

Effects of Branch Degree of CPAM for Retention and Drainage

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ABSTRACT

CPAM has been applied to the paper industry for the purpose of wet-end improvement for a long time. And molecular weight and charge density have been managed most important quality factors to make CPAM for this application. Recently branched CPAM was developed to improve retention and drainage characteristics and we considered branch degree of CPAM as important factor as molecular weight and charge density. In this experiment, we tried to investigate physical and chemical properties to determine branch degree and flocculation efficiency using Arbocell pulp which was recently developed micro size pulp and finally we applied retention and drainage test under the ONP stock condition.

Keywords : polyacrylamide, retention, drainage, branch degree, inverse emulsion, Arbocell

1. Introduction

CPAM (cationic polyacrylamide) has been widely applied wet-end of paper mill. Lower molecular weight CPAM has been applied to the paper strengthening aid to be added to the thick stock and higher molecular weighted CPAM has been applied to retention and drainage aids to be added shear point of near pan-pump or pressure-screen of wet-end. And molecular weight and charge density have been managed most important quality factors of these application. Recently we found

branch degree was as important as molecular weight and charge density. And branch degree of CPAM affects not only retention and drainage in the wet-end but also paper quality including formation, strengthening properties of paper. Normally linear CPAM (L-CPAM) has good flocculation efficiency at lower dosage condition however flocculation efficiency was rapidly decreased when over dosage of the polymer. On the other hand, branched or cross-linked CPAM (B-CPAM or C-CPAM) tend to increase flocculation efficiency even though slightly over dosage of the polymer and also have benefit of better paper formation than L-CPAM somewhat. Polymerization methods to make high molecular weight C-PAM were classified salt dispersion type, powder type and inverse emulsion type. And salt dispersion type CPAM is difficult to increase molecular weight as high as powder or inverse emulsion type because of decreasing stability under the condition of high molecular weight. And it is very difficult to make branched CPAM with powder form also because of insoluble particle generation during drying process. Finally inverse emulsion type CPAM is most suitable to produce not only higher molecular weight but also easy production of branched or cross linked form because it is stabilized in the W/O micelle and there are no difficult process of gel drying and etc..1~2) There are some researchers tried to apply branched polymer to wet end application. First of all Shin jong ho et al applied highly branched CPAM to fine and filler flocculation 4)~5) and we published multiple retention system using branched CPAM, branched APAM and microparticle of bentonite or silica using LBKP with grinded calcium carbonate (GCC) stock condition. 3) And also we can find reference of branched or crosslinked polymer to apply paper retention and drainage aids from a few United states or European patents. 7~8) In this experiment, we tried to investigate physical and chemical properties to determine branch degree and flocculation efficiency using Arbocell pulp which was recently developed micro size pulp and finally we applied retention and drainage test under the ONP stock condition.

2. Materials and methods

2.1. CPAM emulsion preparation

CPAM emulsions were polymerized by typical inverse emulsion manufacturing process as figure-1.

2.2. Analysis of CPAM characteristics by morphology

2.2.1 Analysis of physical and chemical characteristics

Solid contents was measured by IR dessicator with condition of 160 °C and 16 minutes. Viscosity was measured by Brookfield viscometer (LV-2 type) preparing 0.2% active polymer solution. and charge density was measured by PVSU titration method. Sancam flow speed was measured by preparation of 0.2% active polymer solution with addition of 40 ml of polymer solution to the sancap and measure times of flow.

2.2.2 Spectrometric characteristics by colloidal titration

We prepared 100 ml of 0.005% active polymer solution and add HCl to adjust pH between 3.8 and 4.2 and then add 2 drops of 0.1% TB (Toluidine blue) indicator and start titration with 0.0025N PVSU (Potassium polyvinylsulfate) solution. Measure absorbance under the condition of 625 nm wavelength using Hach DR 2500 spectrophotometer 4 times repeatedly by every 4 drops of PVSU solution titration. Report the average of standard deviation of each absorbance of every 4 times measurement as a branch degree.

2.2.3 Flocculation characteristics using Arbocell pulp

Prepare 0.1% of active polymer solution and add 1,000 ppm (Dry pulp base) of polymer to the 0.3% consistency Arbocell pulp and let it stirred during 10 seconds at 1,000 rpm and then measure floc size using Horiba LA-700 particle size analyzer.

2.3. Retention and drainage test

2.3.1 Stock

Stock consisted of ONP which was taken from not-printed area of waste newspaper and whiter water taken from H-paper. After disintegrating of pulp, we adjusted final consistency of stock to 0.18%. And the cationic demand of stock was 4.5 ml of 0.001N polyDADMAC titration and pH of the stock was 7.0.

2.3.2 Retention and drainage test

Retention test was performed by operation of RDA (Retention and drainage analyzer). The consistency of the stock was 0.18% and the volume of the stock was 1,000 ml. Vacuum condition of the drainage part was 200 mmHg at the main and sub tank. The sequence of chemical contacted time of the stock was as followings. At first, stock was introduced to the jar and let it stirred at 1,000 rpm for 15 seconds. And then, C-PAM was added and let it stirred at 1,500 rpm for 15 seconds of 60 (± 10) g/m² paper forming condition. Retention was determined by measuring of FPR by filtering white water using filter paper and let it dry during 8 hours 105°C. Drainage was compared by vacuum releasing curves during RDA test. and Formation of the paper was determined by using Techpap 2D-F sensor.

3. Results and Discussion

3.1. CPAM inverse emulsion preparation

We prepared CPAM inverse emulsion with various morphological conditions by polymerization after emulsification of acrylamide, dimethylaminoethylacrylate methylchloride quaternary salt, water, hydrocarbon oil and surfactants. And we controled branch degree to change dosage of branching monomer. Figure-1 of equipment diagram of polymerization shows well how to make CPAM polymers. To briefly introduce polymerization condition, agitating condition was paddle type impeller at the speed of 300 rpm. We started polymerization to add redox catalyst after charge nitrogen gas sufficiently to remove dissolved oxygen in the monomer

solution. This was exothermic reaction and we have to remove heat using water bath during polymerization. charge density was adjusted to control mole ratio of acrylamide and dimethylaminoethyl acrylate methylchloride quaternary salt monomer. And molecular weight was adjusted to apply same amount of initiator and catalyst. And finally branch degree was controlled by dosage of branching monomer. We did not add branching monomer to L-CPAM polymerization and we increased branching monomer amount by increase of branch degree. After polymerization, we cooled reactor to room temperature and add very high hydrophile-liphophile balance (HLB) nonionic surfactants of inversing treatment to increase solubility in the water. After polymerization, stability of L-CPAM, B-CPAM and C-CPAM were good and we managed bulk viscosity of emulsion bellow 1,000 cPs to maintain fluidity.

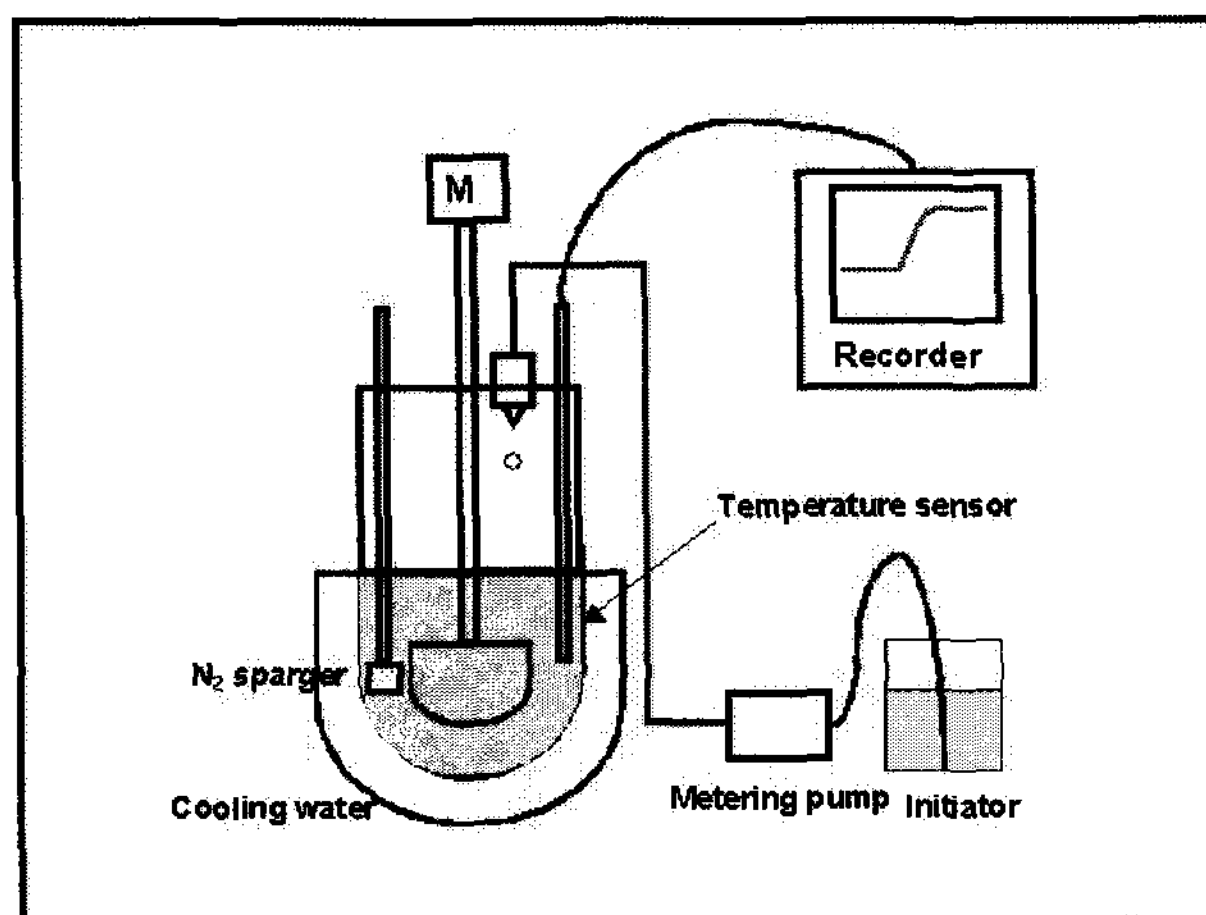


Fig.-1 Equipment diagram of inverse emulsion polymerization

3.2. Analysis of CPAMs

3.2.1 Physical analysis

we show analysis result of L-CPAM, B-CPAM and C-CPAM to table-1. Solid contents and pH of polymers were almost same of about 40% and 5 respectively. There needed extra care not to increase solid contents too high because it can break micelle especially high molecular weight condition and higher pH above 6 can

affect by hydrolysis of cationic functional group of polymer. 0.2% solution viscosity of C-CPAM was highest and lower with order of B-CPAM and L-CPAM. On the other hand, sancap flow speed of C-CPAM was fastest and slower with order of B-CPAM and L-CPAM. Normally speed of sancap flow is lower with higher viscosity but, in this experiment opposite result was observed. And we considered different morphological condition of CPAM related independently with viscosity and sancap flow speed under the gravity. This phenomena can be explained L-CPAM tends to be tangled and combined together to reduce flow speed of sancap however branched or cross linked CPAM tends to get higher viscosity to increase resistance between brookfield spindle and polymers from charge interactions among around polymers but when free flow mode under the gravity, polymers are less combined than linear polymers because of their rigid shape of polymers to increase speed of sancap flow. Actually, we can see different phenomena when we dragged up 0.2% solution of polymers, L-CPAM was dragged bulky formation and B-CPAM and C-CPAM tends to be dragged thin and broken formation because of same reason mentioned above. In terms of charge density, L-CPAM was highest and B-CPAM and C-CPAM were followed in order because steric effects of branch and network formation of B-CPAM and C-CPAM reduced penetration speed of PVS titrator and possibly end point of titration was early finished.

Table-1 Analysis of applied C-PAM

Items	unit	L-CPAM	B-CPAM	C-CPAM
Solid contents	%	40.3	40.5	40.2
Charge density	meq/g	1.4	1.3	1.25
pH at 0.2% solution	~	5.1	5.2	5.1
Viscosity at 0.2% solution	cPs	250	280	380
Sancap flow at 0.2% solution	second	40	32	25
Branch degree	degree	0.25	0.64	1.1

3.2.2 Spectrophotometric characteristics by colloidal titration

When PVSX titration to analyze charge density of CPAM, L-CPAM tends to be stable to maintain blue color of TB indicator during titration and rapidly change to pink color when reach to endpoint because of cationic functional group of L-CPAM is opened and PVSX penetration is relatively quick to response. On the other hand structured CPAM like B-CPAM and C-CPAM seems to have rigid network type structure and there are some hidden cationic functional group and it block penetration of PVSX therefore, color of TB indicator changed frequently during titration. We checked color variation during titration using Hach-2500 spectrophotometer to determine branch degree visually. Figure-2 shows the curves according to various wavelength using both of blue color and pink color of TB indicator, we found 625nm wavelength was selected to distinguish easily blue and pink color. Every 4 drops of PVSX titration, we checked absorbance 4 times repeatedly at 625 nm wavelength to check change of colors. As you see figure-3, we found C-CPAM was more fluctuated and followed B-CPAM and L-CPAM in order. We analyzed this result from calculation of average of standard deviation at the point of every 4 drops periods. We can see the distinctively difference of branch degree of L-CPAM, B-CPAM and C-CPAM at figure-4. This result could be explained the steric effect difference of CPAM can be applied not only measurement of branch degree but also give us indirect evidence of the formation difference of steric condition of each L-CPAM, B-CPAM and C-CPAM.

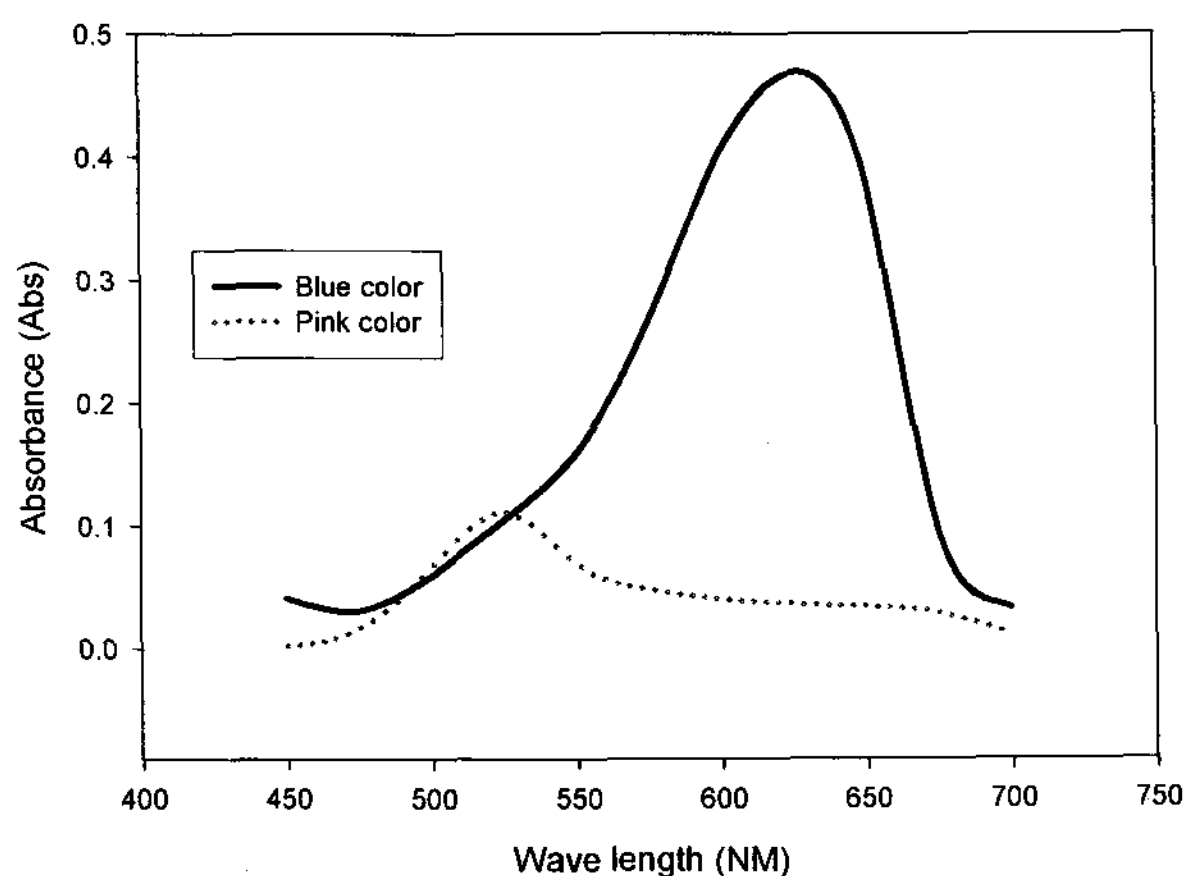


Fig.-2 Absorbance curve of Blue and Pink color of TB indicator (Hach 2500)

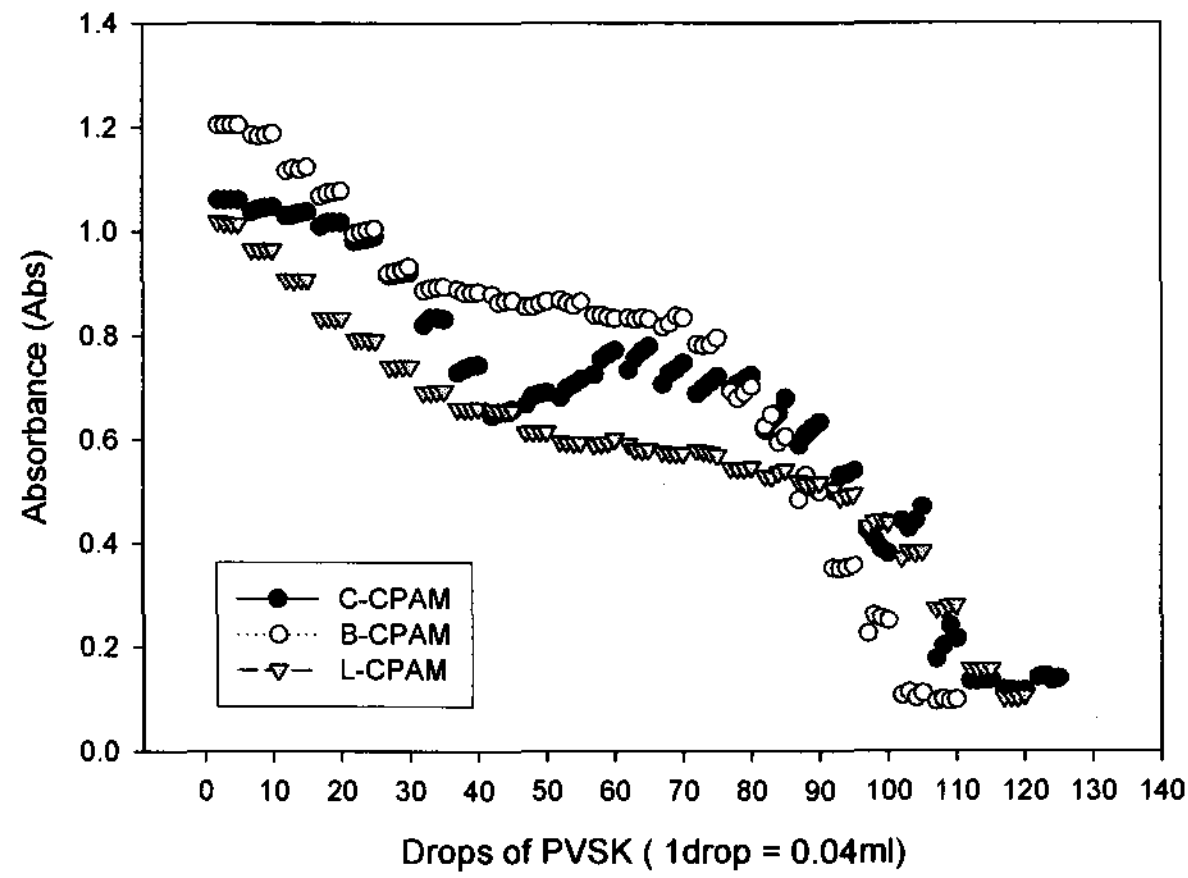


Fig.-3 Absorbance curve by titration of PVSK at 625nm wavelength(Hach 2500)

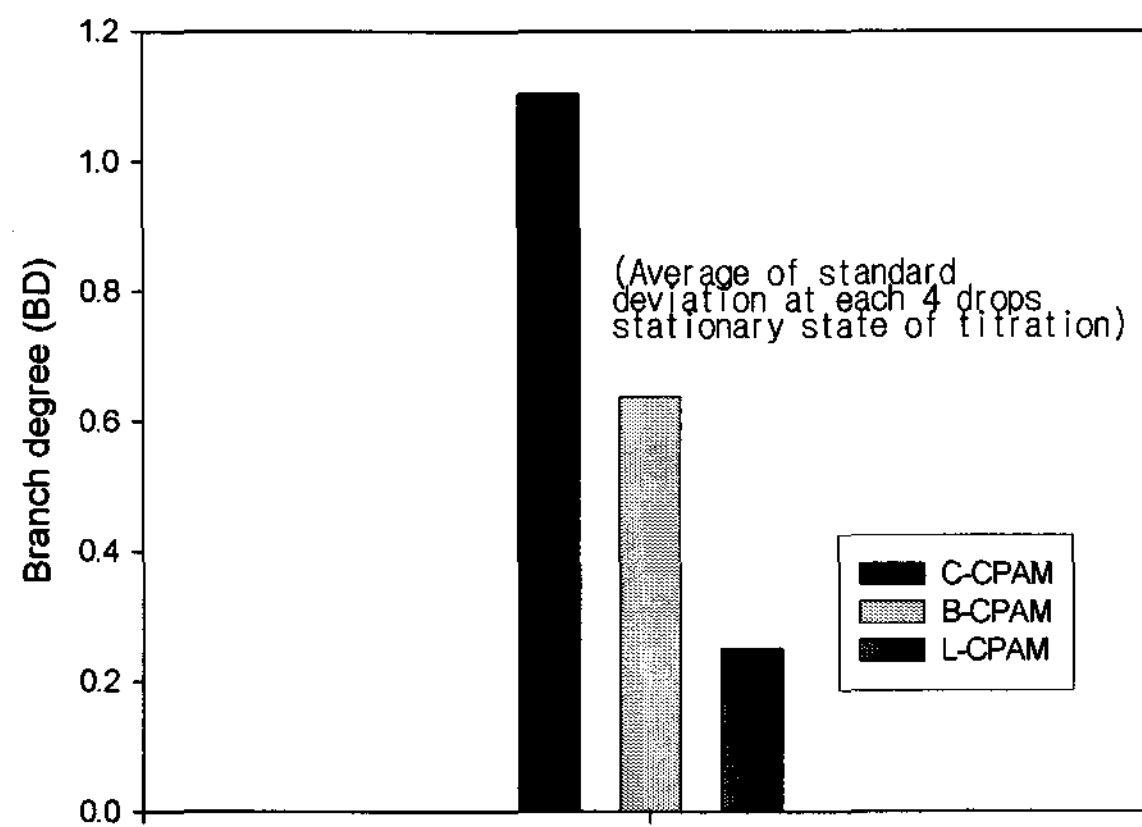


Fig.-4 Branch degree of applied CPAMs

3.2.3 Flocculation characteristics of Arbocell pulp

To evaluate flocculation efficiency by branch degree of CPAM, we used Arbocell C-100 micro pulp which was better to evaluate floc size using particle size analyzer because of its shapes are small and relatively rectangular form to compare ONP which is rather longish shaped pulp as you can see table-2. We found better flocculation efficiency with the increase of branch degree at figure-5. And also found C-CPAM and B-CPAM was much stable to maintain flocculation efficiency

when we add 1M NaCl salt to the pulp to increase conductivity according to figure-6. L-CPAM of tangle and flexible morphology tends to easily shrink by NaCl salt effect but more rigid form of B-CPAM and C-CPAM was considered better performance under the high conductivity pulp conditions. Above benefit of B-CPAM and C-CPAM is expected to be applied to the dirt white water and process water conditions from mill closure of the paper mills.

Table-2 Analysis of applied Pulps

Items (unit)	Arbocell C100	ONP
Average fiber length (μm)	290	784
Average Width (μm)	46	22
Coarseness (mg/m)	3.2	0.17
Kinked fibers (%)	4.1	15
Average Curl (%)	8.3	5.3
Rate in macrofibril length (%)	2.6	1.1
Break end (%)	77.5	34

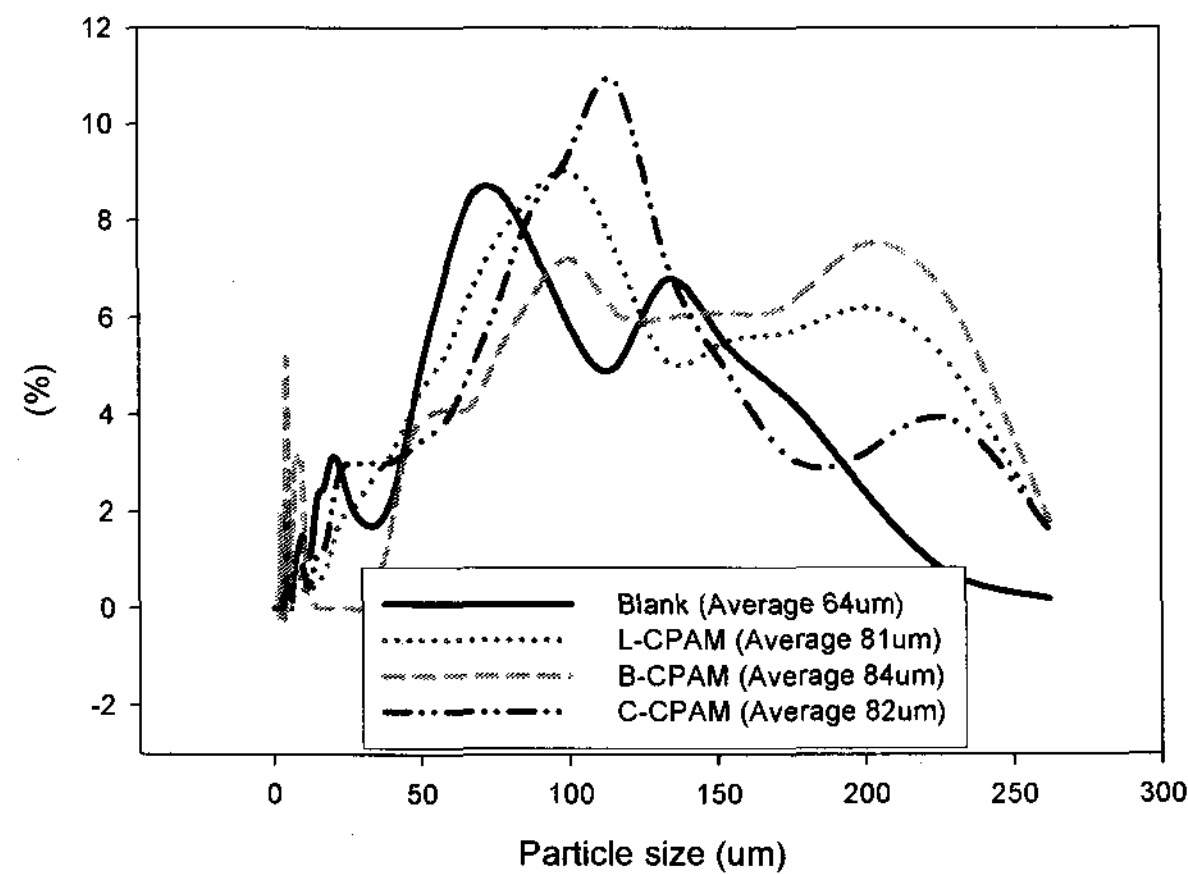


Fig.-5 Flocculation efficiency of Arbocell C 100 by morphology of C-PAMs (Horiba LA-700 particle size analyzer)

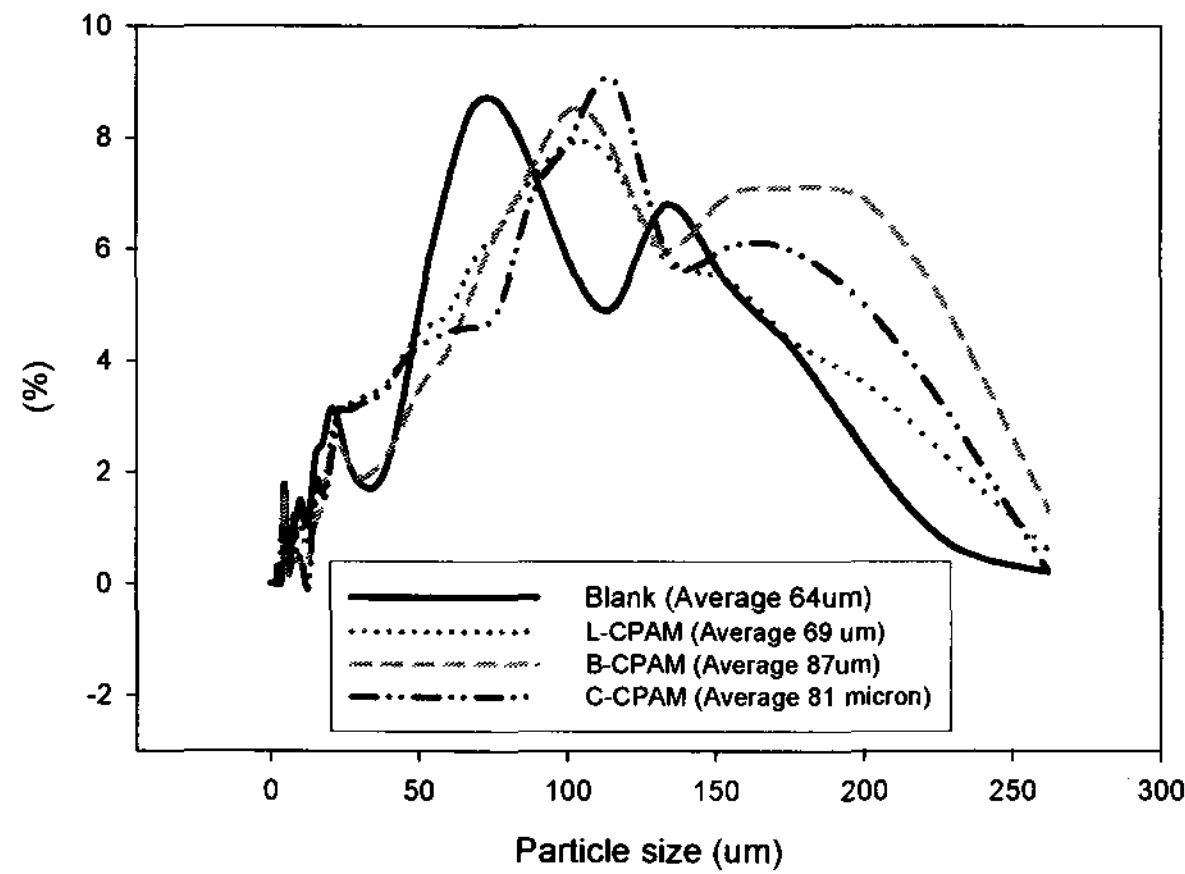


Fig.-6 Flocculation efficiency of Arbocell C 100 with 1M NaCl by morphology of C-PAMs (Horiba LA-700 particle size analyzer)

3.3. Retention and drainage test

We tested retention, drainage and formation characteristics of L-CPAM, B-CPAM and C-CPAM using ONP stock condition. As you can see figure-7, L-CPAM shows fast retention performance at lower dosage of polymer but, it slows to increase performance with increase of polymer dosage. On the other hand B-CPAM and C-CPAM increased retention properties constantly to increase polymer dosage. You can also find drainage result of relatively high polymer dosage of 1,000 ppm at figure-8, it resulted good performance with increase of branch degree. This could be understood that L-CPAM of linear polymer increase the viscosity of stocks from remained polymers tend to tangle and combined each other. On the other hand B-CPAM or C-CPAM of structured polymer seems less affected to increase viscosity by adjacent polymers and also have benefit of resistance to the conductivity by its concrete and rigid formation. Formation comparison of figure-9 shows better result with the increase of branch degree. This result was originated from B-CPAM and C-CPAM of structured polymer less affect agglomeration between fibers and make relatively small and dense floc than L-CPAM. At the result we found branch degree of CPAM is very important to achieve better

retention, drainage and formation with saving chemical cost. Therefore, further study relating not only CPAM but also APAM is needed to investigate and also needed development of measuring technology of branch degree to evaluate current products and developed products in the future.

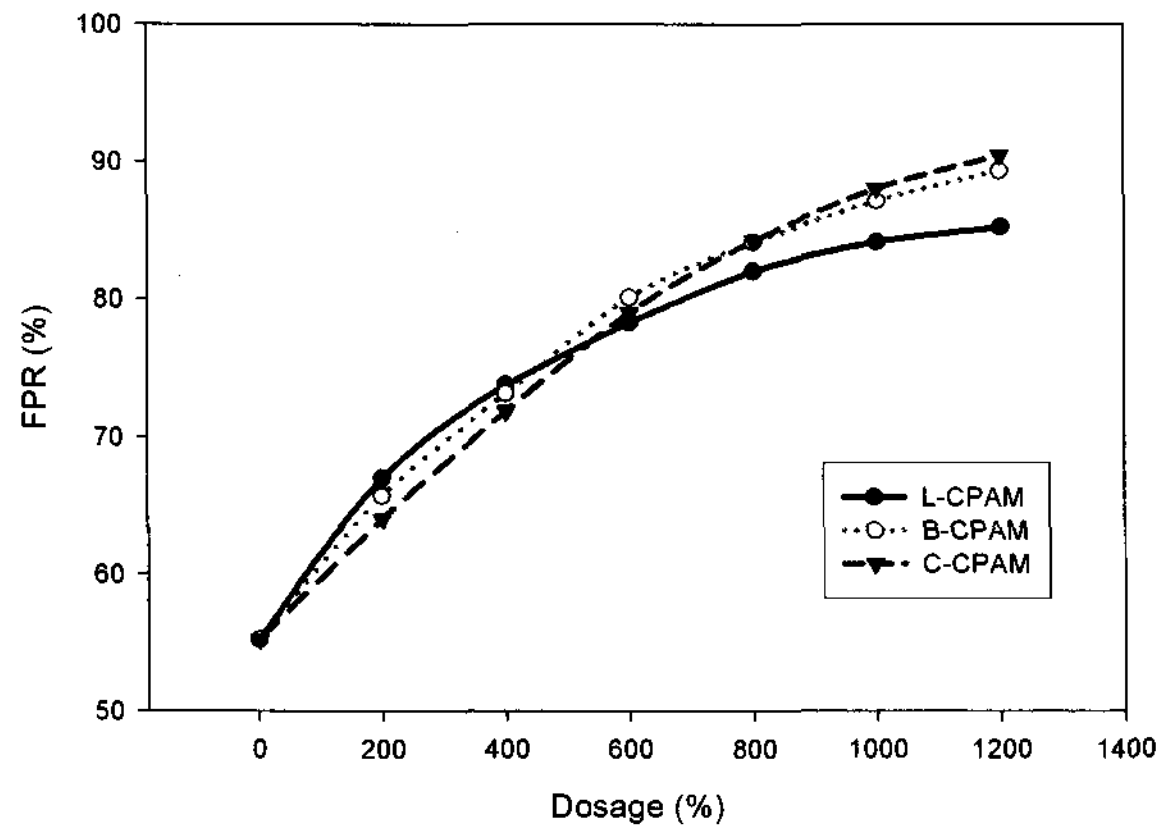


Fig.-7 First pass retention of ONP with various CPAMs

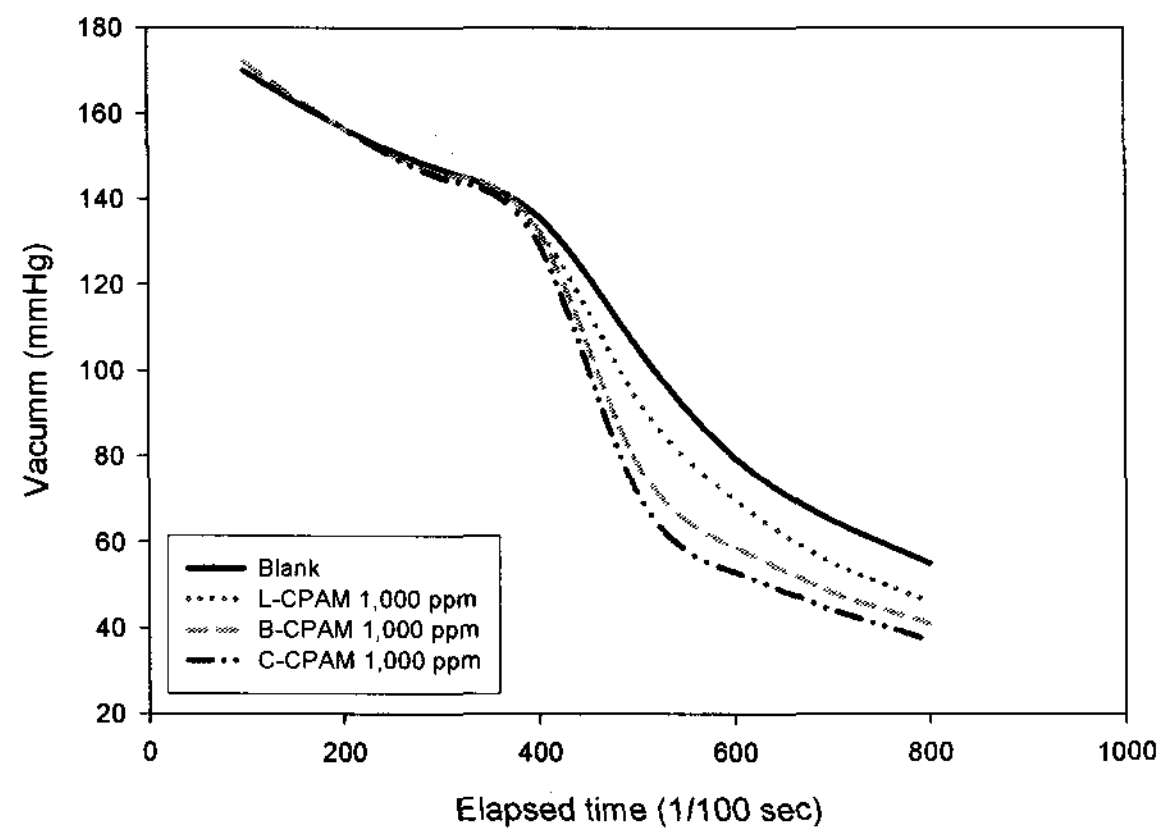


Fig.-8 Drainage curve of ONP with various CPAMs

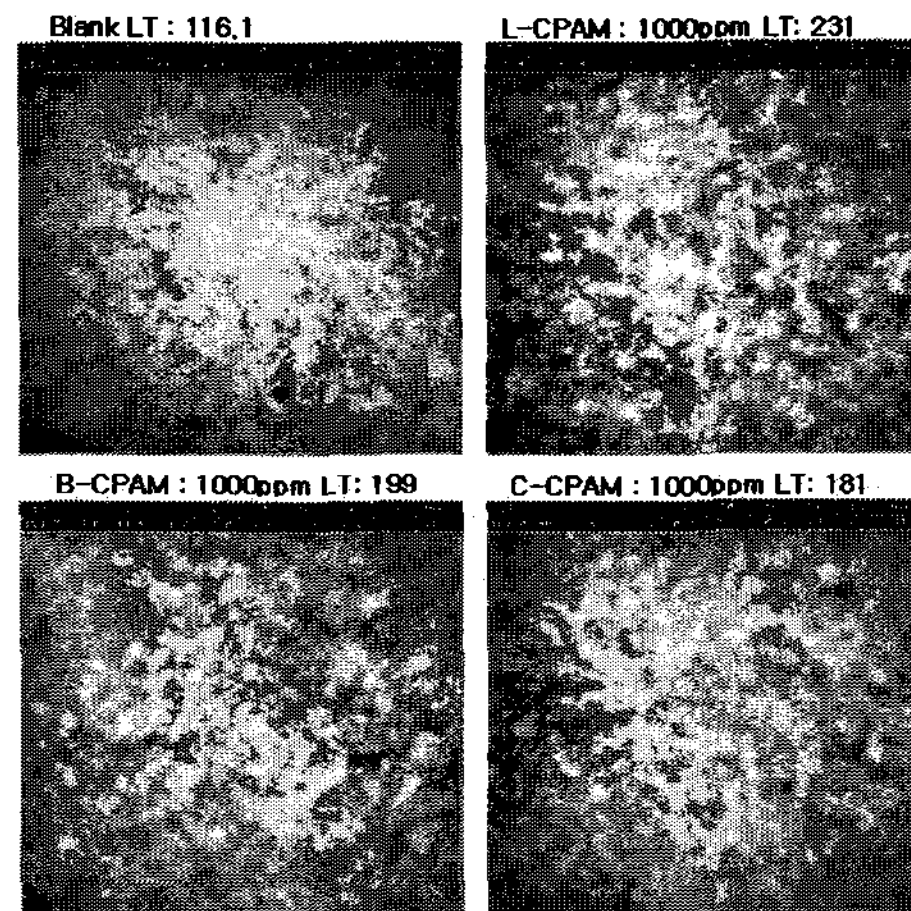


Fig.-9 Formation of ONP with various CPAMs

4. Conclusions

As a retention and drainage aids, branch degree of CPAM is very important and we found inverse emulsion type is much acceptable to control branch degree of CPAM to compare powder and salt dispersion type. With result of analysis of the characteristics according to branch degree of CPAM, charge density is decreased as increase the branch degree because of steric effect of structured polymer shorten endpoint determination. And solution viscosity increased by branch degree increase but, flow rate of sancap reduced by branch degree increase. It shows us when morphology changed, rotational viscosity and flow characteristics under the gravity condition is independently behaved. And we can determined branch degree of CPAM to measure absorbance at 625 nm wavelength to check variation of color during PVSK colloidal titration. With regarding flocculation efficiency using Arbocell of recently developed micro pulp, we found higher flocculation efficiency and better resistance under the high conductivity condition with higher branch degree of CPAM. Finally, we applied retention and drainage test with ONP stock. we found better retention, drainage and formation especially higher dosage polymer condition with higher branch degree. Therefore, we found branch degree is very important

factor to affect retention, drainage and formation and further study of not only CPAM but also APAM and development to evaluate branch degree is also needed in the future.

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