# Effect of Branch Degree of Cationic Acrylamide Copolymers on Flocculation Properties

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## ABSTRACT

Three kinds of cationic acrylamide copolymer with different branch degree were prepared controlling the dosage of N, N'-methylenebisacrylamide. The physical characteristics of the branch-degree-modified copolymers were analyzed by intrinsic viscosity and charge density. The branch degree measurements were investigated by applying the colloidal titration phenomena using a spectrophotometer and comparison with the cationic regain measurement method. The results showed that the absorbance behaviors of spectrophotometer were distinctively different with the branch degree of copolymers. Also, the branch degree determinations and molecular structure estimations of the copolymers were numerically measured by applying the titration phenomena using a spectrophotometer. Finally, three kinds of branch-degree-modified copolymers were applied to flocculation test using arbocel micro pulp for the determination of flocculation behavior by different morphology of cationic acrylamide copolymers.

## 1. Introduction

Flocculation is one of the most important processes in waste water treatment, retention and drainage for papermaking. Acrylamide based copolymers have been widely used for these applications. Anionic polyacrylamide copolymers, prepared by co-polymerization between acrylamide and acrylic acid sodium or ammonium salts and cationic polyacrylamide copolymers, are also prepared by co-polymerization between acrylamide and the methyl chloride salt of dimethylaminoethylacrylate (DMAEA-MC).

In the past few decades, researchers have tried to find a relationship between flocculation efficiency and ionic charge conditions or the molecular weight of polymers. Nasser and Nasser investigated the effects of the surface charge and molecular weight of polyacrylamide (PAM) on the flocculation of kaolinite

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suspensions (1). Bhardwaj et al. found that the effects of the cationic polyacrylamide on the zeta-potential of stock and the effective increase of drainage of secondary fiber pulp (2). Several studies have shown that polymer structure has a great effect on flocculation efficiencies. Ren et al. found that the hydrophobic functional group of cationic polyacrylamide positively affects the flocculation efficiency of kaolin suspension and sugar refinery waste water (3). Larson et al. found that the high molecular-weighted linear CPAM combined with nanosize silica particle produces large network structures giving positive effects on the flocculation (4). Recently studies on the structure modification of branch or cross-linked polyacrylamide have been presented. Ono and Deng found that cationic polymeric micro-particle polyacrylamide can be synthesized emulsion form, and can improve the PCC retention significantly with the cationic dual polymer system (5,6). Naghash et. al succeeded in synthesizing cross-linked nonionic polyacrylamide using the free-radical co-polymerization of acrylamide and N,N'-methylenbisacrylamide using the Ce-based redox initiator system (7). Son and Kim found that branched CPAM, branched APAM and micro-particles of bentonite or the silca multiple dosing system were effective in compensating defects of both linear and cross-linked type polyacrylamide (8). Shin et al. has published conclusions that highly branched cationic polyacrylamide was effective in causing compact flocculation of fillers and better retention maintaining formation of fine retention application (9,10). Wan et al. found that cationic guar gum graft polyacrylamide brings about effective flocculation of tobacco waste water because of its long side chain attached to the backbone of polymer (11).

As introduced above, many researchers have investigated modification of polyacrylamide structures to improve flocculation efficiency. However, there has not been enough evidence of modification of structures, and furthermore, no-one has suggested or presented quantitative analysis of applied structured polyacrylamide.

First of all, Shin et al. has shown evidence of branching by the existence of carbonyl group in the polymer by FT-IR analysis, which explain the bonding of acrylamide and pentaerythritol triacrylate. However, this is not clear because cationic polyacrylamide has already been found to have carbonyl functionality in the methyl chloride salt of the dimethylaminoethylacrylate cationic functional group (9). Yezek and Leeuwen found that cross-linked polyacrylamide, with or without Na-acrylate, showed different characteristics of streaming potential and conductivity, and that this phenomena could be applied to develop branch degree measuring technology (12). Silva et al. presented pore differences using an SEM microscope by cross-linking degrees, and this technology was considered to be effective for analyzing highly cross-linked polyacrylamide (13). Omari et al. has published that higher cross-linking density polyacrylamide gel had better resistance characteristics at a high shear, after study of the properties of structure and rheology of polyacrylamide micro-gel dispersion (14). Nanko et al. has presented the shapes of linear polyacrylamide and branched polyacrylamide on pulp to characterize wet-end performance using a TEM microscope (15). In our opinion, the development of quantitative measuring technology of branch degree of polyacrylamide is required.

In this report, three kinds of branch degree modified copolymers of acrylamide with the methylchloride salt of dimethylaminoethylacrylate(DMAEA-MC) were prepared adjusting the dosage of branch monomer of N,N'-methylenebis acrylamide. The physical characteristics of branch-degree-modified copolymers were analyzed by intrinsic viscosity and charge density. The branch degree measurements and molecular structure estimations were investigated by colloidal titration phenomena using a spectrophotometer. Finally, branch degree modified cationic polymers were applied to flocculation testing using arbocel micro pulp.

## 2. Experimental

### 2.1 Materials

Polyvinylsulfate-K salt(PVSK), toluidine blue(TB) indicator, ammonium persulfate, sodium hydrogen sulfite, N,N'-methylenebis acrylamide and acetone of analytical grade were used. Acrylamide, methylchloride salt of dimethylaminoethylacrylate(DMAEA-MC), hydrocarbon oil, and surfactants of chemical grade were also used. Arbocel C-100 micro pulp was obtained from J. RETTENMAIER & SHEN GMBH CO., Germany. Deionized water was used in the whole experimental process.

### 2.2 Polymerization

The synthesis method described by Son and Kim[8] was used in the preparation of branch degree modified copolymers of acrylamide with DMAEA-MC by the different dosage of branch monomer of N,N'-methylenebis acrylamide. The polymers were synthesized in three steps. First of all, hydrocarbon oil, acrylamide, DMAEA-MC, surfactants and deionized water were emulsified with a homogenizer. Secondly, after charging nitrogen gas sufficiently to remove dissolved oxygen, ammonium persulfate and sodium hydrogen sulfite catalysis were added to the reactor to start polymerization. They were synthesized at 50~70℃ for 3 hrs in nitrogen atmosphere. Finally, the reactor was cooled to room temperature after polymerization and high HLB (hydrophile-liphophile balance) nonionic surfactants of inversing agent were added to increase solubility in water. These polymer emulsions were precipitated and extracted with acetone to recover and were then dried in a vacuum oven at 60℃ for 3 hrs. The yield of the polymerization was calculated with Eq.1 and the related equipment diagram is shown in Fig.1.

Eq. 1.

$$Yield(\%) = \frac{Weight\,of\,recovered\,polymer}{Weight\,of\,total\,monomers} \times 100$$
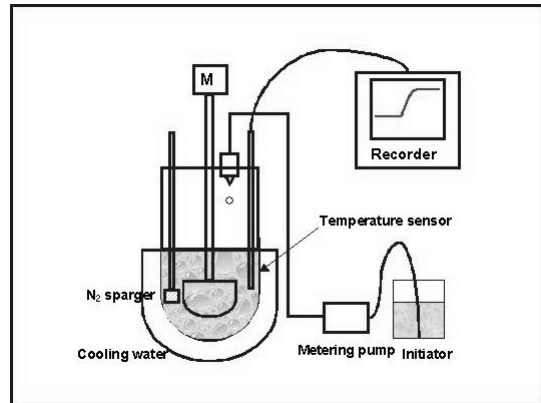


**Fig. 1. Equipment diagram of inverse emulsion polymerization.**

### 2.3 Intrinsic viscosity measurement

The intrinsic viscosity of the polymer was determined by a Cannon Fenske capillary viscometer at 30± 0.0 2℃ in sodium chloride solution (1 mol/L). Intrinsic viscosity is the specific viscosity divided by the concentration which is extrapolated .

$$Eq.\,2.\ \eta_{sp/c} = \frac{t/t_0 - 1}{C}$$

$$Eq.\,3.\ \eta = \lim_{C \to 0} \frac{(t/t_0 - 1)}{C}$$

where, $\eta$ SP/C : specific viscosity, t : time of fall of polymer with 1 N-NaCl, $t_0$ : time of fall of 1 N-NaCl, C : consistency of polymer.

### 2.4 Charge density and ionic regain measurements

Charge density was measured at 100 g of 0.005 % polymer solution with 2 drops of 0.1 % TB indicator using 0.0025 N PVSK titration. Ionic regain was calculated by measuring charge density after stirring at high shear of 10,000 rpm for 5 minutes according to the same procedure above.

$$Eq.4.\ C.D. = \frac{V_{PVSK} \times N_{PVSK}}{10 \times C \times W}$$

where, C.D.: polymer charge density (meq/g), VPVSK : required PVSK volume (mL), NPVSK : normality of PVSK (meq/L), C : polymer consistency (volume %), W : weight of polymer solution.

Eq.5.  $I.R. (\%) = \dfrac{C.D._2 - C.D._1}{C.D._2} \times 100$

where, I.R.: ionic regain, C.D.$_1$ : normal charge density, C.D.$_2$ : charge density after applying shear.

## 2.5 Branch degree and molecular structure estimation

Colloidal titration of 100 mL of 0.005 % polymer solution using 0.0025N PVSK was the same as for the charge density measurement. The 4 measurements of spectrum were carred out at every addition of 0.24 mL addition of 0.0025 N PVSK under the 625 nm wavelength using a Hach 2400 spectrophotometer because 625 nm wavelength is good to compare colors between blue and violet. Branch degree was determined by using the average of standard deviation of the absorbance data from the 4 spectra. Molecular structures were estimated by plotted graphs as in Fig. 2. The smoothly decreasing curve of A represents the soft region as a free open charge neutralization. The slightly stagnating or increasing curve of B represents

the hard region as a hidden charge in the network neutralization. A and B ratios give us the structural information of polymers. The reason of increasing curve of B is considered that hard region blocks PVSK to the inside of the polymer till completion of the reaction between soft region and PVSK. And then PVSK burst to enter to the inside of the polymer by the discrepancy of the consistency of the PVSK between soft region and hard region.

We considered two different ways of concept to classify the structure of cationic polyacrylamide. First, branch degree concept of the polyacrylamide is classified by the different phenomena of fluctuation at each point of titration of PVSK. This idea gives us only reactivity difference between cationic polyacrylamide and PVSK by different morphology of cationic polyacrylamide on the certain point. Second, molecular design is estimated by drawing the curve of the overall behavior of titration. This idea gives us the overall information of the structure of the cationic polyacrylamide to compare proportion of soft region and hard region.

Eq.6.  Branch degree = m $\sigma$

where, m : average, $\sigma$ : standard deviation of absorbance at 625 nm from 4 spectra at every 0.24 mL addition of 0.0025 N PVSK.
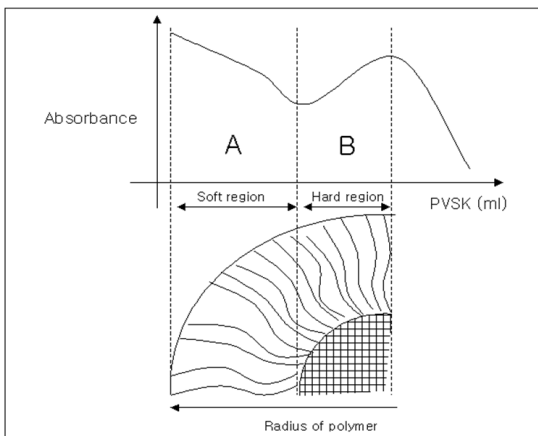
## 2.6 Flocculation test

Polymer solution of 0.1 % on the oven dry pulp was added to a 500 mL of 0.3 % arbocel C-100 micro-pulp slurry with or without NaCl to adjust conductivity. Particle size of arbocel C-100 is 100 $\mu$ m according to manufacturer information. They were mixed by various speeds of 1,000 rpm, 2,000 rpm and 3,000 rpm during 30 seconds using a propeller type agitator. Floc size distributions were determined by using a particle size analyzer (Horiba LA-700). Then the data of the median, the ratio within 10 $\mu$ m diameter and the specific surface area were recorded and floc size distributions were plotted. Our intention to use arbocel



**Fig. 2. Diagram of structure estimation by PVSK titration phenomena with spectrophotometer.**

C-100 micro-pulp instead of normal wood pulp is to characterize flocculation efficiency easily using particle size analyzer because arbocel C-100 micro-pulp is shaped square to circular form.

## 3. Results and Discussion

### 3.1 Effects of dosage of branch monomer on the copolymerization

Three series of copolymers of acrylamide and DMAEA-MC were prepared, in which the dosage of branch monomer of N,N'-methylenebis acrylamide is 0, 2.5 and 5 ppm per total monomers respectively. Branched polymer and cross-linked polymer were differentiated by adjusting the dosage of the branch monomer. The corresponding abbreviations are LCPAM, BCPAM and CCPAM. The L, B and C stands for linear, branched and cross-linked respectively. The
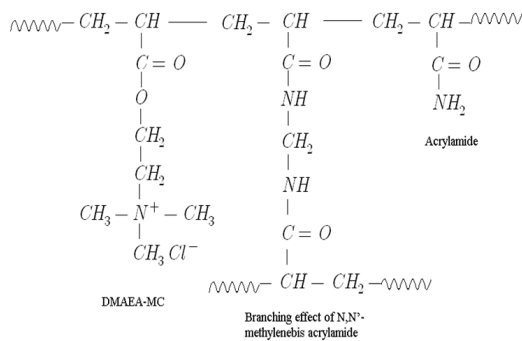


**Fig. 3. Structure of branched CPAM copolymer of acrylamide and DMAEA-MC using N,N'-methylenebisacrylamide.**

molecular structures of branched polymer is shown in Fig. 3.

The branch monomer of N,N'-methylenebisacrylamide has two carbon-carbon double bonds in the molecule and this can form a bridge between molecules. The copolymerization results are summarized in Table 1.

From this table, it can be seen the yield decreased when the dosage of branch monomer per total monomers of the polymer increased. This behavior can be explained as follows. When the dosage of branch monomer increased, the rigidity of molecule tends to increase to break micelle to increase the gel amount as a dreg. The charge density decreased by the increase of the dosage of branch monomer. This is highly related to the fact that the hidden charge in the molecule is increased by branch degree. However, hidden charge revealed by applying high shear. We can estimate branch degree by comparing ionic regain values. From the table, it was indicated that intrinsic viscosity decreased by increase of the dosage of branch degree. This behavior can be explained as follows. When the branch degree increases, the rigidity of the molecule tends to increase too. This makes the molecule hard to be turned into a free radical and be polymerized in the water in oil micelles. Therefore, molecular weight can be decreased by increasing the branch degree.

### 3.2 Branch degree and molecular structure estimation using colloidal titration phenomena with spectrophotometer

The results of branch degree measurement and molecular structure estimation are summarized in

**Table 1. Analysis of copolymerization of acrylamide with DMAEA**

| Sample | Dosage of N,N'-methylenebis-acrylaide/total monomer(ppm) | Yield (%) | C.D.1 (meq/g) | C.D.2 (meq/g) | I.R. (%) | Intrinsic viscosity ($\eta$) (mL/g) |
|---|---|---|---|---|---|---|
| LCPAM | 0 | 95.2 | 2.16 | 2.28 | 5.3 | 141.99 |
| BCPAM | 2.5 | 93.5 | 2.28 | 2.52 | 9.5 | 99.01 |
| CCPAM | 5 | 91.8 | 2.04 | 2.88 | 29.2 | 68.93 |

**Table 2. Branch degree and molecular structure estimation of copolymerization of acrylamide with DMAEA**

| Samples | Branch degree | A (mL) | B (mL) | Soft region (%) (A x 100/(A+B)) | Hard region (%) (B x 100/(A+B)) |
|---------|---------------|--------|--------|----------------------------------|----------------------------------|
| LCPAM | 7.16 | 4.8 | 0.48 | 90.9 | 9.1 |
| BCPAM | 8.94 | 3.12 | 1.44 | 68.4 | 31.6 |
| CCPAM | 10.06 | 1.92 | 3.12 | 38.1 | 61.9 |
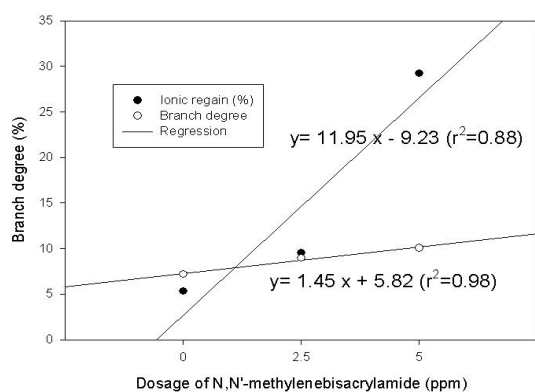


**Fig. 4. Comparison of ionic regain and branch degree method. (107.32, 89.55)**



**Fig. 5. Change of absorbance with colloidal titration.**

Table 2. Branch degree was increased by increasing the dosage of branch monomer. In Fig. 4, the regression lines between branch degree and the ionic regain result were compared. Even though both regression lines of the branch degree and ionic regain had positive gradients, branch degree shows higher reciprocality than the ionic regain method. These phenomena can be explained as follows. End point of titration of ionic regain methods is fluctuated by the branch degree. However, the branch degree method is more accurate and stable for measuring change of colors by morphology using spectrophotometer during PVSK titration. The principle of analysis was based on the different penetration speed of PVSK from the soft region to the hard region of the polymer with different branch degrees. As the branch degree increased, hard region of the polymer increased and the penetration speed became slower than that of LCPAM. Thus, the color of the TB indicator fluctuates more during titration. We schematized the relation between titration

and morphology of the polymer according to Fig. 2 and relevant data listed in Table 2. The region of A is a smooth decreasing part of absorbance during titration and B is an increasing region of absorbance during titration. Their portions are expressed as a soft region and hard region. The former stands for the free open charge region of the polymer and the latter stands for the hidden charge in the network of the polymer. It was found that the soft region diminished by the increase of branch degree. This branch degree method is very useful for estimating polymer structure by morphology.

When every absorbance datum was plotted during titration in Fig. 5, the different phenomena by different morphology of polymers were observed. As the branch degree increased, absorbance data fluctuated more than for the linear polymer.

## 3.3 Effects of shear and conductivity on the flocculation of arbocel micro pulp

**Table 3. Flocculation test result of arbocel micro pulp at low conductivity (20 µS/cm) condition using Horiba LA 700 particle size analyzer**

| Polymer | Blank | LCPAM | | | BCPAM | | | CCPAM | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Agitation speed(rpm) | | 1,000 | 2,000 | 3,000 | 1,000 | 2,000 | 3,000 | 1,000 | 2,000 | 3,000 |
| Median($\mu$m) | 76.1 | 91.3 | 78.5 | 54.5 | 107.1 | 98.7 | 94.5 | 108.4 | 125.5 | 95.6 |
| Ratio within 10 $\mu$m diameter(%) | 7.1 | 3.5 | 4.3 | 6.2 | 3.3 | 3.4 | 2.5 | 3.6 | 3.2 | 2.4 |
| Specific surface area (cm$^2$/cm$^3$) | 1,970 | 1,361 | 1,574 | 2,112 | 1,663 | 1,577 | 1,674 | 2,177 | 1,858 | 1,881 |

Table 3 shows the result of the flocculation test of arbocel at three different shear forces. The LCPAM shows in a considerable decrease in the median size with the increase of shear force, but BCPAM and CCPAM shows that the decreasing rates are relatively small. The ratio within 10 $\mu$ m diameter stood for the ratio of small flocs and LCPAM generates a fairly high amount of fine flocs. However, BCPAM and CCPAM decreased the content of fine flocs by increase of shear force. Also the specific surface area of flocs by LCPAM increased considerably, whereas BCPAM and CCPAM maintained stable.

Fig. 6 shows the effect of shear force on the distribution of the flocs of Arbocel micro pulp by LCPAM. At 3000 rpm, generatio n of fine flocs smaller than 100 $\mu$ m was found considerably. Fig. 7 was the

distribution of the flocs by shear force of BCPAM and it was suspected that the generation of small flocs smaller than 100 $\mu$ m is quite low. Fig. 8 was the distribution of the flocs by shear force of CCPAM and we found that the floc size was increased at 2,000 rpm of the shear force, but fine flocs less than 100 $\mu$ m were generated by 3,000 rpm of shear force. This result was explained that the hard region in the polymer was increased to give resistance to the shear force by the increase of branch degree. Therefore, BCPAM and CCPAM were much stable than LCPAM at high shear condition.

Table 4 shows the result of the flocculation test of arbocel pulp at three different shear force when conductivity was adjusted to 2,000 $\mu$ S/cm by adding NaCl . The LCPAM resulted in a great decrease in the median size with the increase of shear force, but



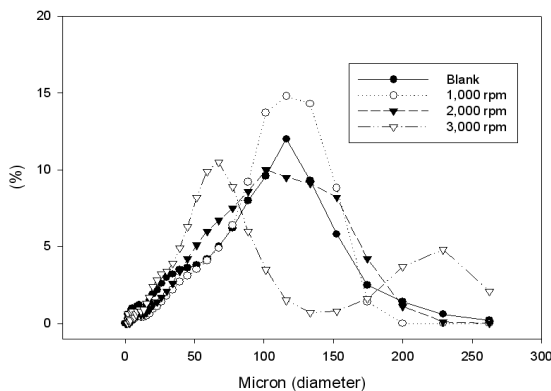**Fig. 6. Floc size distributions of arbocel micro pulp by LCPAM at low conductivity of 20 µS/cm condition at three different shear conditions.**
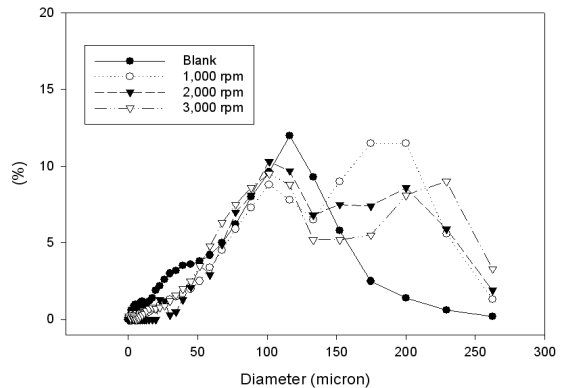


**Fig. 7. Floc size distribution of arbocel micro pulp at low conductivity of 20 µS/cm condition with BCPAM by different shear condition.**

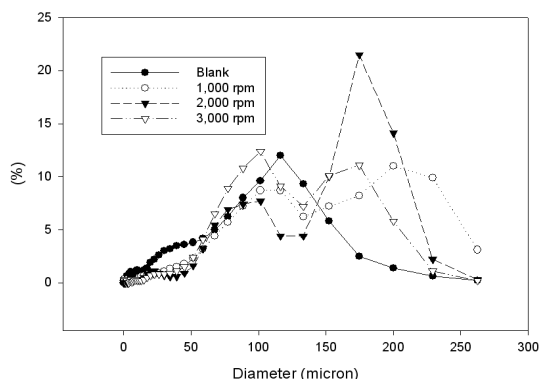**Fig. 8. Floc size distribution of arbocel micro pulp at low conductivity of 20 μS/cm condition with CCPAM by different shear condition.**



**Fig. 9. Floc size distribution of arbocel micro pulp of low conductivity of 2,000 μS/cm condition with LCPAM by different shear condition.**



**Fig. 10. Floc size distribution of arbocel micro pulp of low conductivity of2,000 μS/cm condition with BCPAM by different shear condition.**

BCPAM and CCPAM shows the increase of size. The ratio within 10 $\mu$ m diameter stands for the ratio of fine flocs and LCPAM generates a fairly high amount of fine flocs, although BCPAM and CCPAM decreased fine flocs by increase of shear force. Also, the specific surface area of flocs by LCPAM increased with fluctuation while BCPAM and CCPAM remained slowly decreased.

Fig. 9 was the distribution of the flocs by shear force of LCPAM and it was clear that generation of small flocs less than 100 $\mu$ m was considerable. Fig. 10 and Fig. 11 show the distribution of the flocs at different shear force by BCPAM and CCPAM, respectively. We found that small flocs less than 100 $\mu$ m decreased whereas big flocs higher than 150 $\mu$ m increased considerably. It was suggested flocculation efficiency of LCPAM on the arbocel pulp at high conductivity conditions was somewhat lower than in the low
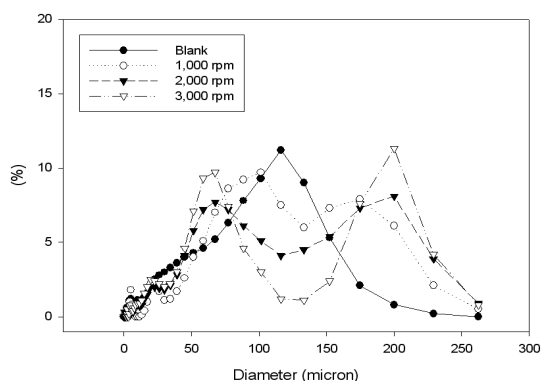
conductivity. However, the BCPAM and CCPAM of structured polymer show a decrease of fine flocs and increase of big flocs considerably. This can be

**Table 4. Flocculation test result of Arbocel C-100 micro pulp of high conductivity (2,000 μS/cm) condition using Horiba LA 700 particle size analyzer**

| Polymer | Blank | LCPAM | | | BCPAM | | | CCPAM | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Agitation speed(rpm) | | 1,000 | 2,000 | 3,000 | 1,000 | 2,000 | 3,000 | 1,000 | 2,000 | 3,000 |
| Median($\mu$m) | 70.8 | 85.0 | 70.9 | 61.8 | 109.1 | 115.8 | 110.8 | 132.0 | 147.8 | 134.1 |
| Ratio within 10 $\mu$m diameter(%) | 7.5 | 4.7 | 5.6 | 5.7 | 3.8 | 3.6 | 3.7 | 4.7 | 3.3 | 3.2 |
| Specific surface area (cm$^2$/cm$^3$) | 2,087 | 1,674 | 2,754 | 1,891 | 1,814 | 1,626 | 1,614 | 2,265 | 1,671 | 1,606 |

**Fig. 11. Floc size distribution of arbocel micro pulp of low conductivity of 2,000 $\mu$s/cm condition with CCPAM by different shear condition.**
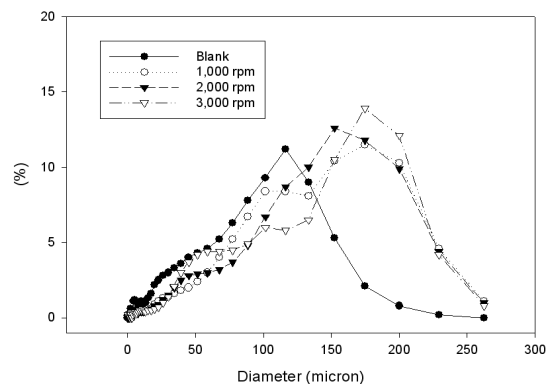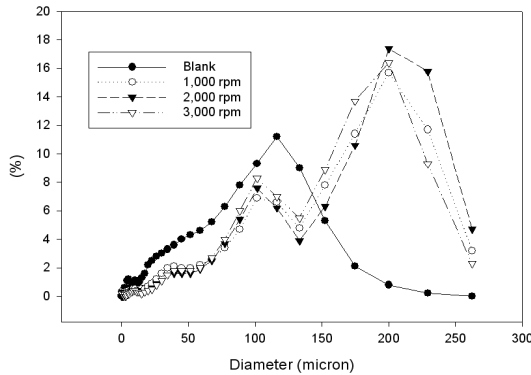
explained by the fact that LCPAM shrinks a lot under the high conductivity conditions, decreasing flocculation efficiency due to its tangle and linear characteristics. However, structured polymers like BCPAM and CCPAM had the shrink resistance under the high conductivity conditions because of their rigid and network characteristics. Thus BCPAM and CCPAM were much more stable quality characteristics than LCPAM on the arbocel micro pulp with high conductivity conditions.

# 4. CONCLUSIONS

(1) Branch degree can be modified to adjust branch monomer of N,N'-methylenebisacrylamide and ionic regain was increased by the increase of branch degree but charge density, yield and intrinsic viscosity were decreased by increase of branch degree.

(2) The branch degree measuring method by PVSK titration using a spectrophotometer was useful to characterize not only the branch degree of polymer but also prediction of CPAM morphology. It was estimated that CPAM consists of soft region and hard region. The former represents the free open charge region of the polymer, the later represents

the hidden charge inside of the polymer network. Also, we found that the soft region decreased and hard region increased by increasing the branch degree. These soft and hard region concepts in the polymer are very useful in estimating morphological condition of the CPAM.

(3) In terms of arbocel micro pulp flocculation, resistance to the shear force as well as conductivity was improved by the increase of branch degree. We considered that the increased hard region gave positive effect to improve resistance against high shear as well as high conductivity.

# LITERATURE CITED

1. Nasser, M. S., and Nasser, A.E., The effect of poly-acrylamide charge density and molecular weight on the flocculation and sedimentation behaviour of kaolinite suspensions, Separation and purification technology, 52(2): 241-251 (2006).

2. Bhardwaj, N. K., Kumar, S., and Bajpai, P. K., Effect of zeta potential on retention and drainage of secondary fibres, Colloids and surfaces A Physicochemical and engineering aspects, 260(1-3): 245-250 (2005).

3. Ren, H., Chen, W., Zheng, Y., and Luan, Z., Effect of hydrophobic group on flocculation properties and dewatering efficiency of cationic acrylamide copolymers, Reactive and functional polymers, 67(7): 601-608 (2007).

4. Larsson, A., Walldal, C., and Wall, S., Flocculation of cationic polymers and nanosized particles, Colloids and surfaces A Physicochemical and engineering aspects, 159(1): 65-76 (1999).

5. Ono, H., and Deng, Y., Flocculation and Retention of Precipitated Calcium Carbonate by Cationic Polymeric Microparticle Flocculants, Journal of colloidal interface science, 188(1): 183-192 (1997).

6. Yan, Z., and Deng, Y., Cationic microparticle based flocculation and retention systems, Chemical engineering journal A, 80(1-3): 31-36 (2000).

7. Naghash, H. J., Massah, A., and Erfan, A., Free-radical crosslinking copolymerization of acrylamide and

N,N´-methylenebis acrylamide by used Ce(IV)/ polyethylene glycol and Ce(IV)/diethylmalonate redox initiator systems, European polymer journal A, 38(1): 147-150 (2002).

8. Son, D. J., and Kim, B. Y., New retention system using branched polymer, J. Korea TAPPI Panpacific conference proceeding, Vol. 2: 251-256 (2006).

9. Shin, J. H., Han, S. H., Sohn, C. M., Ow, S. K., and Mah, S., Highly branched cationic polyelectrolytes: filler flocculation, J. Korea TAPPI, 80(11): 179-185 (1997).

10. Shin, J. H., Han S. H., Sohn, C. M., Ow, S. K., and Mah, S., Highly branched cationic polyelectrolytes: fines retention, J. Korea TAPPI, 80(10): 185-189 (1997).

11. Wan, X. F., Li, Y. M., Wang, X., Chen, S., and Gu, X. Y., Synthesis of cationic guar gum-graft-polyacrylamide at low temperature and its flocculating properties, European polymer journal, 43(8): 3655-4661 (2007).

12. Yezek, L. P., and Leeuwen, H. P., An electrokinetic characterization of low charge density cross-linked polyacrylamide gels, Journal of colloid and interface science, 278(1): 243-250 (2004).

13. Silva, R., and Oliveira, M. G., Effect of the cross-linking degree on the morphology of poly(NIPAAm-co-AAc) hydrogels, Polymer, 48(14): 4114-4122 (2007).

14. Omari, A., Tabary, R., Rousseau, D., Calderon, F. L., Monteil, C. J., and Chauveteau, M. G., Soft water-soluble microgel dispersions: Structure and rheology, Journal of colloid and interface science, 302(2): 537-546 (2006).

15. Nanko, H., Mcneal, M., and Pan, S., Understanding wet-end polymer performance through visualization of macromolecular events by transmission electron microscopy, Panpacific conference proceeding, Vol. 1: 1-18 (2006).