EFFECTIVENESS OF THE BENTONITE AND MICROPOLYMER AS ANIONIC COMPONENTS IN MICROPARTICLE RETENTION SYSTEMS

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ABSTRACT

The microparticle aggregation systems are based on combination of the cationic polymers and anionic microparticles, and have been developed to overcome the limits of the conventional single- and dual-polymer retention systems. The most recently developments include the use of an anionic micropolymer in a two or three component system. This paper presents the comparative results of the microparticle retention systems based on bentonite and anionic micropolymer, which were tested for a fine paper stock. Constant parameters of the stock are 80% hardwood and 20% softwood kraft bleached pulp; 30 % GCC; cationic starch10 Kg/t and 8 Kg/t AKD (16% o.d.). The following retention systems were tested: cationic polycrylamide (PAA); anionic micropolymer (MP): PAA/anionic bentonite (B); PAA/MP; CPAM/B/MP. The results have shown that in the case of a conventional two component microparticle system, total substitution of bentonite by micropolymer leads to a lower retention and drainage rate, but to a better ratio between opacity increase and strength decrease. Halve substitution of bentonite by micropolymer, respectively application of a three component microparticle system (PAA/B/MP), could offer the best solution for balancing the wet end processes and characteristics of printing paper. Main benefits of a three component system are: better relationships between opacity, tensile strength and air permeability, and an easy control of the wet end processes since the system is less dependent of ionic balance.

INTRODUCTION

An effective retention with a uniform distribution of the stock components during sheet formation, and a high drainage rate are key elements in improving paper machine performance. These basic processes – retention, drainage and formation - are so intimately related that it is normally impossible to alter one of them without affecting other. Thus, frequently when the drainage is improved the retention falls, or when retention is increased, a poor formation is obtained. Traditionally, papermakers use chemical additives to control the wet end processes, and often the sheet formation is the result of an optimum compromise between retention and drainage. These processes, as well as the paper characteristics, are influenced by the aggregation degree of paper stock components, which is mainly related to the characteristics of the additives and stock component involved in the aggregation mechanism.

In the wet end systems, the aggregation mechanisms are generally referred as retention mechanisms, and could be divided into the following categories (Gill 1991; Lindstrőm *et.al.*1991; Bobu *et.al.* 1998; Hubbe *et.al. 2001*):
Coagulation involves the destabilization of a colloidal suspension with aluminum salts - *charge neutralization mechanism*, or by low molecular weight, high charge density polyelectrolytes - *patch model mechanism.*
Flocculation involves destabilization of a colloidal suspension by bonding the particles together with a long chain polymer - *bridging mechanism,* or by multi -component additive system - complex *flocculation*. Complex flocculation evolved from a conventional coagulant-flocculant retention system to the microparticle systems with two or three components.

Microparticle flocculation systems. The microparticle flocculation systems have been developed to overcome the limits of the conventional single- and dual-polymer retention systems, especially the decrease in their efficiency under intense shear forces encountered on high speed paper machine. Microparticle systems are based on combination of the cationic polymers and anionic microparticles, which develop flocculation that is reversible or at least partially reversible**.** The first commercial microparticle system utilizing cationic starch and colloidal silica was developed in the early 1980s. The second program introduced several years later is based on the cationic polyacrylamide and modified bentonite. In the standard application, the cationic polymer is introduced first to develop a bridge flocculation; after a shear stage (pumps, screens), the flocs are redispersed; then the anionic microparticle is added to reflocculate the dispersed flocs (Liu 1999). The commonly accepted mechanism is based on the electro-chemical interaction between anionic microparticle and dispersed flocs with positive surface charge, which results in a reversible microflocculation.

The key parameters for microflocculation are the polymer charge density, the shape and surface chemistry of the microparticles, and the conditions of microparticle interaction - addition order of the two components, fiber surface charge, conductivity, CDM concentration and shear level (Lindstrőm *et.al.* 1991; Pelton *et.al.* 1993; Xiao *et.al.*1996; Swerin *et.al.* 1997; Main *et.al.* 1999; Hubbe *et.al.* 2002).

The initial systems were mainly applied in production of the fine paper under alkaline conditions, and their success was due to significant improvements in retention and drainage with no sacrifice in formation (Hubbe et.al. 2001; Bobu *et.al.* 2002; Isermann *et.al.* 2004). During last decade, the microparticle technology was extending to a broader range of papermaking segments. This expansion is due to intense researches in the field concerning a better understanding of the microparticle role in controlling wet end chemistry, along with the development of new microparticles systems. (Hubbe *et.al* 2002; Mirza *et.al.* 2002). The most recently developments include the use of an anionic micropolymer in a two or three component system. All-organic anionic micropolymers are based on branched and crosslinked polymers.

This paper will present a comparative study on the effectiveness of the microparticle retention system based on the anionic bentonite and/or anionic micropolymer. The tasks of investigations are originated by results reported by Ciba Specialty Chemicals on Ciba® TELIOFORM® System (Information Brochure 2003), which combines inorganic microparticle with organic micropolymer. This combination of microparticle offers the opportunity to decouple retention, filler retention, drainage and formation effects, and to optimize each parameter independently.

EXPERIMENTAL

Materials. Basic stock composition included: a typical fibrous furnish for fine printing paper consisting of the hardwood (BHWP) and softwood (BSWP) bleached kraft pulps at a ratio BHWP/BSWP of 80/20 by dry weight, separately beaten in a Valley beater to 30^0SR; ground calcium carbonate at constant addition of 30% related to total solids of the paper stock; *alkyl* ketene dimmer emulsion (AKD) at constant addition of 8 Kg (emulsion of 16.2%)/tone; and 10 Kg/tone cationic starch (substitution index of 0.032) as AKD retention aid.

Following chemicals from **CIBA Specialty Chemicals** were applied in different sequences (see experimental program) as retention/drainage additives: Ciba® *Percol® 3335* - a medium to high molecular weight polyacrylamide (P3335), with a medium cationic charge density; Ciba® *Percol® 63* - a medium to high molecular weight polyacrylamide (P63), with a higher cationic charge density; Ciba® *Hydrocol® OT* – an anionic modified bentonite (B) applied as inorganic microparticle component in retention system; Ciba® *Polyflex® CP.3 - Micropolymer* (MP) – an water soluble, anionic charged polymer with micronetwork structure was used as organic microparticle component in retention systems.

The experimental program (Fig.1) includes five series of experiments, which were designed to develop different aggregation mechanisms: *sseries 1* - bridge flocculation mechanism by cationic polyacrylamide (PAA); *series 2* - microflocculation mechanism by system PAA/B; *Series 3* - microflocculation mechanism by system PAA/MP; Series 4 - microflocculation by a combined microparticle system PAA/B/MP; *Series 5* - bridge flocculation by anionic micrpolymer (MP). First four series of experiments were duplicated for two types of cationic polyacrylamide – Ciba® Percol® 3335 and Ciba® Percol® 63 (P3335 and P63).

Methods. Standard laboratory techniques were applied in order to evaluate effects of different additive systems on the papermaking process and paper properties:
Retention. The Dynamic Drainage Jar (DDJ) was used to determine the total and filler first pass retention, using the following conditions: a screen corresponding to a paper machine wire no.28; stock consistency of 0.5%; additives were added in diluted stock, in following sequencing – PAA/intense shear/ bentonite/micropolymer; finally, first volume of 100mL filtrate was collected and analyzed for total solids and calcium carbonate content.

Free Drainage. Modified Schopper Riegler (MSR) tester was used to measure the free drainage. Diluted stock was taken and additives added in the correct sequencing including the appropriate mixing to provide the right shear before the test was performed. The results were expressed as drainage time (seconds) required collecting 700mL filtrate by central tube, when lateral tube is blocked.

Colloidal titration: charge density (CD) of the chemical additives and cationic charge demand (CCD) of paper stock was determined by direct and back-titration, using standard polymers (poly-DADMAC and Na-PVS) and PCD-02 for isoelectric point detection.

Handsheets characterization. The results regarding effects of different additive systems on the drainage and retention evidenced no significant difference between the two types of polyacrylamides (P_{3335} and P_{63}). For this reason, the handsheets were prepared using only Percol3335 in series 1-4. Handsheets with basis weight of 64 ± 1 (g/m^2) were obtained on a Rapid-Köthen apparatus and the following analyses were performed: calcium *carbonate content* was determined by TAPPI method – T413; opacity *(ISO 2471)* was measured by using a spectrophotometer L&W Elrepho 2000; *tensile strength characteristics* were measured by using a Instron apparatus (ISO1924-1, 1992); *air permeability* was measured on a DL-WEB apparatus, at a pressure drop of 1 KPa.

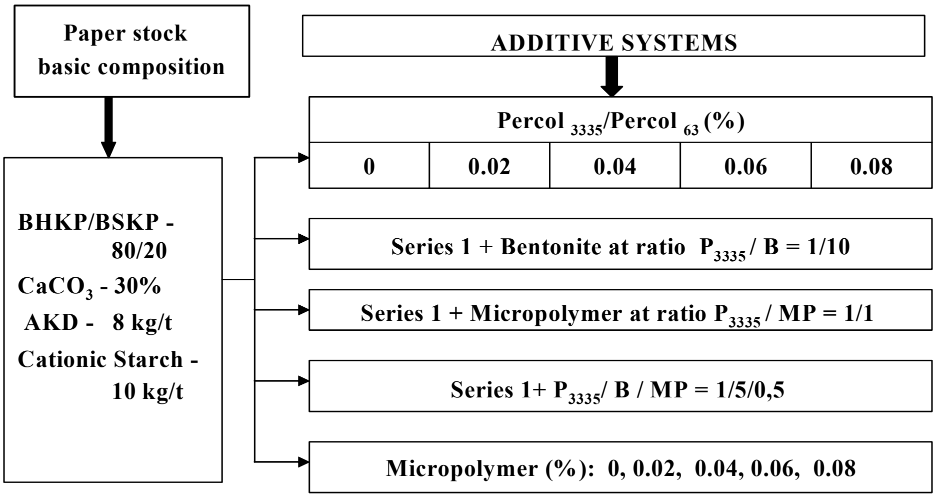


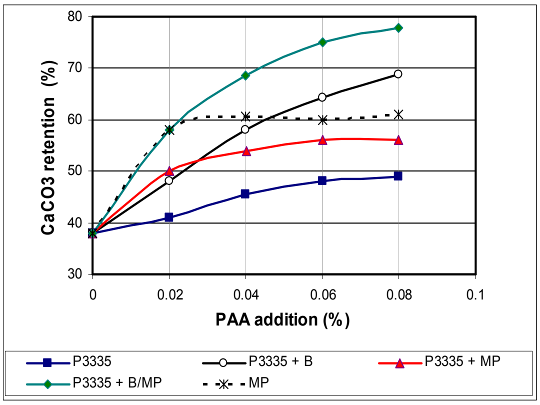
Figure 1 Scheme of experimental program

RESULTS ON RETENTION AND DRAINAGE

The performance of a retention/drainage additive system is influenced by the properties of polymers, the conditions and points of addition, as well as by their interaction with other additives. In this study, the basic stock composition was the same for all experiments, and so were hydrodynamic conditions and order of chemical addition. Thus, each additive system was evaluated under similar conditions, allowing to comparing their effectiveness as retention and drainage aids.

Filler retention. Data presented in graphs of figures 2-3 show clear differences between effects of additive system on the filler retention. The micropolymer alone produces a consistent increase in retention for the lowest dosage and remains constant at higher dosages. On the other hand the combination of polyacrilamide/micropolymer gives a lower level of retention than micropolymer alone, but higher than polyacrylamide alone. These results could be due to difference in aggregation mechanisms: by its branched structure, micropolymer alone could develop a network in solution that will retain filler particle by entrapment. In the case of PAA/MP system, cationic polyacrylamide induces first a bridge flocculation, which after shearing will produce microflocs with slight cationic charge that can interact with anionic micropolymer leading to microflocculation. This mechanism is mainly depending on electro-chemical interaction of dispersed flocs with micropolymer, and generally will result in a more open structure. This hypothesis is sustained by the evolution of drainage rate that is much better for the combination PAA/MP, comparatively with MP alone (Fig. 6-7).

The microparticle systems that include bentonite give the highest values of retention, and a considerable improvement is evidenced in case of the three component microparticle systems (PAA/B/MP), using Percol3335. There are clear differences between microflocculation with micropolymer and that with bentonite, and these are due to higher dosage of bentonite comparatively with micropolymer (ratio 10:1). The bentonite introduce a much large surface area in system with adsorption capacity that will improve fines retention, until the open structure of microflocs will improve drainage.



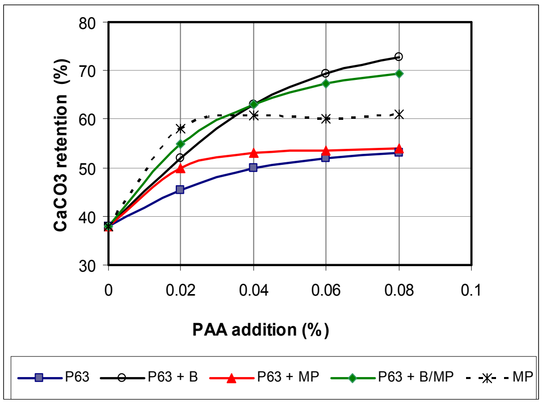
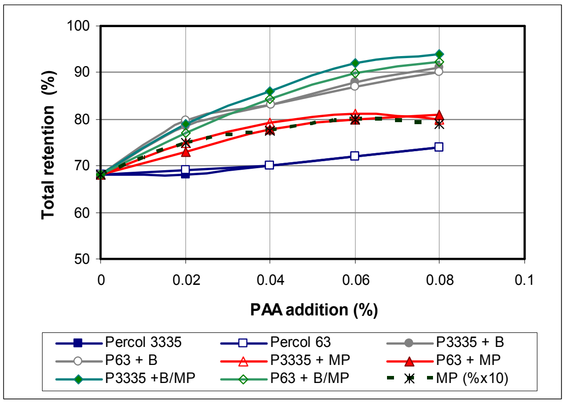


Figure 2 Calcium carbonate retention as a function of PAA (Percol3335/MP) addition, as a single component and in combinations with bentonite and/or micropolymer

Figgie 3 Calcium carbonate retention as a function of PAA (Percol63/MP) addition, as a single component and in combinations with bentonite and/or micropolymer



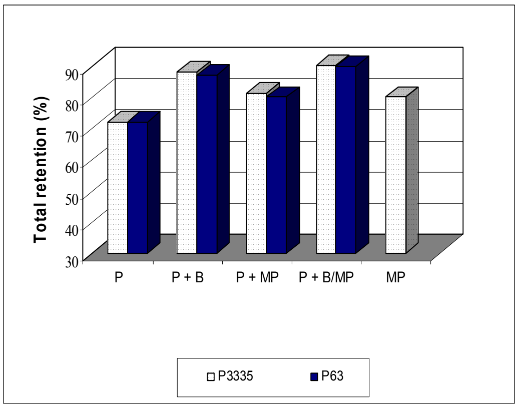


Figure 4 Total retention as a function of cationic PAA addition for different additive systems

Figure 5 Total retention for different additive systems, at 0.06% addition of PAA/MP

Total retention. A similar evolution is remarked for total retention, the higher levels of retention being obtained for the three component systems - PAA/B/MP (Fig.4-5). A comparison between the two polyacrylamide is presented in Figure 5, where there are indicated the levels of total retention at a constant addition of 0.06% PAA. Results show less significant differences between the two types of polyacrylamides (the pairs of curves are almost overlaid), comparatively with calcium carbonate retention.

Free drainage. The drainage time as a function of polyacrylamide addition in different combinations are presented in figures 6 and 7 for Percol3335 and Percol63, respectively. First remark is that mycropolymer tends to increase the drainage time. This effect is evidenced in all combinations with micropolymer and for both types of polymers, supporting the hypothesis of a network flocculation mechanism. The network mechanism is also sustained by the fact that the cationic charge demand tends to decrease when micropolymer is applied in combination with PAA or with PAA and bentonite (Fig.8).

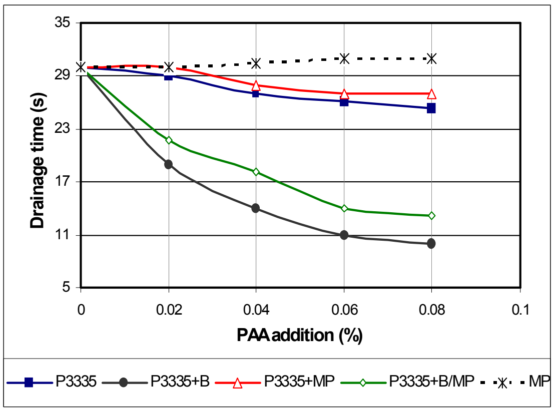


Figure 6 Drainage time as a function of PAA (P3335) addition in different combinations with bentonite and/or micropolymer

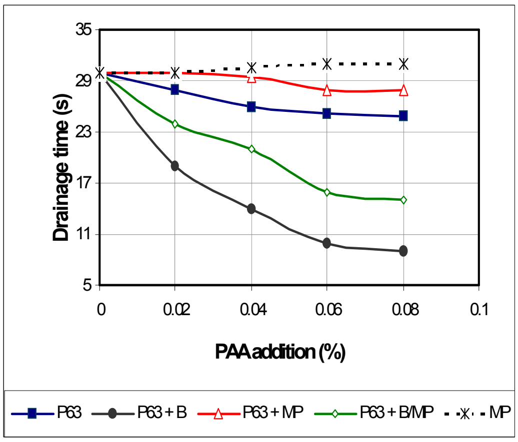


Figure 7 Drainage time as a function of PAA (P63) addition in different combinations with bentonite and/or micropolymer

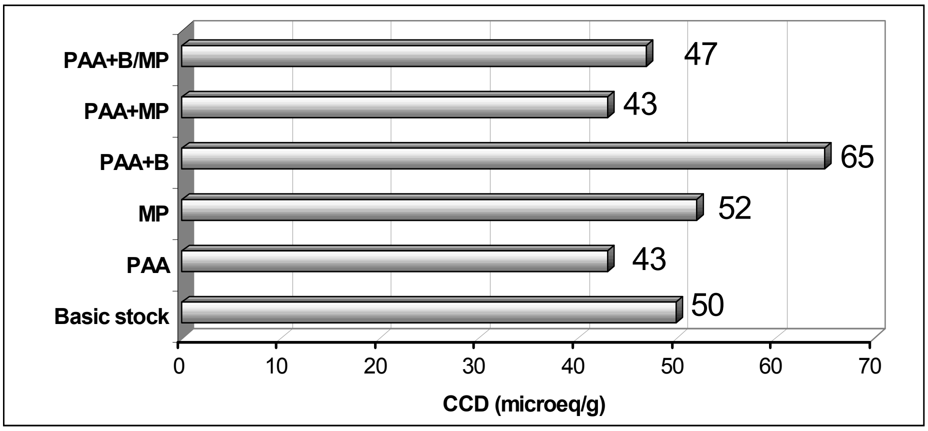


Figure 8 Cationic charge demand of paper stocks prepared with different additive systems (PAA - Percol3335 at constant dosage of 0.06%).

Comparative eeffectiveness on retention and drainage. Diagrams of figures 9 and 10 present level of filler retention and respectively, drainage time for studied additive systems, corresponding to the same addition of 0.06 PAA (most additive systems have shown maximum effectiveness at this level of PAA addition). All combinations with bentonite and/or micropolymer give higher filler retention than polyacrylamide alone, the highest level being reached by the three component system – PAA/B/MP. On the other hand, the drainage rate is higher (drainage time is lower) for combinations with bentonite. It is worth to note that the three component system with Percol3335 gives the highest level of retention and a drainage time close to that of combination PAA/B, which develops the highest drainage rate. This comparison shows that the best balance between filler retention and drainage time is obtained by applying the three component system consisting of Percol3335/Bentonite/Micropolymer. That is why, the handsheets for physical-mechanical tests were prepared only for series of experiments using Percol3335.

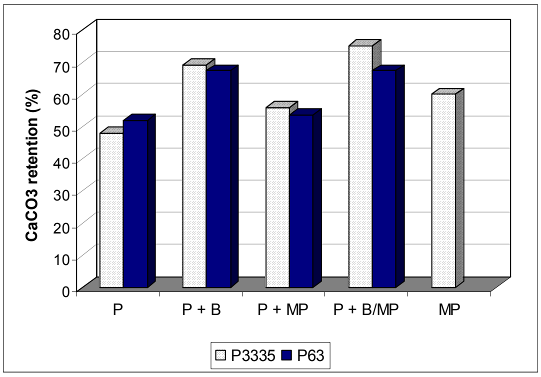


Figure 9 Filler retention for different additive systems, at 0.06% addition of PAA/MP

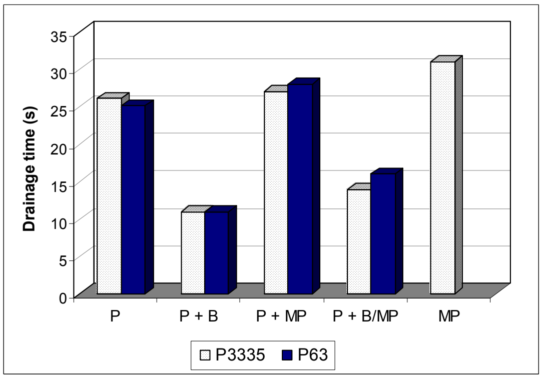


Figure 10 Drainage time for different additive systems, at 0.06% addition of PAA/MP

PAPER PROPERTIES

Opacity and tensile strength. The effectiveness of the printing paper production frequently depends on the solutions for obtaining the desired optical properties. This aspect is very important because some factors that have a positive effect on brightness and opacity (filler content and mechanism of filler retention, low refining, high bleached pulp, and high percent of hardwood pulp) will negatively affect the strength properties and paper machine runnability.

The opacity and tensile strength of printing paper are the two properties with opposite evolution as filler content of paper is increasing (Fig.11-12). Graphs of Figure 11 indicate a better effectiveness of microparticle retention systems in controlling paper opacity, which could be due not only to higher retention of calcium carbonate, but also to a better z-distribution of stock components (origin of curves is for sample without retention additives, and rest of points correspond to PAA addition from 0.02% to 0.08%). The three component system consisting of PAA/B/MP develops the best ratio between opacity increase and filler content (Fig.13), which could be related to an improvement of formation comparatively with PAA/B system.

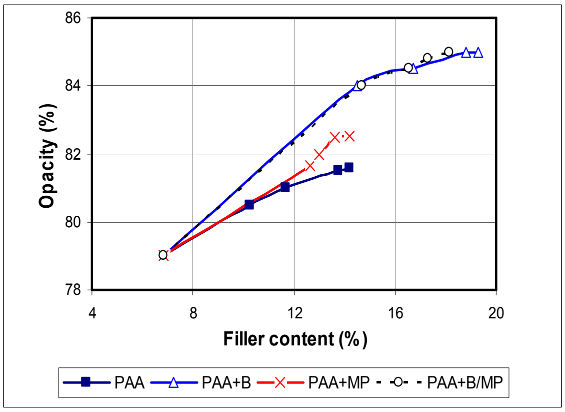


Figure 11 Opacity as a function of filler content, for different additive systems

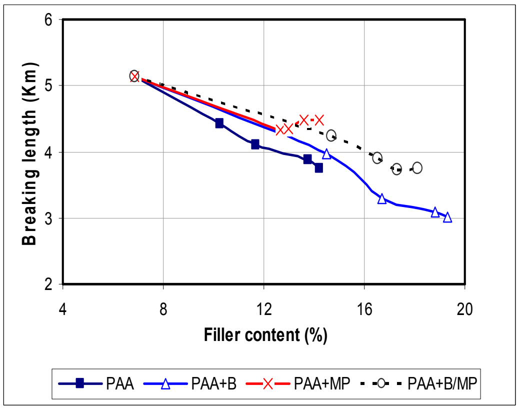


Figure 12 Breaking length as a function of filler content, for different additive systems

The increasing of paper strength is another positive effect of micropolymer. (Fig.12 and 14). It worth to note that in the case of additive system consisting of cationic polyacrylamide and anionic micropolymer (PAA/MP), there is a slight increase of breaking length, though filler content increases too. This evolution could be explained by contribution of both polymers (PAA and MP) by their long and branched chains to strength improvement. The dosages of both polymers increase from 0.02% to 0.06%, until the filler content of paper increases only from 12.5% to 14.5%, and thus is evidenced direct effect of polymer. Therefore, the effect is also remarked in graphs of Figure 14, showing that at constant dosage of 0.06 PAA, the combinations with micripolymer (PAA/MP and PAA/B/MP) develop the best ratio between breaking length and filler content.

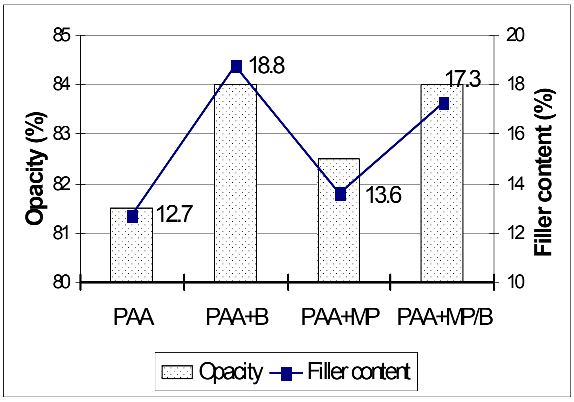


Figure 13 **Opacity and corresponding filler content for different additive systems, at constant addition of 0.06% PAA**

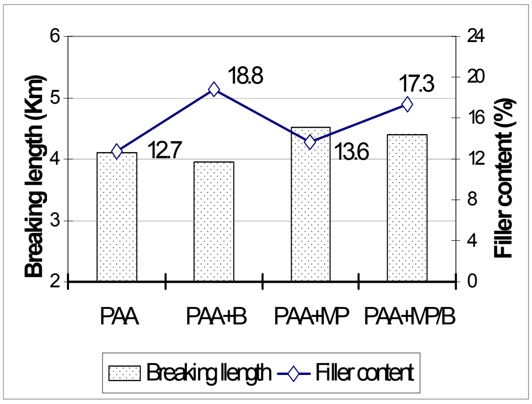


Figure 14 **Breaking length and filler content for different additive systems, at constant addition of 0.06% PAA**

Air permeability. The porous structure of paper plays an important role in the effectiveness of paper for many applications. Beside other, this includes its ability to absorb liquids such as ink, oil, water. Paper porosity is difficult to measure and more difficult to discribe in simple terms. A property that is easy to measure and can ussually correlated with the porous structure of the sheet is air resistance and its inverse air permeability (*Eperen 1991*). Since, the grade of stock aggregation impacts the porous structure of paper, measurements of air permeability could give indications about possible aggregation mechanisms developed by different additive systems and their effects on paper quality.

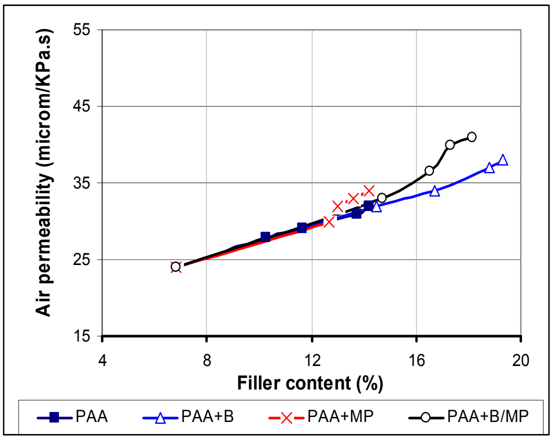


Figure 15 **Air permeability as a function of filler content (resulting of various PAA-dosages in different combinations)**

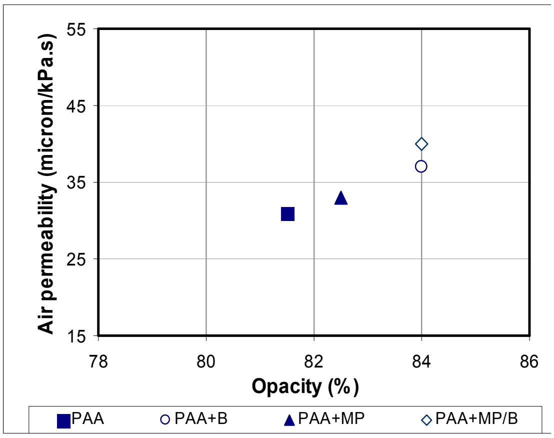


Figure 16 **Air permeability *vs.* opacity for different additive systems, at a constant dosage of 0.06% PAA.**

As it is expecting, air permeability of paper increases wirh filler content, but its evolution differs as a function of additive system (Fig. 15). A definite difference is evidenced at higher contents of calcium carbonate, which correspond to increasing dosages of flocculant. The effect could be explained by a differences in flocculation mechanism and degree of flocculation. At the same content of filler (for example 18%), paper samples obtained with three component system (PAA/B/MP) are characterized by higher permeability than samples obtained with two component system (PAA/B). This is unexpected result because drainage behavior of the paper stock indicated a more open structure of paper web obtained with PAA/B system. An explanation of this result could be a more uniform structure formed of smaller pores, which also is reflected by relationship between air permeability and opacity (Fig.16). At a lower content of filler, the sample of PAA/B/MP (17.3% $CaCO_3$) shows a higher permeability and the same opacity with sample of PAA/B (18.8% $CaCO_3$).

CONCLUSIONS

The results presented here show that it is possible to obtain more benefits from microparticle retention systems by optimum combination of inorganic/organic microparticle (bentonite/micropolymer) with a cationic polyacrylamide.

In the case of a conventional two component microparticle system, total substitution of bentonite by micropolymer leads to a lower retention and drainage rate, but produces a better ratio between opacity increase and strength decrease of paper.

Halve substitution of bentonite by micropolymer, respectively application of a three component microparticle system, could offer the best solution for balancing the wet end processes and characteristics of printing paper. Main benefits of this system are: better relationships between opacity, tensile strength and air permeability, and an easy control of thhe wet end processes, since the system is less dependent of ionic balance.

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REFERENCES

Bobu, E. and Popa V.I. (1998) "Chemical and Colloidal Processes in Papermaking" Ed.Cermi, Iasi, Romania

Bobu, E., Parpalea, R. and Ciolacu, F.(2002), *Wochenblatt f. Papierf.***130** (22): 1510 -1524

Ciba Specialty Chemicals (2003), Ciba® TELIOFORM® System-Information Brochure

Eperen, V.R.H.(1991), „Paper Properties and Testing Procedure" in Pulp and Paper Manufacture Vol.7, Ed.A. Thorp, published by Tappi/CPPA 3rd ed.1991)

Gill, R.I.S, (1991), *Paper technology* **32** (8): 34-38

Hubbe, M.A. (2001), *Nordic Pulp and paper Research Journal* 16 (4) 369-374

Hubbe, M. A. and Wang, F. (2002), *Tappi J.* **1** (1): 28-31

Isermann R.R., Champ, S., Blum, R., and Esser, A. (2004), ipw 1, *Das Papier* T6-2004

Liu, J. (1999), *Paper Technology* **40** (3): 41-45

Lindstrőm, T. (1991), In "Overview of the fundamentals of papermaking" published by The Pulp and Paper Fundamental Research Society, Pira House, England, p.39-117

Main, S. and Simson, P., Tappi J. (1999), **82** (4): 78-81

Mirza, S., Conyngham, M. and Covarrubias, R. (2002), African Pulp and Paper Week, TAPPSA, Durban, October 8 -11

Swerin, A.; Risinger, G.; Ödberg, L. (1997), *Journal of Pulp and Paper Science* 23 (10): 374-77

Xiao, H. , Pelton, R., Hamelic, A. (1996), *Tappi J.* **79** (4):129-135