

Preparation and Papermaking Properties of Dry-Cut Powder from Chemically Crosslinked BEKP

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Chemical crosslinking of cellulosic fibers increases their brittleness, making them more susceptible to dry powdering. In this study, bleached eucalyptus kraft pulp (BEKP) sheets were crosslinked with glyoxal (GO) and citric acid (CA) and subsequently dry cut into powders using a Wiley cutting mill. Key variables in the powder preparation were dosages of GO and CA, as well as their respective catalysts, aluminum sulphate (alum) and sodium hypophosphite (SHP). The average fiber length of the GO and CA crosslinked pulps was reduced, at most down to 0.12 and 0.17 mm by the dry cutting, using a 0.5 mm perforated screen in the final dry-cutting stage. The powders exhibited reduced water retention, lower sedimentation volume in water, and, when dry, showed increased tapped and bulk densities. When mixed with refined BEKP, the powders enhanced dewatering during handsheet formation and improved the resulting sheets' bulk, light scattering, and opacity, while reducing tensile strength. These findings suggest that chemically crosslinked pulp powders have potential as a bulking and dewatering aid in papermaking. Furthermore, due to their low water absorbency and presumable low abrasiveness, the powder may have potential applications beyond papermaking, such as filler of plastics, glues, and coating materials.

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INTRODUCTION

Chemical crosslinking is commonly used to reduce fabric shrinkage and wrinkling caused by the wetting and drying of the fabric. In the chemical crosslinking treatment, cotton fabric is immersed in an aqueous solution of chemical crosslinking agents, which are absorbed into the fabric, its yarns, and fibers. Following absorption, excess solution is removed by pressing the fabric, after which it is dried under tension to maintain a smooth surface. The actual crosslinking reactions between cellulose chains primarily occur during the subsequent heating stage after drying. The resulting crosslinks are supposed to restrict the mutual movement and relocation of cellulose chains during washing, drying, and various mechanical stress in moist and wet conditions. The chemical crosslinking reactions predominantly take place in the amorphous regions of the fibers. As a consequence of the crosslinking treatment, the flexibility and water absorption capacity of fibers' amorphous regions decrease, leading to increased fiber brittleness. Therefore, chemical crosslinking treatments for cotton fabrics are typically optimized to balance shrinkage and wrinkle resistance with the mechanical strength of the fabric (Shindler and Hauser 2004; Dehabadi *et al.* 2013; Mukthy *et al.* 2014; Choudhury 2017).

The suitability of chemical crosslinking for improving the dimensional stability and strength of paper under wet conditions has also been studied. Similar to cotton fabric crosslinking, a drawback of paper crosslinking is the increased brittleness of both the fibers and the paper itself, resulting in decreased tear strength and folding endurance (Eldred and Spicer 1963; Caulfield and Weatherwax 1976; Horie and Biermann 1994; Caulfield 1994; Yang and Xu 1998; Xu *et al.* 2002; Widsten *et al.* 2014; Korpela *et al.* 2023).

The most commonly used chemical crosslinking agents for cotton fabrics are modified dimethyloldihydroxyethyleneurea (mDMDHEU) compounds, typically in combination with a catalyst, such as magnesium chloride (MgCl_2). A key advantage of mDMDHEU compounds is their partial self-polymerization, which extends the length of the chemical crosslinks. This has a beneficial effect on fiber and fabric formability, flexibility, and mechanical strength. A downside of mDMDHEU usage is potential release of formaldehyde residues during the fabric finishing and later on in use (Schindler and Hauser 2004; Choudhury 2017). Due to the concerns, chemical manufacturers have sought to develop formaldehyde-free crosslinking agents for cotton fabrics. Proposed alternatives include dialdehydes, such as glyoxal (GO) and glutaraldehyde, with catalysts such as aluminium sulphate or MgCl_2 , as well as polycarboxylic acids, such as citric acid (CA) and 1,2,3,4-butanetetracarboxylic acid (BTCA), with catalysts such as sodium hypophospite (SHP). In cotton crosslinking, glyoxal's advantage lies in its relatively low required reaction temperature, but its disadvantages include fiber embrittlement, resulting in reduction in fabric strength. Similarly, while CA and BTCA have been investigated as potential "formaldehyde-free" crosslinking agents, their drawbacks include fiber embrittlement, and in addition, a relatively high required reaction temperature and, in the case of CA, the slight yellowing of fibers and fabric during the treatment. The GO and CA reactions with the hydroxyl groups of adjacent cellulose chains are illustrated in Fig. 1 (Lu and Yang 1999; Schindler and Hauser 2004; Dehabadi *et al.* 2013; Mukthy *et al.* 2014; Tang *et al.* 2016; Choudhury 2017).

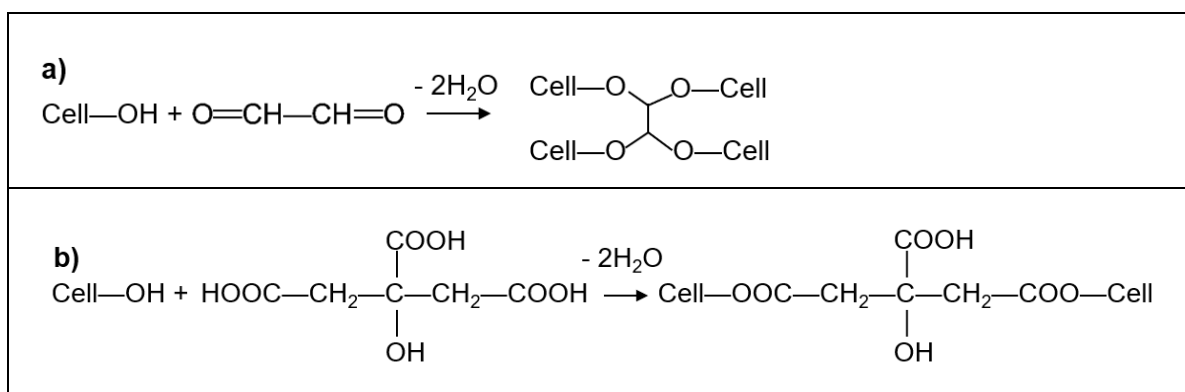


Fig. 1. Crosslinking of cellulose with a) glyoxal (GO), b) citric acid (CA) (Schindler and Hauser 2004)

Depending on the reaction conditions, GO may form either hemiacetal bonds, which are hydrolyzed in the presence of water, or water-resistant acetal bonds between cellulose chains. The formation of more stable acetal linkages is promoted by high reaction temperatures ($>100\text{ }^\circ\text{C}$) and the presence of catalysts like mineral acids, organic acids, and various metal salts, such as alum. The reaction of CA with cellulose is similarly catalyzed by mineral and organic acids and metal salts. Among the catalysts used in published

studies, sodium hypophosphite (SHP) has been the most commonly employed with CA. The reported used reaction temperatures range from 140 to 180 °C, with a few minutes reaction time (Karthik *et al.* 2012; Widsten *et al.* 2014; Tang *et al.* 2016). Most often, authors have aimed not only to achieve the desired effects of the crosslinking treatment, but also to minimize the resulting embrittlement of the treated cellulosic material. In the case of GO, this has been addressed by incorporating co-crosslinkers, such as glycols, which extend the crosslink length, thereby enhancing the flexibility of the crosslinked cellulose (Lee and Kim 2004; Ma *et al.* 2021).

The most severe reported disadvantage of paper crosslinking treatments is embrittlement of the paper, resulting in greatly decreased folding endurance, and strain during the breakage of the paper (Caulfield 1994; Horie and Biermann 1994; Yang and Xu 1998; Korpela *et al.* 2023). The embrittlement is supposed to be a consequence of reduced relative flexibility of the cellulose chains and, thus, reduced formability of the fibers, and paper, by the formed crosslinks. Korpela and Orelma (2020) introduced a method that takes advantage of the embrittling effect to enhance the dry cutting of bleached birch kraft fibers to fine pulp powder. In this approach, pulp sheets were treated with glyoxal (6.0 wt%) and aluminum sulfate (2.0 wt%). The crosslinking treated pulp sheets were first dry cut using a Wiley mill (yielding 84.7% of fibers shorter than 0.20 mm) with 1.0 slot screen and subsequently ground into a more fine powder (D50 = 40 µm) using an air-flow-type micronizer. The crosslinked pulp exhibited significantly increased brittleness and improved processability in the dry cutting the passing time through the Wiley mill being approximately only one-fifth to one-tenth that of the untreated reference pulp. Compared to the fluffy Wiley-milled reference pulp powder, the crosslinked pulp powder had a substantially higher tapped and bulk densities (g/mL) and a smaller average particle size. The non-fluffy character of the dry-cut pulp powder enabled refinement of the material using the air-flow-type micronizer. The water absorption capacity of the crosslinked pulp powder was considerably lower than that of the reference powder. Based on these findings, Korpela and Orelma (2020) suggested that the chemically crosslinked kraft pulp powder could potentially serve as a new type of filler material in paper and plastic applications.

To the best of the authors' knowledge, no studies have been reported in the literature that examine the effects of crosslinking agent and catalyst dosages on cellulosic fiber dry cutting and the properties of the resulting cellulosic powders. This study investigates the effects of GO- and CA-based crosslinking treatments on the dry cutting of crosslinked BEKP fibers in Wiley milling and the properties of the resulting bleached eucalyptus kraft pulp (BEKP) powders. Wiley milling of the pulp sheets crosslinked with different dosages of GO and CA, and their respective catalysts, was performed sequentially through 5 mm, 2 mm, and 1 mm slotted screens; and in the final stage, two times through 0.5 mm slotted screens. The goal of this study was not to produce a cellulosic filler intended to directly replace mineral fillers in paper products or plastics but rather to create a somewhat coarser raw material for papermakers that differs from conventional raw materials. The powder characterization included measurements of fiber length, fines content (< 0.2 mm), water retention value (WRV), sedimentation volume in water, as well as dry pulp powder's bulk density and tapped density. Additionally, the study hypothesizes that the used crosslinking agents, catalysts, and their dosages influence these properties, as well as the expected reduction in paper strength when mixed with ordinary papermaking fibers. This was tested by mixing 20 wt% of the BEKP powders to refined BEKP (°SR 33), followed by measurement of the mixture pulp dewatering properties and laboratory handsheet mechanical and optical properties.

EXPERIMENTAL

Materials

The used pulp was bleached eucalyptus ECF (elementary chlorine free) kraft pulp (BEKP) sourced from a South American pulp mill. It was supplied as A4-sized dried pulp sheets, with a grammage of 1200 g/m² and a dry content of 92.5%. Glyoxal (GO) (40% w/w aqueous solution) was obtained from Thermo Fisher Scientific Inc. (Heysham, Lancaster, UK) and citric acid monohydrate (CA) from VWR International BVBA (Leuven, Belgium). Sodium hypophosphite monohydrate (SHP), which was used as a catalyst for CA crosslinking, was acquired from VWR International BVBA, and aluminum sulfate tetradecahydrate (alum), employed for glyoxal crosslinking, was obtained from Kemira OyJ (Espoo, Finland). All chemicals were of laboratory grade and applied without further purification. Milli-Q water was utilized for all solution preparations and dilutions.

Chemical Crosslinking of Pulp Sheets

The BEKP sheets were immersed in an aqueous solution of crosslinking chemicals at room temperature for 10 min to achieve complete saturation. After impregnation, the sheets were placed between blotting papers, with a metal plate on top, and pressed once back and forth, using a 10 kg roller. The sheets were then dried overnight in a drum dryer at a temperature of 82 to 92 °C. To prevent adhesion, a silicone mesh was placed between the sheets and the drum surface, and blotting paper between the sheets and the dryer fabric. For complete reaction of the GO and CA, the pulp sheets were further heat-treated in an oven for 150 min at 120 or 150 °C, respectively. The sheets were weighed before impregnation and after wet pressing (rolling) and the final heat treatment. The amount of absorbed crosslinking agents were calculated by assuming that the percentage proportions of crosslinking chemicals in the absorbed solutions were the same as the percentage proportions of the immersion solution (Table 1). The wet pick-up of the solutions after the pressing by the roller was around 200% on average, as calculated by Eq. 1.

$$\text{Wet Pick-Up (\%)} = ((\text{Wet-Weight} - \text{Dry Weight}) / \text{Dry weight}) \times 100 \quad (1)$$

Reference sheets were processed identically but without the addition of crosslinking agents. The calculated added amounts of glyoxal (GO) + aluminum sulfate (alum), and citric acid (CA) + sodium hypophosphite (SHP), in the crosslinking treated sheets are shown in Table 2. The reference pulp powders GO Ref and CA Ref were treated in the same way but without the addition of the crosslinking chemicals.

Prior to testing the BEKP powders' dewatering properties and the effects on refined BEKP handsheet properties, the powders were rinsed twice with water (approximately 100 mL per 10 gram), using an open mesh fabric (25-micron mesh opening) in a Büchner funnel to reduce the amount of possible unreacted or unbound crosslinking agents. To minimize the fines loss, the rinsing waters were recirculated during the rinsing process.

Dry Milling of Crosslinked Pulp Sheets

The crosslinked pulp sheets were manually cut into 3 × 3 cm² pieces and subsequently dry cut using a Wiley mill (Standard Model No. 3, Arthur H. Thomas Co, US). The cut pieces were manually fed into the mill, where rotating knives operated against stationary knives to cut and refine the material. The milling was performed in sequential

steps using 5 mm, 2 mm, and 1 mm perforated screens, followed by two passes through a 0.5 mm screen.

Measurement of Powder Particle Size and Poured Bulk and Tapped Densities

Fiber length, fiber width, and fines content of the uncut BEKP and the dry-cut pulps were measured using an L&W FiberTester Plus image analyzer (ABB AB, Kista, Sweden). All measurements were performed in duplicate.

The bulk density of the poured pulp powders was determined by measuring the volume of 1.0 g pulp powder in a 15-mL test tube. Tap density was measured by tapping the test tube from a height of around 3 cm onto a hard surface until no further settling occurred. The results are the mean values of minimum duplicated measurements

Water Retention Value (WRV) and Specific Sedimentation Volume Measurements

The WRV (g/g) of the pulp powders was determined using the centrifugal method according to ISO 23714 (2007). The reported results are the mean values of duplicate measurements. The pulp powders' specific sedimentation volume was measured following the measurement principle described by Marton and Robie (1969). For the measurement 0.50 g pulp powder was mixed with water in a 50-mL test tube, followed by recording the sediment volume (mL) after 6 h, 24 h, and 168 h sedimentation time. The reported results are averages of two parallel measurements.

Photomicrography

Fibers of each sample were separated in water and were examined on a microscope slide as sealed prepares. The unstained samples were examined with a Zeiss Axio Imager M2 microscope (Carl Zeiss GmbH, Göttingen, Germany), using a 10x objective (Zeiss EC Epiplan-Neofluar, numerical aperture of 0.30). Micrographs were obtained using a Zeiss Axiocam 506 CCD color camera (Zeiss) and the Zen imaging software (Zeiss). Representative images were selected for publication.

Refining of Eucalyptus Pulp and Testing of Handsheet Properties

To evaluate the effect of the BEKP powders' papermaking properties, pulp powders were mixed at 20 wt% with refined BEKP. The pulp was refined to a Schopper-Riegler value (°SR) of 33, using a Voith LR1 laboratory refiner (Voith AG, Heidenheim, Germany). The refining process had a specific energy consumption (SEC) of 50 kWh/t and a specific edge load (SEL) of 0.3 J/m.

Laboratory handsheets were prepared using uncirculated ion-exchanged water in accordance with ISO 5269-1 (2005). The target grammage was 100 g/m² at a relative humidity of 50%. Prior to handsheet making, the pH of the pulp suspensions were adjusted to 7.0 to 7.2, using dilute HCl. The test methods used are listed in Table 1.

Table 1. Utilized Pulp and Paper Test Methods

Water Retention Value (g/g)	ISO 23714 (2007)
Schopper-Riegler (°SR) value	EN ISO 5267-1 (1999)
Fines content (%)	ISO 16065-2 (2014)
Grammage (g/m ²)	ISO 5270 (2012)
Bulk (kg/m ³)	ISO 5270 (2012), ISO 536 (2019)
Tensile index (Nm/g)	ISO 5270 (2012)
Optical properties	ISO-2471 (2008), ISO 9416 (2017), ISO 2470-1 (2016)

RESULTS AND DISCUSSION

Table 2 presents the fiber length, fiber width, and fines content (particles smaller than 0.2 mm) of the uncut BEKP, dry-cut BEKP, and the prepared BEKP powders. Samples GO Ref and CA Ref were processed in the same way as the chemically crosslinked dry-cut pulps but without the crosslinking chemicals. According to the results, the fiber length of the crosslinked BEKP powder was substantially lower compared to the reference powders. This occurred despite the samples being dry cut using sieves of the same hole sizes in the Wiley-mill. Thermal treatments of the fibers alone, at 120 and 150 °C (GO Ref and CA Ref), also led to a quite marked reduction in fiber length during dry cutting. This indicates that heating alone also made the BEKP fibers more brittle and thus more prone to cut in the Wiley milling. The effects of both heating and chemical crosslinking were also reflected in a notable increase in the powder fines content (< 0.2 mm). Overall, based on fiber length and fines content, increasing the dosages of GO and CA intensified fiber embrittlement. In contrast, the effect of catalyst dosages was less consistent. It is possible that the applied crosslinking temperature was sufficiently high, and the crosslinking duration long enough, that the catalysts had no significant role in completing the crosslinking reactions in those conditions.

Table 2. Fiber Length, Fiber Width, and Fines Content (< 0.2 mm) of the Uncut BEKP Pulp and the Dry-Cut Pulp Powders measured using an L&W FiberTester Plus Image Analyzer

	Length Weighted Mean Fiber Length (mm)	Mean Width (μm)	< 0.2 mm (%)
BEKP uncut	0.798	18.3	17.8
BEKP dry-cut	0.287	19.5	39.4
GO Ref (120 °C)	0.255	19.6	45.2
+ GO 3.3 %	0.216	20.6	54.2
+ GO 3.1 % + alum 0.1 %	0.213	20.7	54.5
+ GO 3.0 % + alum 1.0 %	0.230	20.8	52.6
+ GO 8.5 %	0.151	21.9	73.8
+ GO 8.8 % + alum 0.3 %	0.154	21.9	73.2
+ GO 8.7% + alum 2.9%	0.124	21.8	82.1

CA Ref (150 °C)	0.257	19.4	44.5
+ CA 2.8 %	0.202	19.8	57.6
+ CA 2.7 % + SHP 0.14 %	0.209	20.0	56.0
+ CA 2.7 % + SHP 1.4 %	0.215	20.3	54.0
+ CA 8.3 %	0.184	20.9	63.6
+ CA 8.4 % + SHP 0.4 %	0.181	21.2	65.3
+ CA 8.5 % + SHP 4.3 %	0.172	21.5	67.1

Optical microscopy images (Fig. 2a-2d) show that the fiber cutting occurred without clear visible fibrillation of the fibers or longitudinal fiber splitting. Wiley milling of non-crosslinked BEKP ($\rightarrow$ BEKP dry-cut) seemed to result in fiber curling and an increased number of fiber kinks (compare Fig. 2a vs. 2b).

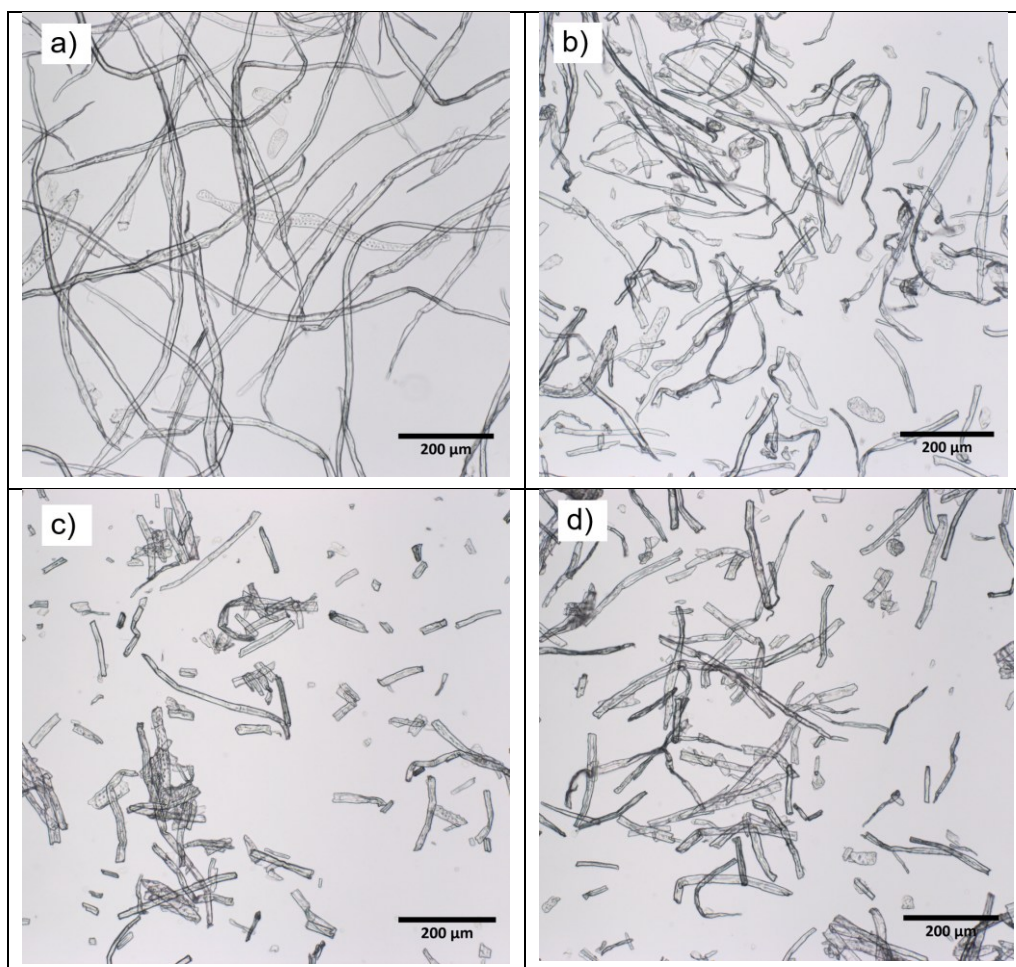


Fig. 2. Optical microscopy image of samples a) BEKP uncut b) BEKP dry-cut c) +GO 8.7% + alum 2.9%, and d) + CA 8.5% + SHP 4.3%. See sample codes in Table 3.

According to the results presented in Fig. 3, chemical crosslinking treatments reduced the WRV values of the pulp powders. The WRV value decreased with increasing dosages of GO and CA. Again, the effect of the used catalysts was minimal. The dry-cutting process alone also led to a reduction in the WRV of BEKP. This may be attributed to mechanical compressive impacts exerted on the fibers during the dry-cutting process, potentially causing irreversible structural changes in fibers that diminish their ability for

water absorption and retention. A similar consequence has been reported to take place during the compression of fibers in paper calendering, resulting in a decrease of the WRV (Water Retention Value) of redispersed recycled fibers (Göttsching and Stürmer 1977).

Figure 4 presents sedimentation volumes of the BEKP powders in water. It is generally acknowledged that a low specific sediment volume of fibers and fines reflects their compact structure, limited internal and external fibrillation, low water absorption, and poor bonding ability (Marton and Robie 1969; Luukko and Paulapuro 1999). Based on the results, the chemical crosslinks did obviously not hydrolyze notably by water but hindered the particles' water absorption and swelling through the 7-day measurement period.

The compact nature of crosslinked pulp powder particles can also be seen in the reduced bulk density and the tapped density of the corresponding dry powders (Fig. 5). In general, a high bulk density and a low ratio between bulk and tapped density indicate good processability of the powder, such as favorable dosing characteristics (Barbosa-Cánovas *et al.* 2006; Kulkarni *et al.* 2010). However, in the present study, this ratio did not show a significant decrease.

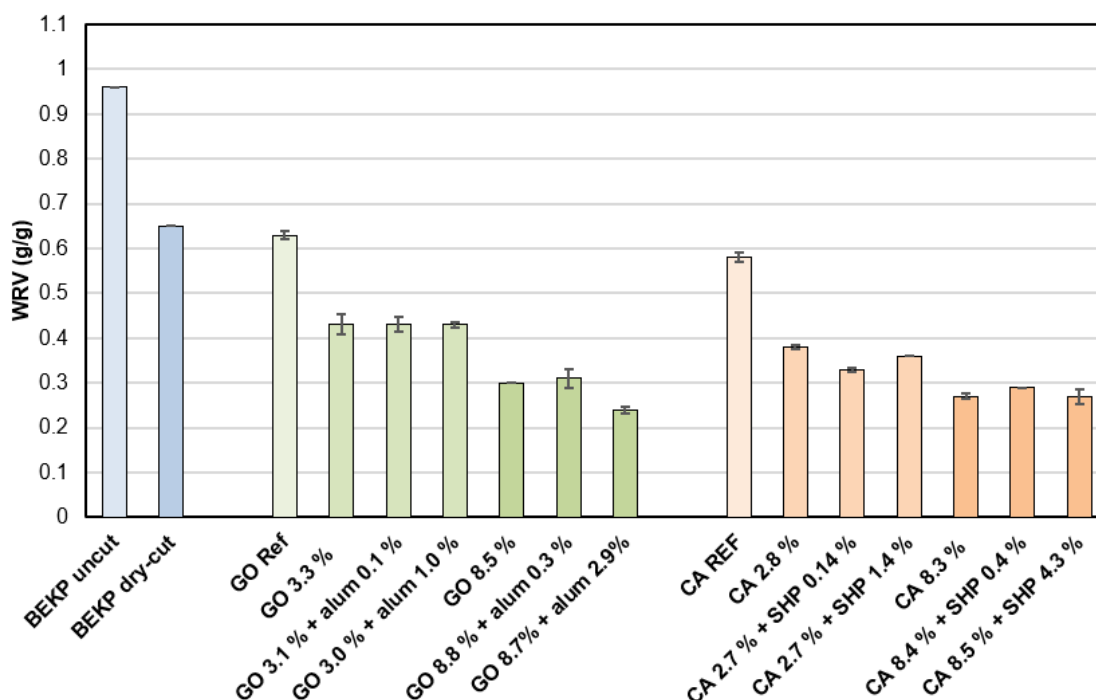


Fig. 3. Water retention values (WRV) of the bleached eucalyptus kraft pulp (BEKP) pulp powders. Samples GO Ref and CA Ref were processed in the same way as the chemically crosslinked dry-cut pulps but without the crosslinking chemicals.

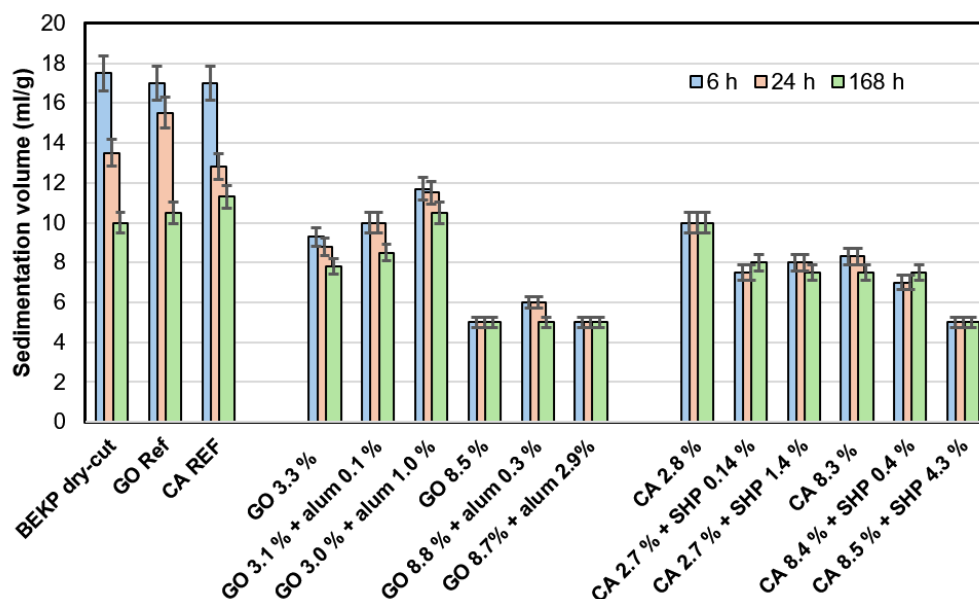


Fig. 4. BEKP powders sedimentation volumes in water. The sedimentation volumes were recorded after 6 h, 24 h, and 168 h sedimentation time. Results are averages of two parallel measurements. Error bars in the figure represent the reading accuracy of the sedimentation volume (approximately $\pm 5\%$).

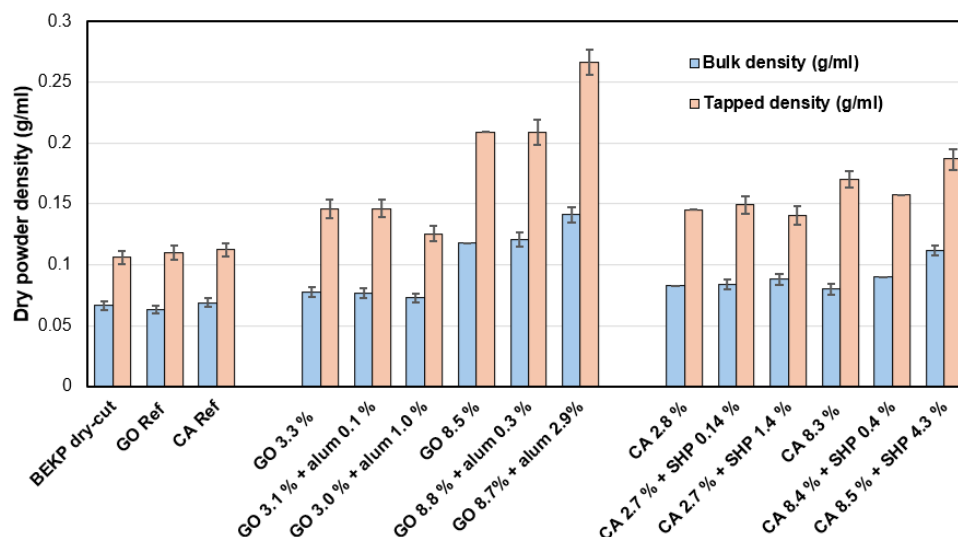


Fig. 5. Effect of BEKP crosslinking treatments on the bulk density and tapped density of dry-cut pulp powder. Bulk density = Mass of fibers (g) / Untapped volume (mL). Tapped density = Mass of fibers (g) / Tapped volume (mL). Error bars in the figure represent the reading accuracy of the powder volume (approximately $\pm 3\%$).

Mixture Pulp Dewatering and Handsheet Properties

The papermaking properties of the cellulose powders were investigated by adding each prepared powder (Table 2) at a dosage of 20 wt% to refined BEKP and measuring the effect of the addition on the dewatering properties of the pulp mixture, as well as the handsheet bulk, strength, and optical properties. Based on the results in Table 3, all added cellulose powders reduced the Schopper-Riegler ($^{\circ}\text{SR}$) value of the pulp mixture, accelerated pulp slurry drainage on the sheet former, and increased the solids content of the laboratory handsheets after the wet pressing stage. GO and CA crosslinking treatments

enhanced these effects quite equally. The results also suggest that a significant improvement in the dewatering properties could be achieved by smaller-than-used crosslinking agent dosages. According to the results, neither the influence of increasing the crosslinking agent dosage nor the catalysts' dosage had a clear and consistent effect on the handsheet properties. As mentioned earlier, it is possible that, under the applied crosslinking conditions, the crosslinking reactions proceeded to completion in all cases regardless of catalyst use.

The observed largest increase in the solids content of wet-pressed handsheets, from 45 % to 48.8%, would in practice lower the amount of water that needs to be evaporated at the paper machine drying section by around 15% per ton of dry paper.

Figure 6 shows that the 20 wt.% BEKP powder additions notably increased the bulk of handsheets made from refined BEKP. These findings are consistent with those previously reported by Korpela and Tanaka (2015) regarding the cross-linking treatment of birch kraft pulp and its effects on the laboratory handsheet properties. The increase is likely due to the bulking effect of the BEKP powders having poor bonding capability due to the crosslinking treatments. The mechanism behind the increased handsheet bulk is presumably similar to that of precipitated and rosette-type calcium carbonate, which, due to their poor bonding capability and bulky morphology, hinder the close packing of papermaking fibers and thereby prevent structural densification of the sheet (Hubbe and Gill 2016). Consistent with the assumed low bonding capability of the BEKP powders, and the resulting increase in handsheet bulk, the crosslinking treatment of BEKP powders reduces both the tensile strength and Z-directional strength of handsheets made from refined BEKP (Fig. 7). These results are also in concordance with the earlier results reported by Korpela and Tanaka (2015). According to a rule of thumb in papermaking, a 10% increase in mineral filler content typically reduces the tensile strength of paper by approximately 20 to 25%. However, the actual effect can vary greatly, depending on the type of filler, as well as its particle size and shape, and papermaking parameters (Bohmer 1981; Hubbe and Gill 2016). The observed 20 to 30% reduction in tensile strength resulting from the addition of 20% BEKP powders aligns closely with the rule of thumb.

Table 3. The Effect of the Dry-Cut Pulp Powders on the Dewatering Properties of Refined BEKP

	°SR	Drainage time (s)	Dry cont. (%)
Refined BEKP 100%	33 (0)	11.2 (0.1)	45.0 (0.8)
+ 20% (GO 3.3 %)	30 (0)	8.5 (0.1)	45.3 (0.5)
+ 20% (GO 3.1 % + alum 0.1 %)	29.5 (0.6)	9.1 (0.1)	48.7 (1.6)
+ 20% (GO 3.0 % + alum 1.0 %)	30 (0)	9.4 (0.2)	48.2 (2.8)
+ 20% (GO 8.5 %)	31.5 (0.6)	8.1 (0.1)	48.0 (-)
+ 20% (GO 8.8 % + alum 0.3 %)	29.5 (0.6)	8.0 (0.1)	48.1 (1.1)
+ 20% (GO 8.7% + alum 2.9%)	30 (0)	9.8 (0.2)	45.8 (1.2)
+ 20% (CA 2.8 %)	29 (0)	7.8 (0.2)	45.7 (0.0)
+ 20% (CA 2.7 % + SHP 0.14 %)	27 (0)	7.5 (0.1)	46.8 (0.5)
+ 20% (CA 2.7 % + SHP 1.4 %)	31 (0)	8.0 (0.1)	47.0 (0.6)
+ 20% (CA 8.3 %)	29.5 (0.6)	7.4 (0.1)	48.4 (0.4)
+ 20% (CA 8.4 % + SHP 0.4 %)	28 (0)	7.8 (0.1)	47.7 (2.6)
+ 20% (CA 8.5 % + SHP 4.3 %)	30 (0)	8.2 (0.1)	48.8 (1.0)

Note: In the mixture, the pulp proportion of refined BEKP was 80 wt% and pulp powder 20 wt%

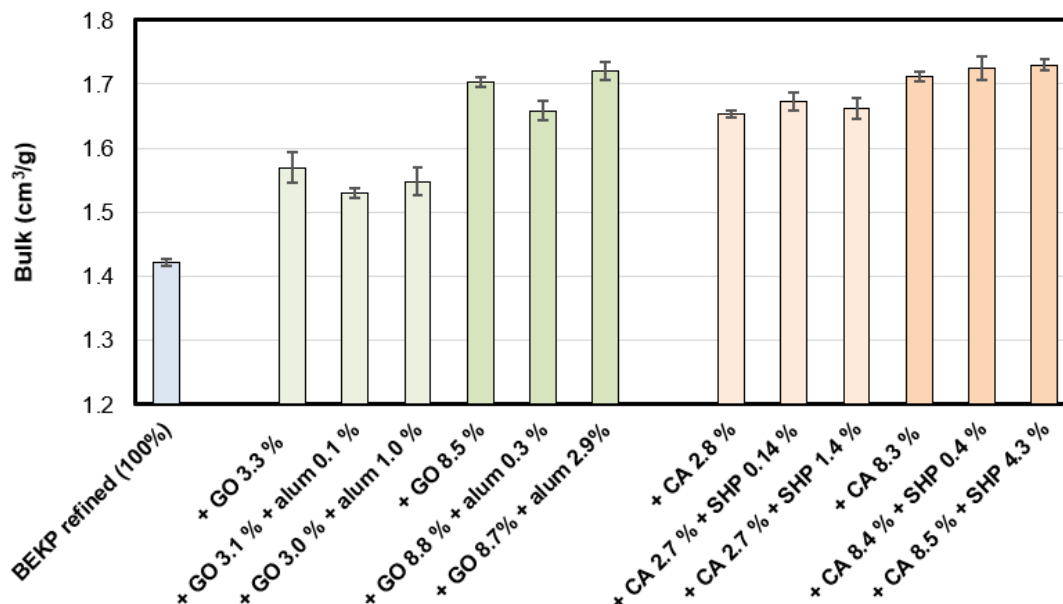


Fig. 6. Effect of crosslinked BEKP pulp powders addition (20 wt.%) on bulk of refined BEKP (°SR 33)

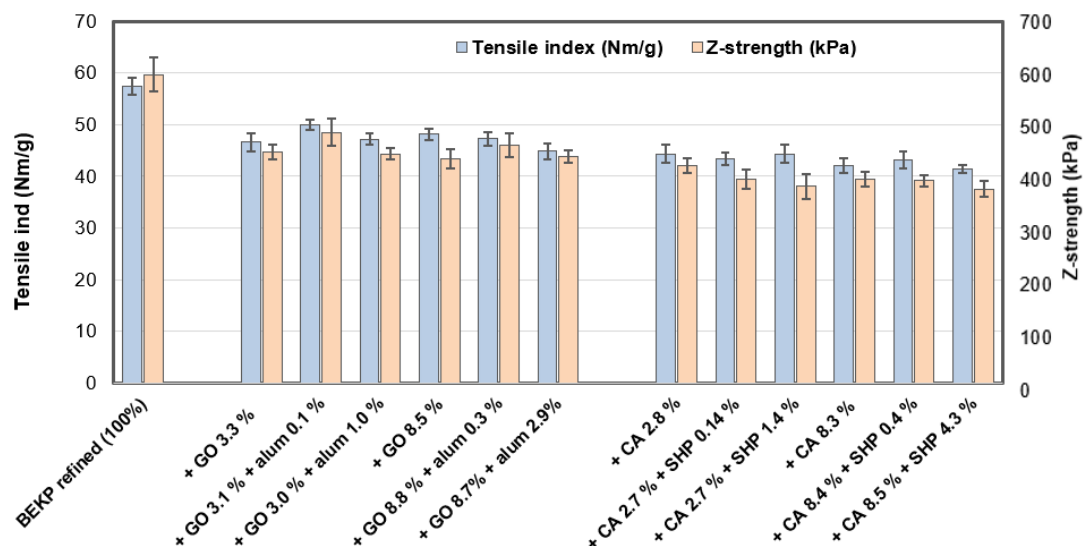


Fig. 7. Effect of crosslinked BEKP pulp powders addition (20 wt%) on the tensile- and Z-directional strength of refined BEKP (°SR 33)

Table 4 shows the effect of the BEKP powder additions (20 wt%) on the optical properties of refined BEKP handsheets. The addition of the BEKP powders increased the light scattering coefficient of the handsheets substantially. The light scattering enhancement was slightly greater for powders crosslinked with citric acid (CA) compared to those crosslinked with glyoxal. The reason for the difference is unfortunately not clear. The use of catalysts did not exhibit a clear or consistent effect on the increase in light scattering coefficients. However, the increased light scattering coefficients are consistent with the increased handsheet bulk.

Table 4. Effect of BEKP Powders (20 wt.%) on the Optical Properties of BEKP Handsheets*

	Light scatt. (m ² /kg)	Light abs. (m ² /kg))	Brightness (%)	Opacity (%)
Refined BEKP (100%)	37.5	0.09	87.1	84.4
+ 20% (GO 3.3 %)	42	0.13	85.8	86.4
+ 20% (GO 3.1 % + alum 0.1 %)	41	0.11	86.4	85.4
+ 20% (GO 3.0 % + alum 1.0 %)	41.7	0.1	86.3	86.1
+ 20% (GO 8.5 %)	42.2	0.13	85.5	86.2
+ 20% (GO 8.8 % + alum 0.3 %)	42.2	0.14	85.6	86.9
+ 20% (GO 8.7% + alum 2.9%)	42.4	0.16	83	87.6
+ 20% (CA 2.8 %)	43.1	0.13	84.9	86.9
+ 20% (CA 2.7 % + SHP 0.14 %)	43.5	0.13	85.1	86.8
+ 20% (CA 2.7 % + SHP 1.4 %)	43.1	0.1	86.5	86.4
+ 20% (CA 8.3 %)	43.4	0.18	81.5	87.6
+ 20% (CA 8.4 % + SHP 0.4 %)	43.4	0.15	82.9	87.6
+ 20% (CA 8.5 % + SHP 4.3 %)	43.5	0.1	86.4	86.4

*Standard deviation of light scattering and absorption coefficients (m²/kg), brightness (%), and opacity (%) measurements were < 1.0 (m²/kg), 0.01 (m²/kg), 1.0 (%), and 0.4 (%), respectively.

The observed increase in the light absorption coefficient of the handsheets is attributed to the yellowing of BEKP fibers resulting from chemical crosslinking treatments, particularly pronounced in powders crosslinked with citric acid (CA) (see Table 4). This discoloration is likely caused by side reactions of CA, which may lead to the formation of oligomeric structures, containing conjugated double bonds, capable of absorbing visible light (Karthik *et al.* 2012; Ye *et al.* 2015; Tang and Sun 2016). According to the results, use of the catalysts' SHP alongside CA mitigates the yellowing effect.

The findings of this study indicate that the crosslinking treatments applied to BEKP induce brittleness in both the sheets and the fibers, facilitating their powdering by dry cutting. The resulting dry powder exhibits higher bulk and tapping densities, and when wetted, significantly lower WRV compared to dry powder produced from non-crosslinked BEKP sheets. When 20 wt% of this powder was added to the refined BEKP pulp, the drainage of the furnish improved, and the solids content handsheets after wet pressing increased. The addition of the powders also led to notable increases in handsheet bulk and light scattering. However, tensile strength and Z-directional strength of the handsheets decreased. These changes are likely attributable to the powder particle smaller length compared to the BEKP fibers, and the reduced bonding capacity of the powder particles caused by crosslinking treatments. Despite the increase in light scattering coefficient, the brightness of the blended sheets slightly decreased, which is explained by an increase in the light absorption coefficient of the BEKP pulp induced by the crosslinking treatments. It should be noted that the reaction conditions used in this study were selected to ensure complete reaction of the crosslinking chemicals. By optimizing chemical crosslinking to occur under milder conditions, the increase of the light absorption coefficient could potentially be reduced compared to what was observed here.

Overall, the results suggest that BEKP powders produced by the dry milling of chemically crosslinked BEKP pulps could be effective in enhancing the dewatering properties of papermaking pulps and increasing the bulk of fiber webs, such as the middle

and back layers of paperboard, or tissue paper. Due to low water absorbency and low density compared to mineral fillers, these powders are also potentially suitable as “lightweight renewable fillers” in plastics and various adhesives. The crosslinking and subsequent dry milling processes involve several key variables, including the type and dosage of crosslinking agents, the temperature and duration of the crosslinking treatment, and the target fineness achieved through dry milling. By adjusting these parameters, the properties of BEKP powders can potentially be optimized for a range of end-use applications. A further interesting research topic is the effect of paper-strengthening agents on papers containing crosslinked pulp powders

CONCLUSIONS

1. The results of this study demonstrate that chemical crosslinking treatments applied to bleached eucalyptus kraft pulp (BEKP) sheets increase the brittleness of both the sheets and their constituent fibers, thereby facilitating their dry processing by cutting mill into fiber powder. The resulting dry powders exhibit higher bulk and tapping densities, and when wetted, significantly reduced water absorption, compared to powders derived from non-crosslinked BEKP sheets.
2. Mixing 20 wt% of these powders into refined BEKP pulp increased the rate of drainage and increased the solids content of wet pressed handsheets, and increased handsheet bulk and light scattering. A downside was decrease of the handsheets' tensile and Z-directional strength. These effects are likely due to the small particle size of the BEKP powders (length weighted average fiber length ranging from 0.12 to 0.23 mm) and the reduced bonding potential of the particle surfaces caused by the chemical crosslinking.
3. Chemical crosslinking resulted in slight yellowing of the chemically crosslinking treated BEKP pulp and the pulp powders made thereof. It is quite possible that the effect could be diminished by using a lower curing temperature and time than in the present study, where the curing conditions were selected to ensure complete reaction of the crosslinking agents.
4. Overall, the findings suggest that BEKP powders produced *via* dry milling of chemically crosslinked BEKP sheets could serve as novel additives for enhancing the dewatering performance of papermaking pulps and for increasing the bulk of fiber-based structures, such as the middle and back layers of paperboard, printing papers, and tissue.

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