

FABRICATION OF HIGH STRENGTH PAPER FROM DIFFERENT TYPES OF PHOSPHORYLATED FIBERS USING HOT PRESSING AND FORMING AGENTS

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Phosphorylated fibers offer a broad range of applications, particularly in thermal insulation, notably with wood fibers, provided they exhibit improved mechanical characteristics. Despite encountering challenges in applying traditional papermaking methods, the creation of paper or board sheets with phosphorylated pulp fibers remains a challenge. Findings suggest that phosphorylation-modified fibers show increased roughness. Moreover, in comparison with unbeaten kraft sheets (KF) and thermomechanical pulp sheets (TMP), those made from phosphorylated kraft fibers (PKF), using a cationic coagulant and a flocculant, demonstrate significant enhancements in burst index, break index, and tensile energy absorption by 2.12 times, 1.7 times, and 2.77 times, respectively. Similarly, phosphorylated TMP sheets, prepared with a dual polymeric system (coagulant/flocculant), exhibit improvements of 1.42 times, 1.33 times, and 1.82 times, respectively, in these properties. The study emphasizes the ameliorating effect of cationic polymeric agents on the charge impact of phosphorylated fibers on overall sheet quality, while also highlighting the substantial influence of hot-pressing lignin-containing paper on all determined physical properties.

Keywords: phosphorylated fibers, physical properties, cationic polymeric agents, hot pressing, thermomechanical pulp paper

INTRODUCTION

The pulp and paper industry is always looking for new opportunities to diversify its products based on wood fibers for value addition. In this regard, the growing interest in fiber modification has led researchers to explore chemical treatments to impart new properties to lignocellulosic fibers. One objective of these treatments consists in adding anionic chemical functions to cellulose, through the formation of carboxylate, sulfonate or phosphate groups.

Carboxylated cellulose is readily obtained by the oxidation of primary and secondary alcohols in cellulose. This reaction is considered as an interesting method to improve the strength properties of lignocellulosic fiber products, and also to prepare cellulose nanofibers by decreasing the mechanical energy required for the process.¹ It also weakens the cellulose structure, which also facilitates the mechanical disintegration of fibers into fibrils.² TEMPO mediated oxidation is a convenient way to oxidize primary alcohols into

carboxylate groups.^{3,4} This oxidation allows the addition of carboxylate groups to the surface of pulp fibers in a selective way, while limiting the degradation of the fibers.⁵⁻⁷ This reaction can be used to prepare fibers bearing anionic charges up to 1500 mmol/kg, creating repulsive forces in the internal structure of the fibers in the water phase.

Sulfonated fibers are another type of highly charged fibers. They are obtained by the chemical-thermomechanical process (CTMP), which is a high yield (82-89%) pulping process based on the sulfonation of lignin.⁸ This type of pulp is used for the production of newsprint and printing paper, where high opacity and light diffusion are more important than brightness or strength.⁹

Finally, phosphorylated fibers can be obtained by the reaction between lignocellulosic fibers and phosphorus derivatives, such as phosphate ester in molten urea. Phosphorylated fibers have many advantageous properties making them very

promising in many applications, such as composite materials,¹⁰ flame-retardant materials,¹¹⁻¹⁴ ion exchange^{15,16} and thermal insulation.^{17,18}

It is widely acknowledged that phosphorylated lignocellulosic fibers are flame retardant. However, this modification reduces the bonding potential between fibers, thereby significantly reducing the mechanical properties of paper sheets produced using these fibers. Recent research has demonstrated that employing a combination of cationic polymers enhances both the sheet formation index and the mechanical properties of sheets produced from phosphorylated kraft pulp fibers. Furthermore, other studies indicate that hot pressing of lignin-rich paper sheets may offer a solution to the challenge of paper strength.¹⁹ Joelsson *et al.*²⁰ found that the strength properties of paper sheets based on high-yield pulp could be notably enhanced by softening lignin and densifying fiber structure through hot pressing. Norgren *et al.*²¹ explored the impact of temperature on material density, revealing that higher temperatures lead to increased product density, consequently improving tensile strength. Moreover, Joelsson *et al.*²² demonstrated that the tensile strength of CTMP paper could be enhanced by up to 100% by subjecting the paper to hot clamping at 200 °C and 6 MPa for 1.5 seconds, followed by a 70-second hold. Regarding phosphorylated fibers, hot wet pressing has been found to improve sheet consolidation and increase creep and deformation, although phosphorylation does not affect thickness recovery after pressing.²³

Phosphorylation of wood fibers to make them fire retardant has already been performed on different type of chemical pulp fibers, but thermomechanical pulp (TMP) fibers have not been studied. For these reasons, the phosphorylation reaction was applied to TMP fibers to obtain high phosphorus contents by extending the phosphorylation to lignin.²⁴ Then, a thermal treatment was applied to lignin-containing pulps by pressing at temperatures close to or above the glass transition temperature of lignin in order to improve their mechanical properties.

This study aims to analyze the morphological formation and mechanical properties of highly charged phosphorylated fibers derived from different types of pulps and to investigate the impact of high-temperature pressing on the mechanical properties of lignin-containing papers,

specifically TMP and CTMP, using kraft pulp fibers as a lignin poor reference. Fiber morphology was assessed using a fiber quality analyzer (FQA), while mechanical properties were evaluated following TAPPI standard methods. Surface changes, including morphology and chemical composition, occurring during fiber modification were characterized using SEM and EDX techniques. The sheet formation was evaluated by measuring the formation index (KFI).

EXPERIMENTAL

Materials

Pulp samples were collected from three different suppliers: unbleached bleached softwood kraft pulp (KF, Kruger Wayagamack, Trois-Rivières, Canada), bleached hardwood CTMP (Innofibre, Trois-Rivières, Canada), and unbleached TMP (Papier Masson Ltd., Gatineau, Canada).

All chemical reagents were used as received from suppliers: 1-decanol (98%), sodium hypochlorite, phosphorous pentoxide (99%) and cetyltrimethylammonium bromide (98%) from Sigma-Aldrich (Oakville, Canada), urea (98%) from Alfa Aesar (Tewksbury, MA, USA). Two cationic polyelectrolytes, a coagulant and a flocculant, were received from Ciba Specialty Chemicals (Mississauga, Canada): poly(diallyldimethylammonium chloride) (PolyDADMAC, Alcofix 111), with a molecular weight of 600 kDa and a charge density around 6.2 meq/g, and polyacrylamide (Organopol 5032), with a molecular weight of 8 to 10 MDa and a charge density of 1.2 mmol/g. Aqueous solutions of both coagulant and flocculant were prepared prior to their use by dissolving the solid powder in deionized water for 20 minutes under magnetic stirring. Two other polyelectrolytes were used for surface charge titration: standardized poly-DADMAC and poly(vinyl sulfate) (PVSU), both 0.100N (BTG Mutek, Mississauga, Canada).

Preparation of phosphorylated TMP and kraft fibers

The phosphorylation process was initiated by combining 1 equivalent of a monodecylphosphate (PE-C10) and 17 equivalents of urea within a small crystallizer. This mixture was then heated to 150 °C in an oven equipped with a gas evacuation and trapping system. Once the urea had melted, 1 equivalent of lignocellulosic fibers was added to the reaction mixture. The mixture was left at 150 °C for 3 hours and 30 minutes. Subsequently, the functionalized TMP (PTMP) and kraft (PKF) fibers were filtered and washed several times with 50 mL of hot water, and then with 50 mL of denatured alcohol. The resulting product was dried in an oven set at 60 °C.²⁵

Handsheet preparation

Handsheets, with a target basis weight of 60 g/m², were prepared according to a modified version of TAPPI T 205. First, 24 g of dry pulp was soaked overnight in deionized water. The pulp suspension was then put in a standard disintegrator at 3000 rpm until all fiber bundles were dispersed. The handsheet machine underwent modifications wherein the original tank was substituted with a 14 cm deep plastic tank, onto which a dynamic drainage jar (DDJ) was affixed. Initially, 800 mL of pulp suspension (0.15% consistency) containing cetyltrimethylammonium bromide (for TMP fibers only), as an additional anionic charge neutralizer, was introduced into the DDJ and stirred for 5 minutes until the foam dissipated. Subsequently, the coagulant was prepared

as per the specified dosages found in Table 1 and poured into the tank while stirring for 60 seconds. Following this, the flocculant solution, also prepared according to the dosages in Table 1, was injected into the DDJ tank and stirred for 3 minutes. The suspension was drained by opening the valve at the conclusion of the mixing step. The injection sequence of the polymers holds significant importance, particularly in a two-component system, requiring specific contact times between each component and the fibers. A summarized injection sequence is provided in Table 2. The prepared sheets were stored in a controlled air-conditioned environment (23±1 °C and 50±1% relative humidity) following TAPPI/ANSI T 402 sp-21 guidelines for subsequent testing.

Table 1
Experimental conditions

	PKF	PTMP
Cetyltrimethylammonium bromide (%)	-	0.6
Coagulant (%)	1	4
Flocculant (%)	0.25	0.25
pH of fiber suspension	9	9
Rotational speed (rpm)	1000	1500

Table 2
Cationic polyelectrolytes injection sequence

Time interval	Task
0 s	Introduction of pulp suspension in DDJ
5 min	Injection of cetyltrimethylammonium bromide (for PTMP only)
0.33 min	Coagulant injection
1 min	Flocculant injection
3 min	Stop agitation

High temperature sheet pressing

A thermal treatment was applied to the lignin containing pulp types (TMP and CTMP) by pressing at temperatures close to or above lignin glass transition. Using a heated press (PowerPress, Amazon, Canada) capable of reaching 230 °C, sheets formed from the lignin-containing fibers were pressure dried at different temperatures between 20 and 200 °C. Higher temperatures were not tested to prevent the activation of the heat-induced fiber protection mechanism with phosphorylated fibers.

Characterization of modified fibers

The total charge of unmodified and modified fibers was measured by conductimetric titration according to the SCAN-CM 65:02 method using a Thermo (USA) Orion conductometer (Model 150) and a Metrohm Brinkmann (USA) automated titrator (Dosimat 765) under an inert nitrogen atmosphere. Approximately 1 g of protonated pulp was added to 500 mL of 1 mM NaCl solution. Before the start of each titration with sodium hydroxide (0.1 M), 20 mL of 0.1 M HCl was added to improve endpoint detection. The total amount

of carboxylic, sulfonic or phosphoric groups could then be determined.

The surface charge of both unmodified and modified fibers was assessed using a PCD-03 Mutek instrument. Back titrations were conducted using poly-DADMAC and poly(vinyl sulfate) standard polyelectrolyte solutions. Initially, 0.2 g of fibers was weighed, and distilled water was added to reach a volume of 50 mL. Subsequently, 10 mL of poly-DADMAC was added, and the mixture was stirred for 30 minutes. To separate the particles, the solution was filtered using a 100 mL flask funnel, and a grade 202 filter paper. Finally, 10 mL of the obtained filtrate was extracted and the excess poly-DADMAC was titrated with PVSU. The surface charge density of the fiber samples was determined by calculating the ratio of the consumed poly-DADMAC to the weight of the dried fiber.

Scanning electron microscopy (15 kV, variable pressure) coupled to energy dispersive X-ray spectroscopy (SEM/EDX, Hitachi SU1510 with Oxford X-max 20 mm²) was used to track structural changes occurring at fiber surface during the

phosphorylation reaction, and to evaluate the phosphorus content and its distribution on the surface of treated fibers. Samples were directly mounted on a conductive double-sided tape, without metallization.

The mean arithmetic fiber length, length weighted percentage of fines and fiber width were analyzed with a Lorentzen and Wettre Fiber Tester Plus fiber quality analyzer (FQA). The analyzer calculates the length of each fiber for about 3 minutes. By comparing the properties of unmodified and modified fibers, this tool can determine the extent of fiber degradation occurring during phosphorylation reactions.

Sheet testing

The Kaptra Vision 9000 Formation Tester was used to examine sheet formation. The system generates a Formation Index (KFI) that reflects sheet uniformity. Lower KFI values indicate better formation. A high-resolution laser scanning confocal microscope (Keyence VK-X1000, Keyence, Mississauga, Canada) was used to observe the three-dimensional surface of sheets. A violet laser of 404 nm was used and a 5 nm resolution was achieved of the z-axis. The physical properties of sheets were measured according to TAPPI standard methods: tensile index (TAPPI/ANSI T 494 om-22), tear index (TAPPI/ANSI T 414 om-21), and burst index (TAPPI/ANSI T 403 om-22).

RESULTS AND DISCUSSION

Mechanism of action of a dual polymeric system (coagulant/flocculant)

The dual-component system typically combines a coagulant with a flocculant to enhance flocculation efficiency. Generally, the coagulant is added first to partially neutralize the negative charge of the fibers, and then the flocculant is used to reform the flocs that have been fragmented by shear stress. This process occurs through a bridging mechanism (Fig. 1). By employing two-component retention systems, it becomes possible to enhance the cohesion of flocs, while facilitating reflocculation, compared to single-polymer-based retention systems. This approach enables the production of more shear resilient flocs, while ensuring the quality of the formation. We have used a retention system consisting of polyDADMAC as a coagulant and a cationic polyacrylamide (C-PAM) as a flocculant. This system is widely used and offers significant advantages, in our case, for sheet formation from fibers highly charged in phosphates.

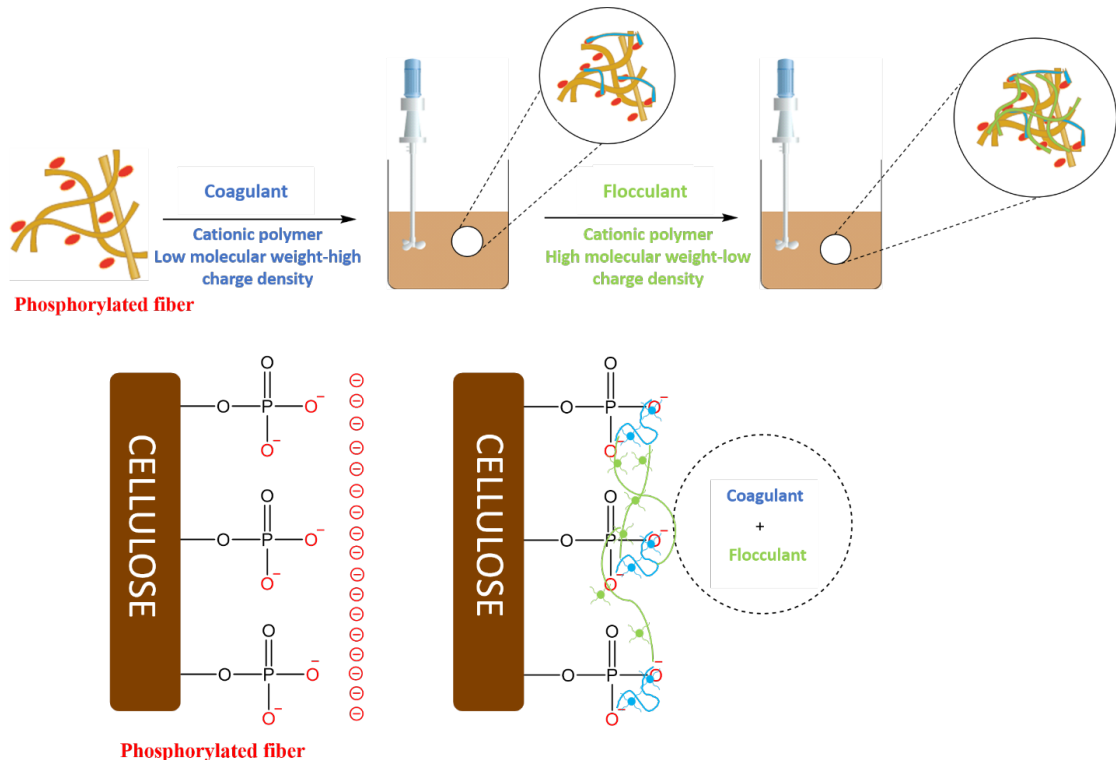


Figure 1: Mechanism of action of a two-component (cationic-cationic) system with phosphorylated fibers

Characterization of modified fibers

Table 3 summarizes the results of phosphorus content, average fiber length, surface charge and

total charge measured before and after the phosphorylation reaction. The phosphorylation reaction led to a significant increase in the total

charge from 230 to 2700 mmol/kg in the case of PKF and from 355 to 3310 mmol/kg in the case of PTMP. It was found that the total charge obtained in the case of PTMP was greater than that obtained with KF when the same phosphorylation conditions were applied. This effect is confirmed by the analysis of total and surface phosphorus by spectrophotometry and EDX measurements. While KF and TMP pulps did not contain any detectable phosphorus, PTMP increased phosphorus content in the case of PTMP compared to PKF (Table 3). The larger increase for PTMP over PKF can be explained by the phosphorylation of lignin hydroxyls that are abundant in TMP.^{26,27}

When KF and TMP are phosphorylated with the same molar ratio of PE, TMP shows a higher percentage of phosphorus than KF. It is possible to explain this increase by the presence of lignin in large quantities in TMP, so the hydroxyls are also phosphorylated (by interaction of free

hydroxyl groups of lignin with PE).²⁴ This confirms the total charge results.

The results of fiber quality analysis show that phosphorylation does not have a significant effect on the average fiber length for kraft fiber. This is one of the main advantages of using PEs instead of traditional phosphorylating agents, such as phosphoric acid, which produce fiber degradation. However, PTMP fibers show a different behavior. Table 3 indicates an important reduction of their average length by 41%. This decrease can be attributed to the fact that the reagents (urea and PE), when combined at a high temperature, can dissolve certain fractions of the substrate, notably lignin, which is present in large quantities compared to kraft pulp, and hemicelluloses. This ultimately results in a reduction in the average fiber length. The increase in diameter of PTMP and PKF, compared to unmodified KF and TMP, can be attributed to the higher inter-fiber repulsion within their structures, resulting in fiber swelling.

Table 3
Charge density and dimensional properties of fibers before and after phosphorylation

Fiber type	Anionic charge		Fiber dimensions (average)		
	Total (mmol/kg)	Surface (mmol/kg)	Length (mm)	Diameter (μm)	Mean fines (%)
Kraft pulp fibers					
Unbeaten (KF)	230 \pm 1	30 \pm 5	2.04 \pm 0.03	25.7 \pm 0.2	0.1
Phosphorylated (PKF)	2700 \pm 20	350 \pm 15	1.99 \pm 0.01	31.9 \pm 0.1	0.2
Thermomechanical pulp fibers					
Unmodified (TMP)	355 \pm 20	40 \pm 15	1.92 \pm 0.03	35.7 \pm 0.2	1.5
Phosphorylated (PTMP)	3310 \pm 30	477 \pm 13	1.14 \pm 0.01	44 \pm 1	2.6

It has been found that the fiber length of thermomechanical pulp is more affected by phosphorylation than the length of kraft pulp. This can be explained by the fact that thermomechanical pulp is subjected to more intense processing conditions than kraft pulp. Thermomechanical pulp is produced by a mechanical reduction process that involves a combination of heat, pressure and motion, which may result in increased fiber fragmentation compared to kraft pulp. It is possible to explain this difference in fiber length by the fact that TMP fibers are naturally shorter. Thus, during processing, it is possible to cut these fibers and save them for later use. However, when processing kraft pulp fibers, there is a tendency to pull fragments from the ends of these fibers. These fragments will be lost during washing,

resulting in a modification of the length of the polar fibers.

Analysis of sheet structure

Figure 2 shows the visual aspect of 60 g/m² sheets prepared with all tested pulp types: KF, PKF, TMP and PTMP. Phosphorylated fiber sheets were also produced with cationic polymers. Several light and dark spots of varying sizes are visible, where the black spots are areas with many agglomerated fibers and the light areas are zones with fewer fibers or even holes. The quality of the formation is confirmed by the determination of a single number KFI index, reflecting the overall uniformity of the sheet. Using positively charged polymeric agents improves the sheet formation index significantly. As shown in Figure 2, the KFI of phosphorylated kraft fiber is reduced from 133

to 17, which is an excellent value compared to unmodified kraft pulp fibers, which have a KFI of 35. In the case of the PTMP, we were unable to make compact sheets without cationic polymers. Cationic coagulants and flocculants were

expected not to increase the retention of fines, but to promote the formation of microflocs that can be agglomerated and thus obtain a good uniformity in sheet formation.

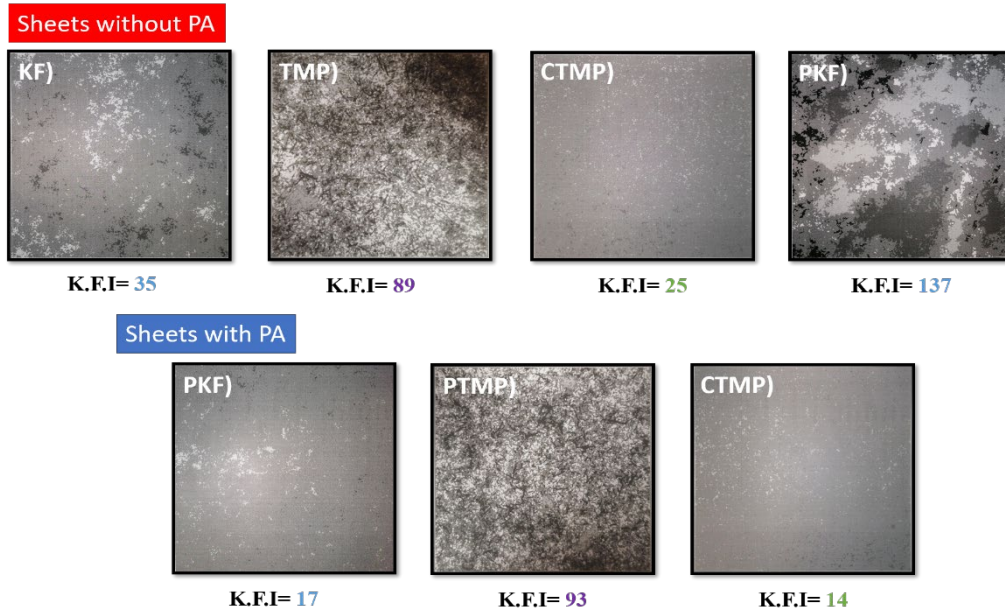


Figure 2: Reconstructed image and formation index of sheets obtained with unmodified and modified fibers

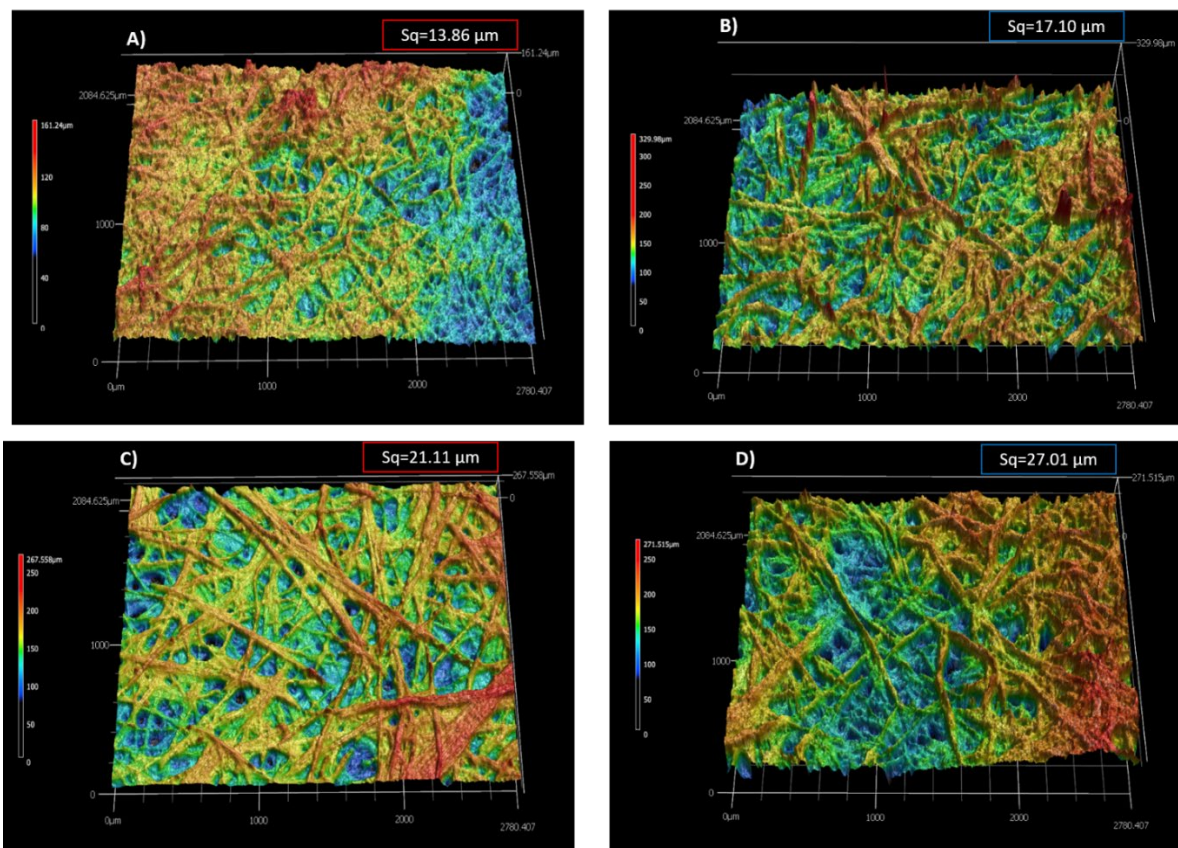


Figure 3: 3D Confocal laser scanning microscope images for (A) KF, (B) PKF, (C) TMP and (D) PTMP

Confocal laser scanning microscopy (CLSM) was used to evaluate the surface morphology of the sheets. Figure 3 shows CLSM phase images of the KF, PKF, TMP and PTMP. It is evident that the S_q value of fibers exhibited a noticeable increase. For the sheets made from kraft pulp, the range was found to be between 13.86 and 21.11, whereas for the sheets made from thermomechanical pulp, it was between 17 and 27. It is generally known that increased surface roughness can lead to greater mechanical interlocking and stronger interfacial bond strength between fibers.^{28,29} In this study, the increase in surface roughness of the thermomechanical pulp

sheets can be explained by the shorter fiber length and the lower degree of fibrillation. This leads to a higher number of protruding fibers and fiber ends on the surface, resulting in a rougher surface. In contrast, kraft pulp fibers have a longer length and are more extensively fibrillated, resulting in a smoother surface. The increased surface roughness can contribute to enhanced mechanical interlocking between fibers, which leads to better sheet formation and strength. Additionally, the higher interfacial bond strength between fibers can also contribute to improved sheet properties, such as tensile strength and tear resistance.

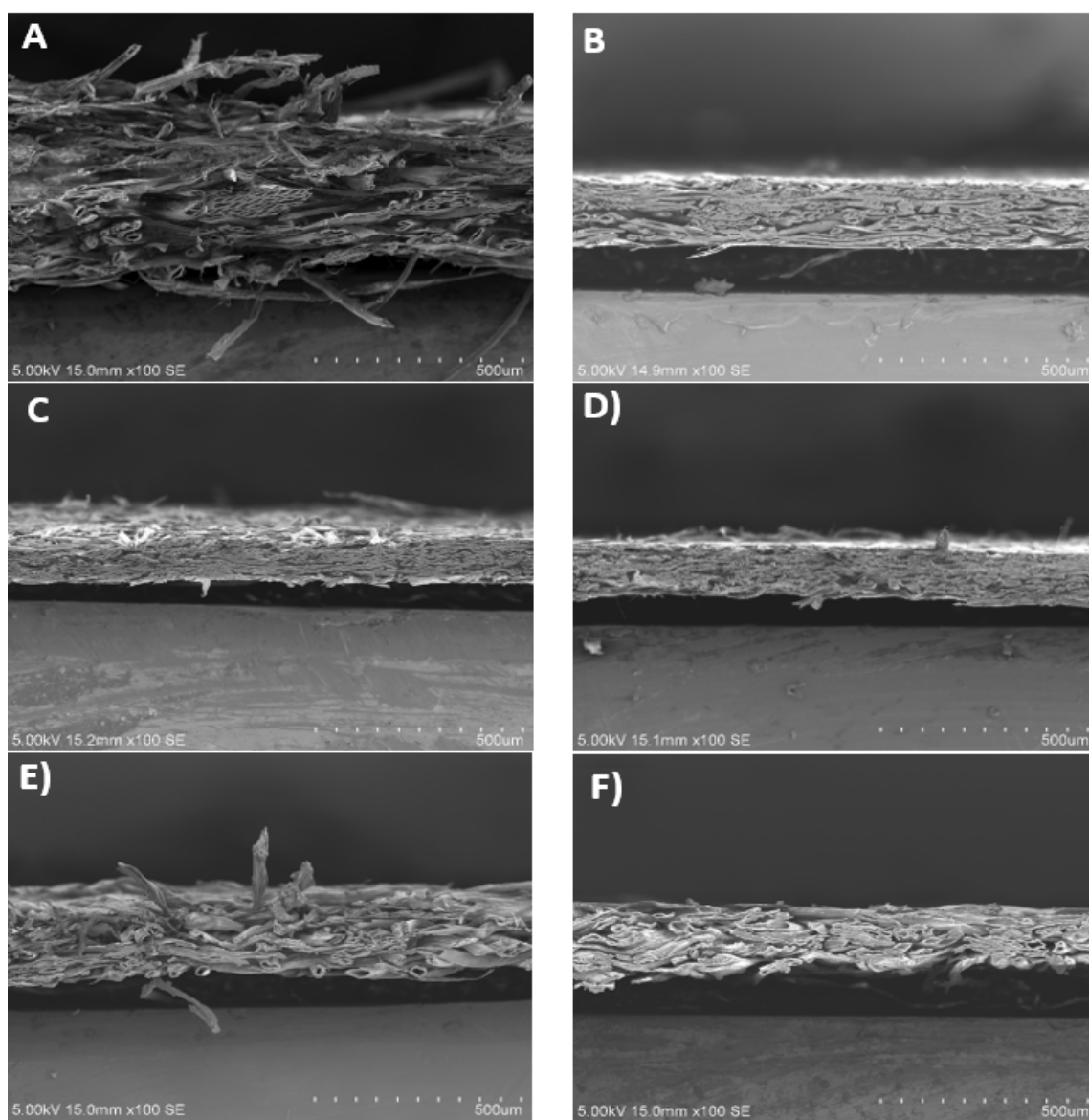


Figure 4: SEM images of cross-sections for three different pulps (TMP, PTMP and CTMP), (A) Unpressed TMP sheet, (B) Pressed TMP sheet at 197 °C, (C) Unpressed CTMP sheet, (D) Pressed CTMP sheet at 197 °C, (E) unpressed PTMP sheet and (F) pressed PTMP sheet at 160 °C

Therefore, the observed increase in surface roughness of the thermomechanical pulp sheets can be beneficial for improving the overall properties of the sheets.

The main objective of this study was to investigate the effect of high temperature pressing on the cross-section of various types of sheets. To accomplish this, we utilized scanning electron microscopy (SEM) to analyze the micrographs of the cross-sections of unpressed and high-temperature pressed TMP, CTMP, and PTMP sheets. The results of this analysis are presented in Figure 4.

The SEM analysis of surfaces for TMP, CTMP, and PTMP sheets illustrated the fiber collapse under high-temperature pressing conditions (Fig. 4, D and F), contrasting with the porous structure of unpressed samples (Fig. 3A, C, and E). Sheets pressed at 197 °C exhibited pronounced fiber consolidation into ribbon-like structures (Fig. 4B, D, and F). Notably, TMP and CTMP underwent a longer treatment at 197 °C for 180 s, compared to PTMP treated for 140 s at 160 °C. Beyond 160 °C, the protective layer of phosphorylated fibers was activated, resulting in dark brown sheets. The unpressed PTMP sheet (Fig. 4E) appeared more compressed than TMP (Fig. 4A), possibly due to the added surfactant effect. This surfactant caused a reduction in surface charge for PTMP fibers, as the long-chain ammonium molecules in the surfactant masked

surface charges, lowering surface energy. Consequently, PTMP fibers exhibited different pressing behavior from TMP fibers, being more charged on the surface and thus showing greater affinity for water molecules, making them more compressible during pressing.

Cross-sectional SEM images of sheet structures (Fig. 4B, D, and F) highlight variations in porosity among different samples. The collapse of the lumen and fiber softening during hot-pressing result in a significant reduction in porosity, potentially diminishing by up to 50%.³⁰

Analysis of sheet physical properties

Figures 5 and 6 illustrate the physical characteristics of the sheets. A comparison between the sheets dried at 23 °C (TMP, PTMP, and CTMP) and those pressed at 200 °C (HP-TMP, HP-PTMP, and HP-CTMP) reveals a notable impact of high-temperature pressing on various physical properties, such as TEA, burst, break, and tear indices. The effect of high-temperature pressing on physical strength properties is particularly evident. For instance, the tensile and break indices of HP-PTMP were 30% higher than those of non-pressed PTMP at high temperature. Similarly, the tensile index of HP-TMP increased by 30% compared to TMP, while for HP-CTMP, the increase was 16.4% in comparison to CTMP.

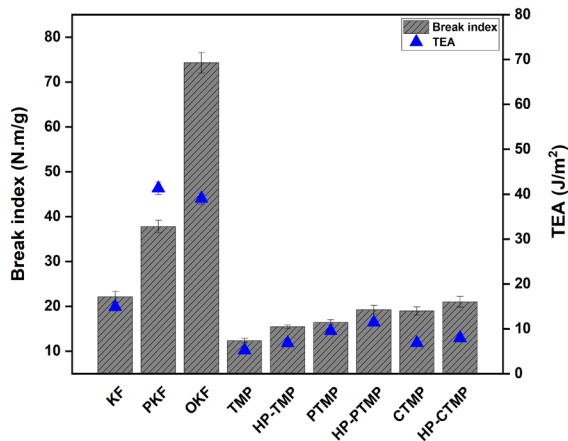


Figure 5: Break index and TEA of sheets formed from different pulps

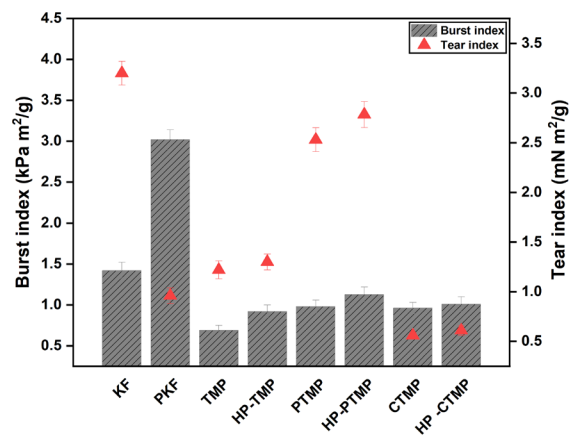


Figure 6: Burst and tear indices of sheets formed from different pulps

The findings depicted in Figure 6 reveal notable increases in the burst index for HP-TMP, HP-PTMP, and HP-CTMP, showing respective increases of 42%, 15%, and 5% compared to non-

pressed fibers at high temperature. Kraft pulp fibers treated with phosphorylation and polymeric agents exhibited significant enhancements over unbeaten kraft pulp fibers, showing

approximately 112% and 67% improvements in burst and tensile indices, respectively. Conversely, the tear index decreased by 68%, representing the sole tested property relying on the inherent strength of fibers rather than on inter-fiber bonds. The incorporation of polymeric retention agents enhances the mechanical properties of paper by binding fibers together, resulting in a more cohesive network and structurally stable form. Sheets produced from fibers rich in lignin exhibited substantial enhancements when subjected to high-temperature pressing. This improvement stems from lignin's softening effect and the densification of fiber structure during hot pressing, resulting in considerable reinforcement of the paper.

CONCLUSION

Sheets made from phosphorylated fibers combined with cationic polymers demonstrate remarkable formation and strength, outperforming sheets made solely from unbeaten kraft pulp or phosphorylated pulp without polymeric retention agents. This finding underscores the significant positive influence of utilizing positively charged polymeric agents. Moreover, hot-pressing proves effective in bolstering the mechanical properties of papers containing lignin. Within the observed range, hot-pressed sheets comprising HP-TMP, HP-PTMP, and HP-CTMP showed superior values for TEA, burst, break, and tear indices, compared to their counterparts made of TMP, PTMP, and CTMP, respectively.

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