Increased Tissue Machine Efficiency and Product Performance Using A Novel, Structured Wet Strength Resin

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ABSTRACT

Wet strength resins are essential performance chemicals used in the production of tissue, towel and napkin grades. Wet strength resins allow these products to retain a significant amount of their tensile strength when wet. A recent innovation has resulted in a step-change in wet strength performance using a technology that employs novel raw materials and a unique manufacturing process. This unique technology has proven to reduce resin dosages by up to forty percent while maintaining wet tensile strength targets and achieving higher maximum wet and dry tensile strength. Lower resin dosage can reduce cost-in-use and reduce the contents of both volatile organic compounds (VOC) and chlorinated by-products. Higher maximum wet tensile strength allows for new grade development, fiber substitution, and other operational improvements such as improved drying and speed capacity through reduced refining. The new wet strength resins can be coupled with unique dry strength chemistries to provide even greater improvements in strength efficiency or tensile development. This paper will demonstrate the improved efficiency and effectiveness of the novel wet strength resin through lab, pilot and commercial case studies.

INTRODUCTION

Tissue products are made from a dilute suspension or slurry of cellulose fibers by drainage of the slurry through a forming fabric to create a wet web. This web is subsequently further dewatered, dried and creped to create the tissue product. Products made from cellulose fibers that have not been treated with a wet strength agent lose their tensile properties rapidly when they become wet and such tissue is said to have very little "wet strength". The wet strength of tissue products is defined as the resistance of the tissue to rupture or disintegration when it is wetted with water. Wet tensile strength of ordinary tissue is only about 5% of its dry tensile strength. Tissue products can range in wet to dry tensile ratios from base levels of about 5% (no chemical wet strength added) to greater than 30% for kitchen towel products.

For decades wet strength resins have been essential performance chemicals used in the production of tissue, towel, napkin and specialty products. Wet strength resins allow these types of products to retain a significant amount of their tensile strength when wet. Various polymer products used to develop wet tensile strength in tissue products have been employed. Polyamidoamine-epichlorohydrin (PAE) wet strength resins have displaced older technologies and are now the primary polymer products used to develop wet tensile strength properties in tissue products.

Wet strength resins are classified as either permanent or temporary, which is defined by how long the paper retains its wet strength after immersion in water. Conventional PAE wet strength resins provide permanent wet strength to tissue products, which means that the tensile properties of the wetted tissue product do not change significantly after prolonged soaking. Conventional resins are typically obtained by modifying polyamidoamine polymers with epichlorohydrin to form the polyamidoamine-epichlorohydrin polymer (PAE), see Figure 1. Most commercially available PAE resins utilize a polyamidoamine backbone synthesized by the step-growth polymerization of a polyalkylene-polyamine and a diacid or diester. This polyamidoamine backbone may be referred to as a

prepolymer. Numerous polyalkylene-polyamine and diacid or diester raw materials are available, but it has been shown that the best permanent wet tensile development has been achieved by PAE resins made from adipic acid and diethylenetriamine (DETA). Crosslinking agents other than epichlorohydrin have also been examined, but the use of epichlorohydrin continues to allow for the best wet tensile development from a modified prepolymer.

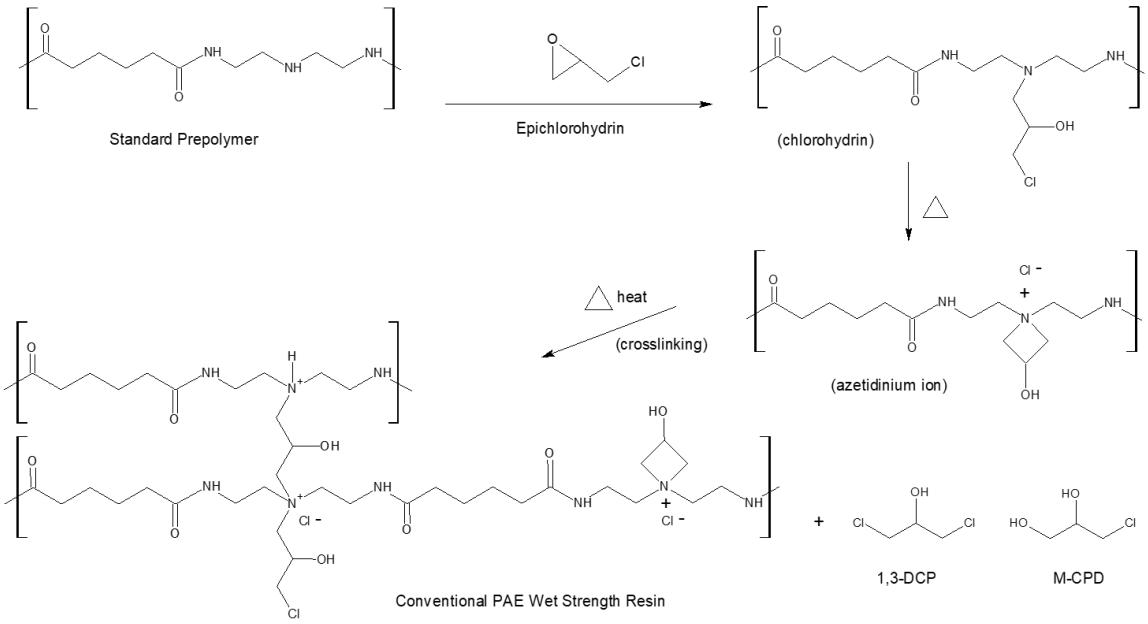

Figure 1. Synthesis of conventional PAE wet strength resin from prepolymer and epichlorohydrin.

Over the past 40 years improvements in PAE resin performance have been gradual and have largely been the result of fine-tuning the existing polymer structure. These incremental improvements in PAE technology have pushed the limits of solids, cost, performance and residual by-product impurities. Further improvements in the development of wet tensile strength in tissue products are gained by effective machine operations and machine process optimizations, but these methods involve many factors operating at once and are difficult and costly to conduct. In order to push the limits of PAE wet strength development in tissue products it was determined that newer technology would need to be developed (1).

It is generally recognized that the wet strength properties of tissue treated with PAE polymers are attributed to the cationic nature and the thermosetting properties of those polymers (2). The two most important characteristics of the molecular structure of a PAE polymer are molecular weight and cationic charge density (3). Molecular weight is generated by crosslinking of the prepolymer backbone with epichlorohydrin, see Figure 1. Charge density is generated by functionalization of the prepolymer free amine with epichlorohydrin to form a cationic azetidinium ion. The reactions that generate molecular weight and cationic charge density are competing reactions, which limits the development of each of these properties in the finished PAE resin products.

New patented technology (4, 5, 6), allows manufacture of high efficiency wet strength resins utilizing a differentiated prepolymer backbone combined with new symmetrical crosslinkers. Further reaction of this new prepolymer intermediate with epichlorohydrin provides a unique polymer structure possessing both high molecular weight and significantly increased cationic charge density that substantially exceeds conventional PAE resin technology. Because the initial molecular weight increase is created from the new crosslinkers, a reduction in epichlorohydrin will achieve the desired final molecular weight necessary to develop good wet tensile strength in paper. Reduced epichlorohydrin affords the new wet strength product possessing lower residual chlorinated alcohol DCP (1,3-Dichloro-2-propanol) and MCPD (3-Monochloro-1,2-propanediol) content than conventional Generation-

1 type PAE resins (DCP and MCPD > 1000 ppm on a liquid basis). This, combined with significant reduction in wet strength usage, allows for an in-use reduction of DCP and MCPD in the papermaking process.

The degree of crosslinking can be easily controlled by the amount of symmetrical crosslinker used, and the reaction yield of crosslinker with prepolymer is essentially 100%. This allows for the molecular weight of the prepolymer – crosslinker intermediate to be selected with high precision in the polymer manufacturing process. The symmetrical crosslinker builds a higher degree of molecular weight and polymer branching than epichlorohydrin does, while consuming less secondary amine on the prepolymer backbone. This allows a greater amount of the azetidinium ion to be formed in the finished wet strength resin product, while also generating the molecular weight necessary to provide differentiated wet tensile development in tissue products. The charge density (meq+/gram solid) of the new commercially available, high efficiency resin is typically 35% higher than that of the best conventional PAE wet strength resins. The high efficiency resin has equivalent molecular weight (range from about 750 to 900 K Daltons, GPC gel permeation chromatography) and Brookfield viscosity (initial range 150 – 170 cP at 25% dry solids) compared to conventional PAE wet strength resins.

RESULTS, ANALYSIS & DISCUSSION

The following lab studies, pilot evaluations and mill trials are provided to demonstrate the greater efficiency and effectiveness of the new structured wet strength technology.

Lab Handsheet Study Premium Towel Grade

An early lab study was conducted to test experimental versions of high efficiency wet strength candidates against standard commercial products prior to a customer trial. Furnish was obtained from a North American tissue and towel producer to prepare handsheets for a premium grade lightweight towel. Commercial resins A and B were obtained directly from a production plant. The relative charge densities of these products compared to the new high efficiency wet strength resins are shown in Table I. The cationic charge density is measured using the Mutek PCD-03 streaming current detector and titration with anionic PVSK. Charge density testing is conducted with very dilute resin in deionized water adjusted to pH 8. At pH 8 the total cationic charge measured is a function primarily of the quaternary azetidinium ion and excludes any unprotonated amine in the polymer. The higher charge densities of the high efficiency resins are a direct indication of their higher azetidinium ion functional group content. There is a linear correlation between the pH 8 cationic charge density and the azetidinium ion ratio measured by quantitative ^{13}C-NMR, see Figure 2.

Table I. Relative charge densities of wet strength resins. High efficiency resin A is a developmental precursor of high efficiency resin B, the current commercial high efficiency product. The two commercial resins are conventional PAE wet strength resin products.

Wet Strength Resin	Relative Charge Density, meq+/gram
Commercial Resin A	0.87
Commercial Resin B	1.00
High Efficiency Resin A	1.20
High Efficiency Resin B	1.35

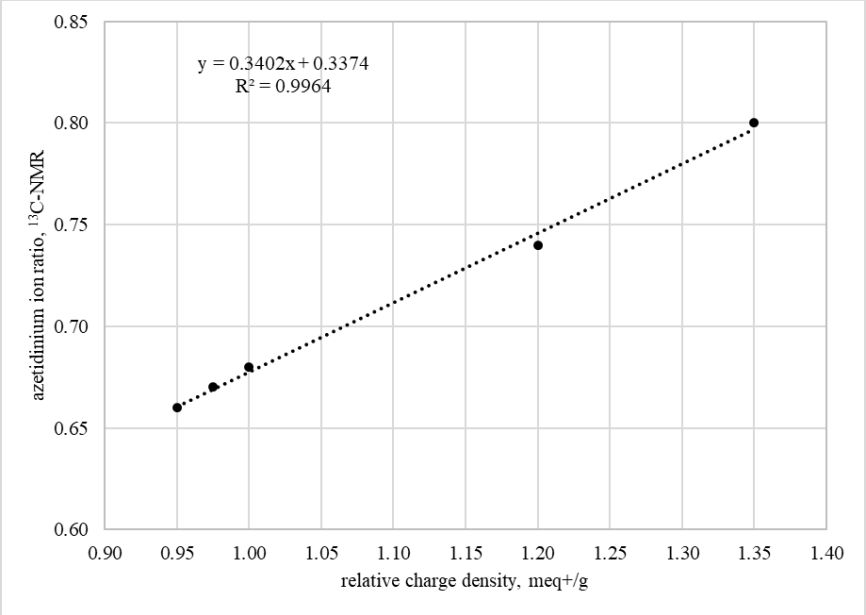

Figure 2. Wet strength resin relative charge density vs. azetidinium ion ratio by quantitative ^{13}C-NMR analysis.

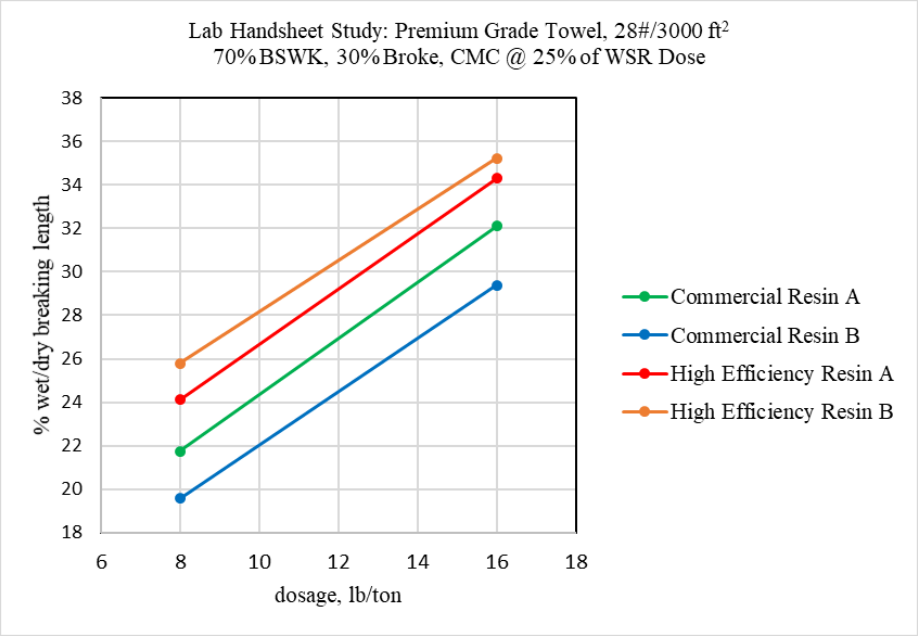

Figure 3. Lab handsheet study for premium towel grade. Wet/Dry breaking length ratio of commercial wet strength resins A and B compared to high efficiency wet strength resin A (developmental phase 1) and B (developmental phase 2, current product).

The results shown in Figure 3 indicate that the high efficiency wet strength resin B provides a 16% dosage reduction to achieve equivalent wet tensile performance compared to commercial wet strength resin A, and a 31% dosage reduction compared to commercial wet strength resin B. This improved performance is a result of the higher azetidinium ion content of the high efficiency resin as indicated in Table I. Higher azetidinium ion content allows for increased polymer retention onto the fiber surface, while also generating a higher degree of resin crosslinking, or cure, in the finished, dried sheet.

Experimental details for a premium grade towel handsheet study. Thick stock was obtained directly from the customer mill. The basis weight target was 28 lb/3000 ft^2. The thick stock consistency was 2.31% at 584 ml Canadian Standard Freeness (CSF) and pH 7.47. The thin stock consistency was adjusted to 1.0% with mill white water. Carboxymethyl cellulose (CMC) was added at 25% of each wet strength dosage level and was added to the furnish after addition of the wet strength resin. Sheets were made with a Noble & Wood sheet former and were pressed once at 40 psi between two blotters. Sheets were passed once around an Adirondack drum dryer at 230 ºF. Sheets were then post-cured in a forced-air oven at 105 ºC for five minutes and then equilibrated to constant moisture content in a CTH room. Wet and dry tensile strength was measured on a Thwing-Albert tensile tester.

Pilot Evaluation in Kitchen Towel Grade on Hybrid TAD Machine

A pilot trial was conducted to evaluate potential strength performance synergies between the high efficiency wet strength resin and a recently commercialized anionic reactive dry strength resin. Programs consisting of cationic wet strength coupled with an anionic dry strength are commonly used in premium towel grades that require high levels of both wet and dry strength for end use performance. The dual polymer combination employing the high efficiency wet strength resin with the reactive dry strength resin presents a unique opportunity to enhance polymeric network reinforcement of fiber-fiber bonding to develop end use requirements for very high levels of wet and dry strength.

Dry tensile results for the dual polymer program, expressed as the dry geometric mean tensile index, are shown in Figure 4. The program dosage rates are expressed in units of kg product actives/MT of dry fiber. The first value is the dose of the high efficiency wet strength resin (WSR) and the second value (if added) is the dose of the anionic dry strength resin (DSR). It is important as the WSR dose increases to balance the added cationic charge with an anionically charged DSR to improve WSR retention and to keep the wet end charge balanced. The percentage increases in dry tensile index are shown above the conditions. The dry tensile more than doubles for a dose of 5 kg/MT of the high efficiency WSR and can further improve to 174% over the control with an added 2 kg/MT of anionic reactive DSR. Finally, a further increase to 7.5 kg/MT of WSR at the same 2 kg/MT DSR improves the dry tensile to 196% over the control value.

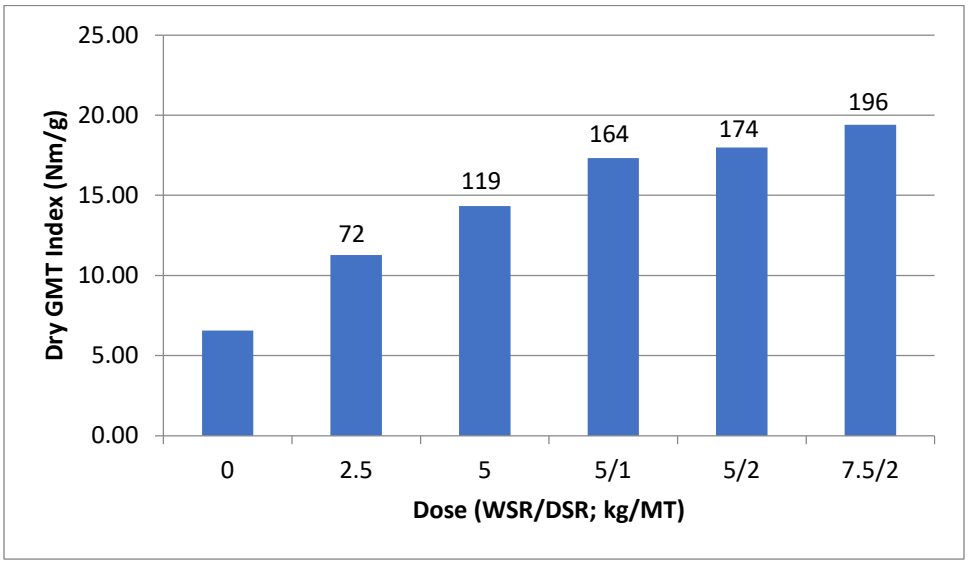

Figure 4. Hybrid TAD pilot machine results for geometric mean dry tensile index on a kitchen towel grade. WSR = high efficiency cationic wet strength resin; DSR = anionic reactive dry strength resin. Values above the bars are the percentage increases in dry tensile compared to the control condition.

Similarly, the wet tensile results for the dual polymer program, expressed as the CD wet tensile index, are shown in Figure 5. The measured wet tensile values are shown above each bar. The wet tensile improvements showed a similar trend as observed for the dry tensile with good improvements provided by the high efficiency WSR by itself and in combination with the anionic DSR.

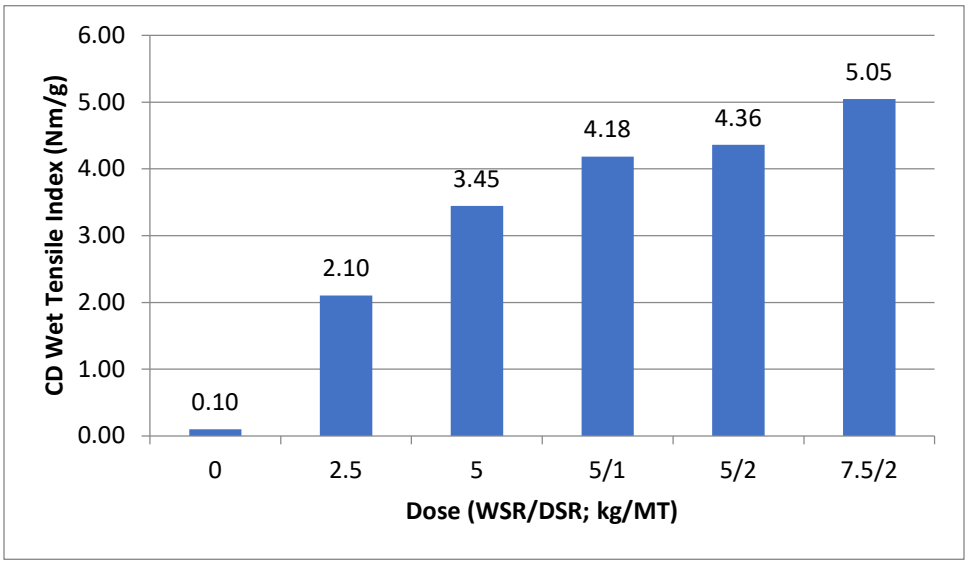

Figure 5. Hybrid TAD pilot machine results for CD wet tensile index on a kitchen towel grade. WSR = high efficiency cationic wet strength resin; DSR = anionic reactive dry strength resin.

Finally, the calculated wet/dry tensile ratios, expressed as a percentage, are shown in Figure 6. The results show a plateau at about 30% wet/dry with the addition of 5 kg/MT of the high efficiency WSR due to approximately equal increases in dry and wet tensile as WSR and DSR dosages are increased. However, a further improvement to 33.5% wet/dry was observed at the highest levels of 7.5/2 kg/MT of WSR/DSR.

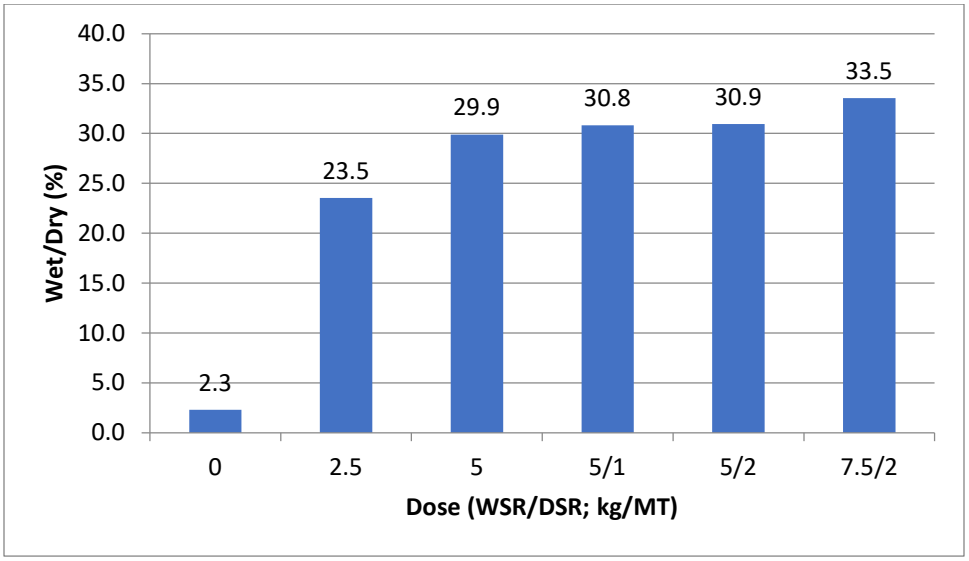

Figure 6. Hybrid TAD pilot machine results for the wet/dry tensile ratio on a kitchen towel grade. WSR = high efficiency cationic wet strength resin; DSR = anionic reactive dry strength resin.

Experimental details for kitchen towel grade pilot evaluation**.** The pilot machine had a Yankee width of 1 meter and was run at a Yankee speed of 1000 m/minute during this trial. The crepe ratio employed was 17%. The

basis weight of the towel was targeted for 21 g/m^2 utilizing a furnish consisting of 60% softwood and 40% hardwood dry lap pulps. The fiber composition was uniform in the z-direction; no layering was employed. The softwood was refined only at a low base level of 40 kWh/T.

Commercial Mill Trial – Recycle Towel and Napkin Grades on a Dry Crepe Machine

A one-week screening trial of the high efficiency wet strength resin was run on a dry crepe machine producing recycle towel and napkin grades. The commercial wet strength resin was a competitive PAE conventional product having lower total resin concentration (21%) than the high efficiency wet strength product (25%). Dosage rates for the two resins are given on a dry solid basis in Figure 7.

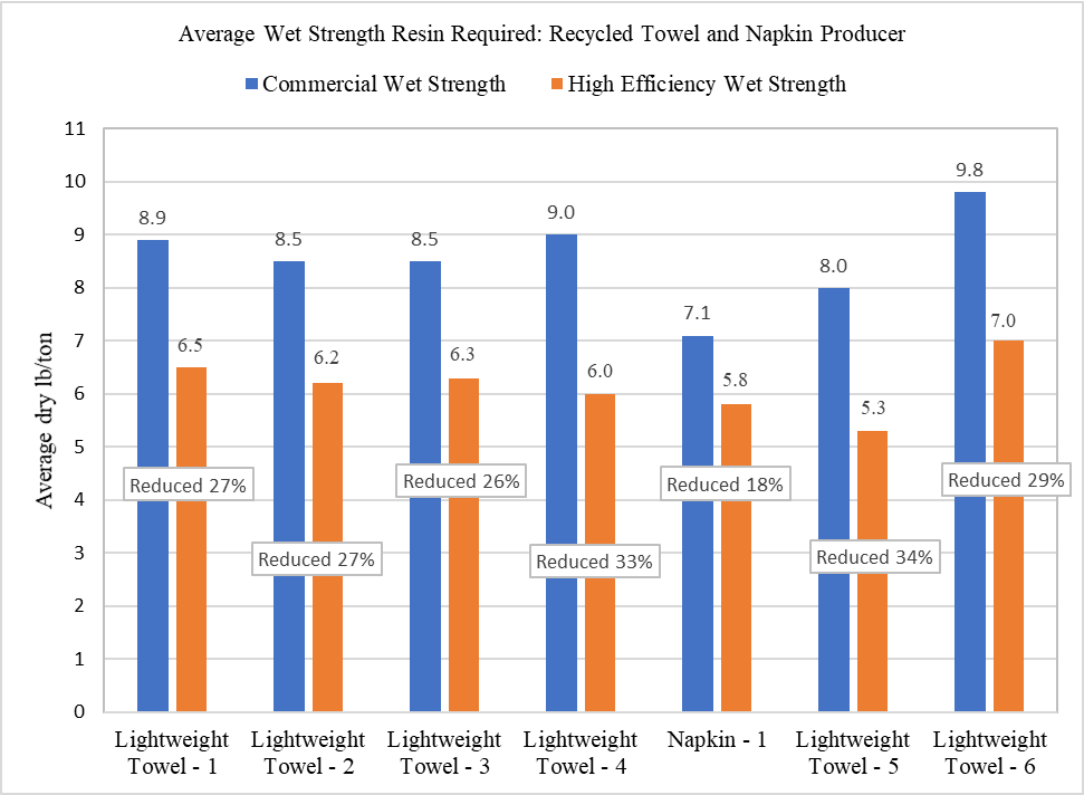

Figure 7. Mill trial on a different recycle towel and napkin grades on a dry crepe machine. Average wet strength resin dosage rates are provided above the bars, and dosage reduction using the high efficiency resin are shown in the boxes.

The wet strength dosage reductions of the high efficiency wet strength ranged from 18 to 33%, with only one grade less than 26% reduction in usage. As shown in Figure 8 the high efficiency wet strength resin generates a higher resin wet tensile index than commercial wet strength products allowing reduced resin dosage rates while delivering equivalent tensile results. The resin tensile index is defined as the CD wet/dry ratio divided by the wet strength dosage rate in dry pounds/ton. This calculation provides the best way to judge wet strength resin performance with fluctuating dry tensiles and is often used as a relative process measurement tool for determining wet strength efficiency. This index is useful in comparing identical grade and basis weight production runs over time as a detection method to flag wet strength process changes attributable to various known, or unknown, process changes. Resin index is a good tool for comparison of various wet strength resins against each other on the same machine and grade of tissue or towel. This index cannot be used across grades, machines, or basis weights.

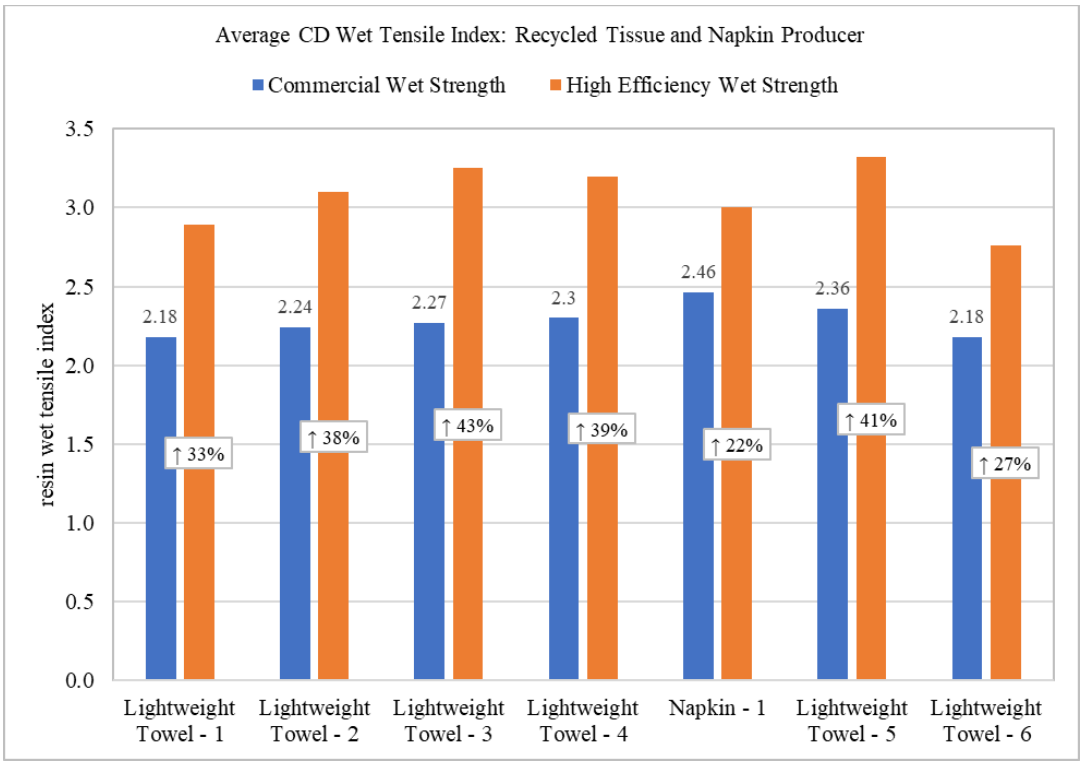

Figure 8. Mill trial on recycle towel and napkin grades on a dry crepe machine. Average CD tensile index of commercial wet strength and high efficiency wet strength resins.

The resin wet tensile index by grade during the trial of the high efficiency wet strength resin ranged from 22% to 44% higher compared to the baseline data. As a result of the performance improvements seen in the screening trial of the high efficiency wet strength product, the trial was extended on the same dry crepe machine producing recycle towel and napkin and virgin towel and napkin grades. The data average for the incumbent commercial wet strength resin was collected over several months leading up to the trial of the new high efficiency wet strength product.

The results in Figure 9 below indicate that during the extended trial the dry dosage level of the new high efficiency wet strength product was able to be reduced an average of 31% across all grades compared to the incumbent commercial wet strength product. Use of the new product allows for an increased operating window where wet tensile targets were consistently met for new developmental heavyweight grades (*heavyweight grade towel 2) that were not met with the incumbent program. During the trial and the subsequent conversion to the new wet strength resin the strength program met the mill target operating expenses. The new high efficiency wet strength resin also has a higher resin concentration than the incumbent product, leading to a considerable reduction in deliveries of wet strength product.

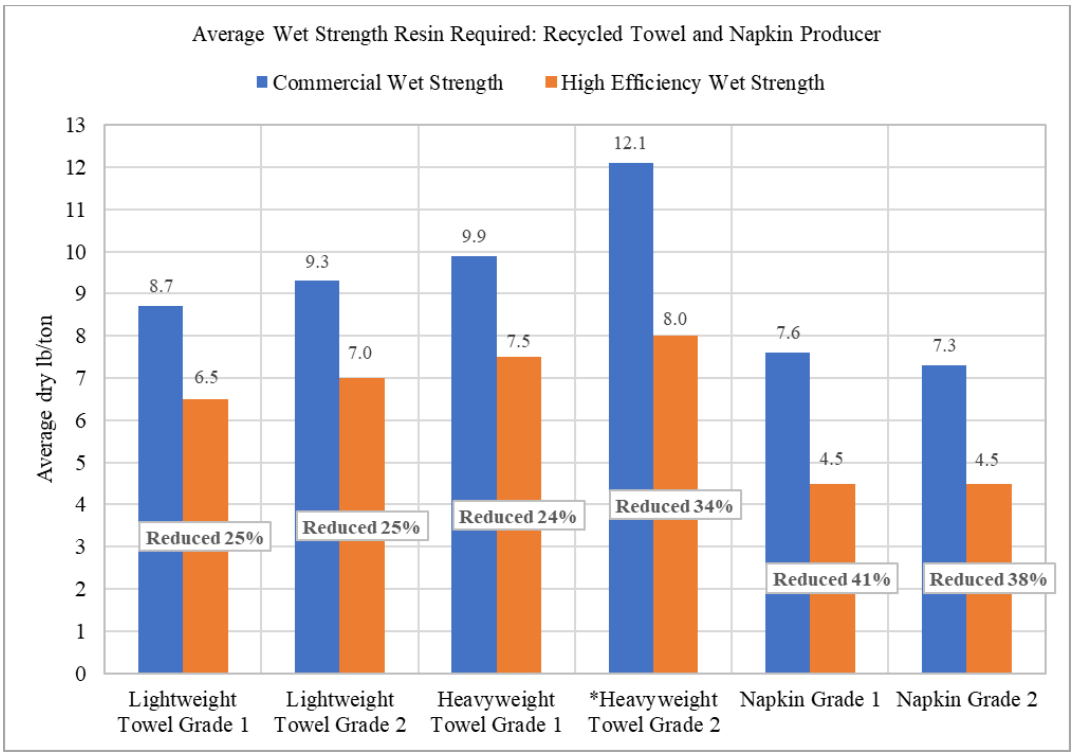

Figure 9. Mill trial and machine conversion on recycle towel and napkin grades on a dry crepe machine. Average wet strength resin dosage rates and percent reduction in dosage rate of high efficiency wet strength by grade. The wet strength dosage reductions for the high efficiency wet strength resin ranged from 24% to 41% on all grades produced.

Mill Trial TAD Towel, Napkin and Facial Tissue Grades

The high efficiency wet strength resin was initially screened over a ten-day period at a major North American producer of towel, napkin and facial tissue on multiple Through Air Drying (TAD) machines. The objective of the trial was to evaluate the new wet strength product for improved wet strength efficiency and cost savings to the mill. Machine runnability had to be maintained and paper quality specifications met. The high efficiency wet strength was trialed in back-to-back comparison with a standard commercial PAE wet strength resin. The high efficiency resin was added at the same addition points as the commercial resin. Wet end testing was conducted throughout the trial and the wet end charge remained consistent with historical testing. Results are shown in Table II and Figures 10-13.

Table II. Mill trial on TAD machine producing tissue, towel and napkin grades. Comparison of dosage rates, dosage rate reduction of high efficiency wet strength resin and CD-tensile index of high efficiency wet strength resin compared to conventional wet strength resin on the same grades. The dosage rates given for each wet strength resin product are the optimized rates (dry lb/ton).

	Optimized Dosage Levels					
Grade	Commercial WSR lb/ton	High Efficiency WSR lb/ton	lb/ton % Reduction	Commercial WSR CD-Index	High Efficiency WSR CD-Index	CD-Index % Increase
Facial Tissue	3.75	3.0	20	4.42	5.67	28
Premium Napkin	6.8	5.7	16	2.59	3.28	27
Facial Tissue	3.1	1.9	39	7.03	10.31	47
Value Towel	5.0	4.6	8	4.00	4.67	17
Premium Towel	5.3	4.1	23	4.09	5.29	29
Value Towel	4.8	4.4	8	4.17	4.64	11
Premium Towel	5.0	4.0	20	4.12	5.30	29
Premium Towel	6.0	5.0	17	NA	NA	NA
Value Towel	9.7	7.5	23	2.25	3.10	38
Napkin	9.7	8.7	10	1.93	2.51	30

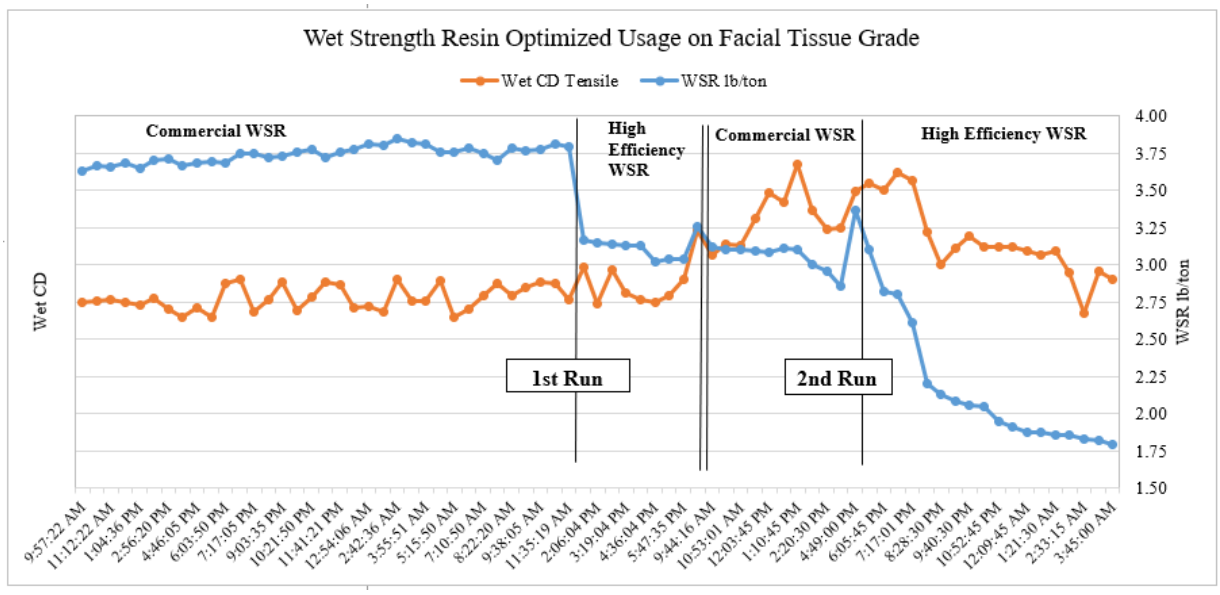

Figure 10. Mill trial on TAD facial tissue grade. The high efficiency wet strength resin provided a 20% reduction in usage in one run and a 39% reduction in the second run, in back-to-back comparisons with the commercial wet strength resin. Wet CD values are not displayed.

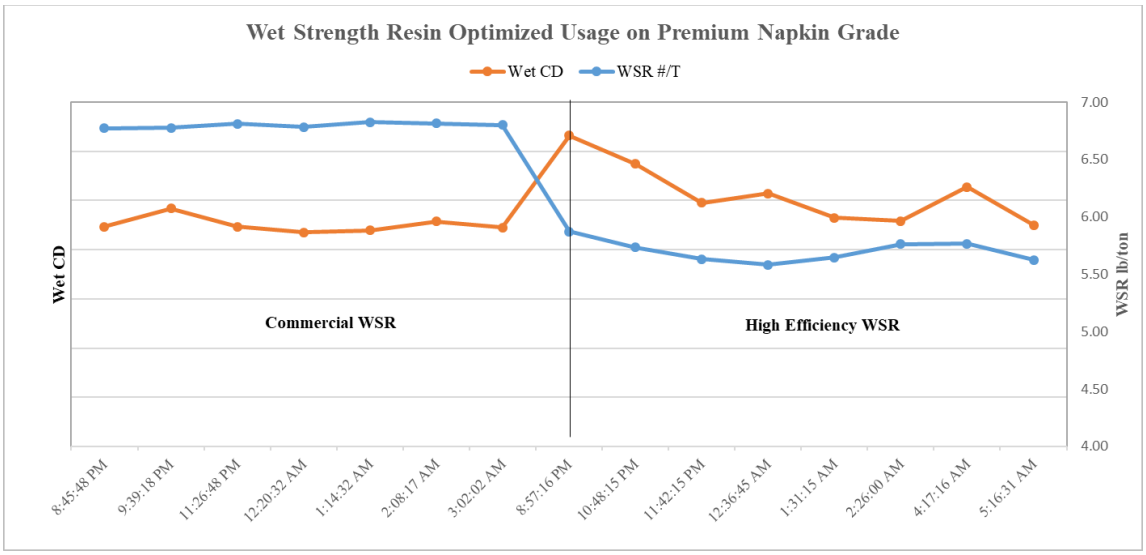

Figure 11. Mill trial on TAD premium napkin grade. The high efficiency wet strength resin provided a 16% reduction in usage in a back-to-back comparison with the commercial wet strength resin. Wet CD values are not displayed.

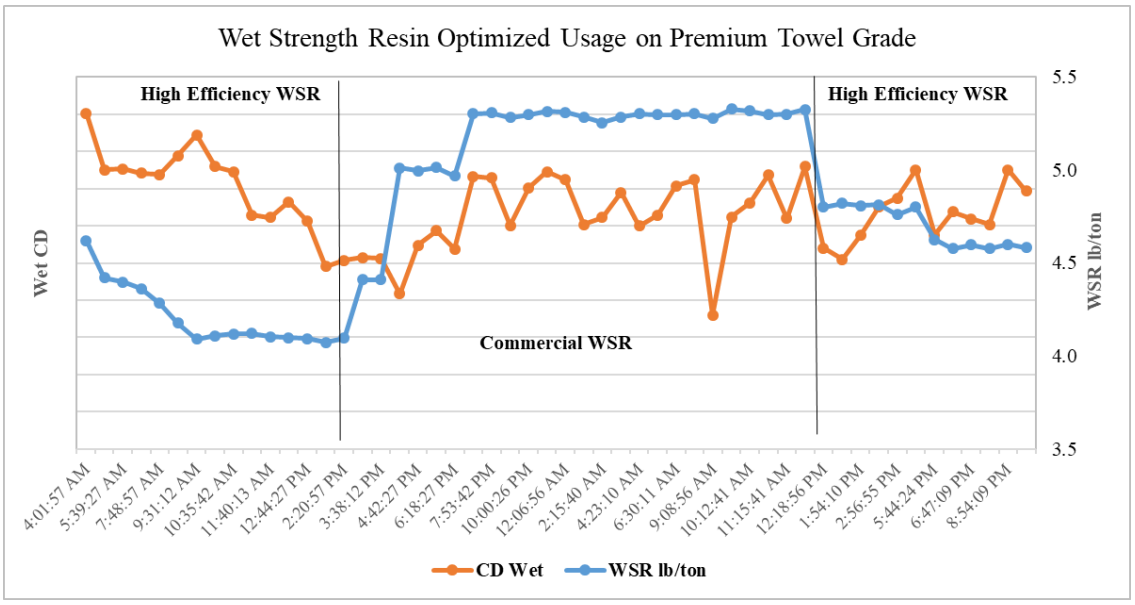

Figure 12. Mill trial on TAD premium towel grade. The high efficiency wet strength resin provided a 23% reduction and a 15% reduction in back-to-back comparisons to the commercial wet strength resin. Wet CD values are not displayed.

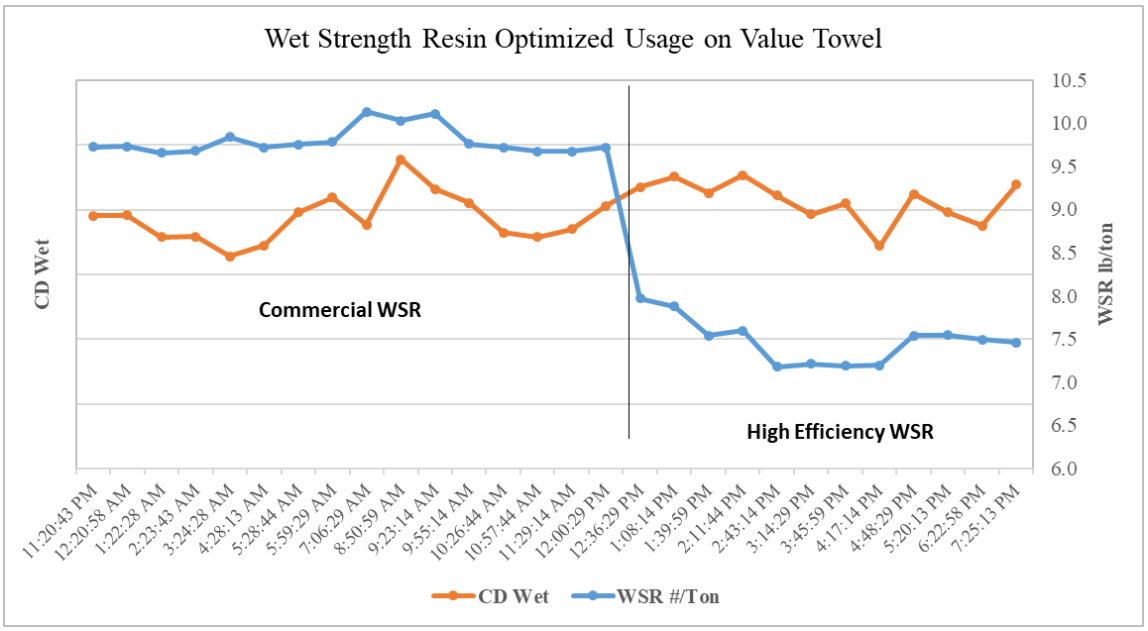

Figure 13. Mill trial on TAD value towel grade. The high efficiency wet strength resin provided a 23% reduction in back-to-back comparisons to the commercial wet strength resin. Wet CD values are not displayed.

After the initial ten day screening trial the mill ran a forty day trial to evaluate the new high efficiency wet strength resin against the same current commercial wet strength product. The trial objective was to convert the mill on a permanent basis to take advantage of the lower wet strength use and cost and higher wet tensile development. The target grades of the trial were TAD premium towel, value towel, napkin and facial tissue. The results of the trial are discussed below in Tables III-IV and Figures 14-15.

Table III. Mill trial on TAD towel, napkin and facial tissue grades. Summary of average wet strength resin dosage rates and reduction in dosage rate of high efficiency wet strength, tensile index and increase in tensile index of high efficiency wet strength compared to commercial wet strength resin.

Grade	Commercial WSR lb/ton	High Efficiency WSR lb/ton	lb/ton % Reduction	Commercial WSR Index	High Efficiency WSR Index	% Difference WSR Index
Napkin	6.2	5.6	10	2.94	3.30	12
Value Towel	6.7	5.7	15	2.82	3.34	18
Premium Towel	7.4	5.8	22	2.82	3.53	25
Premium Napkin	6.2	4.8	23	3.26	4.13	27
Facial Tissue	3.9	3.3	15	5.15	7.22	40
Facial Tissue	3.8	2.6	32	5.55	7.82	41
Value Towel	14.6	11.5	21	1.39	1.94	40
Premium Towel	14.3	11.3	21	1.49	1.80	21
Average			20			28

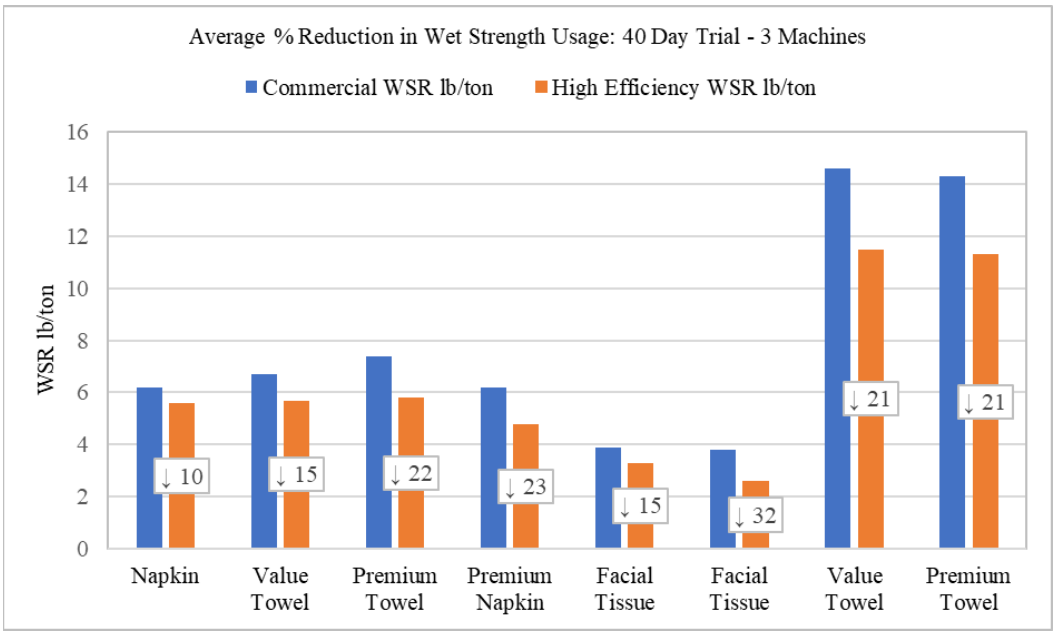

Figure 14. Mill trial on TAD towel, napkin and facial tissue grades. Average wet strength dosage required to meet quality specifications for each wet strength resin and reduction in wet strength usage of the high efficiency wet strength resin compared to the commercial wet strength resin for each grade produced over a forty day trial. The commercial wet strength resin data is the average of a two month run on the same grades before the start of the trial of the high efficiency wet strength resin.

As shown in Table III and Figure 14 the high efficiency wet strength resin allowed for reduction in wet strength dosage rates ranging from 10% to 23% across all grades produced.

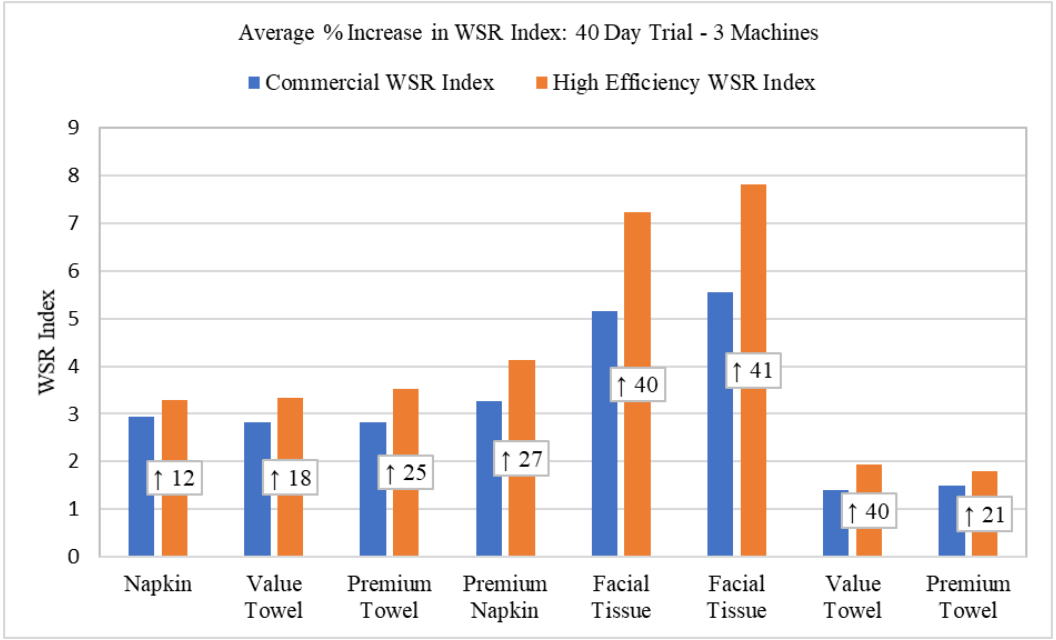

Figure 15. Mill trial on TAD towel, napkin and facial tissue grades. Average tensile index and increase in tensile index of high efficiency wet strength resin compared to the commercial wet strength resin on each grade produced on multiple machines over a forty day trial. The commercial wet strength resin data is the average of a two month run on the same grades before the trial of the high efficiency wet strength resin.

Table IV. Mill trial on TAD towel and napkin grades. Dry strength resin addition rates during runs of commercial wet strength resin and high efficiency wet strength resin on three grades produced on one machine.

Grade	Commercial WSR lb/ton	DSR lb/ton	High Efficiency WSR lb/ton	DSR lb/ton	% Reduction DSR
Napkin	6.2	2.3	5.6	1.8	22
Value Towel	6.7	2.0	5.7	1.4	30
Premium Towel	7.4	4.8	5.8	4.5	6
Average					19

During the trial of the high efficiency wet strength resin on one machine the dry strength resin usage was reduced by an average of 0.5 lb/ton (6 – 30% depending upon grade) while attaining equivalent dry tensile levels. This reduction offers a significant cost savings potential beyond the reduction in wet strength resin use.

The results of the extended trial show that the wet strength usage was reduced across all grades by an average of 20% (a range 10 – 32%) with the use of the high efficiency wet strength resin. The tensile index was increased across all grades by an average of 28% (a range 12 – 41%) with the use of the high efficiency wet strength resin.

The improvement in the wet strength performance of the high efficiency wet strength allowed for new grade development on higher wet test grades, higher wet/dry grades and higher wet/dry with lower dry tensile for improved softness on TAD machines. A reduction in resin usage along with an increase in wet strength resin solids from 21% to 25% reduced the wet strength consumption at the mill by approximately 800,000 lbs/year and allowed for reduced delivery cycles to improve inventory management and improve the safety aspect of handling chemicals. Additional cost savings with conversion to the high efficiency wet strength resin include a reduction of 0.5 lb/ton of the dry strength resin used on one machine and reduced felt filling. The benefits of reduced felt filling with less wet strength usage include longer felt life, improved water removal, increased tonnage and reduced holes and breaks. The high efficiency wet strength resin improved the wet end stability with improved flow consistency compared to the incumbent commercial product.

This mill converted all machines to the new high efficiency wet strength product and strength chemistry program (wet and dry strength resins). The mill ultimately realized a 24% reduction in total annual strength chemistry spend after optimization of the new strength chemistry program.

CONCLUSIONS

This new structured PAE wet strength technology is covered by a patent family protecting the composition, the manufacturing process and the methods of using the technology. The proprietary chemistry and manufacturing technology produce increased wet strength functional group content, greater molecular weight control, increased cationic charge density and reduced AOX (adsorbable organic halogen) compared to conventional Generation 1 PAE products. Greatly reduced resin usage rates allow for further reduced AOX content in-use. The application of this new structured PAE wet strength has allowed for significant wet strength efficiency gains in existing grades and creates potential for the development of new grades. One example of even higher strength development for potential new grades is shown by combining the high efficiency wet strength resin with an anionic reactive dry strength resin.

In every mill trial or conversion using the new high efficiency wet strength product, wet strength resin usage has been reduced by 15 – 40%, varied by grade and machine, with excellent machine operation. This has resulted in cost-in-use reductions by similar margins of 5 – 40%. The new wet strength resin technology has been proven in multiple furnish types including recycle and virgin fiber, both bleached and unbleached. Grade applications have included tissue, towel, napkin and specialty products. Additional benefits have been noted during trials and on

converted machines, including increased dry tensile strength, improved retention and drainage, increased machine speed, reduced felt filling, and significantly reduced material handling.

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