Control of Wet end chemistry by synthetic organic polymers. 1. Effect of molecular weight and charge density of polyacrylamide on retention and drainage in paper manufacture

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SUMMARY

Water soluble linear polyacrylamides of various molecular weights ranging from 50,000 to 6500000 are synthesized in the laboratory. Some of these polymers are converted to cationic derivatives and their characteristics determined by measuring the intrinsic viscosity, weight average molecular weight and charge on the polymer.

These known polyacrylamide polymers are then used to study the wet end chemistry of paper making particularly as retention and drainage aids. The molecular weights of the polymer are found to play a dominant role both in the retention of fillers and improvement of the drainage of the pulp. Thus a polyacrylamide of very high molecular weight 6.5×10^8 and negligible charge density retains TiO₂ on paper handsheets as high as 90% even when dosage of application is only 0.04% based on the weight of pulp; whereas a low molecular weight polyacrylamide of weight average molecular weight 0.22×10^8 and charge density 2.1 megg⁻¹ retains only 60% of the TiO₂ applied indicating that not only the charge density of the polymer is important to act as an efficient retention aid but also its molecular weight polyacrylamides of very little charge density are inefficient to serve as retention aids.

However, optimization of polymer application for retention is very complicated because of many factors coming into play simultaneously. This optimization will depend not only on the chemistry of the polymer but also on the characteristics of the pulp, viz., method of pulping, degree of refining amount of fines and wood based polymers present, etc. Effect of alum on the retention of fillers is investigated. Presence of alum for the retention of Kaolin is found to be very important, perhaps due to presence of high negative charge on the surface of kaolin.

The drainage time is found to be decreased when polyacrylamide is added contrary to finding by some other authors. The effect of addition of polyacrylamide on charge of freeness of the pulp is studied and found that a pulp of initial CSf 240 ml when treated with 0.3 mgg-1 fibre and 3.3 mgg-1 fibre polyacrylamide reached values 270 ml and 625 ml respectively. In this case also the effect of molecular weight of the polymer is found to be noticeable.

The control of wet end chemistry in the manufacture of paper is very important. The properties of the finished paper as well as economy and ecology of the system depend to a large extent on the control of the wet end chemistry.

It is well known that during the manufacture of paper from cellulosic pulp in aqueous medium, quite a good percentage of other additives, viz., fillers, pigments, dyes, sizing chemicals etc., are

IPPTA Convention Issue, 1984

added in order to achieve specific properties in the final sheet. Sometimes, particularly in the manufacture of fine paper, the percentage of these additives may far exceed the cellulose content itself. It is the interaction between these various ingredients used in the manufacture of paper which influences the wet end chemistry of the paper industry.

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Cellulose pulp contains hydroxyl, carboxyl or sulphonyl groups which confer negative electrical charges on its surfaces when suspended in aqueous medium. The non-cellulosic additives are also negatively charged particles. An electrostatic repulsive force, therefore, exists which opposes the contact of the fibres and particles. Some particles and fibres may have certain chemicals absorbed on the surface which act as dispersants and oppose contact of the fibres and particles.

It is evident, therefore, that manipulation of these charges to the best advantage of the sheet formation is of paramount importance. Pulp slurry drainage rate, filler retention and white water clarification all depend to a large extent on manipulation of the electric charges which reside on surfaces in water¹.

Beating and refining operations increase the quantity of pulp fines resulting in increased surface area and increased chemical reactivity. Upon collision, due to attractive force between particles, flocculation may occur. In contrast to the attraction between particles, however, chemical reactivity of fines may produce two major types of repulsive effects, viz., electrical double layer and protective colloid. When the repulsion is sfficiently large, sticking collisions between particles are dis-couraged and aggregation and flocculation will not occur in a reasonable period of time. So finer particles smaller than the pore size of the forming sheet pass into the white water. Improving singlepass retention, then, is concerned with providing means to nullify or circumvent the effects of the electrical double layers of the various particles.

Repulsive potential between the fibres and the additives can be overcome by addition of cations, such as alum or by addition of polymers which by virtue of their either opposite charges or molecular sizes can cause to flocculate the fines onto the fibres.

Simple cations, though affect coagulation cannot produce strong flocks that can withstand the shearing forces of a fast machine². Because of white water recycling these cations may accumulate in the headbox which is also detrimental to retention³. A complete as well as tenacious retention is particularly desirable when using additives such as TiO₂, microspheres and/or latex. Another negative aspect of use of alum in the paper industry lies in the fact that it is acidic in nature whereas the paper industry is toward neutral/ alkaline paper making because it is more cost efficient than the acid process.

Polyacrylamides and their ionic derivatives may be used to control the wet end chemistry in paper industry. They improve drainage¹,²⁰ and

formation⁴ assist in the retention of fibre fines⁴, improve initial wet web strength and final dry strength of paper⁵. Although lot of investigations have been carried out on the use of polyacrylamide to control wet end chemistry, it may be observed that the results are not consistent with one another. It is admittedly an esoteric subject and as described by Swanson⁶ the interpretations are cloaked in sesquipedalian jargon. Thus LaMer⁷ suggests that there is an optimum molecular weight of the polymer to achieve maximum flocculation in a given system. Others⁸,⁹ have shown that there is only a monotonically increasing degree of flocculation with increasing molecular weight. Teot¹⁰ has shown that it is the charge on the polymer which determine flocculation independent of molecular weight. It has been demonstrated¹⁹ that higher drainage rates are obtained with both increasing molecular weight and increasing cationic charge. It is hoped that additional data with known polymers are required in order to better understand the mechanism involved. With this aim in view, we have carried out a series of laboratory scale investigations to control the wet end chemistry of paper making with non-ionic and ionic polyacrylamide which are prepared and characterized in our laboratory. This report describes the effects of molecular weights and charge density of polyacrylamide on retention and drainage properties of paper making furnish.

EXPERIMENTAL

A. Materials :

The acrylamide polymers used in this investigation were prepared in the laboratory by radical polymerization¹⁰,¹¹ and their molecular weights controlled by known procedures¹². They were not fractionated and their weight average mol. wt. ranges from 5×10^4 to 6×10^6 . The cationic derivatives of the polyacrylamide were prepared by the Mannich reaction^{18,14,15} and the charge on the polymer were calculated by Colloid Titration method^{16,17}. The intrinsic viscosity of the polymers were measured by a Oswald Viscometer as usual. Molecular weights of the polymers were determined by light scattering technique.

The pulp used in this investigation was a bleached kraft bamboo pulp. The pulp was made from preserved pulp just before its use. This was done following standard practice¹⁸.

B. Methods

150 g fibres were first torn and soaked for about 4 hours. They were then disintegrated in a laboratory disintegrator for sometime, diluted to 1.5 litte with water. When the fibres were well separated, examined visually, they were beaten at 25°C in a laboratory Noble and Wcod valley beater. 5 litre of water added to the beater and

IPPTA Convention Issue, 1984

roller motor started. The disintegrated stock containing 150 g pulp in 1.5 litre of water was then added to the beater and an additional 3.05 litre of water added to make the consistency of the pulp 1.57% (w/v). After 5 minutes of circulation beating was commenced by weighing the bed pla te lever so as to exert a force equivalent to 10.7 ± 0.1 kg. The freeness was measured after every 15 minutes.

All sheets were made on a laboratory sheet former at 60 gsm basis weight using the Tappi standard¹⁹. The beaten pulp was diluted to $1.2^{\frac{1}{2}}$, consistency. Measured quantity of TiO₂ (water consistency. Measured quantity of 110_2 (water dispersible anatase type) was added and stirred. The pH of the for 5 minutes in a disintegrator. The pH of the stock controlled by adding dil NaOH or dil HCl. The content was used for making the sheet. The sheet was made on a 150 mesh wire. The polymer was added to the stock with a burrette in a beaker and mixed thoroughly before added to the sheet machine. The stock was mixed by moving the perforated disk up and down five times within about 4 seconds and it was then slowly removed. Five second after mixing the drainage cock was opened to form the sheet.

Retention was determined as described below:

The sheet was prepared in the sheet machine as described above using the measured quantity of The sheet was filler and polymer, at desired pH. oven dried at 105°C to a constant wt. The weighed paper was folded carefully and placed in a covered platinum crucible and put in the muffle furnace at The weight of ash was 900°C for half an hour. noted. A blank sheet of paper without added filler and polymer was dried and ashed in an The difference in weight identical procedure. between the two ash contents was taken as the The retention is weight of the filler retained. expressed as the percentage of the initially added TiO₂ after correcting for the ignition loss.

The drainage time was determined as described below :

The volume of stock in the sheet machine was maintained at 8 litres which contain pulp, filler, polymer etc. The stock was mixed by moving the perforated disk up and down 5 times within 4 seconds. A stopwatch was started as soon as the drain cock of the sheet machine opened and stopped when the liquid surface disappeared through the formed sheet. Quoted drainage times are the mean of duplicate determinations. They are corrected to a standard sheet basis weight using formula²¹

IPPTA Convention Issue 1984

$$d_{s} = d (60-k) (r-k)^{-1} + {(rt)^{-1}-1} (d-4)^{-1}$$

where,

- $d_s =$ Standard drainage time reported
- d = Average drainage time obtained
- t = Temperature (°C) of the mixture in the cylinder
- $\mathbf{r} = \mathbf{A}\mathbf{v}\mathbf{e}\mathbf{r}\mathbf{a}\mathbf{g}\mathbf{e}\mathbf{g}\mathbf{r}\mathbf{a}\mathbf{m}\mathbf{m}\mathbf{a}\mathbf{g}\mathbf{e}\mathbf{o}\mathbf{f}$ the o.d. sheet
- $v_t = 100$ times the viscosity of water at temperature t.

Flocculation measurements were performed as follows :

The stock was diluted to 0.2% consistency and taken in a 500 ml stoppered measuring cylinder such that the total volume of the stock after addition of the polymer solution did exactly coincide with the 500 ml mark. The cylinders were closed and mixed by inverting the cylinder several times. A stop watch was started when the cylinder was allowed to stand erect. The subsidence rates were determined by plotting the height of the solid liquid boundary as a function of the time. The optical density of the supernatant clear solution was measured at 546 nm using 1 cm cell with distilled water as reference using a Beckman DU spectrophotometer.

RESULTS AND DISCUSSION

Table-I gives the characteristics of the Polymers used for this investigation. It can be seen from Fig. I that the one pass filler retention without polyacrylamide is very low, which is only about 25%. Alum alone increased the filler reten-The effect of molecular tion to about 40%. weight of the polyacrylamide as a function of filler retention can be seen from Fig. I. As the molecular weight of the polyacrylamide increases, the requirement of the polymer for maximum Low molecular weight retention decreases. polyacrylamides are not efficient in improving retention. Thus it is found that with a polyacrylamide of weight average molecular weight 55000 the retention is less than 40% even when as high as 2 mg.g^{-1} fibre of the polymer is applied. Similar observations were also made by Howard et al²² with non-ionic polyacrylamides. Sakaguchi and Nagasee²³ found that when the intrinsic viscosities of the polymer are higher than 5-6 dlg-1 (viscosity average molecular weight about 1 million) they are very effective flocculant.

When the molecular weight of the polymer is high, the loops and tails it can deposit on the surface of the particles will be longer compared to a low molecular weight polymer. This is the case, however, when the polymer is non-ionic or have a very small charge density.

Poly- acrylamides	Molecular weight	dn/dc (Cm ³ g— ¹) ^b	$A_2^T \times 10^4$ (mole.mlg ²) ^c	$S_{od}^{2\frac{1}{2}}$	Charge density	Intrinsic Viscosity	dl. g—1
	(X10-)-			(A)	meq. g	<u> </u>	
1	0.217	0.136	2.3575	440	2.1		3.2
2	1.458	0.166	2.6872	1525	1.95		5.02
3	3.741	0.128	3.1324	2500	2.4		7.4
4	2.121	0.170	1.3826	2330	2.1		5.6
5	6.68	·	:		Very small	18.2	2.1
6	0.09	<u> </u>	<u> </u>		Very small		·
7	0.055	·			Very small	0.06	;

TABLE—I CHARACTERISTICS OF THE CATIONIC POLYACRYLAMIDES

a. In 0.1 M NaCl at 436 nm using Brice phoenix light scattering photometer

b. Refractive index increment for the dialized solution

c. Osmotic second virial coefficient

d. Root mean square radii of gyration.



Having established the effect of molecular weight of polyacrylamide in retaining filler and pigments, we tried to find out a relation between the concentration and molecular weight of the polymer to have the optimum retention. This is a very complicated issue because of many factors coming into play simultaneously. Perhaps, such an optimization will vary widely, Table-II depicts such an attempt. Since retention is influenced not only by the chemistry of the polymer but also by the characteristics of

the pulp, viz., method of pulping, degree of refining, presence of fines, wood based polymers etc., this optimization becomes problematic and little is published in this regard. Fig. 2 shows the influence of degree of refining on the retention of fillers. It can be seen that the degree of refining influences the retention of filler almost linearly. Fig. 3 shows the dependence of retention on the amount of filler added. However the effect of the filler concentration in its retention is rather negligible.

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IPPTA Convention | ssue, 1984



Alum is used in the paper industry for various purposes. So the experiments in isolation of alum may not be very authentic. A series of experiments were performed in which all the ingredients were maintained constant and retention

values were determined with increased concentration of polymer. The results are shown in Table-II. It can be seen that as little as 0.05% of cationic polymer based on the dry wt. of the pulp is sufficient to achieve retention value over 85% when 5% alum is present in the system. The retention of kaolin clay when the same polyacrylamide but under different environment is shown in Table-III. It is found that there is some influence of alum in retaining the Kaolin clay, because polyacrylamide without alum at 0.01%application retains only about 34% of kaolin whereas introduction of 2% alum at the same polymer application the retention values are almost double. It may be due to very high negative surface charge of kaolin particles. The mol. wt. of polyacrylamide has great influence in flocculation is also shown by Chemlir²⁴ et al who have shown that the sedimentation rate of fine kaolin particles suspended in water is 200 times higher if a small amount (1-4 ppm) of polyacrylamide is added to the suspension. They have also found that the sedimentation on time is reduced from 31.5 secs to 2 seconds when the molecular weight of the polymer is increased from 0.3×10^6 to 5.5×10^6 at polymer concentration of 4 ppm.

TABLE—II HAND SHEETS WITH INCREASED CONCENTRATION ACRYLAMIDE POLYMER

TiO ₂ added	= 5%	based	on	the	wt.	of	dry	pulp
Alum	= 5%	,,	,,		,,	,,	,,	. 99
pH of the	stock m	aintaine	ed 5	5.5				

Expt. No.	Weight of the oven dry sheet	Basis weight of the sheet	Weight of the ash after correcting the ignition loss	Amount of polymer added	TiO ₂ retention $\%$ based on TiO ₂ added
	(g)	(g.m—²)	(g)	$(mg.g-1 \times 10-1)$	
1.	1,864	59.3	0.0384	0	41.2
2.	1.898	60.4	0.0452	0.1	47.6
3.	1.870	59.5	0.0543	0.25	58.1
4.	1.920	61.1	0.0647	0.5	67.4
-5.	1.892	60.2	0.0715	1.0	75.6
6.	1.958	62.3	0.0791	2.0	80.8
7.	1.848	58.8	0.0729	3.0	78.9
8	1.876	59.7	0.0773	4.0	82.4
9	1 904	60.6	0.0813	5.0	85.5
10	1 883	59.9	0.0840	10.0	89.2
10.	1 911	60.8	0.0872	15.0	91.3
12	1 867	59.4	0.0817	20.0	87.6
13.	1.952	62.1	0.0839	25.0	86.0

IPPTA Convention Issue, 1984

Experiment No.	Polymer added to pulp mg.g $^{-1} \times 10^{-1}$	Alum added %	pH of the stock	Retention %
1.	0	0	6.5	21
2.	0	2	5.4	38
3.	1	0	6.5	34
4.	2	0	6.5	45
5.	3	0	6.5	58
6.	5	0	6.5	55
7.	10	0	6.5	69
8.	20	0	6.5	72
9.	2	- 1	5.8	48
10.	5	1	6.0	75
11.	10	1	6.0	78
12.	20	1	6.0	82
13.	1	2	5.5	78
14.	2	2	5.0	84
15.	5	2	5.0	88
16.	10	5	4.5	87
17.	10	5	4.5	87

TABLE—IIIEFFECT OF ADDITION OF POLYACRYLAMIDE ON THE
RETENTION OF KAOLIN CLAY

TABLE—IVEFFECT OF ADDITION OF CATIONIC POLYACRYLAMIDE WITH AND
WITHOUT ALUM ADDITION ON DRAINAGE TIME IN SHEET
FORMATION

Experiment	Polymer added to pulp	Alum added to pulp	pH of the	Drainage time (seconds)	
110.	mg. g—1 fibre	(%)	pulp stock		
1.	0.2	0	4.5	20.5	
2.	0.4	0	4.5	18.5	
3.	0.6	0	4.5	18.0	
4.	0.8	0	6.5	17.5	
5.	1.0	0	6.5	17.0	
6.	0	0	4.5	24.0	
7.	0	0.5	4.5	23.5	
8.	0	1.0	4.5	23.0	
9.	0	2.0	4.5	20.5	
10.	0	3.0	4.5	20.0	
11.	0	4.0	4.5	19.0	
12.	0	5.0	4.5	19.0	
13.	0.4	2.0	4.5	17.0	
14.	0.4	3.0	4.5	17.0	
15.	0.4	4.0	4.5	16.5	
16.	0.4	5.0	4.5	16.0	

Pulp: Bleached Bamboo kraft beaten to 300 ml Csf.

IPPTA Convention Issue, 1984

Table IV and Fig. 4 shows the effect of ACKNOWLEDGEMENT polyacrylamide on the drainage of properties of the pulp. It can be seen from Table-IV that the drainage time decreases as the concentration of polymer in the pulp increases contrary to the finding by some other authors²². The drainage time though decreases as the concentration of alum in the pulp is increased, the effect is comparatively less prominent than that with the polymer. However, a combination of alum and polyacrylami je yields better drainage performance. Fig. 4 shows the effect of addition of polyacrylamide on the degree of ficeness of pulp. Thus a pulp of initial canadian Standard freeness of 240 ml when treated with 0.3 mg.g^{-1} fibre and 3.3 mg g^{-1} fibre of polyacrylamide reached values of 270 ml and 625 ml respectively. The effect of molecular weight of polyacrylamide as a drainage aid can be seen by comparing the values in graph 'A' and 'B' in Fig. 4 'A' is a high molecular weight of palymer haviving weight average molecular weight of 3.75×10^6 and 'B' is a low molecular weight polymer having weight average molecular weight 0.22×10^6 . Both these polymer have identical charge density of 2.1 meg g^{-1} . An inspection of the two graphs will indicate that high molecular weight polymer is a better drainage aid than the low molecular weight one.



CONCLUSION

From the above discussion it may be concluded that molecular weight of the polymer plays a dominant role if it is to be used as a retention and drainage aid.

IPPTA Convention issue 1984

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IPPTA, Convention Issue, 1984