Strength chemistry for board and tissue production: Scientific outlook and end applications

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Abstract
Strength is a key paper characteristic that papermakers must control to produce the sheet of desired quality at a target production rate. In the two dynamic areas of the paper industry, board and tissue, various natural polymers and synthetic resins have found a wide use as flexible and economical tools for paper strength control. There are similarities and significant differences between the strength aids used for board and tissue, driven by their specific end use and paper manufacturing processes. Dry strength aids, based on starch or polyacrylamide, are most commonly used in both board and tissue production. Permanent wet strength aids, based on a polyaminoamide-epichlorohydrin (PAE) resin, are limited to moisture resistant grades such as liquid packaging, napkin and paper towel. Temporary wet strength, based on glyoxalated polyacrylamide (GPAM), is a niche application for producing sanitary products intended for disposal into a septic system. Beyond reinforcing the sheet, some strength aids can play an important role in balancing charge on fines and fibres, providing benefits for improving efficiency of other process and functional additives and improving sheet dewatering. In this presentation, we will review the fundamentals of strength development and strength aid chemistries as well as we will discuss their end applications, both conventional and novel. Industrial case studies will demonstrate practical aspects of the strength chemistry.
Introduction
The board and tissue markets have been the two fastest growing segments of the paper industry in the last 20 years. Globally, the average annual growth from 2000-2007 has been 4.5% for board and 3.6% for tissue compared to 1.8% for printing and writing grades [1]. The board production growth is largely driven by globalization and increased shipping of goods across the globe, whereas the tissue production growth closely follows the increase in GDP and higher standards of living. The recent economic recession slowed down this growth, but the industry outlook is still positive in large due to the growth in the emerging markets [2].

Strength is one of the most important characteristics of paper from the standpoint of both end-use characteristics and manufacturing efficiency. Board and tissue are utilized for unrelated purposes that demand unique characteristics. For example, bending stiffness is required for folding boxboard, whereas handfeel softness (opposite of stiffness) is desired for toilet paper. Despite the obvious differences, the fundamentals of paper strength and the chemistries used for strength control are largely the same for both segments.

The theory and practical aspects of paper strength developments have been extensively reviewed [3-6]. The key factors of strength development are generally recognized as

- Fiber strength and length
- Intrefiber bond strength
- Bonded area (number of bonds per area unit)
- Sheet formation
- Stress distribution

A number of means are available for papermakers to allow for control of the sheet strength. The choice of fibers and their mechanical treatment (refining) are most common. Virgin fibers, especially Kraft softwood, produce the strongest sheet, but this pulp is costly. Driven by the high cost of virgin fiber and also by environmental pressure, both board and tissue industries have moved towards a greater use of less expensive recycled fibers, which inherently produce a weaker sheet. Furthermore, the quality of recycled fibers has been deteriorating dramatically in the latest decade or so, creating significant challenges for the industry [7].

Operational means such as headbox consistency, wire/jet speed ratio or wet pressing can be effective in improving strength but can interfere with other objectives such as production rate or sheet bulk. In case of raw material or operation limitations, chemical means are often used as flexible and economical tools for strength control. A variety of strength chemicals is available in the market. In this paper, the chemistry of these strength aids is reviewed and their benefits for board and tissue production are demonstrated using laboratory data and mill trial results.

Strength chemistries
Various natural polymers and synthetic resins are employed for controlling sheet strength in board and tissue grades. The choice of a strength aid depends on a number of factors, including their effectiveness (or the impact on a specific quality parameter), the program cost, the effect on machine runnability and productivity, ease of use, product availability and shelf life. Below is an overview of the most common strength aids.
Table 1: Common paper strength agents

<table>
<thead>
<tr>
<th>Chemistry</th>
<th>Form of delivery</th>
<th>Charge</th>
<th>Mode of addition</th>
<th>Dry strength</th>
<th>Wet strength</th>
<th>Dewatering effect</th>
<th>Fines Retention effect</th>
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</thead>
<tbody>
<tr>
<td>Natural polymers</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Native starch</td>
<td>Dry</td>
<td>0</td>
<td>surface</td>
<td>Yes</td>
<td>No</td>
<td>Negative</td>
<td>No</td>
</tr>
<tr>
<td>Cationic starch</td>
<td>Dry</td>
<td>+</td>
<td>wet end or surface</td>
<td>Yes</td>
<td>No</td>
<td>Negative</td>
<td>Positive</td>
</tr>
<tr>
<td>Carboxymethylcellulose (CMC)</td>
<td>Dry</td>
<td>-</td>
<td>wet end</td>
<td>Yes</td>
<td>No</td>
<td>Negative</td>
<td>No</td>
</tr>
<tr>
<td>Synthetic resins</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Glyoxalated polyacrylamide (SPAM)</td>
<td>Liquid</td>
<td>+</td>
<td>wet end</td>
<td>Yes</td>
<td>Yes*</td>
<td>Positive</td>
<td>Positive</td>
</tr>
<tr>
<td>Polyamide-epichlorohydrin (PAE)</td>
<td>Liquid</td>
<td>++</td>
<td>wet end</td>
<td>Yes</td>
<td>Yes</td>
<td>Positive</td>
<td>Positive</td>
</tr>
<tr>
<td>Cationic polyacrylamide (CPAM)</td>
<td>Liquid</td>
<td>++</td>
<td>wet end</td>
<td>Yes</td>
<td>No</td>
<td>Positive</td>
<td>Positive</td>
</tr>
<tr>
<td>Anionic polyacrylamide (APAM)</td>
<td>Liquid</td>
<td>--</td>
<td>wet end or surface</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>Amphoteric PAM</td>
<td>Liquid</td>
<td>+/-</td>
<td>wet end</td>
<td>Yes</td>
<td>No</td>
<td>Positive</td>
<td>Positive</td>
</tr>
</tbody>
</table>

*Temporary wet strength

Starch

Starch is the most common strength aid, primarily due to its low cost compared to synthetic resins. However, due to competition with the food industry, the starch prices have significantly increased in the past several years and synthetic alternatives have become more attractive. Potato, wheat, corn and tapioca are most common sources of starch. Starch is a polysaccharide and structurally related to cellulose. Starch can be derivatized with a small amount of cationic reagents to provide charge for self-retention on anionic fibers. The level of cationicity is defined by the degree of substitution (DS) that can typically range from 0,02 to 0,1 but most commonly around 0,03-0,06. With increased system closures, the trend in the past years has gone to higher DS starches. Anionic and amphoteric starches can also be produced but are less common in board and tissue manufacturing.

Native or unmodified starch is applied via a size press. The surface application allows addition of a large amount of starch (1.5-5% of sheet weight) that essentially impregnates the paper sheet and increases its stiffness by 20-25%. However, the downside of the size press application is re-wetting the sheet and a need for additional drying, which slows down the machine often to more than 30%. Extra drying also increases energy costs.

Applying cationic starch in the wet end solves the redrying problem, but its higher cost and discrete fiber surface area limit the starch loading to below 1.5-2%. For higher loading levels, additional retention chemicals are required. Cationic starch is typically added to the thick stock for strength or thin stock for retention.
Cationic starches are believed to improve strength by a combination of three mechanisms [4]:

- Increasing bonded area, resulting in increased sheet density
- Strengthening the interfiber bonds
- Decreasing stress concentrations in paper sheet

Besides the rising cost of starch, there are a number of other negative aspects that papermakers have to consider. Starch is normally supplied in a solid form, which requires a considerable investment in the make-down equipment and an added cost for dedicated personnel to run it. Another drawback of using natural polymers like starch is their tendency to promote biological growth and deposits. In contrast, synthetic resins can provide a similar or better effect on paper strength without the shortcomings of natural polymers.

**CMC**

Carboxymethyl cellulose (CMC) is a natural polymer derived from cellulose by modifying with chloroacetate. The carboxyl group provides anionic charge. The degree of substitution (DS) can range from 1 to 3 depending on the number of hydroxyl groups in a single glucose monomer reacted with chloroacetate.

CMC requires a cationic counterpart in the wet end to assist with retention to anionic fibers. Most typically, CMC is used in a pair with a cationic PAE resin. PAE provides cationic sites on fibers for retention of CMC, whereas CMC rebalances the fiber charge, allowing for additional retention of the PAE resin [7]. This approach is especially typical for kitchen towel production. In production of containerboard, cationic starch or other cationic dry strength aids are sometimes coupled with CMC to boost sheet strength and/or efficiency of the cationic strength aids.

The low cost has made CMC attractive for paper makers. A big drawback of CMC is its handling. CMC is supplied as a solid powder which requires a significant investment into make-down equipment. Like starch, CMC is also prone to biological growth and deposits. Another drawback of CMC is its tendency to disperse fines and mineral ash in papers and thus increase the demand for retention aids. Papermakers often look for economically viable liquid alternatives to CMC.

**GPAM**

Cationic glyoxalated polyacrylamide (GPAM) is a well-known strength resin [5-6] that is often regarded as a benchmark for generating dry strength. The polyacrylamide backbone normally incorporates a small amount of a cationic monomer, e.g. diallyldimethyl ammonium chloride (DADMAC), rendering the polymer self-retaining on fibers (see Scheme 3). GPAM is a reactive polymer that can covalently bind with cellulose upon dehydration as shown in Scheme 4. The result is a generation of both dry and wet strength in paper.
The reaction with cellulose is reversible in water, making the wet strength temporary and has no impact on broke repulping. The design of the GPAM molecule can be altered to control the wet strength decay rate. A slower decay rate is tolerable in board and towel grades, whereas a faster decay is required for manufacturing toilet paper that must be readily dispersed in water at room temperature.

![Scheme 4: Reversible reaction between GPAM and cellulose](image)

One of the most efficient dry strength resins in the market is Kemira’s Fennobond 3000. It tends to be more efficient than traditional GPAM resins due to a secondary structure of the polymer [8]. In the first structure level, the cationic backbone is pre-crosslinked to allow for greater contact points with cellulose fibers. In the second structure level, crosslinking with glyoxal yields a polymer network with optimal molecular weight and the degree of crosslinking to provide high substantivity to fibers and high reactivity towards cellulose.

Fennobond 3000 has been used in most of the board and tissue grades, especially in containerboard, towel and napkin. It can improve compression strength (SCT, CMT, RCT), burst, tensile, internal bond and surface strength. The strength mechanism is primarily through reinforcement of the inter-fiber joints via both hydrogen and covalent bonds [4]. It has also been noted that structured GPAM molecules positively impact sheet dewatering. The dewatering effect primarily comes from improved press dewatering but an increase in free drainage can also occur.

For some special grades, an ultra-fast decay of wet strength is required. Premium toilet paper typically requires additional wet tensile that has to be maintained for a few seconds in moist paper, after which it must quickly diminish in water after paper is disposed of in a septic system. A fast decay of wet tensile is critical for preventing the septic system from getting blocked with undispersed paper. For these purposes, Kemira developed the FennoRez product line (Figure 1) based on the uniquely designed GPAM chemistry [9-11].

Unlike starch, GPAM resins are supplied as solutions in water with 8-20% solids and can be dosed right into the stock stream with an inexpensive pump system. Also,
GPAM resins are not prone to biological activity. The GPAM chemistry is most efficient if pH is maintained below 7 and the sulfite level below 5 mg/L. The chemistry and application aspect of GPAM resins have been reviewed in [5-6].

**PAE**

A polyaminoamide-epichlorohydrin (PAE) resin is the predominant wet strength resin in the market. Its chemistry is based on a polyaminoamide backbone, which is typically made in a condensation reaction between adipic acid and diethylenetriamine. A subsequent reaction with epichlorohydrin results in a crosslinked polymer structure with a significant amount of reactive groups called azetidinium ions. These ions provide to the PAE resin a high cationic charge needed for polymer retention on cellulose fibers and the self-crosslinking ability as shown on Scheme 5.

![Scheme 5: Self-crosslinking of a PAE resin](image)

The crosslinking reaction is accelerated by heat and alkaline pH. Unlike GPAM, a crosslinked PAE resin is not easily hydrolyzed. When retained in the sheet, the PAE resin self-crosslinks, forming a water-proof barrier around the fiber-to-fiber contact points, which prevents water from hydrolyzing hydrogen and ionic bonds. This “water-proofing” of fiber joints provides “permanent” wet strength to the sheet. The PAE wet-strengthened broke normally requires high pH and hypochlorite to break down the crosslinked PAE resin.

The PAE benefits and application in paper have been documented in literature [4-6]. PAE wet strength resins are largely used in paper towels, napkins, facial tissue, liquid packaging and food wrapping paper. In most of the wet strengthened grades, wet tensile or wet burst are normally measured.
In the tissue and towel production, it is also common to follow the wet/dry ratio, which is the wet tensile strength expressed as a percentage of the dry tensile strength. Since a higher dry tensile is associated with a stiffer sheet, a high wet/dry ratio is preferred for tissue and towel to minimize a negative impact on handfeel softness. Kemira’s Fennostrength products, based on PAE resins, can provide wet/dry ratio of up to 30-45%. This ratio will depend on fiber quality, dosages, pH and other chemicals used. Low pH (below 7) and strong oxidants (free chlorine above 1 mg/L) are detrimental to the wet strength development.

Very high levels of a PAE resin are required for kitchen towels and some specialty boards. Typically, a PAE dose above 5-8 kg/ton will overcationize fibers, resulting in poor resin retention on fibers and a loss of the resin efficiency. To assist with retention of excess PAE resin, anionic polymers such as carboxymethyl cellulose (CMC) or poly(acrylamide/acrylic acid) are used.

SPAM

Polyacrylamide (PAM) is a common and versatile chemistry typically utilized in the wet end. Acrylamide-based products found use in water treatment, retention, dry and wet strength applications. The dry strength improvement is primarily due to amide groups, forming hydrogen bonds with fibers and thus increasing inter-fiber bonding as shown in Fig. 2. Acrylamide-based polymers are very versatile and can be manufactured within a wide range of molecular weight and charge.

For dry strength purposes, the molecular weight needs to be high enough to ensure efficient adsorption and hydrogen bonding, but not too high so the polymer would not cause overflocculation and poor formation, which can weaken the sheet [4]. Typical molecular weight ranges from 100-2000 kDa, but can be exceptions. These polymers are supplied as solution in water and are referred to as solution polyacrylamide (SPAM).

The charge of an acrylamide-based polymer is provided by co-polymerizing acrylamide with one or more monomers bearing a charged group in a radical chain reaction catalyzed by an initiator. A cationic PAM typically includes 5-30 mole% of a quaternary ammonium monomer such as acryloyloxyethyltrimethylammonium chloride (ATAM-Cl), methacryloyloxyethyl-trimethylammonium chloride (MATAM-Cl), 3-trimethylammonium propylacrylamide chloride (APTAC), 3-trimethylammonium propyl methacrylamide chloride (MAPTAC) or diallyldimethyl ammonium chloride (DADMAC). Most commonly, ATAM-Cl is used in cationic PAM strength aids, primarily due to availability and a lower cost of this cationic monomer (Scheme 6). Anionic PAMs are copolymers of acrylamides and anionic monomers such as acrylic acid, methacrylic acid and itaconic acid. Amphoteric PAM’s include both anionic and cationic monomers.
Cationic and amphoteric PAMs are self-retaining on cellulose fibers, but can be sensitive to detrimental colloidal and dissolved substances (“anionic trash”), especially in recycled fibers. A high cationic charge (> 10 mole %) can overcome these problems although high cationic charge PAMs tend to be expensive due the high cost of cationic monomers. Food contact regulations (FDA, BfR), which are important for production of towel, napkin and food packaging, also restrict the amount of a cationic monomer in PAM.

Anionic PAMs have found a wider use due to its lower cost and a synergistic effect with other cationic strength aids such as cationic starch or PAE wet strength resin. Anionic PAMs requires a cationic counterpart for retention on fibers. Aluminum sulfate (alum) or polyaluminum chloride (PAC) can assist with retention. The optimum pH will be dictated by the alum/PAC chemistry and the ionization degree of anionic PAM and is typically within the pH 4-5 [3]. High cationic charge polymeric fixatives (polyamine, etc.) are less pH dependent.

Kemira’s Fennobond 85E is an example of an anionic PAM (Scheme 7). It is a copolymer of acrylamide and acrylic acid. Fennobond 85E is especially effective when used in conjunction with a PAE wet strength resin cationic starch.

Figure 3 demonstrates that addition of high levels of a PAE resin (FennoStrength) causes overcationization of fibers and limits further absorption of the resin, which is reflected in the plateauing effect on wet tensile already at 5 kg/ton. Ineffective retention of a PAE resin can lead to resin deposits, felt plugging and excessive foaming. Addition of anionic PAM (Fennobond 85E) reverses fiber charge to anionic (based on zeta potential), providing extra sites for retention of cationic PAE. This results in a wet tensile increase by additional 40%.

Apart from wet end addition, anionic PAM can also be applied to the sheet surface via a size press for improving surface strength, which is needed for reduction of linting. When Fennobond 85E was added via a size press to a testliner, linting was significantly reduced, improving converting efficiency.

**Machine case studies**

**Case study 1: GPAM in testliner for strength improvement, fiber savings and productivity**

A two-layer Fourdrinier machine produces testliner from 100% OCC fibers. It has been difficult to achieve strength targets (especially CMT 30’ and SCT CD) with the current strength chemical program. To meet the targets, basis weight has often been increased above the upper end of the specification.
range, resulting in additional expense. The incumbent chemical program includes cationic starch added into the machine chest, cationic PAM (C-PAM) added into the inlet of the machine chest pump and CMC added into the outlet of the fan pump. The machine is steam limited; therefore, the size press starch is not an option.

Kemira offered FennoBond 3000, a GPAM based product, which was fed into the inlet of the machine chest pump instead of C-PAM. CMC was also off. The trial results are summarized in Figure 4 below.

As demonstrated in Figure 5, addition of FennoBond 3000 at 3 kg/ton (dry basis) resulted in a significant increase in all the strength parameters, allowing the basis weight to remain on target while reducing starch by 11%. As soon as FennoBond 3000 was off and the old strength program was back on the machine, strength went down and the basis weight had to be increased by 3-6% to maintain strength specifications. Higher basis weight resulted in a drop of machine speed by 9%. Overall, the trial results showed an opportunity for significant savings from lowering the basis weight, increased production and reduced starch consumption.

Figure 4: Summary of the testliner trial with FennoBond 3000

Figure 5: Changes in strength parameters, basis weight and machine speed during trial and post-trial
Case study 2: Anionic PAM in folding boxboard for strength increase and fiber savings

A folding boxboard (FBB) manufacturer is looking to increase bending stiffness that could allow for reduction of the basis weight and fiber savings. The FBB sheet has a typical three layer structure with a heavy middle layer (70% of basis weight) made from groundwood/broke and lighter top (20%) and bottom (10%) layers made from a combination of bleached short fibers, long fibers and filler. Cationic starch is normally dosed to each layer at 4.5 kg/ton to control bending stiffness and internal bond strength.

Kemira offered FennoBond 85E (anionic PAM) for addition to all three layers. To ensure retention of anionic PAM, starch was increased from 4.5 to 8 kg/ton. Figure 6 summarizes the trial results. FennoBond 85E allowed for increase in bending stiffness, tensile strength and internal bond strength.

<table>
<thead>
<tr>
<th>Machine overview</th>
<th>Needs</th>
<th>Solution and Benefits</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grade: Folding boxboard</td>
<td>Lighter sheet by improving:</td>
<td>FennoBond 85E (0.4–0.8 kg/t dry) after starch</td>
</tr>
<tr>
<td>Basis weight: 200–330 g/m²</td>
<td>Bending stiffness (top plies)</td>
<td>Starch increased from 4.5 to 8 kg/t to maximize effect of FennoBond 85E</td>
</tr>
<tr>
<td>Machine type: 3 layers, 190 TPD, 150 m/min</td>
<td>Internal bond (middle ply)</td>
<td>Lower basis weight (~6 g/m²) at target bending stiffness</td>
</tr>
<tr>
<td>Furnish: Top: Birch</td>
<td></td>
<td>Higher internal bond strength (+10%)</td>
</tr>
<tr>
<td>Back: Birch, pine</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 7 demonstrates that addition of FennoBond 85E allowed for reduction in the basis weight by 6 g/m², while keeping physical characteristics on target, including the sheet thickness, bending stiffness and tensile strength. Addition of FennoBond 85E into the middle ply improved internal bond by 10% as shown in Figure 8. Overall, the trial showed a potential for 3% savings in expensive fibers from the outside layers and a 10% increase in internal bond.
Case study 3: GPAM in brown towel for dry and wet tensile improvements

A tissue mill producing brown towel from 100% OCC experienced both low wet and dry tensile strength resulting in end-use problems. The towel was torn apart when being pulled out from the dispenser by consumers in order to dry their hands. Kemira offered FennoBond 3000 (GPAM resin) in combination with FennoStrength (PAE resin) to resolve this issue.

As shown in Table 2, the addition of 1,8 kg/ton FennoBond 3000 increased MD dry tensile index by 26%. CD wet tensile index was increased by 17% and the FennoStrength dose was reduced by 19%. In addition, FennoBond 3000 allowed for a machine speed increase by 122 m/min, providing production gains by 11%.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Pre-trial</th>
<th>Trial</th>
<th>% Change</th>
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</thead>
<tbody>
<tr>
<td>FennoBond 3000 dose (kg/ton)</td>
<td>0</td>
<td>1,8</td>
<td></td>
</tr>
<tr>
<td>FennoStrength dose (kg/ton)</td>
<td>4,2</td>
<td>3,4</td>
<td>-19%</td>
</tr>
<tr>
<td>MD dry tensile index (N m/g)</td>
<td>11</td>
<td>14</td>
<td>+26%</td>
</tr>
<tr>
<td>CD wet tensile index (N m/g)</td>
<td>2,2</td>
<td>2,6</td>
<td>+17%</td>
</tr>
<tr>
<td>Reel speed (m/min)</td>
<td>1134</td>
<td>1256</td>
<td>+11%</td>
</tr>
</tbody>
</table>

Case study 4: Anionic PAM in white towel as CMC replacement

A twin wire tissue machine produces white towel using a blend of 60% mixed office waste (MOW) and 40% bleached Kraft softwood (BKSW). Dry tensile and wet tensile are critical targets. A PAE wet strength resin (WSR) at 6-12 kg/ton (dry) is used to control wet tensile. Anionic CMC at 3-6 kg/ton is used to provide dry tensile and to ensure efficient retention of the cationic WSR.
CMC is supplied as dry powder and requires a laborious handling, involving expensive make-down equipment and human resource. The mill is interested in a liquid synthetic alternative to CMC to simplify their process. Kemira offered FennoBond 85E to replace CMC. Figure 9 summarizes the trial results.

As shown in Figure 10, the replacement of CMC at 3 kg/ton with FennoBond 85E at 2 kg/ton maintained the strength targets in both machine- and cross-directions. On transition, when CMC was off and FennoBond 85E was under 1 kg/ton, both dry and wet tensile decreased noticeably, demonstrating the importance of anionic strength aid for both.

**Figure 9: Summary of the towel trial with FennoBond 85E**

**Figure 10: Results for wet and dry tensile and wet/dry ratio (solid lines) from the FennoBond 85E trial relative to the respective targets (dotted straight lines)**
Conclusions
Strength additives are critical components for manufacturing of board and tissue. They provide not only the required strength quality to paper products but can also improve machine productivity and process efficiency. A variety of strength chemistries are available in the market, including natural polymers (starch, CMC) and synthetic resins (PAM, GPAM, PAE). Natural polymers have been dominant in the market due to their availability and a relatively low price. However, synthetic strength resins have been gaining the market share due to their unique benefits, ease of use and versatility.

Kemira offers multifunctional dry strength additives such as FennaBond 3000 (GPAM) and FennaBond 8SE (anionic PAM), the effective permanent wet strength products line, FennoStrength (PAE), and the unique temporary wet strength product line, FennoRez (GPAM). The documented benefits of using Kemira’s strength aids include improved sheet characteristics (strength, bulk), reduced basis weight, a larger use of lower quality fibers, energy savings, increased machine speed, productivity gains and reduced consumption of other chemicals (e.g., starch, wet strength resin, defoamer).

References