

NEW MICROPOLYMER TECHNOLOGIES FOR INCREASED DRAINAGE AND RETENTION FOR BOTH WOOD AND NON WOOD CONTAINING FURNISHES

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ABSTRACT

The ability to control filler performance and fines retention is vital in the development of both filled and non filled grades, respectively. This is very important when achieving the desired sheet structure necessary to maximize machine performance and end user demands. A narrow balance exists in attaining the desired retention and formation particularly in systems with heavier ash loads and producing paper and paper board on higher speed high shear equipment.

A new generation of both cationic and anionic micropolymer technologies has been developed. These water based chemistries are volatile organic compound (VOC) and alkyphenol ethoxylate (APE) free. When these novel micropolymers are applied with linear poly-acrylamide or in conjunction with inorganic microparticle technologies (such as silica or swellable minerals), substantial increases in drainage, fibre retention and ash retention are observed. These improvements have been observed not only in high filled wood and non wood containing grades such as fine paper and super calendared sheets (SCA), but also in low filled newsprint grades. Of particular note is the drainage improvement seen with the application of the cationic micropolymers in unbleached packaging grades with poly-acrylamide.

INTRODUCTION

During paper manufacture a narrow balance exists when achieving the optimal retention in the process for maximizing runnability, while obtaining the desired sheet formation. Dispersed colloids deposit onto fines and fibres to form "flocs" which are retained by filtration [1]. The adsorption of these small particles becomes a greater challenge as the furnish is exposed to increasing hydrodynamic shear stress as machine speed is increased [2,3]. Further complexity is introduced when ash containing furnishes are used and the ash constituent is elevated, intensifying the demand on retention systems.

High molecular weight long chain polymers, poly-acrylamides (PAM's), are efficient for gross retention. These low charged polymers are generally linear. Although branched or structured versions are sometimes used, the linear versions are the most common structure applied. PAM's generally require the development of a larger floc via a bridging mechanism to obtain sufficient retention of fines and filler. The sheet structure created is often referred to as "hard flocced" or macro flocculated. In the presence of filler, PAM's can agglomerate filler particles. By effectively

increasing the average particle size of the mineral, optical efficiency can be compromised. With the changes in filler distribution within the sheet and particle size, both opacity and formation can be adversely affected, as well as other physical properties.

In addition, a substantial level of "bound" water is present within the floc often hindering the pressing efficiency of the sheet. Higher dewatering rates may be observed in the forming section of the paper machine, but the net water removal after the press section may be lower [4]. The result can be slower machine speeds or higher steam demands. Runnability can be also compromised if the bound water becomes excessive resulting in sheet crushing and picking. In manufacturing processes that utilize high efficiency presses such as an extended nip press (ENP), this loss in pressing efficiency can be very prohibitive.

High charged low molecular weight polymers allow for fixation or patch retention of fillers, fines, and detrimental substances. Although they can improve drainage in some systems through soluble charge control, they are limited in their ability to maintain retention because of the lack of floc structure. Moreover, sufficient application rates to obtain the desired drainage effect, can lead to an excessive decrease in cationic demand. This can inhibit retention of other process additives as well as the principle furnish components.

A new generation of micropolymer technology enables a floc and subsequent sheet structure to be created that maximizes drainage in the former without compromising pressing efficiency. This technology is also very efficient for retention of both calcium carbonates and kaolins. These polymers are synthesized with either cationic or anionic charge, which enables this chemistry to be reactive across the majority of wood and non wood containing grades.

PROPERTIES AND MECHANISMS

The following figure illustrates how the charge and molar mass of the cationic versions of the micropolymers relates to the conventional linear cationic PAM's and short chain high charge density coagulants.

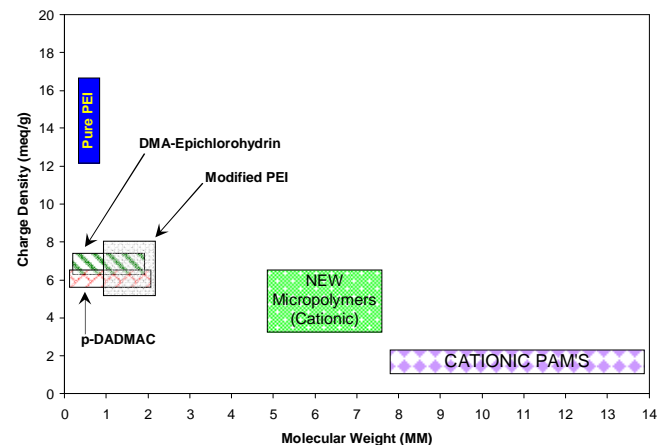


Figure 1. Charge Density versus Molecular Weight for Various Cationic Polymers

The illustration shows the unique combination of molecular weight and charge density of the cationic micropolymers. In

addition to these properties, they possess a unique structure and composition.

These polymers are synthesized using a controlled molecular weight cationic polyacrylamide polymerized within a coagulant matrix. The end result is a system of high charge density low molar mass polymers and higher molecular weight medium cationic polymers. This system is depicted in the following illustration.

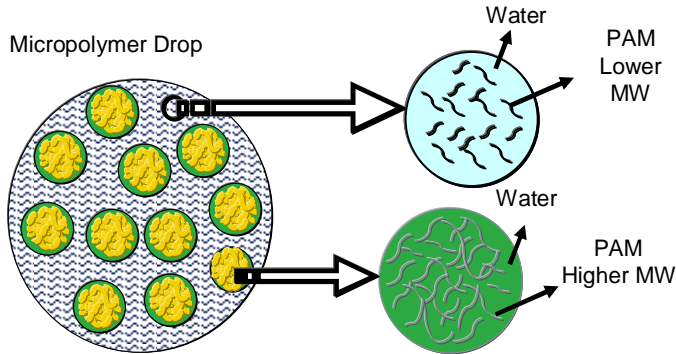


Figure 2. Schematic of New Micropolymer Technology

This chemistry can also be produced using an anionic system of anionic acrylamide, which allows for the development of anionic charged polymers.

The micropolymers are highly structured polymers demonstrating very little linearity. This is largely due to the inclusion of hydrophobic associative groups in the synthesis. These groups increase the number inter and intra molecular interactions as shown in the following figure.

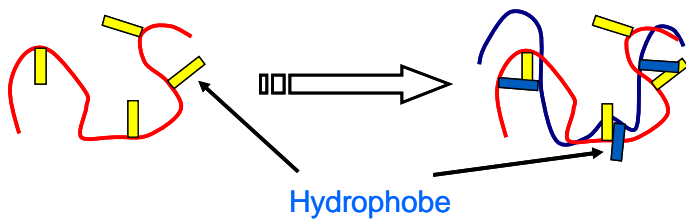


Figure 3. Schematic of Association of Hydrophobic Monomers

These associations or interactions build a very highly structured polymer, creating a three dimensional micro-network that is estimated to be 50 nanometres (nm) in size as determined by Zimm analysis. Because the structure is created without truly cross-linking the polymer constituents, the charge of the polymer is very accessible, increasing reactivity. Recent work has shown that this structure is preferred for retention of clays and carbonates [5]. Data suggests that there is selectivity for ash. The structure is illustrated in Figure 4.

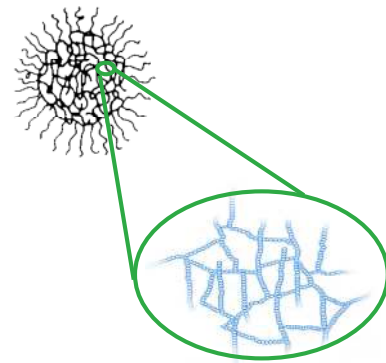


Figure 4. Micropolymer Structure and Network

Although the charge is highly accessible, a considerable portion is buried in the network and requires some shear to expose it. This is referred to as the ionic regain. Consequently, it should be noted that the charge density data for this chemistry in Figure 1 is determined by streaming potential and does not represent the total charge available within the micropolymer structure. This combination of charge and structure allows the polymer to control anionic trash through fixation while retaining fibres and fillers. The control of detrimental substances is necessary in many systems in order to maintain efficiency of process additives such as starch and sizing agents [6]. The floc structure created is not only efficient for retention, but it also improves sheet dewatering through the former and press. Fines and fillers are flocculated along the long fibres as small discrete flocs, which minimizes the level of bound water. This structure reduces the blocking of inter-fibre pores. A greater level of water can be removed from the former and this dewatering can continue through the press section. An illustration comparing the floc structures created with a micropolymer versus conventional long chain linear polymer is shown below.

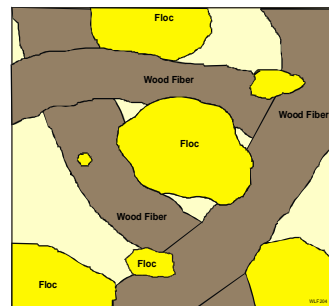


Figure 5a. Conventional System Flocculation Mechanism

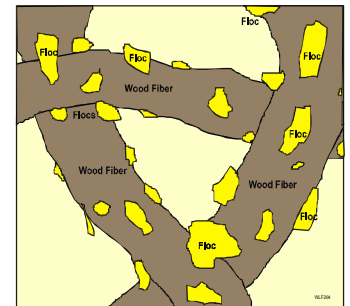


Figure 5b. Micropolymer Flocculation Mechanism

An additional advantage of the floc structure depicted by Figure 5b is the improved fines and ash distribution due to the flocculation along fibre surfaces. This can bring about increases in strength and improved optical properties.

Finally, this micropolymer technology is made without oil. They are not emulsions, and as such, do not contain volatile organic compounds (VOC's) or alkyphenol ethoxylate.

LABORATORY EVALUATIONS

Bench studies were done with a mechanical fibre containing furnish containing precipitated calcium carbonate (PCC) filler. The furnish also contained deinked fibre (DIP) which was very rich in residual ink. The effective residual ink concentration (ERIC) values for the furnish was approximately 220 ppm.

The furnish mixture is approximately 50% thermo mechanical pulp (TMP) and 50% DIP. The ash load ranged between 4% and 8% PCC. The morphology of the PCC was scalenohedral. Retention studies were conducted using a Dynamic Drainage Jar (DDJ) and stock drainage was determined using the Modified Schopper Reigler Drainage Tester (MSR). In addition optical properties, in particular brightness was determined via handsheets. Figure 6 shows the impact of various polymer technologies on brightness. The cationic micropolymers vary by molecular weight, charge, and the type of coagulant chemistry.

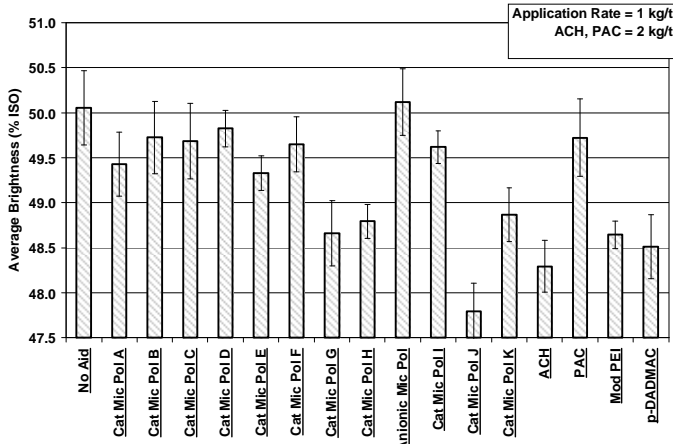


Figure 6. Brightness Impact for Various Polymer Technologies
Error Bars Represent +/- 1 Standard Deviation

The data shows that anionic micropolymer has the least impact on brightness, although several of the cationic micropolymers reduced brightness values by less than 1/2 a point compared to the non treated sample. (The data shows that the average for two standard deviations is approximately one brightness point). The familiar brightness reversion associated with the some of the more common organic coagulants, such as polyethyleneimine (PEI) and diallyldimethyl ammonium chloride (p-DADMAC), is also observed. The retention and drainage data is presented in the following graph.

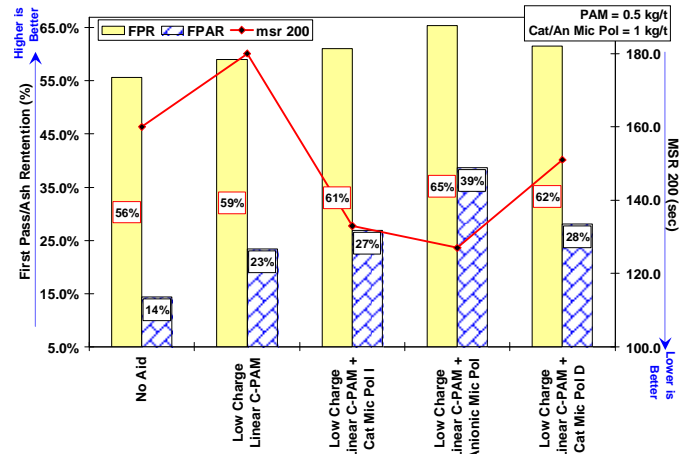


Figure 7. Retention and Drainage Data for Micropolymer Technologies

The data shows reactivity of the anionic micropolymer with respect to the improved drainage and ash retention. This is novel for anionic micropolymers, since most emulsion anionic micropolymer do not sustain their reactivity in highly contaminated furnishes, particular those containing mechanical fibre. Figure 8 shows the brightness response with increasing PCC load for both the anionic micropolymer and cationic micropolymer systems.

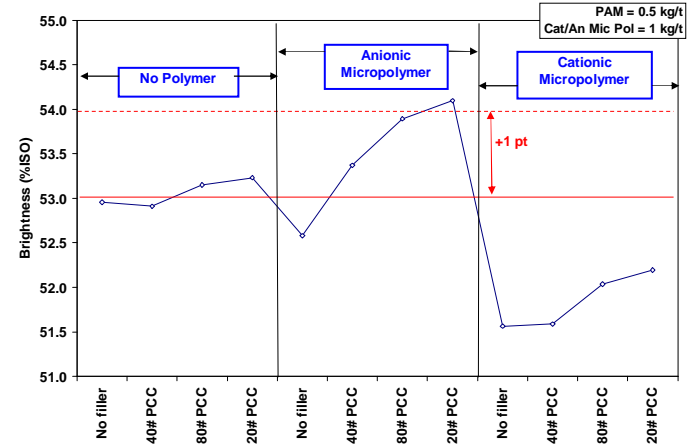


Figure 8. Brightness versus Ash Load with Micropolymer Technologies

The high ash retention observed in Figure 7 coupled with increase in brightness demonstrates the selectivity for ash, when using the anionic micropolymer in the ink rich environment. This is in contrast to the cationic micropolymer which is able to increase brightness as the ash load is ramped up, but it is not sufficient to overcome the brightness loss due to the retention of ink and low brightness fines.

PILOT STUDY

A pilot machine evaluation was conducted using 100% old corrugated container (OCC). The stock was pulped on mill site and then refined in the pilot process to a freeness of 395 CSF. The fines content was approximately 47% defined as all fibre with a length less than 0.20 mm. The pilot machine ran at a speed of 1.7 m/min with the press was set at a load of 140 PLI (pounds per linear inch). The white water system was charged with a mixture of process white water and

fresh water. The equilibrium soluble charge was 80 meq/L and the zeta potential was -14 mV (millivolt) measured at the headbox.

Several cationic polymers were evaluated. Each chemistry was evaluated in conjunction with a dry anionic PAM and alumina chlorohydrate. A list of the cationic polymers is shown:

- Modified PEI
- Three (3) Cationic Dispersion Micropolymers
 - Varying molecular weight, charge density, and coagulant chemistry

The primary objective of the evaluation was to determine the pressing efficiency for each chemistry. And relate it to the resulting sheet structure. The sheet structure was determined by Gurley porosity measurement. Pressing efficiency was determined by measuring the solids rise of the sheet between the couch roll and the exit of the single nip press. The data is shown in Figure 9.

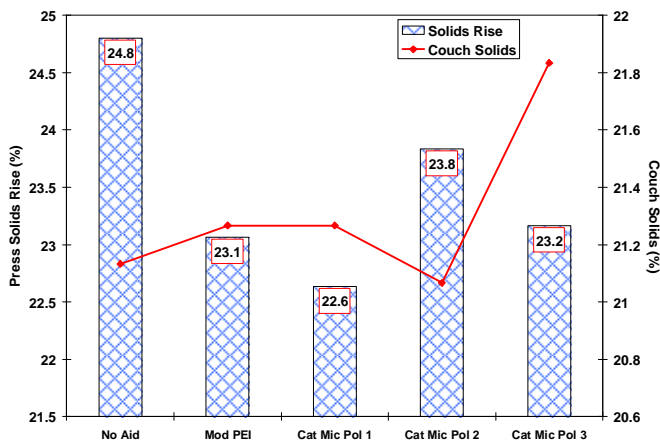


Figure 9. Press Solids Rise and Couch Solids for Pilot Machine Evaluation

The data shows two of the three cationic micropolymers equalling and improving the press solids rise compared to modified PEI, which has been established as an efficient chemistry for pressing [4,7]. The highest press solids rise is achieved with the zero application condition. With minimal floc structure, there is little or no bound water. Because dewatering occurs both on the former and in the press section, the impact of not treating the stock needs to be considered on the former drainage. The data from Figure 9 does not show appreciable differences in the couch solids due to the very low turbulence associated with the low machine speed associated with the pilot machine (1.7 m/min). This coupled with the minimal vacuum in this system make it difficult to differentiate the table drainage. To better quantify sheet drainage, stock from each condition was tested using a Dynamic Drainage Analyzer (DDA). The results are shown in Figure 10.

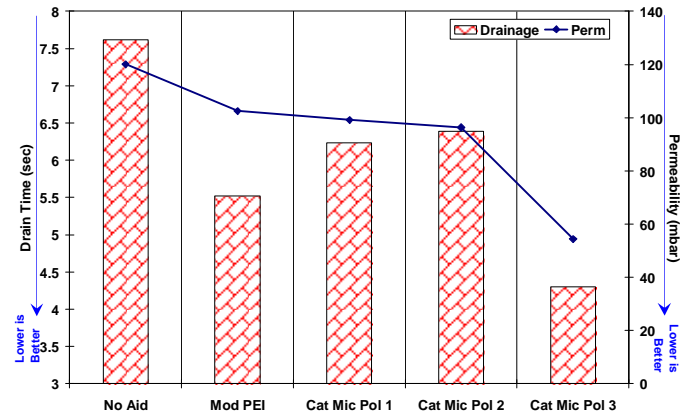


Figure 10. Dynamic Drainage Analyzer Evaluation

A loss in drainage is observed when the stock is not treated (no aid). Drainage is comparable for the treated samples, although cationic micropolymer 3 increases the drainage rate beyond the other samples. This is also shown in the permeability data, which gives an indication of the residual moisture.

Figure 11 shows the Gurley porosity data for each polymer condition run on the pilot machine.

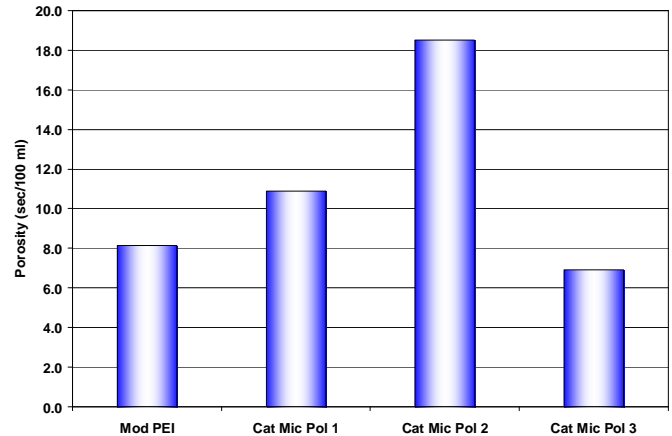


Figure 11. Gurley Porosity Data

The three cationic micropolymers impact the sheet structure differently. The polymer molecular weight and coagulant chemistry type may be driving these differences. The chemistry choice allows for the control in achieving the desired sheet properties (closed versus open sheet).

MILL CASE A

An application using the anionic dispersion micropolymer technology has been evaluated on a North American uncoated freesheet machine. This fourdrinier machine produces opaque and offset grades. The wet end chemistry includes ASA (alkenyl succinic anhydride) sizing, along with alum, cationic starch, precipitated calcium carbonate (PCC), and dye stuffs. The incumbent retention program consisted of an anionic PAM followed by the addition of colloidal silica and an (oil in water) anionic emulsion micropolymer (AEMP). The primary goal of the

evaluation was to replace the AEMP with the new anionic micropolymer dispersion technology (New Technology). It was applied in conjunction with the existing anionic PAM and silica applications.

Replacing the AEMP with the New Technology allowed for equal or better performance at significantly lower application rates of both the New Technology and the colloidal silica. This is illustrated below.

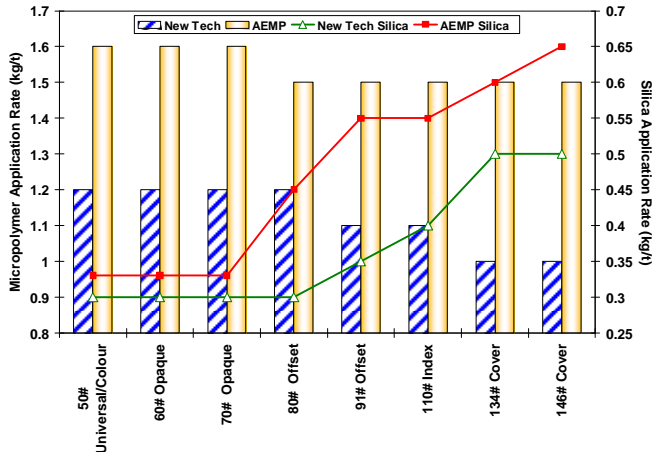


Figure 12. Comparison of Application Rates of AEMP versus New Anionic Micropolymer Technology

Silica reduction between 20% and 30% were realized coupled with a 25% - 35% reduction in micropolymer application rate. At these lower dosages, *production was not compromised*.

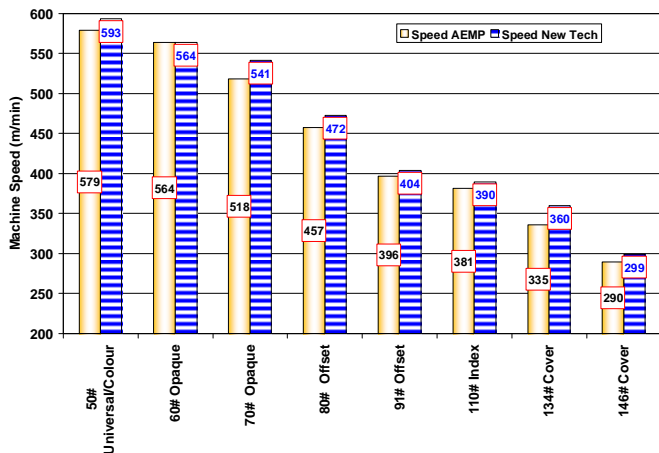


Figure 13. Machine Speed by Grade for AEMP and New Technology

The speed with the New Technology is equal or better than the AEMP program with the reduced application rates as shown in Figure 13. The retention data for some of the lightweight grades shows a similar trend in Figure 14.

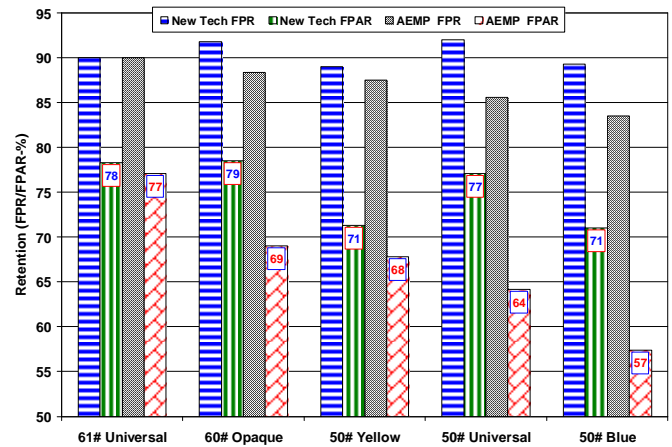


Figure 14. Retention Comparison AEMP versus New Technology

The novel characteristics of the new anionic micropolymer dispersion, with respect to structure and accessible charge, have allowed for significant increases in ash retention. In addition, speed increases have been realized with some grades. This has been achieved with substantially lower application rates of the retention and drainage components, resulting in significant savings.

MILL CASE B

An alkaline fine paper machine producing light weigh opaque, offset, and text grades has recently been converted to a program utilizing the anionic dispersion micropolymer technology. The incumbent program consisted of bentonite and cationic polyacrylamide (C-PAM). This integrated mill uses ASA (Alkenyl Succinic Anhydride) size and precipitated calcium carbonate (PCC) for filler, along with cationic potato starch. Titanium dioxide (TiO₂) is also used periodically for the opacity sensitive grades. The sheet ash target ranges from 12% to 16% depending on the grade. Optical brightening agents (OBA) are used at both the size press and in the wet end.

The primary objective was to replace the bentonite/C-Pam program in order to improve formation and increase production. The new application utilizes the anionic dispersion micropolymer technology applied post screen (shear) along with an application of anionic poly-acrylamide (A-PAM) pre screen (shear). Poly-aluminium chloride is applied pre A-PAM.

A significant increase in production rate was observed with the transition to the anionic micropolymer dispersion program, across the majority of the grades. The production data is shown in Figure 15.

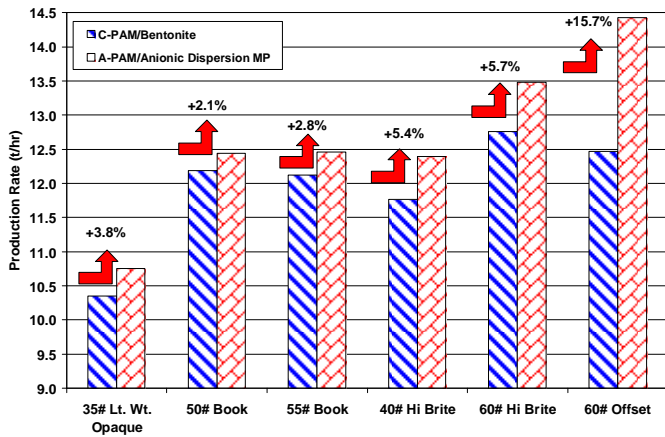


Figure 15. Production Data Bentonite versus Anionic Micropolymer Dispersion

It should be noted that this increase was achieved in addition to reducing the pre size press moisture target by as much as 0.7%. The bentonite program pre size press moisture target average was approximately 1.6%.

A marketed improvement in formation across many of the grades was observed with implementation of the new micropolymer technology. At a minimum, the formation was equal. This is illustrated below.

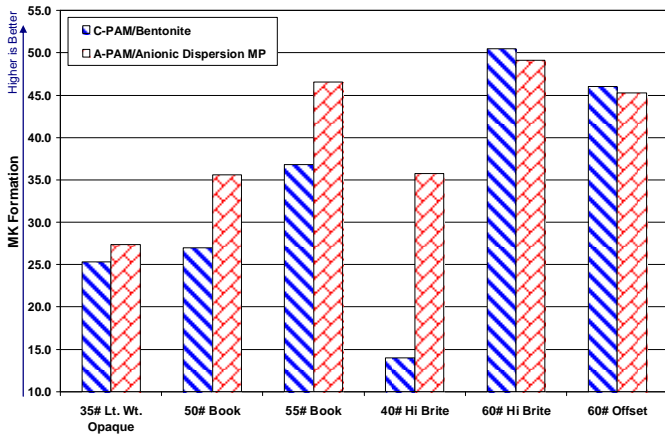


Figure 16. Formation Data Bentonite versus Anionic Micropolymer Dispersion

On the grades where the formation improvement was most apparent (40#, 50#, 55#), a half point increase in opacity was seen. The grades where the formation difference was not so apparent were the grades where the production improvement was greatest. This was due to a marketed increase in (former) drainage. This high degree of drainage offers opportunity to improve formation through optimization of slice position/geometry, headbox flow, table vacuum amongst others.

Finally, the new program had the added benefit of improving efficiency of other process additives, in particular wet end starch. A reduction in wet end starch application was observed across all of the grades and is illustrated in Figure 17.

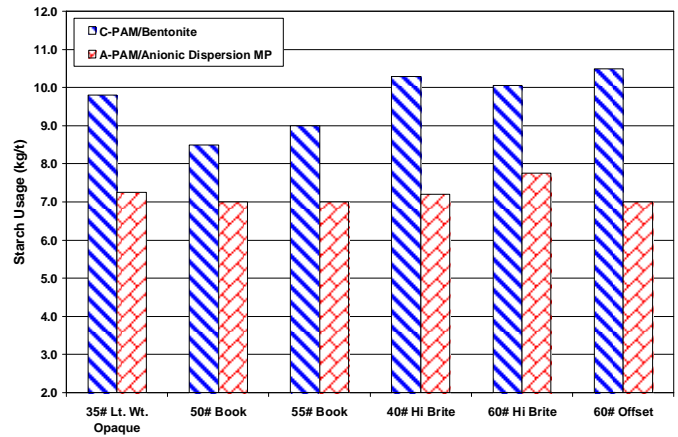


Figure 17. Starch Efficiency Bentonite versus Anionic Micropolymer Dispersion

The reduction in starch application ranges between 1.5 kg/t and 3.0 kg/t depending on the grade. With this reduction retention was not compromised nor was any quality specs. First pass ash retentions up to eight percent (80%) were achieved. Sizing response was not impacted with the starch reduction. HST (Hercules Size Test) values were equal or better than those attained with the bentonite program at equivalent or lower ASA application level.

MILL CASE C

An evaluation of the new anionic micropolymer dispersion technology was done on an alkaline fine paper machine producing offset and xerographic grades with a typical sheet ash of 15% to 18%. The incumbent program uses cationic potato starch and colloidal silica. ASA size and alum are used, along with PCC. OBA is used in both the size press and wet end.

The primary objective was to improve ash retention and strength to potentially increase sheet ash load. This was to be done by applying the anionic micropolymer dispersion with the existing colloidal silica program. The dispersion is applied with the silica in a post screen (shear) application point. The cationic potato starch is applied pre screen (shear).

Significant increases in ash retention were achieved across all the grades. This is shown in Figure 18.

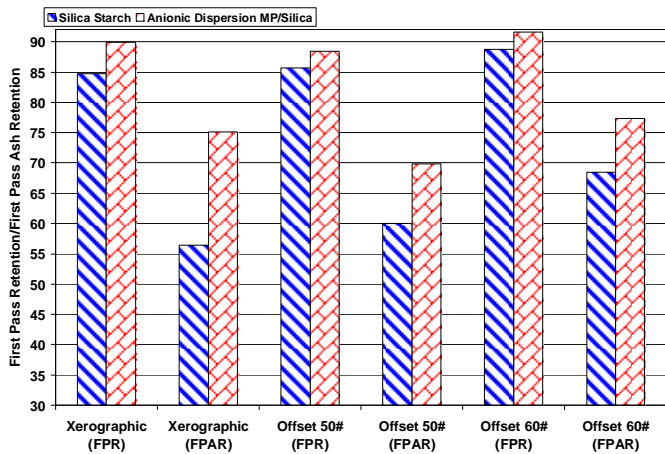


Figure 18. First Pass Solids/Ash Retention Silica versus Silica + Anionic Micropolymer Dispersion

The ash retention improvement was achieved with a 40+% reduction in silica application. With the high level of retention, higher cost potato starch could be substituted for a lower cost corn starch. Although there was some loss of efficiency, the dispersion technology plus silica program provided retention that exceeded values obtained by the incumbent program using potato starch. The starch change provides significant savings to the mill.

Strength improvements were observed across the majority of grades. This was seen in both the tear and tensile data. The tear data is shown below.

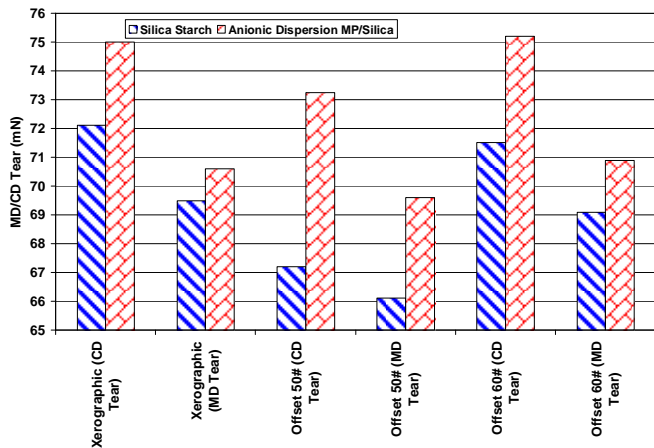


Figure 19. MD and CD Tear Data Silica versus Silica + Anionic Micropolymer Dispersion

Similar improvements are illustrated in the tensile and burst data in Figure 20.

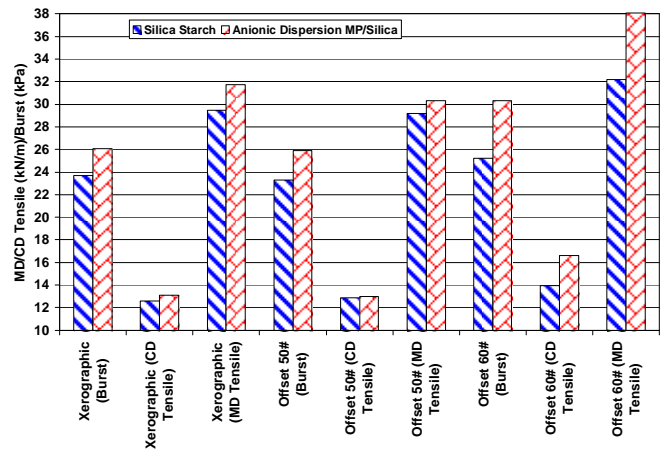


Figure 20. MD and CD Tensile Data Silica versus Silica + Anionic Micropolymer Dispersion

The strength improvement seen in all the parameters has given the opportunity to increase sheet ash. Preliminary evaluations have allowed for sheet ash increases of up to 3%, without increasing the retention program application rate.

MILL CASE D

An evaluation of a cationic micropolymer dispersion in salt solution (CatMP-SS) was done on an alkaline machine using PCC to produce super calendared (SC) grades. The machine included a top wire former and a 4th press. The furnish is largely pressure groundwood that is hydrogen peroxide bleached. Kraft is also a constituent and can account for up to 30% of the furnish. Cationic starch and optical brightener are also applied to the wet end.

The primary objective of the evaluation was to improve productivity on new higher grammage grades focussed on customers between the light weight coated (LWC) and SC segments. Speed limitations were anticipated with the new grade grammage target of 70 g/m².

The current retention system included the application of cationic polyacrylamide (C-Pam) and bentonite, with the C-Pam applied post screen and the bentonite applied pre screen. The CatMP-SS was applied in-line with the C-Pam, while the bentonite application rate remained constant. Application rates for the C-Pam and CatMP-SS are shown in Figure 21.

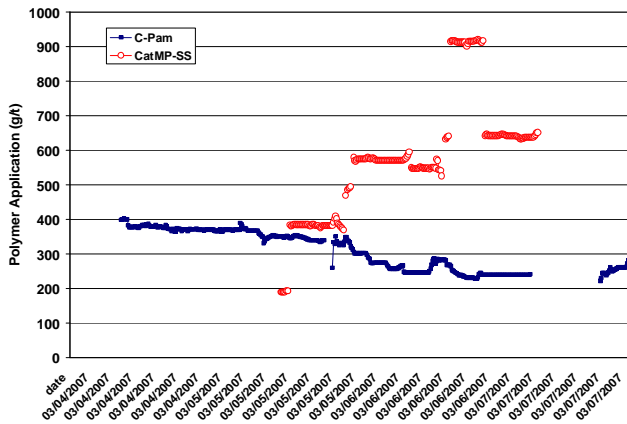


Figure 21. Polymer Application Rates

With the application of the CatMP-SS, the C-Pam was reduced by over 30%. Drainage was improved dramatically as is illustrated in the steam demand data of Figure 22.

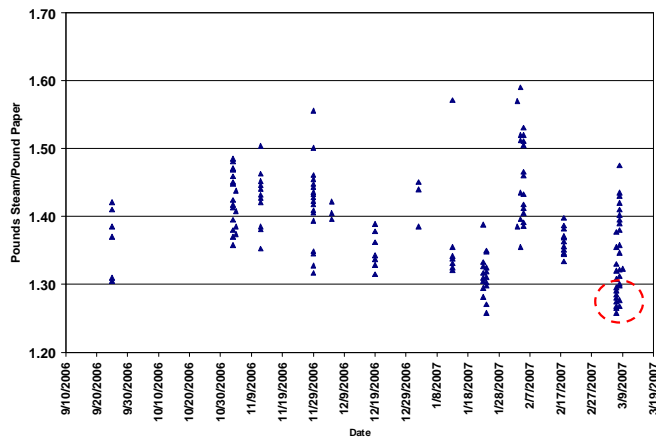


Figure 22. Overall steam / paper ton / speed of reel

It should be noted that other than the trial date, circled in the figure, steam data represents runs at 65 g/m² and not the trial 70 g/m². With lower steam demand, production was increased which is illustrated in Figure 23.

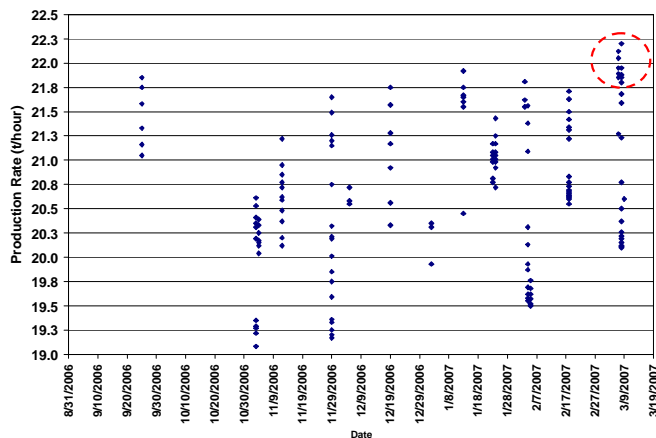


Figure 26. Production Rate

The drainage improvement allowed for increases in headbox dilution. This coupled with the decrease in linear C-Pam application had the benefit of a formation improvement at higher grammage.

CONCLUSIONS

A new generation of both cationic and anionic micropolymer dispersions has been developed. These chemistries are robust enough to be applied in a wide range of furnishes. The unique composition and structure allow them to increase sheet dewatering while increasing retention in both low and high ash environments. Machine evaluations suggest that these anionic dispersions outperform the anionic emulsion micropolymer versions.

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