CELLULOSE CHEMISTRY AND TECHNOLOGY

FROM FIBRE SURFACE TO SHEET STIFFNESS: A COMPREHENSIVE STUDY OF REFINING EFFECTS

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This work studied the effects of refining on the physicochemical and mechanical properties of five pulps: three softwood kraft (KP1, KP2, KP3), one hardwood kraft (KE1) and one NSSC eucalyptus pulp (NE1). The freeness, specific surface area, surface charge, water retention value and Young's modulus were measured at different refining levels. It was found that refining increased surface charge and the ratio of surface-to-total charge in a quite consistent way for all pulps, indicating increased accessibility of fibre surfaces rather than changes in bulk fibre chemistry. Specific surface area also showed an increase with refining, confirming external fibrillation and generation of fines. The Young's modulus increased steadily with decreasing freeness for all the tested pulps due to increased bonding between fibres and consolidation of fibre network. KE1 reached the highest final modulus (5271 MPa), whereas KP1 and KP3 had a good stiffness development after moderate refinement. Linear regressions showed that Young's modulus was strongly correlated with surface charge, freeness and water retention value. These results emphasized refining as one of the primary ways of optimizing stiffness in papermaking.

Keywords: Young's modulus, pulp refining, surface charge, specific surface area, freeness, fibre bonding

INTRODUCTION

The mechanical behaviour of paper originates in a web of interactions inside its fibre network. Since paper is a mesh of fibres bonded at numerous points, its stiffness depends on how many hydrogen bonds there are, how strong those hydrogen bonds are, how tightly the fibres are packed and how easily fibres can slide or deform within the sheet. A hydrogen bond forms when a hydrogen atom sitting on one oxygen is drawn toward an oxygen on a neighbouring fibre; these weak but numerous links are what holds the fibres together in a sheet of paper. Among the main mechanical properties, Young's modulus stands out as a primary measure of stiffness. It indicates the level of stress required to cause a given degree of elastic deformation in a material under tension or compression. Understanding what controls Young's modulus is critical for making papers with the desired attributes for printing grades, packaging grades, specialty applications, and high strength applications. The literature suggests that a number of fibre- and sheet-level variables determine stiffness, including freeness, fibre charge, fibre surface area, and sheet density. Each provides a somewhat different perspective on fibre interactions within the sheet, the number of hydrogen bonds between fibres, and the efficiency of stress transfer within the network. Overall, the four preceding variables are widely regarded as key predictors of Young's modulus.

Freeness, for instance, has had a long history as a practical measure of the ease with which pulp drains. Although freeness is an indirect measure, it shows several changes in the pulp caused by refining: more external and internal fibrillation, fibre swelling, fibre becoming shorter, increased flexibility, and the production of fine particles.[1] These refining effects directly influence how the fibres conform together when making sheets and how many hydrogen bonds are formed in the paper. As refining increases and freeness decreases, fibres become more flexible and can flatten more easily. This improves bonding because more surface area becomes available for fibre-fibre contact

Fibre surface area represents how much external area is exposed on the fibre and available for bonding. Refining increases surface area by peeling off outer fibre layers and creating fibrils that extend from the fibre surface. These fibrils create more places for hydrogen bonds to form. Since hydrogen bonding is the main mechanism of bonding in paper, an increase in fibre surface area allows more hydrogen bonds to form. When the bonded area increases, the sheet becomes stiffer and stronger. Lindström and Carlsson (1982) were among the early researchers to show that external fibrillation increases bonding ability.[2]

Cellulosic fibres usually have a natural negative charge when they are in water. This happens because they contain acidic groups in hemicelluloses and lignin that can release ions. The overall charge on a fibre is influenced by several things: what the fibre is made of, how many of these acidic groups are ionized, and what other materials or chemicals may be stuck to the fibre surface. The number of ionizable groups changes depending on where the fibres come from and what chemical processes they have gone through, such as pulping or bleaching. The mechanical treatment the fibres receive also strongly affects the condition of the fibre surface and, therefore, the charge it carries. When fibres have more carboxyl groups on their surface, they usually form stronger hydrogen bonds with each other.[3,4] Many studies on different pulps have shown the same pattern: more carboxyl groups lead to greater swelling, which then leads to higher tensile strength. For example, Chen, Wan, Dong, and Ma found that pulps with a higher carboxyl content developed better fibre–fibre bonding and showed higher tensile strength.[5] Other work has shown that fines can increase this effect. Fines often have a much higher surface charge than whole fibres, absorb more water, and swell more. When they are properly retained, they can meaningfully improve bonding in the sheet.[6]

When acidic groups on the fibre surface become ionised, the negatively charged sites inside the fibre start to repel each other. This repulsion causes the fibre wall to swell. Earlier studies by Grignon and Scallan (1979-1983) explained this behaviour, and later work showed that swelling depends on the type of counter-ions, how strongly they dissociate, and the ionic strength of the surrounding solution.[7-9] Swelling is closely tied to tensile strength because swollen, flexible fibres bond more effectively during sheet formation.[2]

Gharehkhani *et al.* reviewed how pulp refining changes the structure of fibres, including fibrillation, fine formation, fibre length, curl, crystallinity, and the surface chemical composition.[10] Many researchers have studied how refining changes the fibre charge and electrokinetic behaviour of different pulps.[11-20] Fibre charge also influences how easily fibres absorb water and swell, which is important because swollen, flexible fibres form stronger hydrogen bonds. This connection between charge, swelling, and bonding has been highlighted in earlier research.[17] Higher fibre charge usually leads to greater swelling and hydration. When fibres swell, they become softer and easier to shape. This helps them form better hydrogen bonds when the paper is made. Several studies show that the strength of the hydrogen bonds between fibres is closely connected to electrokinetic properties, especially the surface charge.[13,14,21]

The ability of pulp to form strong hydrogen bonds depends on how much the fibres can swell, and water retention value (WRV) is a direct way to measure this.[22] One way to measure how much internal fibrillation has happened is by looking at WRV, which increases as fibres swell more during refining.[23,24] Refining mainly works by loosening and breaking the hydrogen bonds within and on the surface of cellulose fibres. This process changes the fibre structure so the fibres can swell, bend, and bond better during papermaking. Several structural changes in the fibres affect WRV, including swelling of the fibre wall, the peeling or brushing of the outer surface (external fibrillation), and the formation of fines. WRV is a good way to judge how much the fibres have fibrillated at the micro- and nano-scale. Gu *et al.* showed that WRV gives results that match what is seen in SEM and TEM images, making it a dependable indicator of fibrillation.[25] WRV is a standard test used to find out how much water a pulp sample can hold. Almost every step in pulping and stock preparation, including bleaching, drying and refining, affects this water-holding ability as measured by WRV.[6]

Sheet density, or specific volume, represents how tightly fibres are packed in the sheet. A denser sheet generally presents more fibre-fibre contacts, more hydrogen bonds per unit area, fewer voids, and better stress transfer between fibres. Sheet density is a widely recognised indicator of fibre network consolidation and is strongly correlated with Young's modulus. Since Young's modulus represents the ratio of stress to strain within the linear elastic portion of the stress–strain curve, a dependence of mechanical behaviour on density implies a strong correlation between sheet density and Young's modulus.

In this study, the goal was to see how refining affects several key pulp properties like freeness, specific surface area, surface charge, total charge, water retention value, sheet density, and Young's modulus. The findings observed across various pulps were compared, and an effort was made to identify relationships between these properties to better understand how they contribute to Young's modulus of paper. Because these properties relate to bonding and structure, these can be used to develop regressions for Young's modulus of paper. Efforts were made to develop relationships between the pulp properties discussed above and Young's modulus of paper.

EXPERIMENTAL

Source of pulps

Five pulps were used: three high-yield, unbleached softwood kraft pulps (labelled as KP1, KP2, KP3) from *Pinus radiata* (Kappa number ≈ 95) taken from a commercial mill after the wash press, and two laboratory-cooked eucalyptus pulps (KE1 and NE1) made by kraft and NSSC processes following conventional conditions.

Refining of pulps

After centrifuging, 360 g (o.d.) of each pulp was dispersed in deionized water to 23 L to make 1.57% consistency. Refining was done in a Valley beater at room temperature to different freeness levels following TAPPI T 200 sp-96. About 2 L of slurry was taken out at set times for later tests. Freeness was measured by TAPPI T 227 om-99. The refined pulp was drained under vacuum on a Büchner funnel to produce wet fibre pads, and the filtrate was passed through the pad a second time to minimise the loss of fines. Pads were adjusted to 20 ± 2% solids and stored at 4 °C until testing.

Chemicals

Analytical-grade NaOH, HCl, and NaCl were used. Poly-DADMAC (≈150–200 kDa) and sodium poly(ethylene sulfonate) (PESNa, ≈19.1 kDa) were reagent grade (ATA Scientific Pty. Ltd.). All solutions were prepared in deionized water (conductivity 8×10^{-4} mS/cm) to the required concentrations. Nitrogen gas was used during conductometric titrations to prevent CO_2 uptake.

Wet pulp characterization

Freeness was measured according to TAPPI T 227 om-99 using a Canadian Standard Freeness (CSF) tester. Pulp slurries were prepared at the standard test consistency (≈0.3%) with deionized water and gently mixed to remove air. The slurry was poured into the CSF tester and allowed to drain; the filtrate volume (mL) was recorded as CSF. Each sample was tested in triplicate, and results are reported as the average CSF at room temperature.

Specific surface area was measured using the Pulmac method. About 5 g (o.d.) pulp was diluted to 0.5% and deaerated. A uniform mat (~20 mm) was formed by controlled-rate filtration. A permeable piston with a spacer set the mat thickness. The pad was prepared according to standard procedures and weighed after oven drying to a constant weight at 105 °C.[13,14]

Water retention value (WRV) is defined as the percentage of water retained by a pulp after centrifugation with respect to the dry fibre mass. WRV reflects fibre swelling and the cohesion of the fibre network, and is commonly used as an indicator of internal fibrillation/swelling. A centrifuge fitted with steel tubes, each with a short inner sleeve and a coarse grid supporting a 100-mesh screen above the tube bottom, was used for the measurements. Pulp was prepared at 1 g o.d. in 100 mL water. For each run, the slurry (equal to 1 g o.d.) was poured onto the screen and centrifuged at 900 g for 20 min. The moist pad was removed and weighed immediately, then dried at 105 °C to determine moisture. WRV (%) was calculated as the water retained after centrifuging, expressed as a percentage of the oven-dry fibre.[24,26]

Determination of charge

Before measuring charge, pulp was fully protonated by soaking a 1% pad in 0.01 M HCl for 16 h. It was then vacuum-filtered on a Büchner funnel and washed with deionized water until the filtrate pH ≈ 6. The carboxyl groups were converted to the Na form following an earlier described procedure.[27] Fibre mass was found gravimetrically by filtering onto pre-weighed paper and drying at 105 °C to constant weight.

Polyelectrolyte titrations

Charge was measured with a Mutek PCD-02. A 0.5 g pulp sample was mixed with 100 g of 0.001 N poly-DADMAC and stirred 2 h to neutralize anionic sites. Solids were removed on a #100 mesh sieve. 10 mL filtrate was titrated with 0.001 N PES-Na (rate 0.1 mL/min) to a 0 mV streaming-potential endpoint. A blank (poly-DADMAC vs PES-Na) was run.

Charge density: $q = (Vp - Vb) \cdot c \cdot 1000/w$ (mmol/kg) (1)

where Vp is titrant volume for pulp (mL), Vb is titrant volume for blank (mL), c is concentration of titrant (mol/L), and w is pulp solids content (g).

The procedure followed established methods as described earlier.[14,15]

Conductometric titrations

About 0.5 g of protonated pulp was suspended in 100 mL of 1 mM NaCl, and 0.5 mL of 0.05 M HCl was added prior to starting the titration. Samples were titrated at 25 °C with 0.05 M NaOH using an autotitrator; conductivity was recorded every 30 s. Conductance first fell (HCl neutralization), then levelled (weak-acid buffering), then rose. Charge was calculated from the NaOH volume between the first and second inflection points. All tests used 1 mM ionic strength. The procedure followed established methods as described earlier.[14,15]

Handsheet making and paper testing

Handsheets (120 g/m^2) were prepared from each refined pulp using a standard handsheet former following TAPPI T 205 sp-95, with one change: sheets were additionally pressed at 2 bar to improve water removal and consolidation. Sheets were conditioned at 23 °C and 50% RH for 48 h before testing. Tensile properties were measured on an Instron 5566. Each sheet was cut into 15 mm-wide strips; the grips were set to a 100 mm span. Specimens were pulled at a constant crosshead speed of 25 mm min^{-1} until failure. The elastic modulus was obtained from the linear portion of the stress–strain curve between 0.3–0.7% strain. For each pulp, six replicates were tested and the mean value was reported. All tests were performed in the same conditioned room to ensure consistent temperature and humidity.

RESULTS AND DISCUSSION

For each refined pulp, we measured freeness, specific surface area, surface charge, water retention value, and Young's modulus. Total charge was determined by conductometric titration, while surface (accessible) charge was measured by polyelectrolyte titration using poly-DADMAC. Fibre-charge results are reported as the average of at least three repeats per sample.

Figure 1 shows a plot of $(C/Rp)^{1/3}$ against pulp-mat density for kraft pine (sample 1KP, 715 CSF). These data were used to compute the pulp's specific surface area with the Robertson–Mason relation:[28]

$$(C/Rp)^{1/3} = (1/(k\,Sw^2))^{1/3}\,(1-V\,C) \qquad (2)$$

with

$$Rp = A^2\,\Delta P/q\,W\,\eta \qquad (3)$$

$$C = W/A\,L \qquad (4)$$

where C = pad density ($g\cdot cm^{-3}$); Rp = specific flow resistance ($cm\cdot g^{-1}$); k = Kozeny factor (5.55); Sw = specific surface area ($cm^2\cdot g^{-1}$); V = specific volume of pulp ($cm^3\cdot g^{-1}$); A = pad area (cm^2); ΔP = pressure drop ($dyn\cdot cm^{-2}$); q = water flow rate ($cm^3\cdot s^{-1}$); W = pad mass (g); η = water viscosity (P); L = pad thickness (cm).

Effect of pulp refining on pulp charge (surface, total and surface/total)

Refining consistently increased surface charge across all pulps as freeness decreased. The rise was accompanied by a higher surface-to-total charge ratio, showing that refining exposes and creates access to charged sites at (or near) the fibre surface. This effect was the strongest for NE1 (NSSC eucalyptus), which reached the highest surface/total ratio, indicating pronounced surface accessibility after refining. For KP1 pulp, the surface charge increased from 48.7 mmol/kg to 80.6 mmol/kg and surface to total charge ratio increased from 0.36 to 0.60 as the CSF dropped from 745 to 270 mL. For KP2 and KP3 pulps, the surface charge increased from 42.2 mmol/kg to 68.9 mmol/kg and 58.5 mmol/kg to 93.1 mmol/kg, and surface to total charge ratio increased from 0.32 to 0.52 and 0.33 to 0.52 as the CSF dropped from 745 to 285 mL and from 715 to 275 mL, respectively. For KE1 pulp, the surface charge increased from 63.3 mmol/kg to 74.2 mmol/kg and surface to total charge ratio increased from 0.55 to 0.64 as the CSF dropped from 410 to 265 mL. For NE1 pulp, the surface charge increased from 45.6 mmol/kg to 64.2 mmol/kg and surface to total charge ratio increased from 0.59 to 0.83 as the CSF dropped from 585 to 235 mL. The rising surface/total ratio reflects greater accessibility of charges after refining rather than new bulk charge creation. Similar observations were reported by Bhardwaj *et al.*, who found that refining raised the fibre surface charge without altering the total charge, and that the gain in specific surface area resulting from refining contributed to enhanced surface charge and stronger inter–fibre bonding.[14]

Figure 2 demonstrates a clear increase in Young's modulus with surface charge for all pulps. Higher surface charge reflects the presence of more ionisable carboxyl groups, improving fibre–fibre adhesion through hydrogen bonding. KP1 and KP3 develop higher modulus values compared to KP2 at similar charge levels, suggesting stronger fibre interaction. This trend supports previous findings that electrostatic interactions enhance fibre bonding and stiffness development in cellulosic networks. Banavath *et al.* showed that, as the surface charge of bagasse pulp increases, its tensile index also goes up.[29] Hirn and Schennach estimated the energy contributions of different bonding mechanisms between fibres, such as mechanical interlocking, hydrogen bonds, and van der Waals interactions, and demonstrated that fibril interlocking in refined pulp accounts for a 30–55% improvement in bond energy.[30] In contrast, the total charge for each pulp stayed nearly constant with refining, implying that the chemistry of the bulk fibre did not change appreciably; rather, accessibility changed. In spite of this, the total charge differed by pulp type and quality. Among the pulps, KP3 showed the highest total charge – of 179.8 mmol/kg, KE1, KP1 and KP2 were intermediate, and NE1 was the lowest at 77.8 mmol/kg.

Table 1
Characterization of various wood pulps

Pulp	Freeness, mL CSF	Surface charge, mmol/kg	Total charge, mmol/kg	Charge ratio (Surface/Total)	Surface area, m^2/g	Sheet density, g/cm^3	Elastic modulus, MPa
KP1	745	48.7	134.0	0.36	-	0.31	1342
	700	49.8		0.37		0.44	2074
	655	56.7		0.42		0.52	3264
	620	54.6		0.41		0.56	3300
	560	63.9		0.48		0.60	3648
	460	69.9		0.52		0.64	4079
	335	76.0		0.57		0.65	4143
	270	80.6		0.60		0.66	4625
KP2	745	42.2	132.0	0.32	-	0.30	533
	705	49.8		0.38		0.38	1086
	655	51.5		0.39		0.46	1530
	575	57.6		0.44		0.51	2009
	510	54.7		0.41		0.53	2276
	445	58.1		0.44		0.55	2341
	350	63.5		0.48		0.57	2527
	310	68.6		0.52		0.61	3265
	285	68.9		0.52		0.62	3391
KP3	715	58.5	179.8	0.33	1.48	0.46	2578
	630	61.0		0.34	2.73	0.55	3544
	565	63.8		0.35	3.13	0.57	3762
	515	71.3		0.40	4.37	0.59	4213
	445	73.7		0.41	4.68	0.60	4290
	400	81.1		0.45	5.39	0.62	4258
	340	82.9		0.46	5.98	0.62	4234
	275	93.1		0.52	7.58	0.63	4414
KE1	410	63.3	116.0	0.55	2.50	0.58	3439
	350	65.4		0.56	3.43	0.61	4120
	310	69.6		0.60	3.54	0.64	4514
	265	74.2		0.64	4.37	0.69	5271
NE1	585	45.6	77.8	0.59	1.90	0.43	1896
	545	-		-	2.24	0.47	2156
	500	48.5		0.62	3.32	0.49	2395
	445	-		-	3.55	0.54	3001
	400	53.0		0.68	4.30	0.56	3216
	305	59.9		0.77	5.03	0.59	3491
	235	64.2		0.83	5.75	0.60	3887

Effect of pulp refining on physical properties of pulps

Refining significantly improved sheet properties for all pulp types. With the reduction of freeness by refining, the sheet density increases due to fibrillation and tighter fibre packing, which increases the strength of inter-fibre bonding and increases the elastic modulus since the internal structure is becoming stronger. Elastic modulus measures the material stiffness, which is given by the amount of elongation for a given applied load. Figure 3 shows that Young's modulus increases with a reduction of freeness for all five pulps (KP1, KP2, KP3, KE1, and NE1), which is indicative of the improving effect of refining on fibre bonding. Reduced freeness corresponds to greater external fibrillation, leading to an increase in the bonded area between fibres and network stiffness. KP1 exhibits the highest modulus at lower freeness, showing better refining response than KP2 and

KP3, consistent with earlier reports on refining–stiffness behaviour. Banavath *et al.* found that when refining lowers the freeness of bagasse pulp, its tensile index increases.[29] The link between sheet density and elastic modulus was not exactly the same for all pulps; it changed depending on the type of wood or raw material used.

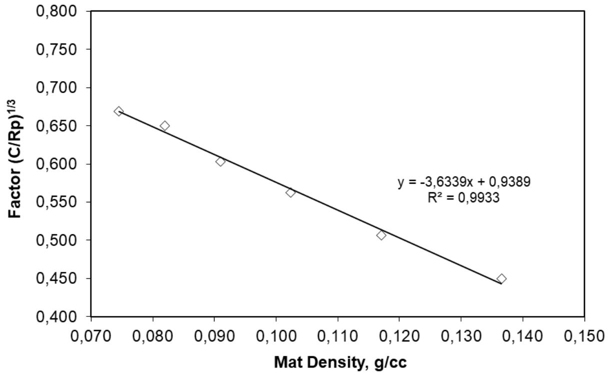

Figure 1: A plot of factor $(C/R_p)^{1/3}$ *versus* pulp mat density used in calculating specific surface area for kraft pine pulp (sample KP1, 715 CSF)

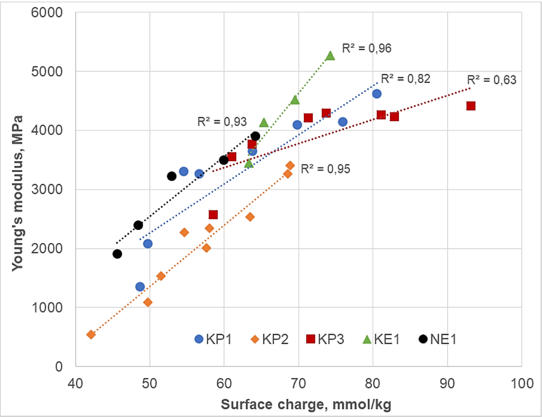

Figure 2: Effect of surface charge on Young's modulus of different pulps

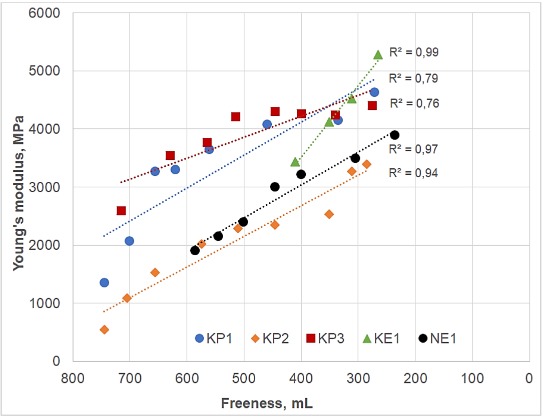

Figure 3: Effect of freeness on Young's modulus of different pulps

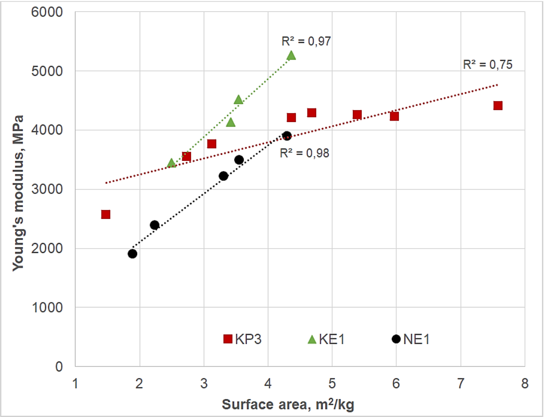

Figure 4: Effect of surface area on Young's modulus of different pulps

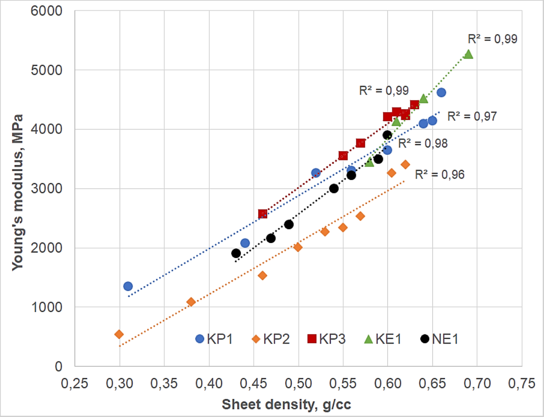

Figure 5: Effect of sheet density on Young's modulus of different pulps

Pulps such as KP1 and KP2 displayed a steady rise in elastic modulus from low to high refining levels, while KP3 showed high stiffness even at moderate refining, indicating species-specific fibre characteristics. NSSC eucalyptus pulp NE1 also followed the same trend, but achieved lower stiffness than kraft eucalyptus pulp KE1. Overall, elastic modulus strongly depended on sheet density and refining intensity.

Specific surface area describes how much surface a wet pulp presents for each gram. More fibrillation on fibre surfaces and more fines raise this value. Where measured, specific surface area improved sharply with refining (highest rise for KP3) with reduced pulp freeness of the same pulp, consistent with external fibrillation and fines generation. For KP3 pulp specific surface area improved from 1.48 to 7.58 m^2/g, whereas for KE1 and NE1 pulps, this value increased from 2.50 to 4.37 m^2/g and 1.90 to 5.75 m^2/g, respectively under the refining levels studied. Figure 4 indicates a positive correlation between specific surface area and Young's modulus. Increased surface area is primarily attributed to fibrillation and fines production during refining, allowing more inter-fibre contact points. KP1 shows the steepest increase in modulus with surface area, while KP2 shows comparatively lower stiffness development. These results agree with studies highlighting the importance of surface development in improving fibre bonding efficiency and mechanical strength.

The structural changes generated by pulp refining, where comparable, produced higher sheet density, *i.e.*, more compact packing and improved bonding; KE1 reached the highest final density. The increase in sheet density was from 0.46 to 0.63 g/cm^3, 0.58 to 0.69 g/cm^3 and from 0.43 to 0.60 g/cm^3 for KP3, KE1 and NE1 pulps, respectively. Denser sheets relate to higher fibrillation/bonding, and in most cases, the strength of paper increases with sheet density.[31] A denser sheet presents more fibre-to-fibre contact, thus offering more inter-fibre bonding. The elastic modulus, the initial slope of the stress–strain curve, is also a measure of stiffness, and this property again shows considerable dependence on the strength of inter-fibre bonds. Figure 5 illustrates that Young's modulus increases with sheet density for all pulps. Higher density means better packing and consolidation of fibres, and thus higher stress transmission within the fibre network. Again, KP1 and KP3 show higher elastic modulus values than KP2 at comparable densities, proving better conformability and ability to form hydrogen bonds with fibres. This pattern shows that tightening the sheet structure is important for increasing stiffness. Motamedian *et al.* looked at how different changes caused by refining influence the tensile strength of paper sheets. Their tests showed that refining made the sheets stronger, stiffer, and denser, which is what we normally expect. These improvements were mostly due to the sheets becoming more compact and the fibres bonding more effectively.[32] Even though fibres are pressed during papermaking, they can still be compressed through the thickness of the sheet, which makes density an important factor in how paper behaves mechanically. Lang *et al.* studied how density and thickness compression influence the in-plane mechanical properties of paper and paperboard. They ran uniaxial tensile tests on lab-made papers refined at different energy levels and on commercial paperboard with directional differences. Their results showed that density had a strong impact on the stress-strain curve, elasticity, and plastic deformation of the sheets.[33]

These microstructural improvements reflected in the mechanical properties included the following: Young's modulus was increased for all pulps, with KE1 reaching the highest final stiffness, thus indicating substantial bonding potential for hardwood kraft at similar freeness. More precisely, the elastic modulus increased from 1342 to 4625 MPa for KP1, from 533 to 3391 MPa for KP2, from 2578 to 4414 MPa for KP3, from 3439 to 5271 MPa for KE1, and from 1896 to 3887 MPa for NE1, according to different refining levels. Overall, refining improved all the pulps, with kraft eucalyptus (KE1) showing the greatest final modulus.

WRV increases with the increasing number of refining revolutions and with decreasing freeness value. This means that more heavily beaten fibres hold more water. During beating, the fibre cell walls start to open and delaminate into layers, forming small pores inside the fibres. Due to internal delamination, fibres that undergo more refining develop a greater internal surface area and are able to hold more water. The consistent increase in WRV with increasing beating indicates that these internal structural changes are more pronounced in well-refined fibres. Refined fibres are able to hold more water and develop stronger hydrogen bonds with each other.[34]

Comparing among the different pulps, refining increased accessible (surface) charge, specific surface area, sheet density, and tensile stiffness for all pulps. Kraft hardwood, KE1, most effectively converted surface development into highest sheet density and stiffness; kraft softwoods, KP1–KP3, showed large surface-area gains, particularly KP3; and NE1 showed the greatest increase in surface accessibility relative to its total charge in terms of surface to total charge. Overall, the data tied a coherent chain: refining → higher accessible surface charge and surface area → denser sheets → higher tensile stiffness.

Practically, these results suggest tuning refining to target a balance: enough surface development for bonding and stiffness, without excessive fines that hurt dewatering. For mills, hardwood kraft can deliver higher end-stiffness at a given freeness, while tailored refining of softwoods (*e.g.*, KP3) can maximize surface development when strength is the priority.

Development of relationships between various physical properties of pulps

The relationship between Young's modulus (E) and key fibre characteristics – surface charge (σ), specific surface area (Φ), freeness (F) and water retention value (W) – was investigated for five pulp types: KP1, KP2, KP3, KE1 and NE1. The regression coefficients (a and b), coefficient of determination (R^2) and percentage root mean square error of estimation (%RMSEE) for each pulp and model are summarized in Table 2.

$$RMSEE = \sqrt{\frac{\sum_{i=1}^{N}(\hat{y}-y_i)^2}{N}} \qquad (5)$$

where $\hat{y}$ is the value of the property measured by the model for sample i; y_i is the actual property, reference value for sample i; and N is the number of samples in the calibration set. %RMSEE is a percentage-based version of the RMSEE, calculated by dividing the standard RMSEE by the mean of the observed values and multiplying by 100.

Table 2
Relationships of fibre surface charge, specific surface area, freeness (CSF), water retention value of pulps and Young's modulus

Pulp	Nr data points	Freeness range	Model	a	b	R^2	%RMSEE
KP1	8	745-270	E = a + bσ	-1.8938	0.0832	0.82	13.12
	8		E = a + bF	6.3977	-0.0057	0.79	14.24
KP2	9	745-285	E = a + bσ	-3.8350	0.1039	0.95	9.33
	9		E = a + bF	4.7941	-0.0053	0.94	10.59
KP3	8	715-275	E = a + bσ	0.9445	0.0405	0.63	8.96
	8		E = a + bF	5.6635	-0.0036	0.76	7.16
	8		E = a + bΦ	2.7093	0.2722	0.75	7.41
	8		E = a + bW	-1.8032	0.0216	0.81	6.39
KE1	4	410-265	E = a + bσ	-6.2952	0.1560	0.96	3.00
	4		E = a + bF	8.4581	-0.0124	0.99	1.79
	4		E = a + bΦ	0.9239	0.9862	0.97	2.54
	4		E = a + bW	-5.3357	0.0357	0.99	1.74
NE1	5	585-235	E = a + bσ	-2.5399	0.1017	0.93	6.78
	7		E = a + bF	5.3102	-0.0057	0.97	3.78
	7		E = a + bΦ	0.9546	0.5121	0.96	4.74
	4		E = a + bW	-4.1418	0.0275	0.98	4.51

Fibre surface charge (σ), Canadian standard freeness (F), Specific surface area (Φ), Water retention value (W) and Young's modulus (E)

These findings emphasize that the physicochemical properties of fibres control the stiffness and bonding potential of pulp networks, which in turn determine the mechanical properties of paper. Banavath *et al.* similarly demonstrated that refining increased the specific surface area, specific volume, and water retention value of five different pulps, and that total fibre charge remained unchanged while surface charge rose with refining, reinforcing the role of surface accessibility in bonding development.[13]

In kraft pulps, KP1 and KP2, the best linear correlations were obtained between Young's modulus and fibre surface charge (E = a + bσ), with $R^2 = 0.82$ and 0.95, respectively. The positive slope values of 0.0832 for KP1 and 0.1039 for KP2 indicate that an increase in surface charge improves the bonding due to increased swelling and greater interaction of fibrillated surfaces. Refining increases fibre surface charge by exposing carboxyl groups. Such fibres become more flexible and are able to form stronger inter-fibre bonds, which results in higher sheet modulus. In an earlier study, Banavath *et al.* found a strong linear relationship between surface charge and tensile index in handsheets.[13] Their results showed very high correlations for bamboo, hardwood, and bagasse pulps, with R^2 values around 0.99, 0.99, and 0.97. For wheat straw and softwood pulps, the correlations were also strong, with R^2 values of 0.93 and 0.89. Freeness, F, was inversely related to Young's modulus in these pulps with $R^2 = 0.79$ for KP1 and 0.94 for KP2, indicating that lower drainage resistance (lower freeness) corresponds to an increase in fibre flexibility and bonding area. Earlier, Banavath *et al.* showed a strong linear relationship between pulp freeness and the tensile index of handsheets.[13] Their results reported very high correlations for bamboo, wheat straw, and bagasse pulps, with R^2 values of about 0.99, 0.99, and 0.98. Hardwood and softwood pulps also showed strong correlations, with R^2 values of 0.97 and 0.90.

The behaviour of KP3 was more heterogeneous: for most fibre properties, the correlations between Young's modulus have been moderate in comparison with other pulps, with $R^2 = 0.63–0.81$. Of the fibre properties tested, W, water retention value, a measure of fibre swelling showed the strongest positive correlation with Young's modulus, with $R^2 = 0.81$, and %RMSEE = 6.39%. This implies that swelling-induced flexibility results in better fibre conformability and contact area within the fibre network. The specific surface area, Φ, showed a reasonable correlation with $R^2 = 0.75$, which can be interpreted as fibrillation increasing network stiffness through an increase in available bonding sites.

Among all pulp types, the kraft eucalyptus pulp KE1 showed the best general correlations. Extremely high R^2 values were found for freeness (0.99), water retention value (0.99) and specific surface area (0.97), suggesting that refining has a more homogeneous and predictable effect on hardwood fibres. The highest slope was obtained for $E = a + b\Phi$ ($b = 0.9862$), confirming that the increase of specific surface area significantly improves the bonding capacity. This is in good agreement with the fact that eucalyptus fibres are fine and flexible, showing more pronounced fibrillation upon refining, which increases surface area and enhances sheet stiffness.

Similarly, the neutral sulfite semi-chemical pulp, NE1, showed a high level of predictability for Young's modulus from fibre characteristics. Indeed, the best model was obtained with water retention value, $R^2 = 0.98$, followed by freeness, $R^2 = 0.97$, specific surface area, $R^2 = 0.96$ and surface charge, $R^2 = 0.93$. Having a coarser origin than chemical pulps, refining-induced fibrillation and collapse of NE1 fibres considerably enhanced bonding, as reflected in a stronger mechanical response.

The %RMSEE values reported in Table 2 reveal that for the linear models relating pulp properties to Young's modulus, predictive accuracy varies with pulp type and parameters. %RMSEE values for kraft pine pulps, KP1–KP3, are relatively higher (6.39–14.24), reflecting moderate prediction accuracy. Among these, KP3 gave a better estimation performance for both water retention value, W, and freeness, F, models (%RMSEE 6.39 and 7.16, respectively), than surface charge, σ. Hardwood eucalyptus pulp, KE1, revealed the lowest %RMSEE values (1.74–3.00), exhibiting excellent model reliability, particularly for water retention value and freeness parameters. Similarly, NE1 also showed very good prediction capabilities (%RMSEE 3.78–6.78), and freeness provided the best correlation. Generally, water retention value and freeness were the most reliable predictors of Young's modulus, as reflected by consistently lower %RMSEE values across pulps when compared to surface charge and specific surface area.

Among all the pulps, freeness and water retention value were found to be reliable predictors of Young's modulus, indicating that fibre flexibility and network consolidation are both key components in the development of stiffness. Fibre surface charge was also strongly influential, in particular for kraft pulps, whereas specific surface area assumed greater importance in pulps subjected to extensive fibrillation.

The results clearly indicate that Young's modulus is directly improved as the fibre bonding potential increases, as achieved with refining-induced fibrillation, swelling, and charge development. However, the strength of each relationship differed according to pulp type, morphology and chemical composition. These findings underscored the significance of choosing an appropriate refining strategy given the characteristics of the pulp to achieve gains in paper stiffness without over-refining or energy losses.

CONCLUSION

The study showed that refining directly improved paper stiffness by modification of fibre surface chemistry, morphology, and bonding potential. Across all five pulps, refining raised the surface charge, specific surface area, and sheet density, which led to improved fibre–fibre interactions and higher Young's modulus. For instance, the surface-to-total charge ratio of NE1 surged from 0.59 to 0.83, the highest gain among all pulps. KP3 recorded the sharpest rise in specific surface area, from 1.48 to 7.58 m^2/g. Sheet density for KE1 went from 0.58 to 0.69 g/cm^3, the highest final value. In terms of stiffness, Young's modulus for KE1 rose from 3439 to 5271 MPa, the best overall, while KP1 increased from 1342 to 4625 MPa, the largest absolute gain among softwoods.

The increase in Young's modulus strongly correlated with declining freeness, indicating that refining enhances network consolidation through fibrillation and fibre collapse. Regression analysis showed that water retention value and freeness followed by surface charge and specific surface area were the most reliable predictors of Young's modulus, with R^2 values reaching 0.99 for KE1. The results suggest that mill can fine-tune refining to get the right balance between bonding and stiffness without excessive energy input or producing too many fines.

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