변성 폴리아크릴아미드의 합성 및 제지 공정의 보류 시스템에 응용

Synthesis of modified polyacrylamides and their applications for the retention system of papermaking

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1. Abstract

The purpose of this study was to improve not only wet-end performances but also paper characteristics by the modification of various factors like molecular design and ionic characteristics of polyacrylamides.

First of all, physical characteristics were observed after modify molecular design of the cationic polyacrylamides to linear, branched and cross-linked. In addition it was found analysis method to confirm branch degree of cationic polyacrylamides to combine ionic titration characteristics and spectroscopic behavior. After application of these structure modified polyacrylamides to the multiple retention systems with inorganic microparticles, it was found adjusting of branch degree of polyacrylamides was very important to optimize wet-end improvement.

Second, After polymerization of amphoteric polyacrylamide to have both of cationic and anionic functional group in the polymer, we observed not only physical characteristics but also wet-end improvement to apply recycled pulp and found that the improvement of solution stability to prevent hydrolysis and increase of ash retention dramatically to compare traditional cationic polyacrylamide retention aid.

Finally, After polymerization of anionic polyacrylamide, we observed not only wet-end improvement but also paper characteristics to apply preflocculation of PCC and it was found the improvements of flocculation efficiency, retention, ash retention, optical properties of the paper and bursting strength to compare traditional preflocculant of cationic polyacrylamide.

2. Materials and methods

2.1 Experiment

2.1.1. Materials

Nonionic monomer of acrylamide (50% active contents), anionic monomer of acrylic acid, cationic monomer of methyl chloride salt of dimethylaminoethylacrylate and branch monomer of N, N'-methylene bis acrylamide were obtained from Eyang chemical co. ltd.

Emulsifier of Span-80 (Sorbitan mono-oleate), inverting agent of Brij-96 (Oleyl alcohol) and mineral oil (Isopar-L) were obtained from uniquema.

Chain transferring agent of Na-formeate and initiator of ammonium persulfate, sodium hydrogen sulfite and AIBN were chemical grades. And deionized water was used all process of polymerization.

2.1.2. Determination of molecular structure

Branch degree and molecular structure estimation were measured using colloidal titration phenomena using spectrophotometer methods described by Son (44). Colloidal titration of 100 ml of 0.005% polymer solution using 0.0025N PVSK was the same as for the charge density measurement. 4 times of spectrum at every 0.24 ml addition of 0.0025N PVSK were repeatedly checked under the 625 nm wavelength using a Hach 2400 spectrophotometer. Branch degree was determined using the average of standard deviation of the data at each 4 times of spectrum. Molecular structures were estimated comparing plotted graphs as in figure 21. 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.

$$Branch\ degree = \frac{\sum \sigma}{n}$$

here σ : Standard deviation of 4 times of spectrum at every 0.24 ml addition of 0.0025N PVSK under the 625 nm wavelength.

3. Results and Discussion

3.1. Molecular structure analysis

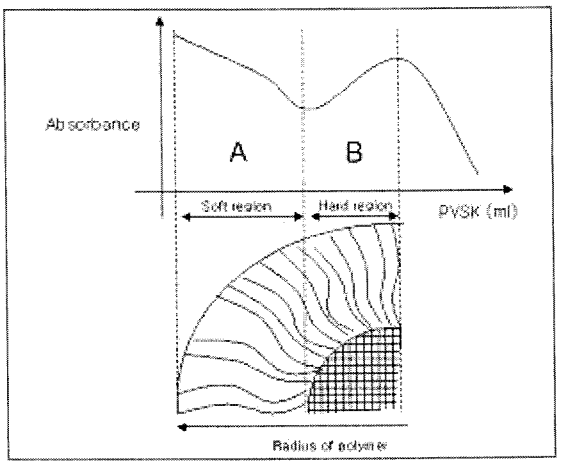

Figure 1. Diagram of structure estimation by PVSK titration phenomena with spectrophotometer

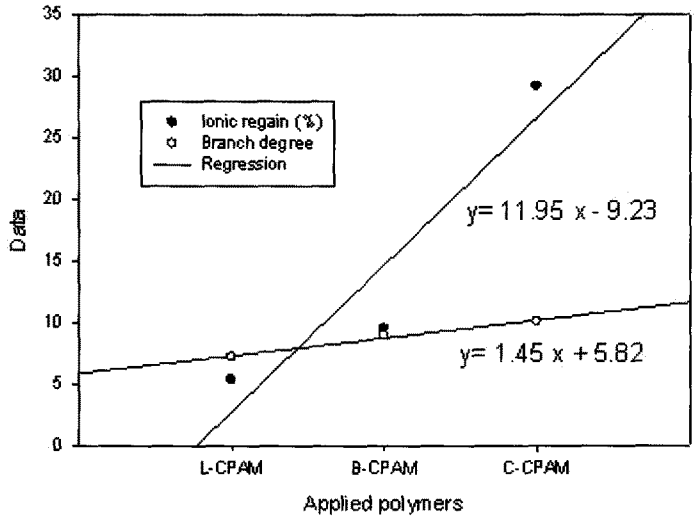

Figure 2. Comparison of ionic regain and branch degree method

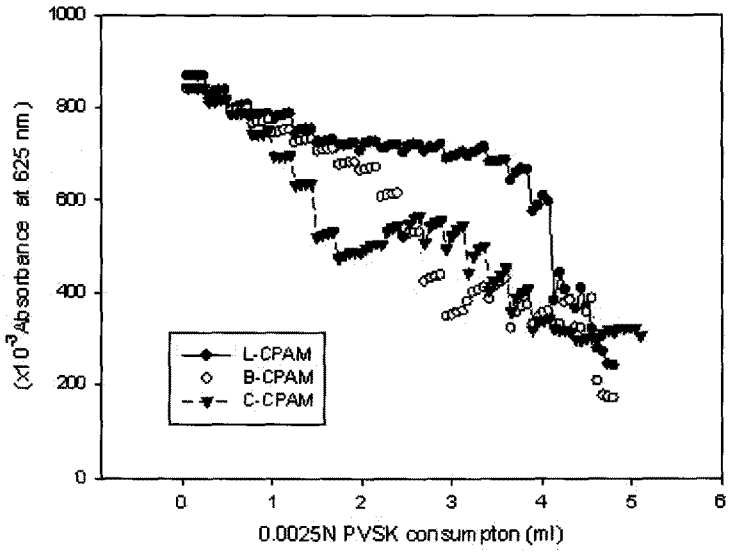

Figure 3. Comparison of colloidal titration phenomena using spectrophotometer

Table 1. 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)
L- cationic polyacrylamide	7.16	4.8	0.48	90.9	9.1
B-cationic polyacrylamide	8.94	3.12	1.44	68.4	31.6
C-cationic polyacrylamide	10.06	1.92	3.12	38.1	61.9

The results of branch degree measurement and molecular structure estimation were summarized in Table 1. Branch degree was increased by increasing the dosage of branch monomer. As you can see from Figure 2, we compared the regression line between branch degree and the ionic regain result. Even though both regression lines of the branch degree and ionic regain had positive gradients, branch degree shows better agreement between data and regression curve than the ionic regain method. These phenomena can be explained as follows, end point of titration of ionic regain methods was fluctuated by the branch degree. However, the branch degree method was more accurate and stable for measuring fluctuation of colors by morphology using spectrophotometer during PVSK titration. The principle of analysis was based on the different penetration speeds of PVSK from the soft region to the hard region of the polymer by different branch degrees. As the branch degree increases, hard region of the polymer increased and the penetration speed became slower than L-cationic polyacrylamide. Thus, the color of the TB indicator fluctuated more during titration. We schematized the relation between titration and morphology of the polymer according to Figure 1 and relevant data was listed in Table 1. The region of A is a smooth decreasing part of absorbance

during titration and B is an increasing region of absorbance during titration. Their percentages were 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 and the hard region was increased by the increase of branch degree. This branch degree method seems very useful for estimating polymer structure by morphological difference. We plotted every absorbance data during titration in Figure 3 and we can see the different phenomena by different morphology of polymers. As the branch degree increases, absorbance data fluctuates more than for the linear polymer.

4. Conclusions

We tried to polymerize to modify polyacrylamides. cationic polyacrylamides were polymerized by the modification of branch degree of linear, branched and cross linked. Anionic polyacrylamide was polymerized to high molecular weight after neutralization with NaOH. And finally, amphoteric polyacrylamide was polymerized to add acrylic acid to the similar to the linear cationic polyacrylamide formulation.
Branch degree measuring technology was developed of cationic polyacrylamide using spectrophotometer and polyvinylsulfate K salt titration. And this technology was useful to characterize cationic polyacrylamides by their structures and we also classified soft region and hard region of the polyacrylamides by branch degree of the polymer.