The effect of laboratory mixing at medium pulp concentration on radiata pine kraft pulp

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SUMMARY

Medium pulp concentration (MC) treatment of radiata pine pulp in a high intensity laboratory mixer modified pulp and handsheet properties compared with untreated control pulp. The treatment had little effect on pulp viscosity and freeness while Kappa number decreased; pulp was weaker as indicated by reductions in tear, tensile, and wet zero span tensile compared with untreated control pulp.

Treatment increased fibre wall dislocations and enhanced fibre curl, and thus improved stretch.

Reaction temperature and pH were identified as significant. Increasing reaction pH increased sheet density and tensile, but elevated temperatures during treatment had the opposite effect. The relative contribution of either refining and/or curling of the fibres appears to be controlled by the process conditions during treatment.

Unrefined pulp handsheet properties induced by MC treatment were maintained following PFI mill refining when compared with control pulps. However as refining proceeded the magnitude of the differences were reduced.

New Zealand market kraft pulp mills produce bleached kraft pulp utilizing medium pulp concentration (MC) processes (8–15%).

During 1990 PAPRO purchased a laboratory high intensity mixer from Quantum Technologies Inc, Ohio, USA capable of performing pressurized, high temperature bleach treatments on MC pulp. High intensity mixing of pulp allows the instantaneous addition of bleach chemicals.

Fibre suspensions at medium pulp concentration behave as non-Newtonian fluids and require substantial energy input for homogeneous processing (1). The dissipation of this energy in the pulp suspension has the ability to not only induce effective mixing but also to modify fibre physical properties. De Grace and Page (2) reported that increasing extensibility of pulps through a kraft pulp bleach plant was directly correlated with the mechanical treatment the fibres received from unit operations such as mixing and pumping. Seth *et al* (3) identified similar enhancement of sheet stretch associated with softwood kraft pulps produced by the same mill before and after converting to a MC bleaching process.

Comprehensive studies of complete softwood kraft mill fibrelines have also identified reductions in pulp strengths through a modern bleach plant. MacLeod (4,5) measured the tear-tensile delivery (%) for one such fibreline, where strength delivery was a measure of the change in pulp strength compared with a laboratory reference pulp (Fig. 1). These results suggest that modern bleaching processes may further reduce strength delivery by at least another 10%.

Mechanical treatment in the presence of water is usually termed refining and is routinely performed prior to papermaking to develop the physical properties of the paper sheet. In addition to developing new fibre surfaces, refining increased fibre flexibility and fibre collapse. As a result sheet density increases allowing greater interfibre bonding and ultimately enhanced tensile strength (6).

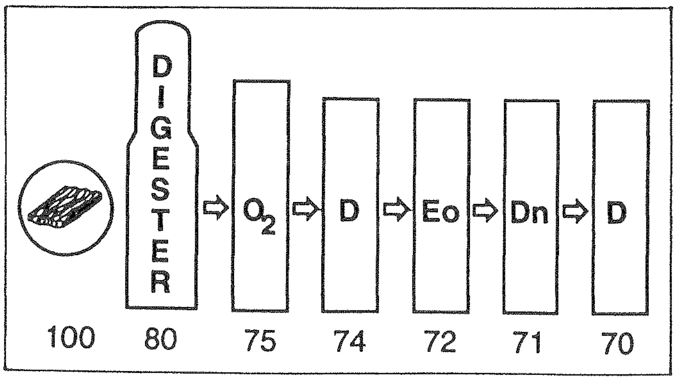

Fig. 1 — Softwood kraft pulp bleaching, tear-tensile strength delivery (%) (4,5).

Introduction of fibre kink and curl results in increased sheet bulk as fibres consolidate less during sheet forming. A decrease in the number of fibre to fibre contact points reduces interfibre bonding and as a result tensile strength normally decreases (3).

Introduction of fibre wall dislocations is commonly associated with mechanical treatment and is often accompanied by other effects of mechanical treatment such as fibre curl. Increased levels of fibre wall dislocations enhance handsheet stretch and tearing resistance (7). In addition, concentrated zones of dislocations could be expected to affect fibre strength.

This study was planned to quantify the overall effect of mixer treatment at MC on kraft pulp quality and also to identify the role of process or bleaching conditions during mixing. Changes to pulp quality were observed by measuring the handsheet properties of unrefined and refined mixer-treated and untreated control pulps.

EXPERIMENTAL

Pulp

Commercial unbleached kraft pulp was obtained from Tasman Pulp & Paper Co Ltd, Kawerau at 11% pulp concentration (p.c.) following brown stock washing. Laboratory washing was performed by dilution to 1% p.c. with hot water followed by intermittent agitation to allow all remaining carryover to be leached over a 12 hour period. Pulp was then thickened to *c.* 30% p.c. by centrifuge prior to fluffing and storage at 5 °C. Kappa number was 27.3 and viscosity 32.9 mPa.s.

pH adjustment

Kraft pulp (150 g o.d.) was treated over a 12 hour period at 10% p.c. to obtain target pulp pH before mixer treatment as follows:

- pH 7–8 by addition of water.
- pH 9–10 by addition of 2% $NaHCO_3$–NaOH buffer (10.5 *m/m* ratio).
- pH >12 by addition of 2% NaOH.

Experimental design

A 2^3 factorial experimental design was performed to assess the effect of reaction temperature, pH, and mixing speed on handsheet properties (Table 1).

Four replicate pulps were produced at the mid-point conditions of the design to estimate pure error variance. Duplicate blank treatments, without pH adjustment or mixing, were also produced as control pulps.

Laboratory mixer treatment

Kraft pulp (150 g o.d.) was treated in the laboratory mixer at 10% p.c. for 10 minutes at varying temperature, pH and speeds according to the experimental design.

Pulp was heated to within 5 °C of the desired reaction temperature in a microwave oven then placed in the preheated mixer bowl and brought to reaction temperature over a five minute period. Once at reaction temperature, pulp was subjected to high intensity treatment of four seconds duration. The pulp remained in the mixer for 10 minutes total reaction time with heat transfer mixing at 600 r/min every minute.

Following treatment, the pulp was thickened to 20% p.c. and the filtrate pH recorded. Dewatered pulp was washed by dilution to 1% p.c. with warm tap water and soaked for one hour. Pulp was then thickened to *c.* 20% p.c. and fluffed before analysis for Kappa number, viscosity, and handsheet properties.

Pulp samples were retained for microscopic analysis, to measure Kajaani fibre length, fibre wall dislocations, and fibre curl index.

Analyses

Kappa number was determined according to Appita method 204m-86 and viscosity according to TAPPI standard method T230 om-89. Handsheet testing was performed according to AS1301.208s-89 after PFI mill refining at 0, 1000, 2000, 4000 and 8000 rev. Wet zero span tensile index was measured on paper samples normally tested for burst index according to AS1301.459rp.

Quantitative estimates of fibre wall dislocations were made using polarized light microscopy according to the method developed by Kibblewhite (7).

Measurement of changes in fibre geometry were estimated by measuring fibre curl index. Approximately 400 fibres for each pulp sample were measured using image processing, according to a previously developed method (8). Kajaani fibre length distribution was measured according to TAPPI standard method T271 pm-91.

Table 1
Experimental design

Factors	Low level	Mid-point	High level
Reaction pH	7 – 8	9 – 10	> 12
Reaction temperature, °C	60	80	100
Mixer speed, r/min	1400	1800	2200

Table 2
Kappa number, viscosity and freeness, following mixer treatment at experimental design

Sample	Average pH	Average temperature °C	Mixing speed r/min	Kappa number	Viscosity mPa.s	Freeness CSF
Control	–	–	–	27.3	32.9	715
1	7.1	69.0	1400	25.6	35.4	690
2	7.4	61.9	2200	24.7	34.7	725
3	7.6	102.9	1400	24.4	31.2	715
4	7.3	104.1	2200	23.2	32.6	715
5	11.6	69.5	1400	23.0	30.7	725
6	12.3	63.0	2200	23.2	31.3	700
7	12.0	98.6	1400	23.3	31.9	695
8	11.9	102.5	2200	22.5	34.9	730
9	9.5	83.1	1800	25.2	30.8	690
10	9.4	82.3	1800	25.5	29.5	730
11	9.5	83.3	1800	26.4	31.5	710
12	9.4	85.1	1800	25.6	33.4	745

RESULTS

Pulp properties

All mixer-treated pulps showed decreased Kappa number following treatment compared with untreated control pulp while pulp viscosity and freeness were relatively unaffected (Table 2).

Unrefined handsheet properties

The tensile index of handsheets from mixer-treated pulps were in general reduced compared with control pulps (Fig. 2), but showed considerable variation. The wet zero span tensile index of mixer-treated pulps also showed a general decrease compared with control pulps, while stretch was enhanced by laboratory mixing (Fig. 3,4).

The intent behind the experimental design was to discover which process variables influenced pulp quality during MC mixing. Statistical analysis of the experimental data identified those factors which produced significant

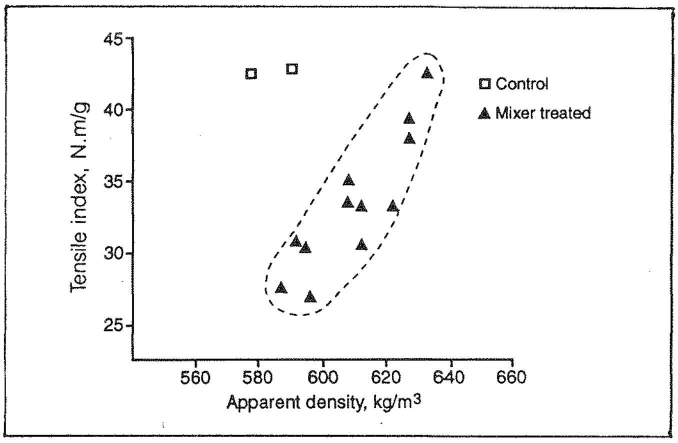

Fig. 2 — Tensile index of unrefined mixer-treated and control pulps.

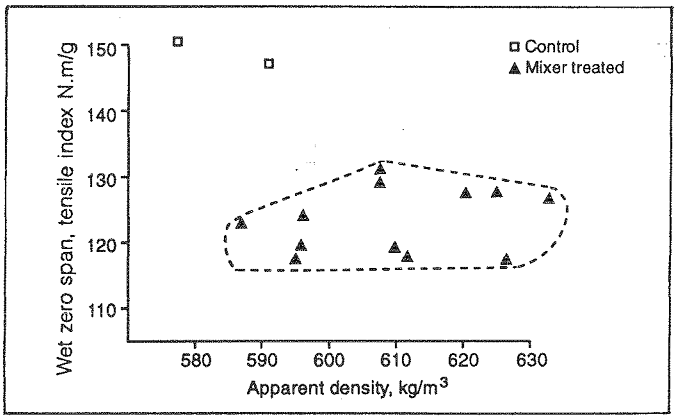

Fig. 3 — Wet zero span tensile index of unrefined mixer-treated and control pulps.

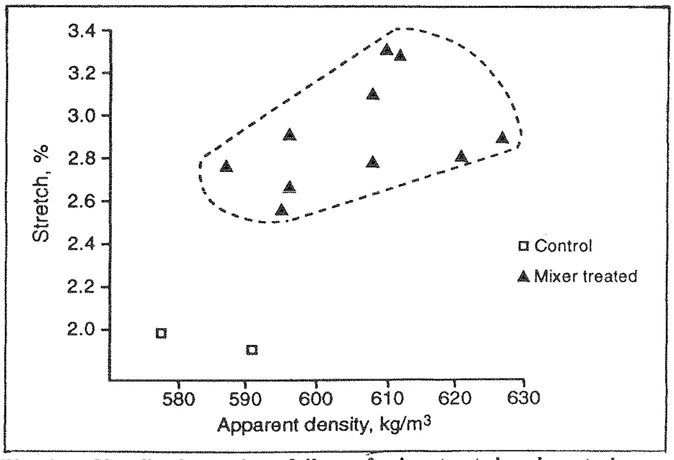

Fig. 4 — Unrefined stretch at failure of mixer-treated and control pulps.

differences between responses at varying process conditions. The response models for mixer treatment factors (temperature, pH, mixing speed) are presented in Table 3. Factor coefficients indicate the predicted change in the response variable when the factor increases from 0 to +1 level, i.e., mid-point to high level (Table 1). The response models include all factors which showed statistical significance at the 95% level.

Reaction pH was identified as a significant factor for Kappa number and tear index response (Table 3). Tensile strength was significantly affected by pH, temperature, and the interaction of temperature and mixing intensity (Table 3).

All three experimental factors were significant for apparent density response (Table 3). Increasing treatment intensity increased apparent density which is consistent with an increased refining effect. Reaction pH and temperature were identified as significant but opposing effects: increasing pH increased density but increasing temperature decreased it.

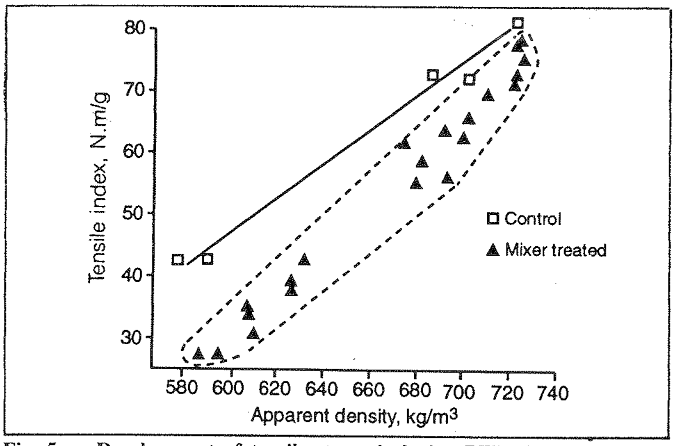

Fig. 5 — Development of tensile strength during PFI mill refining.

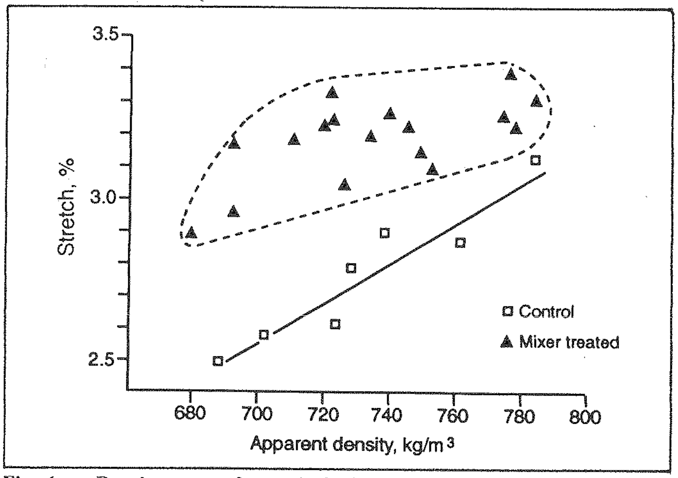

Fig. 6 — Development of stretch during PFI mill refining.

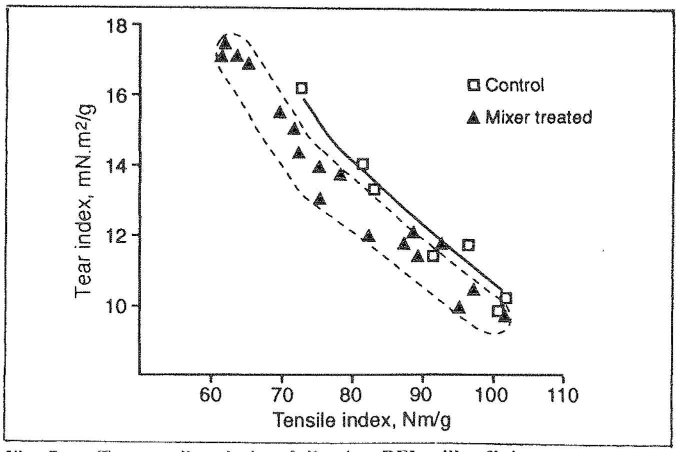

Fig. 7 — Tear-tensile relation following PFI mill refining.

A sheet with decreased density or increased bulk contains many more surfaces or interfaces to reflect light and increase light scattering. Thus mixing conditions producing a negative effect on sheet density should promote a positive effect on light scattering. Statistical response model coefficients confirm this trend for the mixer-treated pulps (Table 3).

Fibre properties

Two unrefined pulps at either end of the apparent density range (Fig. 2) were selected for comparison with control pulps (Table 4). Least significant difference values were estimated for differences between means to statistically determine real differences between samples.

In general, mixer treatment significantly increased fibre wall dislocations and fibre curl index.

Refined pulp handsheet properties

The change in tensile strength for mixer-treated pulps was maintained during initial PFI mill refining, i.e., up to 2000 PFI mill rev (Fig. 5). Enhanced sheet stretch due to mixer treatment was maintained throughout PFI mill refining (Fig. 6). Mixer treatment altered the tear-tensile relation compared to untreated control pulps following refining (Fig. 7).

Table 5 outlines the statistical response models for experimental pulps following PFI mill refining. The response models include all factors which showed statistical significance at the 95% level.

DISCUSSION

Pulp properties

Statistical analysis identified that reaction pH had a significant effect on Kappa number following mixer treatment (Table 3). Increasing pH during high shear treatment decreased the resulting Kappa number. A 7% decrease in Kappa number was predicted with increasing reaction pH from neutral to alkaline (pH 12) conditions.

Leaching of lignin from kraft pulps at elevated pH and temperature, as opposed to chemical delignification at the same conditions, has been reported by MacLeod and Li (9). The Kappa number of a kraft pulp decreased from 28.9 to 20 when treated in a flow-through type reactor at pH 13 and

Table 3
Statistical response model coefficients for mixing process conditions — unrefined pulp

$$\text{Response} = C_0 + C_1X_1 + C_2X_2 + C_3X_3 + C_{12}X_1X_2 + C_{13}X_1X_3 + C_{23}X_2X_3 + C_{123}X_1X_2X_3$$

Factor	Kappa number	Tensile index N.m/g	Tear index mN.m²/g	Apparent density kg/m³	Scattering coefficient m²/kg
Main effects					
X_1 pH	−0.86	2.36	1.40	7.75	0.30
X_2 temperature		−4.44		−11.50	0.70
X_3 mixing intensity				4.75	−0.35
Two factor interactions					
X_1*X_2					
X_1*X_3					
X_2*X_3		−1.14			
Three factor interaction					
X_1*X_2*X_3					
Constant	23.86	34.16	24.0	612.2	21.92
Adjusted R_2	0.92	0.98	0.82	0.92	0.96

Coefficients significant at 95% level.

Table 4
Fibre properties of selected unrefined pulp samples

Sample	Reaction pH	Reaction °C	Wall fractures No. per mm	Curl index	LWL mm
Control 1			29.5	0.233	2.67
Control 2			30.4	0.247	2.67
Mixer 3	7	100	50.3	0.331	2.57
Mixer 4	7	100	48.5	0.341	2.57
Mixer 5	12	60	43.2	0.311	2.60
Mixer 6	12	60	40.9	0.287	2.62
LSD* (95%)			0.95	0.040	0.07

* Least significant difference.

Table 5
Statistical response model coefficients for mixing process conditions — PFI mill refined pulp (4000 rev)
Response = $C_0+C_1X_1+C_2X_2+C_3X_3+C_{12}X_1X_2+C_{13}X_1X_3+C_{23}X_2X_3+C_{123}X_1X_2X_3$

Factor	Tensile index	Tear index	WZST
Main effects			
X_1 pH	2.09		−3.79
X_2 temperature	−2.49		
X_3 mixing intensity			
Two factor interactions			
X_1*X_2			
X_1*X_3			
X_2*X_3	−1.04	0.26	
Three factor interaction			
X_1*X_2X_3			
Constant	89.01	11.51	139.9
Adjusted R^2	0.95	0.56	0.68

Coefficients significant at 95% level.

100 °C for 15 minutes. A similar mechanism of alkaline leaching was proposed for the decrease in Kappa number observed following pulp pH adjustment and mixer treatment.

Pulp viscosity and freeness following mixer treatment were similar to those of the untreated control pulps (Table 2). Previous work in the Quantum laboratory mixer also failed to detect any significant changes in freeness following mixer treatment (10), while MacLeod also detected little change in viscosity during leaching of kraft pulp at elevated pH (9).

Unrefined pulp handsheet properties

Overall MC mixing effect: Pulps treated in the laboratory mixer according to the experimental design showed reduced tensile strength and increased apparent density compared with the untreated control pulps (Fig. 2). Such a result was unexpected as the decrease in tensile strength was not accompanied by decreased apparent density. Treatments that induce curling of pulp fibres reduce tensile strength through reduced apparent density and interfibre bonding (3,6). Our results showed mixing reduced tensile strength without decreasing apparent density (Fig. 2). The reduction in tensile strength was attributed to reduced bonding and/or reduced fibre strength.

The wet zero span tensile (WZST) test eliminates sheet bonding influences and gives an estimate of intrinsic fibre strength (11). Mixer-treated pulps all exhibited reduced WZST compared with untreated control pulps (Fig. 3). Cellulose integrity was maintained since viscosity remained unchanged (Table 2). Therefore, the reduction in WZST suggested that mechanical treatment during MC treatment weakened the pulp fibres.

However, the reduction in WZST with mixing only partly related to reduced fibre strength since WZST is also influenced by fibre curl and wall dislocations (12). Further evidence to support the hypothesis that MC treatment weakened the pulp fibres was shown by a reduction in the tear-tensile relation following refining (Fig. 7).

Increased levels of wall dislocation and fibre curl were observed for mixer-treated pulps (Table 4). These observations agree with previous authors and confirm that MC treatment induces fibre curl and wall dislocation (2,7). Stretch increased following mixer treatment since fibre curl and wall dislocation enhance sheet extensibility (Fig. 4) (3).

Mixer-treated pulps exhibited reduced fibre length (LWL) when compared with control pulps (Table 4). Although the reduction in length was measurable, the statistical significance was marginal (Table 4). It is likely that the reduction in LWL is related to the optical measurement technique where curled fibres are measured from a projection on one plane of view. Further work is needed to evaluate fibre contour length by image analysis. This method will determine whether the fibres are shortened, cut or curled during mixing.

Process condition effects: Statistical analysis of the handsheet data identified reaction pH, temperature, and the interaction of temperature and mixing intensity, as significant factors influencing unrefined tensile strength response (Table 3). Increasing reaction pH increased tensile strength (positive coefficient) while increasing temperature decreased tensile strength (negative coefficient). The interaction of temperature and intensity of treatment also decreased tensile strength (negative coefficient). High temperature combined with high intensity of treatment produced the greatest decrease in tensile strength (Fig. 2,8).

Figure 8 depicts the effects of pH and temperature on the tensile-density relation. Increasing pH (at constant temperature and treatment speed) was associated with increasing tensile strength and apparent density, while increasing temperature (at constant pH and speed) produced decreasing tensile strength and apparent density. The relative magnitudes of the competing effects appear to be controlled by the process conditions. Increasing reaction pH pushed the pulp properties in the same direction as would refining treatments. Lindstrom *et al* (13) reported similar results for the effect of pH during refining on the strength of unbleached kraft pulp. Tensile strength increased with increasing pH during refining and sheet forming, reaching an optimum at pH *c.* 11. Lindstrom concluded that increasing pH assisted strength development through polyelectrolyte swelling of the fibre wall. The chemical conditions that favoured a high degree of swelling as determined by water retention value (WRV), also favoured an increased rate of tensile development.

Increasing temperature during treatment decreased tensile strength and apparent density (Fig. 8). Similarly, high reaction temperature produced the greatest increase in fibre curl and wall dislocation (Table 4). Elevated temperatures may increase the susceptibility of pulp fibres to curl and wall dislocation due to thermal softening.

Over the experimental temperature and pH ranges, temperature had the predominant affect on pulp properties (Fig. 8). This is confirmed by the larger response model coefficient for the effect of temperature on tensile strength and apparent density (Table 3).

PFI mill refining

Mixer-treated and control pulps following PFI mill refining exhibited typical development of tensile strength (Fig. 5). However when compared at a common apparent density the mixer-treated pulps had reduced tensile strength (Fig. 5). Hence the decrease in tensile strength established for unrefined pulps was maintained during PFI mill refining.

The differences between mixer-treated and control pulps decreased with refining (Fig. 5). Although fibre properties of refined pulps were not measured, some mixer treatments effects may be reversed since PFI mill refining reduces fibre

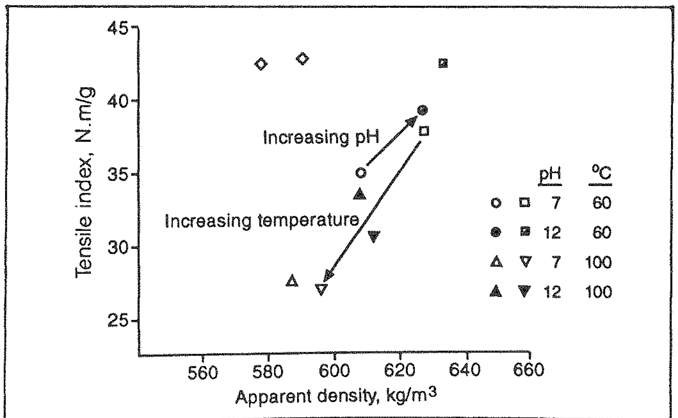

Fig. 8 — Effect of pH and temperature on tensile and density (Pairs of symbols: 1st = 1400 rev/min; 2nd = 2200 rev/min).

curl and relaxes zones of wall dislocation (7,14). A similar trend was observed for stretch where PFI mill refining minimized the original mixing effect (Fig. 6).

Reaction pH and temperature were identified as significant factors affecting the tensile strength response of refined pulps (Table 5). Previous discussion of these effects for unrefined pulps is also valid for pulps following PFI mill refining. However the magnitude of the model coefficients is reduced for refined pulps since PFI mill refining may reverse some MC mixer effects.

A two-factor interaction was the only significant process variable identified for refined tearing resistance response (Table 5). Unfortunately the response model explained little of the data variation ($R^2 = 0.56$, Table 5). The lack of significant process variables is likely due to experimental variation combined with the reduced effect of pH and temperature since refining may reverse some mixer treatment effects.

The response model for WZST at 4000 PFI mill rev was only modest in explaining the variation in the data ($R^2 = 0.68$, Table 5). However, reaction pH was identified as a significant factor on WZST response. Increasing pH during mixer treatment decreased the WZST of refined pulps. Although fibre dislocation and curl can influence WZST (12), further investigation of these effects is necessary to establish validity.

Changes in the tear-tensile behaviour of kraft pulps can highlight fundamental changes in fibre strength (6,11). Figure 7 clearly illustrates the altered tear-tensile relation for mixer-treated pulps compared to control pulps. These laboratory results suggest that similar changes to pulp quality are likely within modern kraft pulp bleach plants.

Future work

Further work is planned with the objectives to determine the mechanism of strength reduction during MC treatment and to understand further the mechanisms of change due to reaction temperature and pH.

CONCLUSIONS

MC treatment of radiata pine kraft pulp in a high intensity laboratory mixer modified pulp and handsheet properties compared with untreated control pulps. Unrefined mixer-treated pulps generally exhibited reduced tensile strength without decreased apparent density due to reduced bonding and/or reduced fibre strength.

The process appears to be responsible for the reduction in pulp strength as the chemical interactions during treatment had little effect, since pulp viscosity remained unchanged. Mixing increased the number of fibre wall dislocations and enhanced fibre curl. Such damage to pulp fibres can be irreversible having a direct effect on the quality of pulp produced from modern kraft pulp mills. Correlation of laboratory results with commercial MC mixers will be important to establish the extent of fibre damage present in commercial operations particularly where multiple mechanical treatments may produce greater reductions in pulp quality.

Reaction temperature and pH were identified as significant but opposing factors influencing tensile strength during MC mixing. Elevated pH increased sheet density and tensile strength as would refining treatments, but elevated temperature had the opposite effect as would inducing fibre curl and wall dislocations. Reaction temperature had the predominant effect on pulp properties, producing the largest response model coefficient for the effect on tensile strength and sheet density. The reaction conditions present during modern MC bleaching stages will influence the way the fibres respond. High temperature bleach stages such as oxygen delignification may be where the majority of changes to pulp quality originate.

Unrefined handsheet properties induced by MC treatment were maintained following PFI mill refining when compared with control pulps. However as refining proceeds the magnitude of the differences was reduced for refined pulps since PFI mill refining may reverse some MC mixer effects.

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REFERENCES

(1) Bennington, C. P. J., Kerekes, R. J. and Grade, J. R. — *J. Pulp Paper Sci.* **15**(5):J186 (1989).
(2) De Grace, J. H. and Page, D. H. — *Tappi* **59**(7):98 (1976).
(3) Seth, R. S., Francis, D. W. and Bennington, C. P. J. — *Appita J.* **46**(1):54 (1993).
(4) MacLeod, J. M. — *Paperi Puu* **72**(8):780 (1990).
(5) MacLeod, J. M., McPhee, J. F., Kingsland, K. A., O'Hagan, T. J., Thomas, B. C., Tristram, R. W. and Kowalska, R. E. — Proceedings TAPPI Pulping Conf, San Diego, Vol 1 (183-192 (1994).
(6) Page, D. H. — Trans 9th Fund Res Sym, Cambridge (1-38) (1989).
(7) Kibblewhite, R. P. — *Cell. Chem. Tech.* **10**(4):497 (1976).
(8) Miller, P. R. — *Appita J.* **42**(2):125 (1989).
(9) MacLeod, J. M. and Li, J. — *Tappi J.* **76**(12):159 (1993).
(10) Duff, M. A., Piechuta, M. E., Yant, R. E. and Hurst, M. M. — CPPA Annual Meeting Montreal, Vol B (67-74) (1988).
(11) Clark, J. — **Pulp technology and treatment for paper**: Miller Freeman: (1978).
(12) Mohlin, U-B. and Alfredson, C. — *Nordic Pulp paper Res. J.* **5**(4):172 (1990).
(13) Lindstrom, T. and Kolman, M. — *Svensk Papperstidn.* **85**(15):R140 (1982).
(14) Page, D. H., Seth, R. S., Jordan, B. D. and Barbe, M. C. — Trans 8th Fund Res Sym, Oxford (183-227) (1985).

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