Cationisation of thermomechanical pulp fibres. Part 2: Influence on strength and retention

By D. Montplaisir, B. Chabot and C. Daneault

Abstract: This study was undertaken to develop a process to improve paper quality and to lower production costs by a chemical modification of thermomechanical pulp (TMP) fibres. TMP pulps were grafted with a quaternary amine to optimise paper strength and retention of fillers in hand-sheets. This grafted pulp had a lower anionic net charge compared to untreated TMP. Results show that cationised fibres significantly improved sheet strength. Retention of anionic fines and fillers with various retention aids were also improved.

The main components in papermaking are chemical and mechanical fibres, fines and inorganic fillers. All of these components repel each other due to their anionic character. Drawbacks related to this effect include poor retention of fines and fillers, weak interfibre bonding, and drainage issues. Cationic additives are used mainly to lower the overall negative charge, and hence increase the attractive force between those particles. Fast, modern paper machines and high shear rates tend to detach adsorbed cationic polymers, affecting retention, drainage, and interfibre bonding development. Covalent bonding of a quaternary amine directly to fibres can decrease the negative charge of fibres, and give better shear resistance than polymers, resulting in improved strength and retention.

CATIONISATION AND INTERFIBRE BONDING

The covalent addition of a quaternary amine to polysaccharide is used extensively in cationic starch production [1]. This grafting reaction has also been applied to cotton fibres to improve anionic dye fastness [2]. Grafting of chemical pulp has been investigated in many publications [3,4,5]. It is well established that cationised chemical pulp can improve both the retention and strength properties of papers [6]. The reaction mechanism and optimization method for our study was previously described [7]. Medium and high consistency processes were developed. The main advantage of the high consistency process was that the bleaching reaction did not interact with the grafting reaction. For this reason, this study will cover only the high consistency process.

In the headbox of the papermachine, at less than 1% consistency, the interfibre bonding is mainly affected by electrostatic repulsive and van der Waals attractive forces [8]. The grafting of cationic charges can reduce the repulsion by decreasing the surface potential, as indicated by the following equation [9,10] for two spheres of the same radius:

\[ V_r = \frac{4\pi \varepsilon \varepsilon_0 \alpha e^{\left(-\frac{H_o}{2a+H_o}\right)}}{\left(2a+H_o\right)} \]

where:
- \( V_r \) = Repulsion force.
- \( \varepsilon \) = Solution dielectric constant.
- \( \alpha \) = Ionic radius.
- \( \varepsilon_0 \) = Surface potential.
- \( \psi_0 \) = Surface potential and charge density factor.
- \( 1/K \) = Electronic double layer thickness.
- \( H_o \) = Distance between spheres.

Interfibre bonding of paper is related to several parameters [11]. Chemical bonds within the cellulose molecules, and acid-base interactions between them. Intermolecular van der Waals bonds and hydrogen bonds. Entanglements of polymer chains. Interfibre bonds: the zone where two fibres are so close that chemical bonding, van der Waals interaction, or molecular entanglement may occur.

The van der Waals bonds have an energy in the range of 2-8 kJ/mol for dipole-induced attraction and hydrogen bonds in the range of 8-32 kJ/mol. Grafting of a cationic charge gives an ion-induced dipole interaction of 65-72 kJ/mol [12] and can contribute significantly to paper strength.

EXPERIMENTAL

Unbleached eastern Canadian spruce: balsam (70:30) TMP was sampled after twin-wire press at the Kruger Trois-Rivieres mill. Pulp consistency was approximately 32-38%. Distilled water was used for all dilution and washing processes carried out during the experimental procedures. For each experiment, the pulp was mixed with the suitable amount of water and chemical reagents in a Hobart laboratory mixer for 15 minutes, and was placed in a temperature-controlled bath for the retention time defined by the experimental design. An aqueous solution of 2,3-epoxy-propyl-tri-methyl ammonium chloride (EPTMAC) was used in all cases as a cationic grafted monomer.

The fibre surface cationic charge (SCC) was measured by colloidal titration with poly-vinyl sulfonyl acid potassium salt (PVSK) and poly-diallyl-dimethyl ammonium chloride (polyDADMAC). The pulp was diluted to approximately 0.5% consistency and the pH was adjusted to 2.5 in order to eliminate the negative charge from the car-
boxylic acids, which start to dissociate at a pH of 2.9. An excess of the anionic polymer (PVSK) was added to the pulp slurry and, after a few minutes, the unreacted PVSK was back-titrated using the cationic polymer (polyDADMAC). The amount of polymer which reacted with fibres is a measure of the SCC of fibres in milliequivalent per kilogram of fibre.

Retention evaluation was made in a Britt jar at 0.8% consistency (similar to headbox consistency) with neutral, anionic and cationic polyacrylamides at different dosages and furnish compositions, as required by the experiment design. A 80 mesh stainless steel screen was used with the rotational speed at 1200 rpm.

Optical and physical testing of pulps were done according to PAPTAC standard testing methods.

**RESULTS**

The CAT-TMP was prepared with the optimum conditions, see Table I, as previously published [7].

The maximum SCC was achieved without any bleaching chemicals, Fig. 1. Peroxide bleaching gave more SCC than percarbonate, but lower brightness, Fig. 2. It seems that a less efficient bleaching reaction consumes less alkali, and this alkali can react with EPTMAC to give more cationic groups at the surface.

Addition of EPTMAC did not negatively affect the percarbonate bleaching stage. According to Fig. 3, it seems that a less efficient bleaching reaction consumes less alkali, and this alkali can react with EPTMAC to give more cationic groups at the surface.

Scott bond is certainly the property that responds most to internal bonding. Delamination is z-directional, and mostly interfibre bonding is involved. According to Fig. 3, bleaching and alkali treatment increased Scott bond by approximately 30%, but grafting added another 20% to 40%. The unbleached reaction produced better properties, relative to the higher SCC. Peroxide and peroxide bleaching gave similar results.

Burst index also responds to interfibre bonding because of the multidimensional aspect of this test, but to a lesser extent than the Scott Bond. According to Fig. 4, burst index increased by approximately 5.5%, and grafting added another 10-25%. Better results were achieved without any bleaching. The trend is similar to Scott bond results, but to a lower extent.

Tensile strength was increased by both bleaching and grafting, by 21% for bleaching and an extra 9-21% for grafting.

**TABLE 1. Optimum conditions and results at high consistency.**

<table>
<thead>
<tr>
<th></th>
<th>TMP</th>
<th>TMP</th>
<th>CAT-TMP</th>
<th>CAT-TMP</th>
<th>CAT-TMP</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Alkali Bleaching</td>
<td>No-Bleaching</td>
<td>Bleaching 1</td>
<td>Bleaching 2</td>
<td></td>
</tr>
<tr>
<td>EPTMAC (mmole/kg)</td>
<td>–</td>
<td>0</td>
<td>420</td>
<td>420</td>
<td>420</td>
</tr>
<tr>
<td>Alkali ratio</td>
<td>–</td>
<td>–</td>
<td>4</td>
<td>4</td>
<td>4.5</td>
</tr>
<tr>
<td>NaOH (mmole/kg)</td>
<td>–</td>
<td>1750</td>
<td>1750</td>
<td>1750</td>
<td>1890</td>
</tr>
<tr>
<td>Sodium carbonate (%)</td>
<td>–</td>
<td>2</td>
<td>2.5</td>
<td>10</td>
<td>–</td>
</tr>
<tr>
<td>Sodium percarbonate (%)</td>
<td>–</td>
<td>10</td>
<td>0</td>
<td>–</td>
<td>3.5</td>
</tr>
<tr>
<td>Hydrogen peroxide</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>75</td>
<td>75</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>120</td>
<td>120</td>
</tr>
<tr>
<td>Time (minutes)</td>
<td>–</td>
<td>75</td>
<td>75</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>SCC (mmole/kg)</td>
<td>0</td>
<td>–</td>
<td>60.4</td>
<td>34.2</td>
<td>45.6</td>
</tr>
<tr>
<td>Brightness (% ISO)</td>
<td>56.2</td>
<td>58.6</td>
<td>39</td>
<td>58.9</td>
<td>53.73</td>
</tr>
</tbody>
</table>

**FIG. 1. Surface cationic charge.**  
**FIG. 2. Brightness of the optimum conditions.**  
**FIG. 3. Scott Bond for optimum conditions.**  
**FIG. 4. Burst for optimum conditions.**
ing. Figure 5 shows the breaking length in meters.

Increasing interfibre bonding decreases the mobility of fibres in the sheet, resulting in a reduction of tear strength [12]. The tear was reduced by 12% for the bleaching treatment, and an additional 0-12% with grafting, Fig. 6. The worst case was achieved when grafting without any bleaching chemicals, where the SCC was at the maximum.

An experiment was designed involving 8 different polyacrylamides, as listed in Table II. Three polyacrylamide dosages, combined with a quadratic mixture design, were used to understand the role of CAT-TMP in the retention of fines and filler in optimum conditions. This mixture design involved clay, TMP and CAT-TMP.

Table III describes the range used for every quantitative parameter. A total of 52 runs were needed, based on D-Optimal criteria.

Comparison of the different polyacrylamides at the intermediate clay level show that the polymer C10 was the best, followed very closely by the anionic A10, Fig. 7.

At higher filler levels, the polyacrylamide A10 gave much better results than the C10, Fig. 8. For this reason, the A10 was used for the rest of the retention study.

At 15% headbox ash content, an increase in filler retention was observed with the addition of CAT-TMP. But the CAT-TMP was detrimental for fibre retention. The loss of fibre retention was low compared to the increase in filler retention. In a mechanical speciality grade production, the filler retention is much more important than fibre retention. For that reason, the effect of CAT-TMP is considered beneficial for wet-end chemistry. Fig. 9 shows the retention curve for 15% ash content. By increasing CAT-TMP, the ash retention increased by 11% and the fibre retention was reduced by 4 points.

At high headbox ash content, the situation was different. The CAT-TMP had no significant influence on retention of either fibre or clay, as seen in Fig. 10. The SCC seems to be saturated by clay and cannot interact in the retention mechanism. The system is governed by the amount of clay particles, instead of fibre surface potential.

**CONCLUSIONS**

High consistency cationic grafting, combined with oxidative bleaching, can improve overall paper strength, specifically increasing:

Scott bond, by 60%,
Burst by 35%, and
Breaking length by 24%.
As with any other treatment to increase
interfibre bonding, there is a tear loss. In
this case, tear was reduced by about 12%.
This treatment can be used in the pro-
duction of mechanical speciality grade to
decrease the amount of Kraft pulp or to
increase the level of filler, without sacri-
ficing too much strength.
The best retention for this blend of
clay, CAT-TMP and TMP was achieved
with the highest charge on both cationic
and anionic polyacrylamide. But an
anionic polymer was more effective for
higher clay dosage, and efficient at lower
clay content.
The CAT-TMP can improve retention
of clay for moderate amounts of clay, up
to 20%, in the headbox. However, fibre
retention was partly sacrificed. The overall
performance improved the wet-end chem-
istry. No interaction was observed at high
clay content such as 30% and more.

ACKNOWLEDGEMENTS
The authors gratefully acknowledge
Kruger Inc. and the Canada Research
Chair in Value-Added Paper for their
financial support.

LITERATURE
1. WURZBURG, O.B. Modified Starches: Properties
and Uses. CRC Press Inc., Boca Raton, Florida, US,
pp.113-129 (1986).
2. SEONG, H.S., KO, S.W. Synthesis, Application and
Evaluation of Cationising Agents for Cellulosics Fibres.
3. SCHEMPP, W., KAUFER, M., KRAUSE, T. Cation-
ization of Pulp Reactions and Kinetics. Proc. TAPPI
Int. Dissolving Specialty Pulps Conf., Boston, p. 171-
175 (1983).
4. GRUBER, E., GRANZOW, C., OTT, T. New Ways for
5. GESS, J. M., HARDING, M. J., GAINES, R. C.
Cationic Cellulose Product and Method for Its Prepa-
6. GRUBER, E., GRANZOW, C., OTT, T. Cationization
of cellulose Fibres in View of Applications in the Paper
7. MONTPLAISIR, D., DANEault, C., CHABOT, B.
Cationisation of Thermomechanical Pulp Fibres. Part
1: Grafting Reaction Optimisation. PAPTAC 90th
8. CARRE B. Contribution to a better understanding
of the retention and flocculation mechanism occuring
during papermaking. Doctoral thesis, Polytechnics
9. DERJAGUIN B. V., LANDAU L. Theory of stability
of highly charged lyophobic sols and adhesion of
highly charged particles in solutions of electrolytes.
10. VERWEY E. J., OVERBEER J. T.G. Theory of the sta-
11. GULLICHSEN, J., PAULAPURO, H. Papermaking
Helsinki, Finland (2000).
12. GULLICHSEN, J., PAULAPURO, H. Papermaking
Science And Technology: Papermaking Chemistry, Vol. 4, 1st

Résumé: Cette étude a été entreprise afin de développer un procédé permettant d’améliorer
la qualité du papier et de diminuer les coûts de production par une modification chimique des
fibres d’une pâte thermomécaniques (PTM). Des fibres de PTM de résineux ont été greffées avec
une amine quaternaire pour augmenter les propriétés de force de la feuille et l’adsorption des
fines et des pigments. Cette pâte greffée a montré une charge cationique nette supérieure à la pâte
PTM non traitée. Les résultats indiquent que les fibres cationisées améliorent significativement les
propriétés de résistances mécaniques. La rétention des fines et des charges minérales anioniques
aussi étaient améliorées.

QC, Canada, February 7-10, 2005. Not to be reproduced without permission of PAPTAC.
Manuscript received November 15, 2005. Revised manuscript approved for publication by the

Keywords: THERMOMECHANICAL PULPS, SOFTWOOD PULPS, CATIONIC COM-
PONDS, RETENTION, MECHANICAL PROPERTIES, QUATERNARY COMPOUNDS.