial bio-TMP blend. Addition of PCC increased the brightness of both blends, but the 9% brightness gap is carried through to 73% ISO for the control TMP sheet filled to the highest level and 64% ISO for the bio-TMP. There appears to be no advantage of filled bio-TMP in strength or brightness differential compared with the control TMP when PCC is introduced by direct loading. Pre-bleaching the mechanical pulp blends with hydrogen peroxide removes the brightness differential between the control and bio-TMP blends. Previously, we found that the bio-TMP blend requires 60% more H_2O_2 to meet the target brightness of 72% ISO compared with the control TMP (Horn, E., Akhtar, M., Mann, D., unpublished data, 2000).

In contrast, when both the control and bio-treated TMP–GW blends were bleached during simultaneous fiber loading with 2% H_2O_2 and 20% Ca $(OH)_2$ required to achieve approximately 9% $CaCO_3$ in the final handsheets made after blending with 50% SWBK, the bio-TMP sheets displayed a significant advantage in strength properties (Table III). In addition, the 9 brightness point gap between the control and bio-TMP was removed. The brightness of both blends was 67% ISO at ~9% filler level in handsheets, an increase of 12% ISO for the bio-TMP compared with 3% ISO for the control. Unfortunately, 67% does not meet the brightness target for the blend (72%).

Table III. Effect of paper properties of fiber-loaded control TMP–GW and bio-TMP–GW after blending with 50% SWBK[a]

Sample ID	Burst index (kN/g)	Tearing index (mN-m^2/g)	Tensile index (Nm/g)	Breaking length (m)	ISO-brightness (%)	Printing opacity (%)	Scatt. coeff. (m^2/kg)	Density (kg/m^3)	Specific volume (cm^3/g)	$CaCO^3$ content in sheet (%)
Control	1.56	9.95	21.1	2,153	67	96	60	577	1.73	9.4
Treatment	1.69	11.07	23.9	2,435	67	97	64	568	1.76	8.7

[a]TMP, thermomechanical pulp; GW, groundwood; SWBK, bleached mixed softwood kraft.

Table IV. Effect on paper properties of decreasing SWBK by 5% and 10% and substituting with 5% and 10% additional fiber-loaded bio-TMP–GW in furnish[a]

Sample ID	Burst index (kN/g)	Tearing index (mN-m^2/g)	Tensile index (Nm/g)	Breaking length (m)	ISO-brightness (%)	Printing opacity (%)	Scatt. coeff. (m^2/kg)	Density (kg/m^3)	Specific volume (cm^3/g)	$CaCO^3$ content in sheet (%)
Control 50/50	1.56	9.95	21.1	2,153	67	96	60	577	1.73	9.4
Treatment 50/50	1.69	11.07	23.9	2,435	67	97	64	568	1.76	8.7
Treatment 55/45	1.64	10.52	23.7	2,413	68	98	72	567	1.77	9.1
Treatment 60/40	1.57	9.90	21.5	2,190	68	99	79	559	1.79	11.0

[a]TMP, thermomechanical pulp; GW, groundwood; SWBK, bleached mixed softwood kraft.

Clearly, the 20% Ca $(OH)_2$ charge needed for fiber loading to achieve ~10% ash is considerably in excess of what is required for 2% H_2O_2 bleaching. How is it possible to apply such an excess of alkalinity and achieve bleaching rather than significant alkaline darkening? While high alkalinity swells fibers and provides good diffusion of bleach chemicals into the fiber, nonbrightening and darkening are caused by high peroxide consumption relative to the alkali consumption (22). Because the temperature of fiber loading is less than 45°C and introduction of carbon dioxide lowers the pH during formation of calcium carbonate, much of the peroxide remains latent during the fiber loading process. Subsequent elevation of temperature activates the peroxide for actual bleaching at a point when the hydroxide has been converted to carbonate, essentially "consuming" the alkali.

The most significant benefit of combining bio-treatment and fiber loading is the superior paper strength indices (1.69 burst; 23.9 tensile) compared with both the fiber-loaded control blend (1.56 burst; 21.1 tensile) and the bio-treated blends direct loaded with PCC at a comparable filler level (~1.37 burst; ~20 tensile) (Table IV). This strength advantage permits a substitution of 5% to 10% expensive kraft with the bio-treated TMP blend without compromising the strength (1.64 and 1.57 for burst and 23.7 and 21.5 for tensile at 5% and 10% substitution, respectively) while increasing the handsheet opacity by 2% and 3% and the scattering coefficient 12% and 19% at 5% and 10% substitution, respectively. The handsheets made from the 10% kraft substitution blend contained ~2% additional carbonate compared with 5% kraft substitution, explaining the large increase in optical properties; however, the strength properties remained intact even at higher filler content (11% compared with 9%). Other benefits of consolidating the bleaching and fiber loading steps include cost savings for additional sodium hydroxide and the advantage of substantially decreased chemical oxygen demand (COD) discharged into process water compared with traditional bleaching.

Because it is possible to use alternate sources of alkalinity for bleaching, we compared the bleach response of 2% H_2O_2 with either 2% Ca $(OH)_2$ or 2% NaOH on direct-loaded bio-TMP–GW before blending 50:50 with SWBK for handsheet preparation. Results of the handsheet properties for the separately bleached and direct-loaded pulps are compared with properties of fiber-loaded bio-TMP sheets (Table V). The direct-loaded handsheets contained ~9.7% filler, slightly higher than the fiber-loaded bio-TMP counterpart, which was 8.7%. As expected, the strength properties of the post-bleaching with either alkali are comparable. The brightness of these handsheets, however, was higher by 3% ISO for the NaOH than either the Ca $(OH)_2$ post-bleach or handsheets made from the simultaneously bleached and fiber-loaded bio-TMP. The scattering coefficient of the post-bleached sheets is decreased by 8% and 5% for NaOH and Ca $(OH)_2$, respectively, compared with the simultaneously bleached and fiber-loaded sheets at slightly less filler. However, parameters for Ca $(OH)_2$ bleaching were not optimized. It is possible a different charge of Ca $(OH)_2$, temperature, or retention time would give different results; however, most references conclude that NaOH is superior for brightness response.

A final comparison was made for fiber loading and bleaching (Table VI). The control and bio-TMPs were fiber loaded first followed by a separate bleach stage using 2% H_2O_2 and 2% NaOH. This procedure resulted in superior

Table V. Effect on paper properties of post-bleaching fiber-loaded bio-TMP–GW[a] furnish using either 2% NaOH or $Ca(OH)_2$ and 2% H_2O_2

Sample ID	Burst index (kN/g)	Tearing index (mN-m^2/g)	Tensile index (Nm/g)	Breaking length (m)	ISO-brightness (%)	Printing opacity (%)	Scatt. coeff. (m^2/kg)	Density (kg/m^3)	Specific volume (cm^3/g)	$CaCO^3$ content in sheet (%)
Treatment, direct loaded NaOH 50/50	1.63	10.70	23.9	2,445	70	95	56	578	1.73	9.6
Treatment, direct loaded $Ca(OH)_2$ 50/50	1.58	10.57	23.6	2,411	67	96	59	564	1.77	9.8

[a]TMP, thermomechanical pulp; GW, groundwood.

Table VI. Effect on handsheet properties of fiber loading the control TMP–GW and bio-TMP–GW followed by 2% H_2O_2 and 2% NaOH bleaching stage prior to blending with 50%, 45%, and 40% SWBK[a]

Sample ID	Burst index (kN/g)	Tearing index (mN-m^2/g)	Tensile index (Nm/g)	Breaking length (m)	ISO-bright-ness (%)	Printing opacity (%)	Scatt. coeff. (m^2/kg)	Density (kg/m^3)	Specific volume (cm^3/g)	$CaCO^3$ content in sheet (%)
Control 50/50	1.64	10.2	21.9	2,227	72	94	58	617	1.62	10
Treatment 50/50	1.84	11.6	25.3	2,581	72	94	56	634	1.57	9.3
Treatment 55/45	1.71	11.04	24.8	2,530	71	95	58	630	1.59	8.2
Treatment 60/40	1.67	10.10	21.4	2,185	70	96	59	623	1.60	8.9

[a]TMP, thermomechanical pulp; GW, groundwood; SWBK, bleached mixed softwood kraft.

strength and optical properties. In this instance, the target of 72% ISO was achieved on both the control and bio-TMP blends, resolving the need for more peroxide to meet that target for the bio-TMP. The strength properties were equally impressive, permitting a substitution of as much as 10% kraft. The fiber-loaded bio-TMP–GW blend mixed 50:50 with SWBK followed by NaOH bleaching gave a tensile index of 25.3, which permitted a 10% substitution of mechanical fiber for SWBK while nearly matching the 21.9 tensile index of fiber-loaded control TMP at 50:50 blend.

Parameters for the combined technologies are not yet optimized, especially for simultaneous fiber loading and bleaching. Possibly a slightly higher temperature than 60°C for a shorter retention time would be beneficial. Residual H_2O_2 was not checked in the final pulp, which could dictate the possible alternatives for optimum brightness development. It has been suggested that divalent bases have a stabilizing effect on peroxide that obviates the silicate and magnesium sulfate requirement when carried out at high consistency in a screw mixer (23). However, chelation prior to bleaching would be more critical if silicate were not used. Elimination of silicate would be desirable from both an economic and processing standpoint.

Only our most recent data are presented in this paper. These data confirm work that was done previously on fiber loading mechanical pulps and blending with kraft (24, 25). This was the first time that bio-treated pulp was fiber loaded or bleached simultaneously with fiber loading. These technologies, fiber loading and biopulping, interact synergistically to produce paper with either reduced grammage based upon enhanced fiber properties or decreased bleached kraft portion of the furnish used during conventional processing. We plan to optimize the parameters of fiber loading and confirm the synergy of these technologies on a pilot plant scale.

CONCLUSIONS

Our results clearly indicate that

- Simultaneous fiber loading with the inclusion of 2% H_2O_2 economically resolves the optical property limitation of bio-treated TMP as well as prohibitive bleach cost.

- Fiber loading the mechanical pulp portion of this furnish followed by post-bleaching with 2% H_2O_2 and 2% sodium hydroxide results in superior paper properties compared with those of simultaneous bleaching and fiber loading using conditions that were not yet optimized.

- Simultaneous fiber loading and bleaching with H_2O_2 successfully increases both optical and strength properties of bio-treated TMP compared with control TMP, permitting reduction of the SWBK component by as much as 10%. Conventional addition of PCC by direct loading the pulp does not exhibit this synergism.

- Simultaneous bleaching during fiber loading eliminates the NaOH requirement and thereby reduces the COD content of process water and saves both the cost of the NaOH and that for remediation of the process water.

- Substitution of TMP–GW for part of the kraft fiber could resolve the decreased sheet bulk characteristic of highly filled papers made by fiber loading.

Optimization of these combined technologies should only improve the results reported here.

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