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Utilization of Calcium Carbonate-Coated Wood Flour in Printing Paper and Their Conservational Properties

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Abstract: Wood flours (WFs) are bulky lignocellulosic materials that can increase the bulk and stiffness of paper. To be used in printing paper for replacing chemical pulp, WFs were first fractionated by a 200-mesh screen to improve smoothness; second, they were coated with calcium carbonate by an *in-situ* $CaCO_3$ formation method (coated wood flours, CWFs) to improve brightness. The performance of CWFs for printing paper was compared to those of bleached wood flours (BWFs) and bleached chemical pulp. Equivalent brightness and much higher smoothness were obtained for the CWFs compared to the BWFs. Furthermore, BWFs caused a significant loss of yield and required wastewater treatment in the bleaching process, while the CWFs increased the yield greatly by attaching $CaCO_3$ to the wood flours, and caused no wastewater burden. An accelerated aging test showed that the CWFs caused lesser brightness and strength loss than the bleached chemical pulp and BWFs. CWFs still had room for improvement to replace chemical pulp, but showed slower aging in optical and close strength properties.

Keywords: wood flours; *in-situ* $CaCO_3$ formation; brightness; smoothness; printing paper; conservational property

1. Introduction

Wood flours (WFs) are used in the filler layer of multiple paperboards and papers to achieve high bulk [1–5]. If higher paperboard bulk than necessary is achieved, one can reduce the basis weight of the paperboard down to the customer-acceptable bulk and achieve savings in wood fiber and drying energy without losing essential board properties. The use of WFs may also be extended to printing paper [6–10]. If WFs can be used in printing paper without causing optical and physical problems, the bulk and stiffness will be greatly improved, and again, basis weight reduction may be possible while essential properties are kept at acceptable levels. Therefore, the aim of this study was to find a technology that enables us to use WFs in printing paper more effectively. In reality, printing paper containing WFs always suffers from low brightness, low smoothness, and fast color deterioration caused by aging. To improve the brightness of WFs, Shin et al. [7] applied an alkaline pulping process. After pulping, they mixed WFs and GCC together for further pulverizing to reduce their size and to improve optical properties. Kim et al. [8] applied a bleaching process. They prepared WFs that passed 200mesh screen, and applied two-step bleaching process by using chlorine dioxide and peroxide. Their results showed that the addition of bleached wood flours still gave low brightness and high roughness, but high bulk in printing paper. Later, Kim et al. [9] tried to add an optical brightener in addition to wood flour bleaching, and obtained more improved brightness by addition of optical brightener.

In-situ $CaCO_3$ formation on the surface of lignocellulosic materials [10–12] greatly improved brightness without loss of yield. In contrast, applying pulping and bleaching processes to WFs caused significant yield loss and water contamination [10]. Seo et al. [10] claimed that the *in-situ* $CaCO_3$ formation on WFs increased furnish yield without water contamination because the attached calcium carbonates on wood flours became the inexpensive part of the entire furnish. Low smoothness caused by WFs is generally due to their large size and rigid structure, and can be improved by optimizing wood flour size and size distribution. To overcome low smoothness, we used a 200-mesh hole type screen to control the maximum particle size in this study.

Wood flours contain lignin, and those wood-containing papers become dark when they are exposed to the air, sunshine, and heat for an extended period. Calcium carbonate-coated WFs or *in-situ* $CaCO_3$ formed WFs (CWFs) may exhibit a different aging behavior from typical WFs during the aging process. It was presumed that hydrogen peroxide bleached WFs (BWFs) may exhibit faster color changes than CWFs. An accelerated aging test was performed to reveal the effect of $CaCO_3$ coated WFs on aging. All properties of the WFs-containing sheets (WFs, CWFs, and BWFs) were also compared to those of bleached chemical pulp sheets.

2. Materials and Methods

2.1. Wood Fibers

Bleached kraft softwood pulp (mixture of Hemlock, Douglas fir, and Cedar, Canada) in 20 wt%, and hardwood pulp (mixture of Aspen and Poplar, Canada) in 80 wt% were mixed together, and refined in a valley beater until freeness (Canadian standard freeness. ISO-5267-2) reached 500 mL. We added WFs, CWFs, and BWFs to this mixed pulp in 5 and 10% to compare their properties.

2.2. Wood Flours

WFs were donated by Korea N Company that were the mixture of hardwoods imported from China. We selected this material because the biggest paper mill in Korea already used the same materials in large quantity for the manufacture of commercial paperboard. The important specification of the wood flours were the size and the composition (mainly from oak) when Korea N company supplies them to the paper mill. However, those wood flours did not make smooth surfaces for printing paper because of their large size. They were further pulverized to pass through the 200-mesh screen. To increase their brightness, hydrogen peroxide bleaching was applied to the WFs (5 wt% H_2O_2 based on dried wood flour weight, sodium silicate, pH13 initially controlled by NaOH, liquid ratio 1:10, 80 °C, 90 min. duration). These bleached WFs (called as BWFs) lost about 32.8% of their initial weight during the bleaching process [10].

To prepare the *in-situ* $CaCO_3$ formed WFs, the screened ones were first mixed with CaO by 169 and 281 wt% based on the dry weight of WFs for making 1:3 and 1:5 ratios of wood flour: $CaCO_3$, respectively, in the reaction vessel initially in 10% concentration. Second, we injected carbon dioxide to the aqueous mixture while stirring at 350 rpm until a neutral pH was reached. The pH was checked until a pH change was not detected for 3 min at neutral pH. These resultant WFs look like the coated WFs with $CaCO_3$, and we called them CWFs.

2.3. Preparation of Handsheets and Testing Methods

Handsheets of 60 g/m^2 basis weight were prepared from chemical pulp with and without WFs according to the standard method (TAPPI Test Methods T205, 1995). Composition of the handsheets are shown in Table 1. Cationic PAM (cationic polyacrylamid, +5 meq/g, CIBA Specialty Chemicals Korea, Seoul, Korea) was used for retention (0.1% based on sheet weight). The ash content (TAPPI Test Method T 413 om-93, 1993), density and bulk (TAPPI T410 om-98, T411 om-97), breaking length (ISO 1924-1, 1992), bending resistance (TAPPI T543 om-00), Bekk smoothness (TAPPI T479 cm-99), brightness (ISO 2470, 1977), and folding endurance (ISO 5626) of the handsheets were measured according to the respective standards. For tensile test, we used 20 mm/min. of loading speed and 10 specimens (15 mm width × 150 mm length) per each sample conditioned overnight at 23 °C and

50% RH before testing. The results were converted to breaking length in km. An accelerated aging treatment was performed based on the dry heat treatment method at 105 °C (ISO 5630-1:1991(e)) for 5, 10, and 20 days.

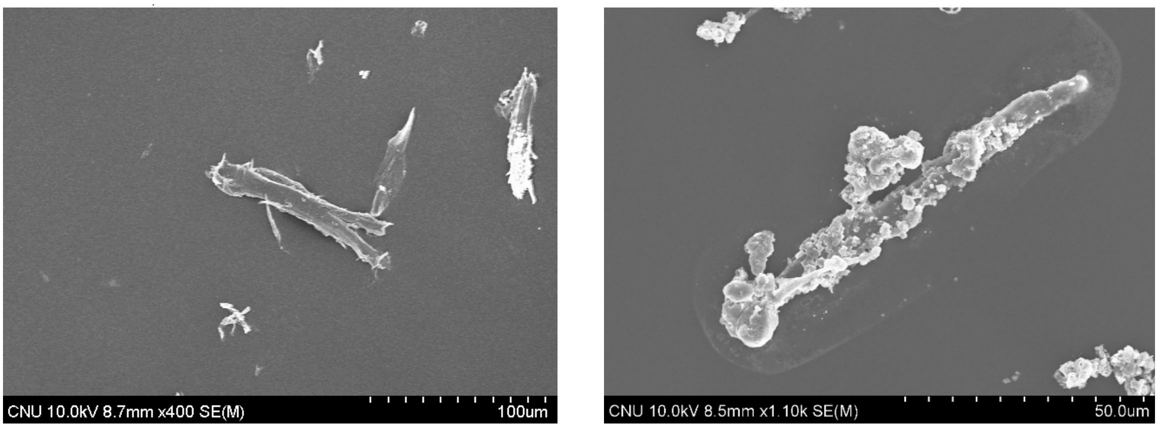
Table 1. Composition of the handsheets in percent.

Sample Name	Wood Fibers	Wood Flour 200 Mesh Passed	Wood Flour: In-situ $CaCO_3$ = 1:3	Wood Flour: In-situ $CaCO_3$ = 1:5	Bleached Wood Flour
Pulp only	100				
Wood flour, 5 (WFs)	95	5			
Wood flour, 10 (WFs)	90	10			
In-situ 1:3 WF, 5 (CWFs-3)	95		5		
In-situ 1:3 WF, 10 (CWFs-3)	90		10		
In-situ 1:5 WF, 5 (CWFs-5)	95			5	
In-situ 1:5 WF, 10 (CWFs-5)	90			10	
Bleached WF, 5 (BWFs)	95				5
Bleached WF, 10 (BWFs)	90				10

3. Results and Discussion

3.1. Morphology of the in-situ $CaCO_3$ Formed WFs

Morphologies of WFs with and without $CaCO_3$ coating are shown in Figure 1. Most of the WF surface was covered with newly formed calcium carbonate for the CWFs, and there were almost no loose $CaCO_3$ around the CWFs in Figure 1b. It seemed that most of the $CaCO_3$ formed were attached to the WFs. Using an electron microscope, it was not possible to differentiate between a 1:3 and 1:5 (WF: in-situ $CaCO_3$) ratio for the CWFs.



(**a**) WFs only. (**b**) *In-situ* $CaCO_3$ formed WFs.

Figure 1. Morphologies of WFs with and without in-situ $CaCO_3$ coating WFs: *in-situ* $CaCO_3$ = 1:5).

3.2. Physical Properties

The brightness and smoothness of the paper containing WFs are the most critical properties in this study. Figures 2 and 3 show the changes in brightness and Bekk smoothness. Adding 5% WFs to wood pulp caused a brightness drop from 82.8% (Pulp only) to 65.1% (17.7% difference). Through peroxide bleaching of WFs, the brightness decreased by 5.4% from the 'Pulp only' sheet. The *in-situ* $CaCO_3$ formation method caused a brightness drop of 6.1% for the 1:5 case. Adding 10% CWFs caused a larger brightness drop.

The Bekk smoothness for papers containing WFs or BWFs decreased greatly. The greater the amount of WFs or BWFs, the less smoother the papers are. This indicates that WFs smaller than the ones that passed through the 200-mesh screen are required. However, the CWFs exhibited much higher smoothness than the other WF-containing sheets. We believe this is because the CWFs consist of mostly $CaCO_3$, not WFs. The CWFs consist of 75% and 83% $CaCO_3$ for the 1:3 and 1:5 ratios, respectively. WFs are bulky, rigid, and rough, but the CWFs are denser than WFs and occupy less volume inside the paper sheet at the same addition level, thereby allowing for less of a chance to lower smoothness. Furthermore, CWFs seem to be slightly deformable under the wet pressing pressure because the calcium carbonates formed on the surface of wood flours are not chemically attached, but instead adsorbed on the wood surface, resisting the turbulence of the process water. In short, CWFs can result in brightness as high as BWFs but can produce much higher smoothness than BWFs. If the improvement in smoothness and brightness of CWFs containing sheets is evident, it may be the correct approach to utilize more CWFs in printing paper than WFs or BWFs.

The bulk of the handsheets were shown in Figure 4, where we observed that WFs, whether bleached or not, resulted in very high bulk. The CWFs produced less bulk than WFs, although still much higher than the 'Pulp only' case. In summary, CWFs can result in brightness as high as BWFs but produce much higher smoothness than BWFs while still producing high bulk. The improvement in smoothness and brightness of CWFs-containing sheets is evident that we believe it is the effective approach to utilize more CWFs in printing paper.

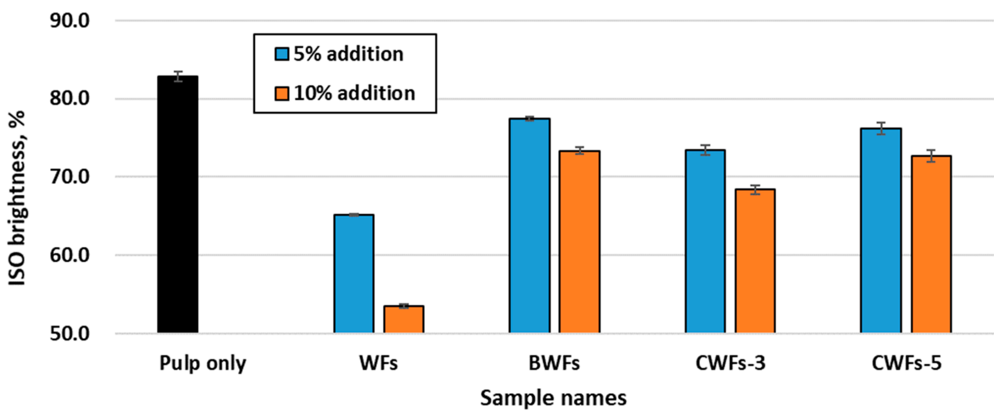


Figure 2. Brightness changes caused by the addition of pre-treated WFs (Standard deviation bars were included).

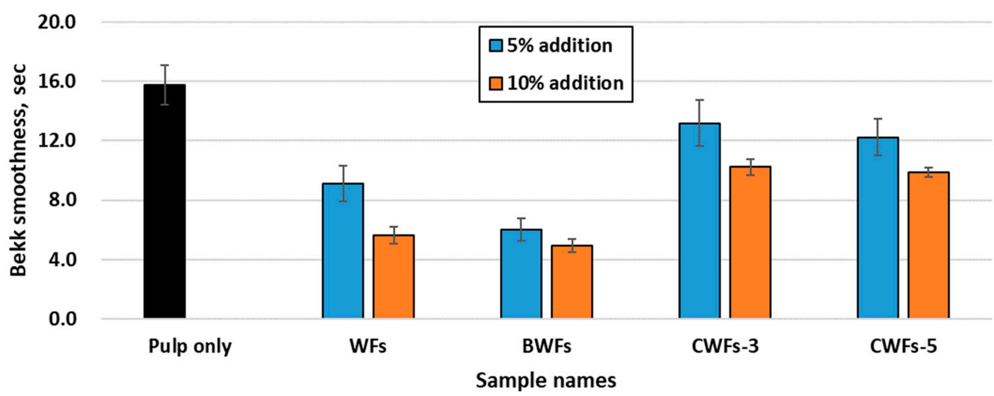


Figure 3. Bekk smoothness changes caused by the addition of pre-treated WFs (Standard deviation bars were included).

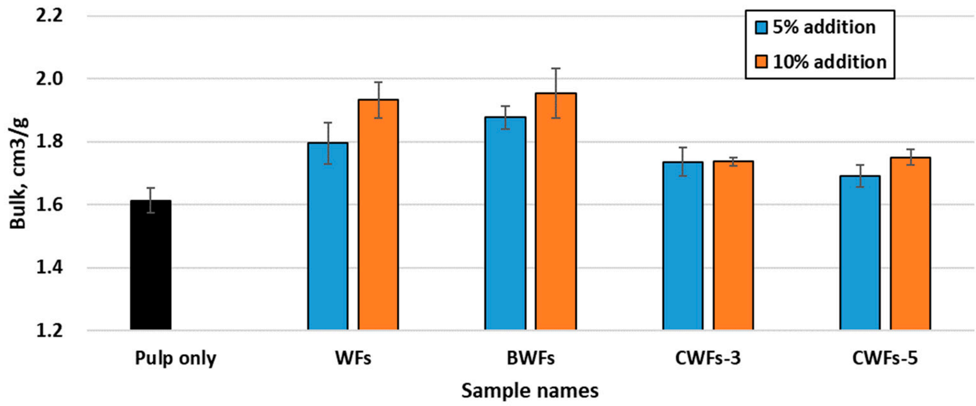


Figure 4. Bulk changes caused by the addition of pre-treated WFs (Standard deviation bars were included).

3.3. Strength Properties

The use of WFs in paper increased bulk as expected, but a decrease in strength properties is unavoidable. Breaking length, which is the measure of tensile strength after compensating for the basis weight differences of paper sheets, of the sheets were shown in Figure 5, where breaking length was higher for the CWFs than for the other WF-containing sheets. We surmise this is because CWFs have less specific surface area than the other WFs do. WFs and calcium carbonate make very little, if any, or no hydrogen bonds with wood fibers. More surface area of either WFs or CWFs per unit weight means less bonding. The WFs and BWFs have more surface area per unit weight than CWFs because the WFs and BWFs consist of wood flours only, but the CWFs both wood flours (usually wood density of 0.4–0.8 g/cm^3) and calcium carbonates (density of 1.5 g/cm^3), respectively. Figure 5 shows there were no differences in breaking length development between the WFs and their bleached ones (BWFs).

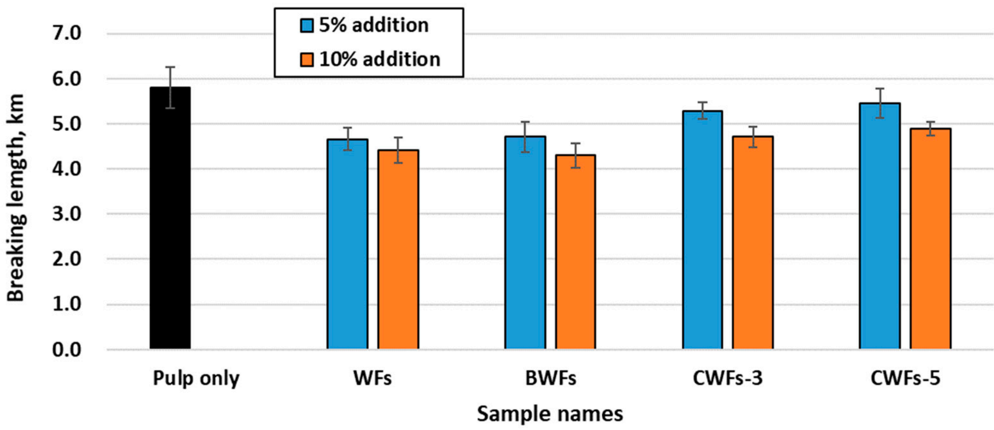


Figure 5. Breaking length changes caused by the addition of pre-treated WFs (Standard deviation bars were included).

The substitution of expensive chemical pulp with other inexpensive materials is successful only when physical properties including brightness, smoothness, and strength properties are acceptable to customers or equivalent to those of the chemical pulp sheet. Out of essential strength properties, stiffness is usually most difficult to increase, and that is why WFs are under current consideration. Figure 6 shows stiffness changes caused by the application of WFs. All WFs-containing sheets exhibited higher stiffness than 'Pulp only' sheets, but the CWFs showed lower stiffness than the other WFs-containing sheets. However, CWFs containing sheets gave 15%–20% higher stiffness than the 'Pulp only' sheet. Sheet bulk is the most important factor for developing high stiffness because stiffness is proportional to the cube of sheet thickness. The bulk is the reciprocal of the thickness.

In Figure 4, the bulk of the CWFs were lower than that of the WFs and the BWFs but higher than the 'Pulp only'.

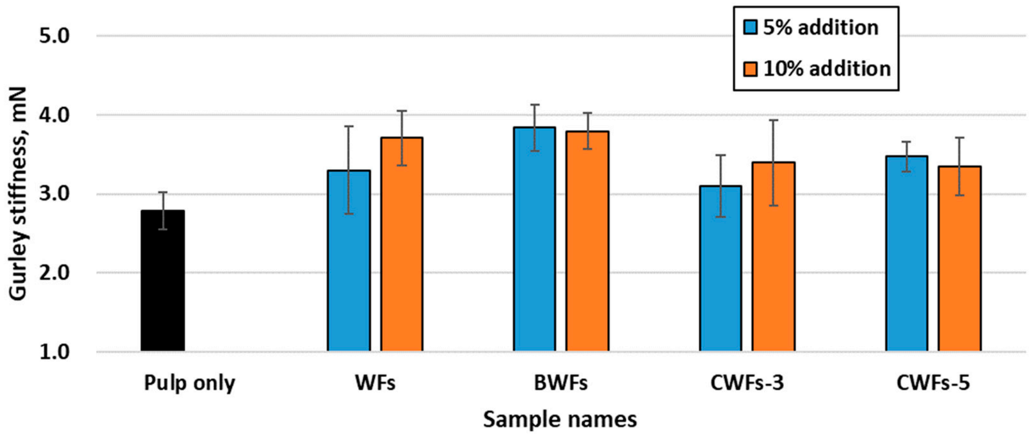


Figure 6. Stiffness changes caused by the addition of pre-treated WFs (Standard deviation bars were included).

Double folds, which is the measure of how many times a paper sheet can endure folding under a given tensile load until failure, are shown in Figure 7. Large differences between 'Pulp only' and WFs-containing sheets are evident. The application of CWFs in printing paper needs to improve folding properties and thus needs to use more long fibers in the wood pulp part.

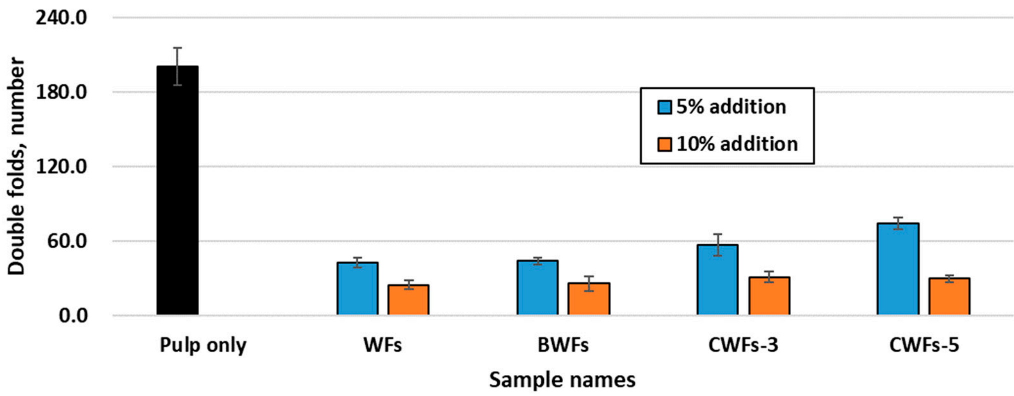


Figure 7. Double folds changes caused by the addition of pre-treated WFs (Standard deviation bars were included).

3.4. Accelerated Aging Test

The use of lignin containing materials in printing paper should cause color change or aging problems. Furthermore, strength properties of those papers deteriorate faster than wood-free paper. Accelerated aging (ISO 5630-1:1991) of paper and board by dry heat treatment at 105 °C may provide information concerning the natural changes that may occur in the material over a period of years. Figures 8–11 show the results of WFs-containing papers after accelerated aging for 20 days at 105 °C.

Brightness decreased greatly due to accelerated ageing for the WFs-containing and 'Pulp only' sheets, but decreased much more slowly for the CWF sheets (Figure 8). There might be large color changes in the WFs within the CWFs, but calcium carbonate on the surface of WFs seemed to partially conceal these color changes. After 20 days, the brightness of the 'Pulp only' sheet was close to that of the CWFs containing sheet.

The slow deterioration of breaking length (Figure 9), stiffness (Figure 10), and double folds (Figure 11) can be explained in the same way. That is, calcium carbonate has not changed its color and bonding properties by the prolonged exposure to the temperature of 105 °C, and the surface of CWFs consist of mostly calcium carbonate. However, chemical pulp and WFs lose their brightness and strength properties quickly by accelerated heat aging. Thus, the CWF sheets had slow deterioration and showed nearly identical strength properties to the 'Pulp only' sheet after 20 days of aging (Figures 9–11).

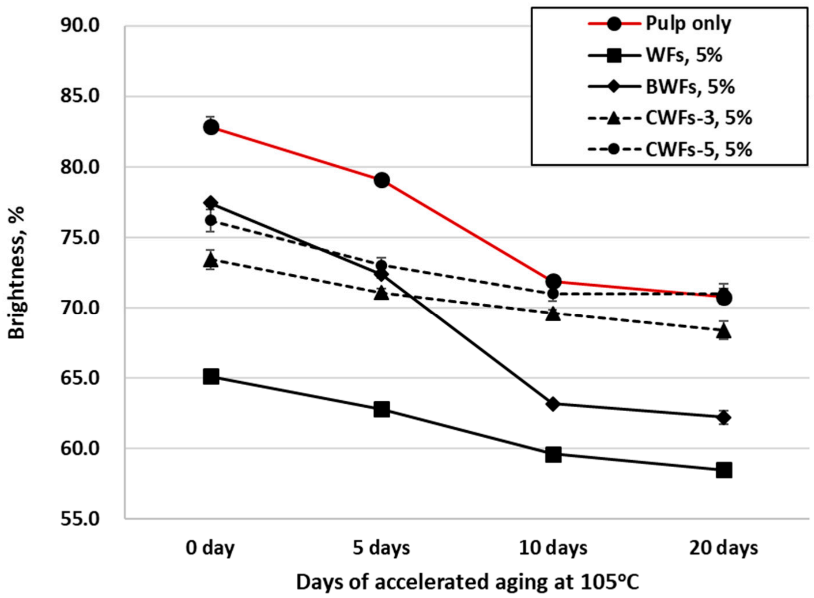


Figure 8. Brightness changes by accelerated aging for the WFs-containing sheets (Standard deviation bars were included).

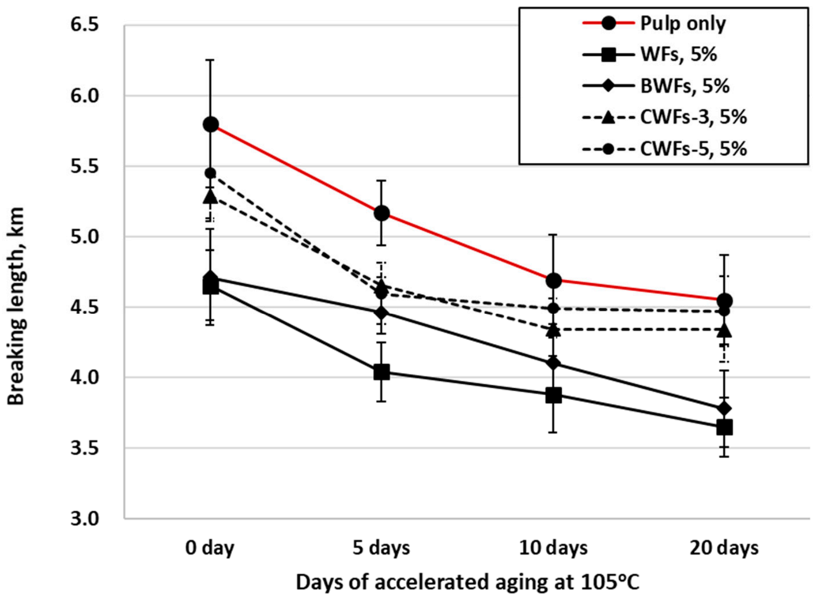


Figure 9. Breaking length changes due to accelerated aging for the WFs-containing sheets (Standard deviation bars were included).

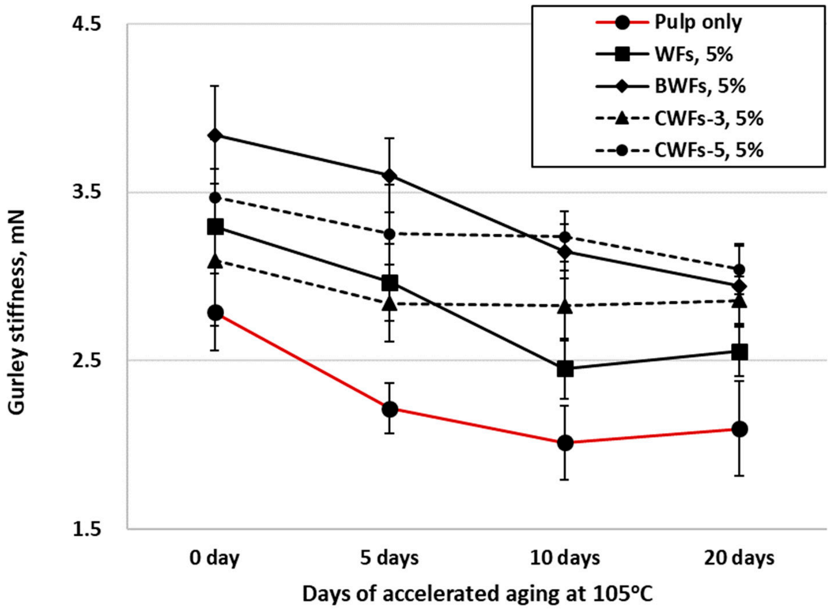


Figure 10. Stiffness changes due to accelerated aging for the WFs-containing sheets (Standard deviation bars were included).

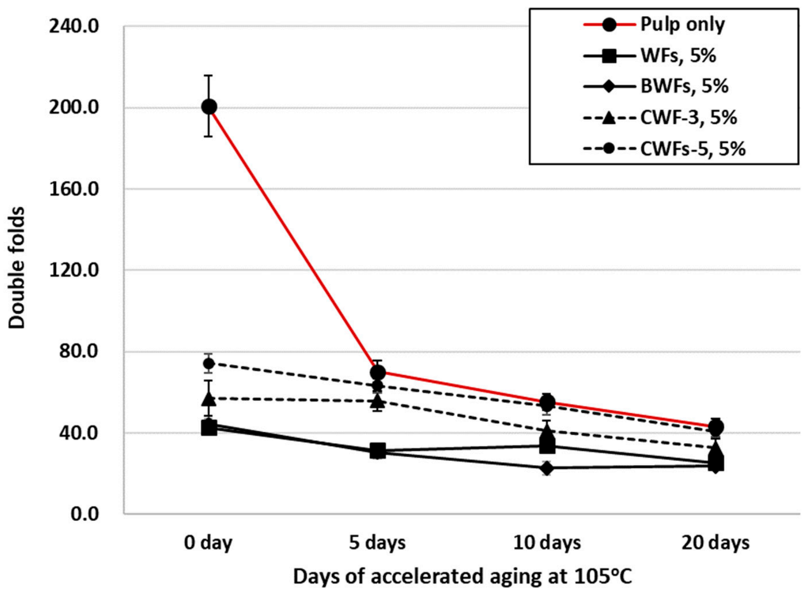


Figure 11. Double folds changes due to accelerated aging for the WFs-containing sheets (Standard deviation bars were included).

3.5. Cost Consideration of the in-situ $CaCO_3$ Formed WFs (CWFs)

To make bleached WFs with 5% H_2O_2 requires chemical costs, process energy, and wastewater treatment. The yield loss was about 32.8% (Seo et al., 2018). On the other hand, for the CWFs with a 1:5 ratio, yield increases 500%. The price of a 200-mesh pass WFs should be more than 2 times higher than the price of calcium carbonate. Bleached WFs should be much more expensive than unbleached ones. Therefore, the cost of preparing CWFs should be much less expensive than the WFs and BWFs used in this study. Furthermore, there is no need to treat wastewater for the CWFs.

4. Conclusions

The wood flours (WFs) that passed through a 200-mesh screen, were added to the bleached chemical pulp in 5% and 10% by weight after H_2O_2 bleaching (BWFs) or after $CaCO_3$ coating (CWFs) to replace the bleached chemical pulp, but turned out to be slightly inferior in brightness and strength properties other than stiffness. It is believed that the size of the 200-mesh screen-passed WFs was not small enough to develop equivalent smoothness to that of the chemical pulp. The CWFs resulted in similar brightness but much higher smoothness and could be prepared in a much less expensive way than the BWFs. Accelerated aging showed that the calcium carbonates on the surface of CWFs conceal the color change of the WFs inside, resulting in much slower deterioration of strength and optical properties in the CWF containing sheets. Compared to the BWFs, the CWFs developed better properties and rendered lower production costs. Therefore, further development of the CWFs for replacing bleached chemical pulp should be promising.

Author Contributions: D.S.K. and J.S.H. participated in the experimental design, actual experiments and data analysis. Y.B.S. conceived the idea of wood flour utilization in printing paper, experimental design, and all the writing. All authors approved read and approved the final manuscript.

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Conflicts of Interest: The authors declare no conflict of interest

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