# Research Concerning the Use of Synthetic Polymeric Flocculants in Industry

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The paper shows in its first part the role, efficiency, types, factors and mechanisms of using the synthetic polymeric flocculants in the paper industry. The experimental part shows the research carried out to determine comparatively the efficiency of using the single component retention systems, with micro/nano particles in the modern alkaline paper production compared to the conventional acid process.

*Keywords:* paper, flocculation, retention aid, zeta potential, micro/nanoparticles.

As a rule, a sheet formation is similar to a filtration process, that consists in water removal from the pulp slurry. Fibers settle out on a continuous movement wire making a fibrous layer.

Two major factors affect the sheet formation and thickness: circulation conditions in the headbox and flocculation condition of the pulp stock settled on the wire.

Efficiency of solid-liquid separation can be improved a lot by applying the synthetic polymeric flocculants.

The "flocculation" term relates to stabilization by adsorption of some big polymer molecules that make a communicating bridge between particles [1,2].

Paper stock flocculation takes place by aggregation of paper stock components and formation of "flocs" that do not pass through the wire mesh. (fig. 1).

Flocculation of pulp fibers, flocculation of fines and filler and adhesion of fines and filler on the fiber surface take place in this process.

The flocculation degree (size of flocs) influences formation, paper quality, retention and drainage capability.

The use of synthetic polymeric flocculants is enforced by a series of process modifications such as conversion to the neutral/alkaline sizing process, increase of using recycled fibers, an increasingly advanced closure of water systems and the occurrence of new polymers and polymeric systems.

In the field of paper making, the benefits of using synthetic polymeric flocculants (retention aids) refer to:

-lower material losses (fillers and fibrous material) therefore a lower pollution;

-steam saving, paper sheet entering with a lower moisture at the drying section;

-improvement of wire and felt wear.

Of all additional benefits we notice the increase of paper machine speed, an improvement of paper opacity and printing by 1-2%, reduction of porosity and duble sideness.

Figure 2 shows the efficiency of using the retention aids in papermaking [3,4].

In the last period various synthetic polymeric based retention systems have been carried out, the research of particularities (requirements, mechanisms) as regards their use and ways of flocculation optimization and control being required [5,6].

It can be stated that by means of the flocculation process control is possible to optimize the main processes carried out on the paper machine wire table – retention/formation/ dewatering.

# Types of synthetic polymers used in the paper industry

Synthetic polymers currently used in the paper industry can be classified in five groups [7-9]:

- polyacrylamides (PAA);
- polyamidamines (PAAM);
- polyamines (PA);
- polyethyleneimines (PEI);
- polyvinylamines (PVAm).

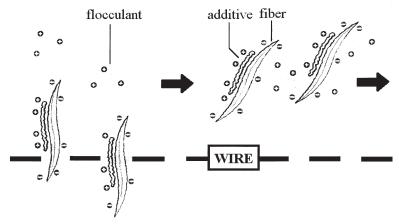


Fig. 1. Paper stock flocculation

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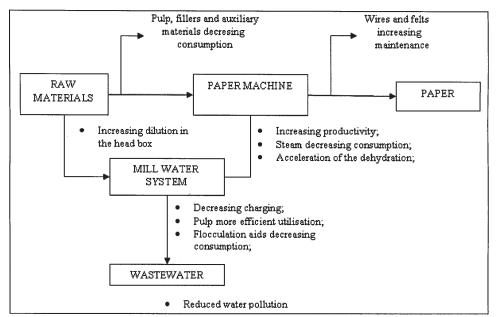


Fig. 2. Retention aids effiency

Table 1
SYNTHETIC POLYMERS USED IN THE PAPER INDUSTRY

Group of products	Primary products	Active chemical groups
Polyacrylamides	Acrylamide	Aminic
		Carboxylic
	Amines	
Polyamidamines	Dicarboxylic acids	Aminic
	Epichlorohidrine	Amidic
	Dicloroethane	
Polyamines	Amines	Aminic
	Epichlorohidrine	
	Ethilimine	
Polyethyleneimines	Amines	Aminic
	Dichloroethane	
	Modified components	

Polyacrylamides (PAA)

Non-ionic polyacrylamides are obtained by polymerization of acrylamides. For retention, cationic and anionic PAA are used. They are obtained by incorporating the suitable groups in the molecule. Cationic PAAs contain amino groups and the anionic ones contain carboxylic groups.

Polyacrylamides are delivered as: solids, in aqueous solution of 3-5% d.s. and can be diluted directly with water and emulsion.

Table 1 provides a general view over the synthetic polymers in the paper industry, mentioning the characteristic chemical groups that are aminic, amidic and carboxylic groups.

The functional groups provide various important properties to the polymeric systems they are attached to [5-10].

The effect of synthetic polymers, as retention aids is driven not only by active chemical groups but also by the general structure of the product (linear polymers, chained structure and network structure polymers).

#### Polyethilenimines

By ethileneimine polyaddition cationic polymers are obtained.

Fig. 3. Ethilenimine polymerization

The polymerization process takes place through the cationic mechanism, especially in the presence of acids, as a rule with formation of linear polymers, up to 10<sup>6</sup>, that sometimes can have a chained structure, too.

PAAs often contain free radicals that allow development of various reactions and are an aqueous solution with a 20-25% d.s. concentration and a medium viscosity. As regards electric charge they have an average up to a strong cationic nature.

Polyetilenimines act at an optimum *p*H between 6 and 8 and can be used as retention aids and for increasing wet strength in papermaking. They are sensitive to the action of aluminium sulphate and are effective in the paper industry only for neutral or alkaline pulps.

Polyethilenimines have a negative impact on optical brightners, causing paper ageing and are not recommended in bleached paper making.

Polyethilenimines can be used for a fast dewatering and for the treatment of waste water resulted in waste paper processing.

Modified polyethilenimines are also used in dual polymer or microparticle retention systems.

Polyamines (PA) have a secondary role for a number of specific applications (TiO<sub>2</sub> retention in neutral medium). They are an aqueous solution with a 20-25% d.s. concentration and have a medium viscosity.

#### Polyamidamines (PAAMs)

PAAMs are condensation products based on aliphatic polyvalent acids with polyvalent apliphatic amines. They are an aqueos solution with a 20-25% d.s. concentration, a medium viscosity and have a strong cationic nature. These products are efficient in the acid medium as well.

Tabelul 2
RETENTION AIDS – CHEMICAL AND PHYSICAL CHARACTERISTICS

Retention aid type	Abbreviation	Characteristical chemical group	Ionic charge	Molecular weight	Commercial product aggregation form
Polyethyleneimine	PEI	NH <sub>2</sub> -(CH <sub>2</sub> -CH <sub>2</sub> -NH) <sub>n</sub>	++	$3-6 \cdot 10^4$	aqueous
Polyamine	PA	NH <sub>2</sub> -(CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -NH) <sub>n</sub>	+++	$3-8 \cdot 10^4$	aqueous
Polyamidamine	PAM	NH- $(CH_3)_2$ -NH- $(CH_2)_2$ -NH- $C = O$   ( $CH_2$ ) <sub>4</sub>   NH - $C = O$	+ sau ++	5 – 10 • 10 <sup>4</sup>	aqueous
Cationic polyacrylamide	PAA	$ \begin{array}{c} - \left[ \begin{array}{cccc} \text{CH}_2\text{-}\text{CH} - \text{CH}_2\text{-}\text{CH} - \\ &   &   &   \\ & \text{C} = 0 & \text{C} = 0 \\ &   &   &   \\ &   & \text{NH}_2 & - & \text{NH}_2 \end{array} \right] n \\ - \left[ \begin{array}{cccc} \text{CH}_2\text{-}\text{CH} & - & \text{CH} & - & \text{CH} \\ &   &   &   &   \\ &   &   &   &   \\ & \text{C} = 0 & \text{C} = 0 & \text{C} = 0 \\ &   &   &   &   \\ &   &   &   &   \\ &   &  $	+	1 - 10 • 104	poudre aqueous emulsion

Polyvinylamines (PVAm)

BASF launched on the market a new class of substances named polyvinylamines (PVAm). Vinylformamide is used in order to obtain this polymer.

If molecular weight is high enough, and electric charge density lowers, excellent flocculants are obtained.

Another advantage of polyvinylamines is that they do not contain organic bonded chlorine and formaldehide.

Table 2 shows the characteristics of some synthetic polymeric flocculants used in the paper industry.

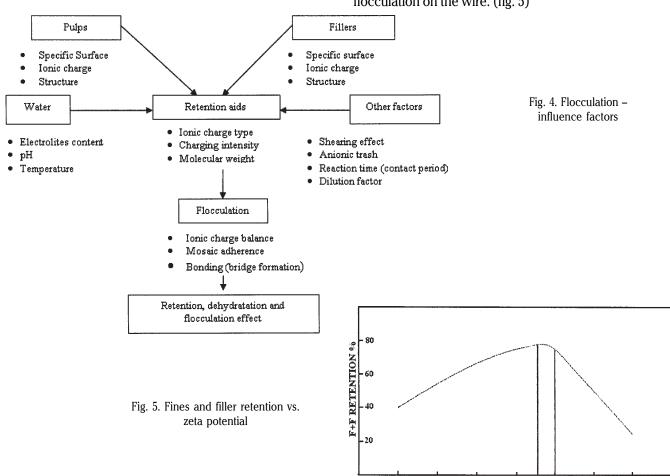
# Factors influencing flocculation

Retention of fillers is not total but partial, depending on several factors of which is noticed zeta potential [10] (fig. 4)

Of the basic influence factors, the issue of zeta potential is noticed representing an interesting mean of assessing the behaviour of suspended particles.

The hachured area represent the optimum zeta potential area for a maximum retention of fibers and fiber.

The higher the zeta potential the higher the rejection between particles is hindering agglomeration, their flocculation on the wire. (fig. 5)



-25

-10

ZETAPOTENTIAL inv

15

Table 3 VALUES OF ZETA POTENTIAL FOR VARIOUS RETENTION DEGREES

Retention characteristics	Zeta potential, mV
Excellent retention	±5
Satisfactory retention	$\pm 10 \text{ to } \pm 20$
Poor retention	$\pm 20 \text{ to } \pm 40$

Table 3 shows the indicative values of the zeta potential for various retention degrees.

The advantage of a retention aid is that, on the hand, it can modify the zeta potential, and on the other hand, it serves as an adhesive in order to bind the fines and fill the cellulosic fibers at surface.

A maximum retention is obtained when charging the cationic polymers in order to get a zeta potential equal to zero. A further rise of charging polymers over this point results in lowering retention as the zeta potential becomes positive. In [13, 14]it is issued and confirmed the assumption that Zeta potential can impact the basic operations in the paper stock preparation, with repercussions over some final qualitative paper characteristics.

The most important issue for the operation mechanism of synthetic flocculants is first of all, their molecular weight.

The higher molecular weight of polyacrylamide is, the higher is flocculation. The order of magnitude as regards polyacrylamides used at present varies between 500.000 and 5.000.000 showing a rise of flocculation efficiency of three times for a higher weight.

However, there is a limit for its size, driven by economic and technical considerations, such as: obtaining a uniform activity product, possibility to dilute easily having a low content of residual monomer and quite economically to be produced.

Flocculants may act only within a certain pH range, their load depending on pH (fig. 6).

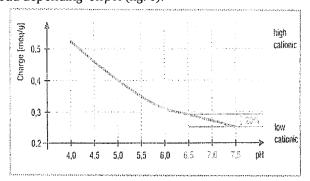


Fig. 6. Charge depends on pH-value

As regards structure both linear polyacrylamides as well as branched and cross-linked polyacrylamides are used.

#### General flocculation mechanisms

Flocculation can be caused by a high number of processes, with various complexity degrees, of which the following can be mentioned:

- a)Simple flocculation mechanisms
- Bridge model aggregation
- Polymer network aggregation
- b)Complex flocculation mechanisms
- Dual system aggregation (bicomponent)
- Multicomponent system aggregation

Bridge model aggregation

This mechanism assumes the requirement that polymers have chains long enough to create bridges between particles following their collision. The mechanism consists of two stages: (fig 7)

- In the first stage, the polymer adsorbs with one of its ends on the particle surface, the remaining chain remains in solution as an extended form.
- In the second stage, the other end or loop created by the polymer in solution is adsorbed on other particle during

Figure 7 illustrates briefly the flocculation mechanism created by polymer bridges [15].

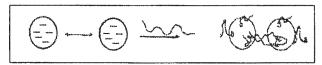


Fig. 7. Flocculation mechanism by means of polymer bridges

To aggregate by polymer bridges the most important factors are: molecular weight, density of polymer loading, ionic loading of fines particles and ionic concentration.

Polymer network aggregation

In the first stage, it involves the interaction of two or several polymers in solution.

Complex flocculation mechanisms: dual-polymer systems

The dual polymer systems are usually made of two polymers, a cationic polymer and an anionic polymer. The cationic polyelectrolyte with average molecular weight and high density of loading the first system is added, so that in the first stage neutralization and reversal of loading take place in some areas located at the solid particle surface

("patch model").

In the second stage, the high molecular weight polymer and low anionic load is attracted and adsorbed by electrostatic attraction forces on the positively charged areas created by the cationic polymer. The ends of macromolecular chain extend in a solution due to the repulsive force between polymer and electronegative surrounding areas, therefore they can be adsorbed on other surfaces, setting bonds by polymer bridges. In case of the dual polymer systems it is shown schematically in figure 8 [14].

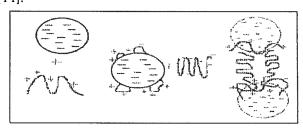


Fig. 8. Flocculation mechanism at the "dual polymer" system

Complex flocculation mechanisms - microparticle systems

Microparticle systems replace the anionic polymer with anionic microparticles in the "dual polymer" system. Apart the "dual polymer" systems in case of microparticle systems, reflocculation is partly reversible and is carried out at micro scale, so that paper formation is not affected. Paper sheet dewaters more easily both on wire table and drying section.

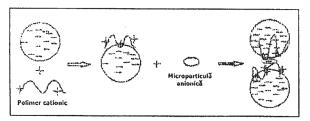


Fig. 9. Polymer-microparticle aggregation mechanism

Of the most common combinations of cationic polymers and anionic microparticles the following systems are mentioned:

- modified starch or cationic polyacrylamide in combination with modified anionic bentonite (HYDROCOL);
- cationic starch or cationic polyacrylamide in combination with an anionic aluminium hydroxide precipitate (HYDROSIL).

The polymer-microparticle aggregation mechanism is shown briefly in figure 9 [15].

#### **Industrial retention systems**

The most common retention systems can be divided in:

- a) single component systems
- b) two soluble component systems
- c) microparticle systems

Single component systems

The single component systems are the simplest of all retention systems and are still used enough for some cases in practice.

Their action principle is based on a connection of negatively charged components of the paper stock slurry with synthetic polymers having molecular weights higher than 10<sup>6</sup> g/mol (polyacrylamides and polyethilenimines).

Two soluble component systems (dual systems)

On the one hand with increasing the waste paper tonnages used and an increasingly advanced closure of water systems on the other hand, as well as the increasingly higher requirements concerning paper quality and functionality of paper machines, it has occurred the necessity of improving the single component systems and their completion with substances that are able to neutralize the amount of harmful substances, in a continuous development on the paper machine [16].

Under these circumstances, the following systems are noticed:

(+) polyacrylamide + cationic polyacrylamide with high molecular weight

- (–) polyethileneimine (modified)

- (+) cationic polyacrylamide with high molecular weight

- (-) polyethyleneimine (modified) + anionic polyacrylamide with high molecular weight.

The bicomponent systems (dual) can run by means of: - additivity – when the total action is equal to the sum of

the system components, apparently the two components act differently: - antagonism – when the system components seem to

work against each other. For the same effect, in this case

higher amounts of flocculants are required. synergism - when the action of flocculants is simultaneous and complementary.

In the field of retention all the three cases are noticed. the synergism and antagonism being more common.

Microparticle systems

The principle of these systems is based on the use of a water soluble polymer and an anionic microparticle (inorganic and organic).

The polymer drives a more or less marked flocculation of fibers, fines and filler. Anionic microparticles insoluble in water having a high specific area and a negative charge will result in a dense, fine flocculation.

Currently, there are various microparticle systems:

Cationic polymer + colloidal polysilicateCationic polymer + bentonite

- Cationic polymer + bentonite + cationic starch

- Non-ionic polymer + bentonite

The main problem of all microparticle systems consists in the fact that it introduces another anionic component (potentially harmful substance) in the paper stock slurry, in a quantity that is not negligible.

The efficiency of microparticle systems depends on both the nature of microparticles and the type of flocculant used

in the mixture [17,18].

The benefit of the microparticle systems is that reflocculation is partly reversible as connection is set by means of microparticles, that in the production process can decompose at microparticle interface on the particle cationic surface.

Another important issue is that reflocculation is carried out at "micro" scale therefore it does not affect paper sheet formation.

The nanoparticle systems increase the operating range of each paper machine providing new ways of obtaining the quality characteristics and of the specific ones that enable the operation at higher speed by advanced dewatering on the wire table, wet press part and drying section.

#### Materials and methods

It has been worked with a paper stock sized in alkaline medium (pH = 7-7.2) with the following composition:

-70% hardwood pulp;

-30% softwood pulp;

- -0.3% Aquapel 210 D (alchildimerketen, synthetic sizer)
- -30% ground calcium carbonate;

-Stock consistency 0.5%.

Quantification of effects regarding the synthetic polymeric flocculants in the papermaking has been done following the filler determination, ash retention, and determination of paper physico-mechanical and optical properties.

Filler retention has been calculated as the ratio between the filler amount retained in paper and that introduced in

the paper stock [19].

Table 4 shows the synthetic polymers used in the experimented retention systems [20]. As it is noticed, synthetic polymers are of polyacrylamidic nature and have been selected from the following reasons:

- polyacrylamides are water soluble

polyacrylamides can be made reproducible with various chain length (molecular weight)

- without diminishing the necessary water solubility, polyacrylamides can be produced with maximum molecular weights (between synthetic flocculants up to  $MM = 2 - 10^6$ 
  - pure polyacrylamide is practically non-ionic
- polymers with anionic properties can be produced by copolymerization with acrylic acid, and by including cationic monomers, polymers with graduated cationic properties can be produced.

Table 4
CHARACTERISTICS OF RETENTION AIDS USED IN WRITING - PRINTING PAPER
AND TOILET PAPER MANUFACTURING

		Toilet paper grades				
Characteristics	FO 4140 PG	FO 4240 PG	AN 934 PG	EM 235	EM 235	CARTARETINE F
Apearance	White powder	White powder	White powder	Aqueous solution with 29% a.d.	Aqueous solution with 30% a.d.	Yellowish clear liquid
Chemical character	PAA mild cationic	PAA medium cationic	PAA anionic	PAA medium anionic	PAA mild anionic	Cationic polyamidamine
Density (20°C) g/cm <sup>3</sup>	0.8	0.85	0.8	-	-	1.06
Brookfield viscosity LVT3, 20°C, 30 rot/min, mPa x s	30 CP la 1gr/l	55 CP la 1 g/l	250 CP la 1 g/l	2000 CP la 5 g/l	700 CP la 5 g/l	450-1000
pH (sol. 0,5%)	-	-	-	-	-	6.5-7.5
Stability at storage (25°C), months	8	10	10	6	6	12
Maximum dissolving concentration, g/l	10	10	5	5	5	-
Dissolving time, min.	90	60	30	-	-	-

Table 5
CHARACTERISTICS OF NADAVIN-DHZ

Composition	Aqueous solution of an PPE resin with a low content of AOX and formaldehyde				
Charge	Cationic				
Dry substance content	$12.5 \pm 0.5\%$				
Viscosity	$50 \pm 20$ mPas (at 25°C with ball viscosimeter)				
Density (at 20°C)	1.04 g/cm <sup>3</sup>				
pH	$2.8 \pm 0.5$				
Can be dilluted	Can be dilluted in any proportion				
Storage stability	6 months at 20°C				

 Table 6

 CHARACTERISTICS OF COLLOIDAL SILICA

Composition	
Charge	Cationic
Dry substance content	$12.5 \pm 0.5\%$
Viscosity	50 ± 20 mPas (at 25°C with ball viscosimeter)
Density (at 20°C)	1.04 g/cm <sup>3</sup>
pH	$2.8 \pm 0.5$
Can be dilluted	Can be dilluted in any proportion
Storage stability	6 months at 20°C

Experiments at first step have been carried out with the DDJ device (Dynamic Drainage Jaar). The DDJ allows the direct measurement of colloidal retention in controlled turbulence conditions and independently of mechanical retention. Measurement of retention in dynamic conditions is very important as starting from stock preparation up to launching and even in the initial formation area, the paper stock is in a dynamic state. The device has a simple construction, the main difference compared to other drainage devices consists in the variable speed agitator ranged between 0 and 3000 rpm.

In order to determine the efficiency of some retention systems with micro/nanoparticles two polyacrylamides with different charges have been selected (FO 4140 PG with low charge and FO 4240 PG with medium charge), a PPE resin (NADAVIN-DHZ), in combination with anionic colloidal silica (Levasil 300 F/ 30%).

The colloidal silica is a jell consisting of compact particles obtained following stabilization of sodium silicate solution and prevention of particle aggregation, so that their rise is carried out by molecular disintegration [20].

Tables 5 and 6 show the characteristics of NADAVIN-DHZ and colloidal silica.

In order to quantify the effect of polymer charge density it has been worked with a steady charge of colloidal silica (0.03% compared to absolutely dry material).

### Results and discussions

Tables 7-9 show the efficiency of using monocomponent and dual retention systems.

As a rule, it is noticed that retention of fillers in the alkaline system is higher than the acid system, by 6% up to 47% even if a monocomponent or a dual retention system is used.

The synthetic retention aid has a major role in the efficiency of sizing as well as in the filler retention, used as a rule in charges higher than 10%.

Thus, compared to the paper produced in the acid process that have an ash content of 5-10%, papers made in the alkaline process a higher ash content was obtained. This content varies between 10% and 19.5%.

# Table 7 MONOCOMPONENT RETENTION SYSTEM

		Alkaline					
CHARACTERISTICS	Acid	FL-45	FO-4140	FI-4240	CARTARETINE		
					40CE		
Filler retention (Rm.u.) %	50	44.8	64.4	89	97		
Ash, %	5-10	9.97	12.19	17.84	19.5		
Opacity, %	89	93	96	96.5	97		
MECHANICAL				·			
CHARACTERISTICS	-	-	-	-			
Breaking length, kgf	5-5.5	8.3	8.0	6.5	5.5		
Burst strength, kgf/cm2	2.5-2.8	3.4	3.5	2.6	2.6		
Tear strength, gfcm/cm	40-50	52	52	66	60		

 Table 8

 DUAL RETENTION SYSTEM (CATIONIC/ ANIONIC)

		FO-4140				FO-4240		
CHARACTERISTICS	Acid	AN	EM	EM	AN	EM	AN	AN
		945	235	533	934	533	934	945
Filler retention (Rm.u.) %	50	50.5	50.4	74.3	56.5	51.5	68.7	62
Ash, %	5-10	10.3	10.2	15	11.7	10.6	13.8	12.4
Opacity, %	89	90.6	92	96.5	91.2	93	68.7	62
MECHANICAL								
CHARACTERISTICS	-	-	-	-	-	-	-	-
Breaking length, kgf	5-5.5	7.5	7.4	7.55	7.8	7.85	8.6	8.4
Burst strength, kgf/cm2	2.5-2.8	3.2	2.8	3.2	3.4	3.5	3.5	3.2
Tear strength, gfcm/cm	40-50	60	52	52	58	60	48	54

 Table 9

 DUAL RETENTION SYSTEM (ANIONIC/CATIONIC)

CHARACTERISTICS	Acid	EM 235	EM 522	EM 225
CHARACTERISTICS	Acid	EMI 233	EM 533	EM-235
		FL-45	FL-45	FO-4240
Filler retention (Rm.u.) %	50	71	59.3	91
Ash, %	5-10	14.2	11.87	18.5
Opacity, %	89	97.4	94.2	95
MECHANICAL				
CHARACTERISTICS	-	-	-	-
Breaking length, kgf	5-5.5	6.5	7.4	7.0
Burst strength, kgf/cm2	2.5- 2.8	2.9	2.9	3
Tear strength, gfcm/cm	40-50	52	58	52

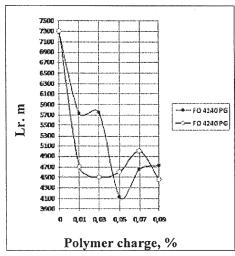


Fig. 10. Variation of breaking length vs. charge of the two polymers

Within synthetic polymers, PAAs are noticed thanks to their high efficiency. The mechanical strength characteristics (breaking load, burst strength and tear strength) increased up to 21%.

The correct use of PAAs is very important, their effect depending on the solution preparation and the metering place in the system. In case of the nano/microparticle system, in order to quantify the effect of charge density concerning polymers, it has been worked with a colloidal silica charge (0.03% compared to absolutely dry material).

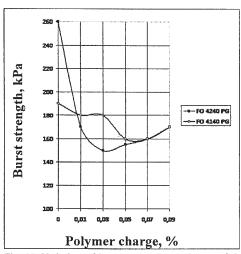


Fig. 11. Variation of burst strength vs. charge of the two polymers

The efficiency of using the micro/nanoparticle (cationic polyacrylamide, anionic colloidal silica) with polymer charge is shown in figure 10-16.

In case of the two polymers, regardless the loading extent, it si noticed that in case of using the micro/nanoparticle systems, the paper mechanical properties go down up to a polymer concentration of 0.05%. It is normal as the pronounced retention of calcium carbonate weakens the inter-fiber bonds. At polymer charges higher than 0.05%, the main effect is improvement of breaking length (here the higher charge density of polymer results in a more favourable effect).

The more pronounced decline of the burst and tear strengths of the PO 4240 PG polymer, shows a paper sheet formation worse than in case of the other polymer (fig. 11)

Considering the results obtained, tests with the multicomponent system FO 4140 PG + anionic colloidal silica have been carried out.

The content of anionic colloidal silica varied from 0.1% to 1.5% (fig. 12-16).

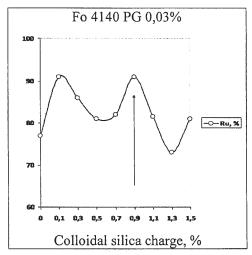


Fig. 12. Variation of filler retention vs. colloidal silica charge

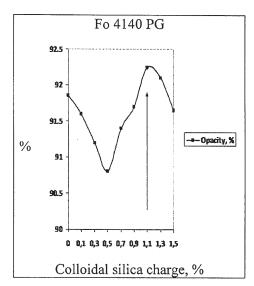


Fig. 13. Variation of opacity vs. colloidal silica charge

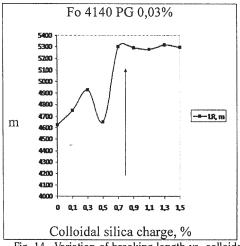


Fig. 14. Variation of breaking length vs. colloidal silica charge

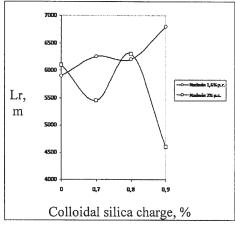


Fig. 15. Variation of breaking length vs. colloidal silica charge

The strength and optic properties of paper are in line with a 0.7-0.9%. silica charge. A major rise of the filler retention (R m.u. > 90%) is also noticed with a positive effect over the load extent of waste water (low pollution).

Following the tests carried out an efficient micro/nanoparticle retention system made of cationic polyacrylamide FO 4140 PG (0.03%) + anionic colloidal silica (0.8-0.9%) was established.

Another polymeric retention system was the system where cationic polyacrilamide has been replaced by an PAAE resin –NADAVIN DHZ (1.6%, 2% concentration), that is an excellent wet strength aid [22].

In this case, a different behaviour of the retention system is noticed according to the component charge.

At a 0.7% colloidal silica charge and a 1.6% dosage of NADAVIN –DHZ, an increase of the breaking length is noticed (opposite to metering 2% product) (fig.15).

An important conclusion is that the efficiency of microparticle based systems decreases while increasing the polymer charge.

It is noticed that for different polymer charges, efficiency of microparticle based systems depends on the charge of the second component, in our case anionic colloidal silica [23].

Thus for a charge of 1.6% Nadavin, good results are obtained with 0.9% silica while with 2% Nadavin, satisfactory results are achieved at 0.8% silica charge.

The paper sheet optic properties are improved by using the microparticle based retention systems (fig. 16).

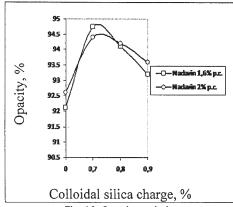


Fig. 16. Opacity variation

The effect of charge order as regards components of microparticle based retention systems has been also studied, using the systems set previously:

- FO 4140 PG 0.3% + 0.8% anionic colloidal silica;

- 1.6% NADAVIN DHZ and 2% marketed product + 0.8% and 0.9% anionic colloidal silica.

By reversing the charge order of the microparticle system components, it has been noticed the decrease of paper strength and optical properties as well as the rise of loading degree concerning effluent systems of the paper machine.

#### **Conclusions**

The efficiency of solid/liquid (cellulosic fibers + fillers/water) separation can be improved a lot by applying the synthetic polymeric flocculants.

Filler retention is greatly influenced by the type of the polymer used, its molecular weight and charge density.

The use of high molecular weight polymer drives the fiber bonding through polymer bridges by means of electronegative charge areas resulting in a significant improvement of retention.

The use of PAAs causes an intense flocculation process with the formation of some flocs resistant to hydrodynamic forces.

The flocculation degree (floc size) drives paper formation, quality, retention and dewatering capability.

The flocculants may act only within a certain *pH* range. Efficiency of retention aids is required by lots of factors of which the impact of shearing forces and anionic trash.

Paper machines with a small or medium working speed can use the monocomponent or dual component retention systems while those with a high working speed can use the microparticle system.

Compared to the monocomponent or dual retention systems, multicomponent systems with micro/nanoparticles show obvious benefits as far as the paper optical properties are concerned as well as retention and reduction of suspension content in waste water.

The modern chemical systems concerning retention based on synthetic polymers provide the opportunity to explore new runs by using some higher quantities of fillers and improvement of paper qualitative characteristics.

#### References

1.BOBU, E., POPA, V.I., Procese chimico-coloidale la fabricarea hârtiei, Ed. Cermi Iași, 1998

2.PIERRE, C., Mesure de la floculation dans les suspension de pâte en écoulement performances de quelques agents de réténtion, Doc. C.T.P. Nr. 1475/1989

3.STANCIU, C., AVRAM, N., BUTEICĂ, D., Retention and retention aids in alkaline paper sizing. The 5th Meeting of Pulp and Paper Industry of Balkan countries, Constanta, Mamaia, 7-9 1998

4.STANCIU, C., BUTEICĂ, D., SECARĂ, C., GHEORGHE, N., PĂVĂLEANU, T., ISAIC, P., AVRAM, N., Agenţi de retenţie utilizaţi la fabricarea diverselor sortimente de hârtie. Third International Symposium Ceprohart Brăila "High performance process and equipment for the pulp and paper industry", 30 May- 1 June 2000, p1

5.ROSE, G., World pulp and paper technology, 1999/2000, p52 6.AUHORN, W., World pulp and paper technology, 2001, p14 7.AUHORN, W., A.T.I.P., 37, nr.3, 1983, p117

8.BICU, I., MUSTAŢĂ, F., Mat. Plast.., **39**, no. 4, 2002, p205 9.GERLI, A., BERGHOUT, S., CARDOSO, X., Pulp and Paper Europe, May/June 2002, p21

10.HULUBEI, C., Mat. Plast., 39, no. 4, 2002, p209

11.POPPEL, E., Rheologie und electrokinetische vogange in der papier technologie, VEB, Fachbucverlag, Leipzig, 1977.

12.MIYANISHI, T., SHIGERU, M., Tappi Journal, 80, nr. 1, 1997, p262 13.BICU, I., Teza de doctorat, Universitatea Tehnică "Gh. Asachi" Iaşi, 1972

14.OBROCEA, I., Teza de doctorat, Universitatea Tehnică "Gh. Asachi" lași, 2002

 $15. RODRIGUEZ, J.M., Micro\ and\ Nanoaparticles\ in\ Papermaking,\ Tappi\ Press,\ Atlanta,\ 2005$ 

16.STANCIU, C., NEDEFF, V., GAVRILĂ, L., CANTEMIR, GH., Modelling and Optimization in the Machines Building Field, Vol. 3, Ed. Alma Mater, Bacău, 2007, p280

17.STANCIU, C., Research concerning achievement and efficiency of some multi-component retention systems with micro/nanoparticles in the paper industry, XIVth International Symposium in the Fields of Pulp and Paper, Packaging and Graphics, Zlatibor, Cigota, June 17th-20th, 2008

18.BENGSTON, G., World Pulp and Paper Technology, 2002, p48 19.OBROCEA, P., BOBU, E., GAVRILESCU, P., Tehnologia celulozei şi hârtiei. Aplicații, Vol.II, Ed. I.P.I, 1987

20.\*\*\* SNF Floerger, Franţa, Polymers used in paper industry, 1996 21.DESHARNAIS, L., DANEAULT, C., CHABOT, B., MORNEAU, D., A.T.I.P., 58, nr. 1, 2004, p19

22.BAYER AG., Produits pour l'industrie du papier

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