Structure–Control of Amphoteric Polyacrylamide and Its Performance as Dry Strength Resin

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Abstract

Dry strength resin is known as multifunctional chemicals to enhance paper/paperboard strength, drainage and retention. Especially, polyacrylamide (PAM) based dry strength resin is widely used in various paper/paperboard grades in Japan. Linear, Low-branched, and high-branched PAM containing both anionic and cationic groups were obtained with free radical polymerization. Molecular weight and structure of PAM were determined by gel permeation chromatography coupled on line to a multi-angle laser light scattering detector (GPC–MALS). The higher degree of branching, the more compact a polymer chain, which leads to decrease in the viscosity of aqueous solution.

The effects of structure and molecular weight of amphoteric PAM on the performance of dry strength resin were investigated. The high-branched PAM with higher molecular weight showed greater performance in retention of PAM and paper strength. The zeta-potential of amphoteric PAM increased with the increasing of the degree of branching. The high-branched amphoteric PAM was able to form polyionic complexes in high salt concentration (electro conductivity, 650 mS/m). The effective iconicity of amphoteric PAM could be controlled by changing the structure of polymer.

Keywords : Polyacrylamide, High-branched, Structure Control, Polyionic Complex, Paper Strength, Drainage

1. Introduction

Amphoteric polyacrylamide (amphoteric PAM) is commonly used in paper and paperboard manufacturing to improve not only dry strength but also runnability of paper machine in many ways like better drainage and dewatering, higher retention of wet end additives, like sizing agent, and fillers like calcium carbonate. Dry strength resin clas-

sified as amphoteric PAM is made by co-polymerizing acrylamide, a main component, with other kinds of monomers such as anionic monomer, cationic monomer and functional monomer, and is supplied to customers in aqueous solution.

PAM of higher molecular weight is more retained on pulp fiber¹⁾, and improves dry strength. The solution of high-molecular-weight PAM, however, gets very viscous, causes troubles in shipping and handling, and practically is not acceptable. Moreover, too much coagulation on fiber disturbs sheet formation, which results in poor dry strength. To cope with those problems, PAM has to be po-

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lymerized to a large molecule without increasing the viscosity of its aqueous solution by restraining the spread of its molecular chain. So, PAM that is branched in its molecule (branched PAM) has been developed²⁻⁴⁾.

Branched PAM can be structured to poly-ionic complexes, a kind of pseudo-macromolecule, which is formed by the interaction of electrostatic force, by controlling positions of ionic groups in its molecule. Several studies are going on to improve drainage by forming branched PAM to poly-ionic complex^{5,6)}. But recent trends like followings are unfavorable for using wet end chemicals. Recycled pulp is used in a larger and larger ratio, paper machines are becoming larger and running faster, and electro-conductivity of water is increasing due to closed water loop in wet end. So, amphoteric PAM that could be effective in such severe conditions is wanted.

We investigated on improving effectiveness of amphoteric PAM by focusing on its structural parameters such as the radius of gyration, molecular weight and the degree of branching.

2. Experiment

2.1 Amphoteric PAM

Six kinds of amphoteric PAMs were synthesized by radical polymerization, using itaconic acid as an anionic monomer and *N,N*-dimethylaminoethylmetacrylate as a cationic monomer. Their ionic monomer contents are the same though they had different molecular weight, structure and radius of gyration. Their characteristics are summarized in Table 1.

2.2 Determination by GPC-MALS

Gel permeation chromatography (Prominence UFLC by Shimadzu Corporation) was coupled on line to an intensity detector (RI-101 by Shodex Co.) and also to a multi-angle laser light scattering detector (DAWN EOS by Wyatt Technology Co.).

2.3 Viscosity measurement

Viscosity was measured by Brookfield viscometer (TVB-10 by Toki Sangyou Co.) equipped with M 4 rotor at 25°C. The revolution of the rotor was selected based on specimen's viscosity.

2.4 Intrinsic viscosity

An amphoteric PAM sample was diluted with 4 % sodium chloride solution to a pre-determined consistency. Using capillary viscometer of Ubbelohde type, its flow down time was measured at 25°C. After making a Huggins plot⁷⁾ with measured specific viscosities η_{sp} , its intrinsic viscosity $[\eta]$ was calculated.

2.5 Light transparency of diluted Amphoteric PAM

Using ion-exchanged water of which electric conductivity was adjusted to 150 mS/M with $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, 0.1 % amphoteric PAM solution was prepared. After adjusting its pH to 3 with 0.05 N sulfuric acid, a sample solution was set to an automatic titrator equipped with pH electrode and light intensity detector (620 nm). Titration was carried out with sodium hydroxide solution of 0.1 N to follow changes of pH and light intensity. Another solution was also prepared of which electric conductivity was adjusted to 650 mS/m by adding $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ to the former solution of which electro-conductivity was 150 mS/m. Titration was done in the same way as before.

2.6 Handsheet preparation

Waste corrugated board was refined to 350 Canadian Standard Freeness. Its pulp consistency was adjusted to 2.4 % and its electric conductivity was controlled to 150 mS/m. Under stirring, aluminum sulfate and then amphoteric PAM solution (1.2% consistency) were added. The dosage of aluminum sulfate was 1 % per pulp, and that of amphoteric PAM was 1 % per pulp for samples I ~ VI. Handsheets were prepared under the pH of 7. Drainage was evaluated by dynamic drainage jar. Pulp slurry was prepared in the same way by adding chemicals, and drain-

Table 1 Characterization of amphoteric PAM

Sample	Mw $\times 10^{(a)}$	Mw/Mn ^{a)}	Rg ^{a)} (nm)	$[\eta]$ ^{b)} (dL/g)	Viscosity ^{c)} (mPa·s)	Structure ^{a)}
I	260	2.8	55	1.5	7,000	Low-branched
II	380	3.9	65	2.0	18,000	Low-branched
III	590	4.1	76	2.6	73,000	Low-branched
IV	280	3.0	67	3.5	50,000 ^{d)}	Linear
V	330	2.9	55	1.2	3,500	High-branched
VI	560	4.2	64	1.9	7,000	High-branched

^{a)}Determined by GPC-MALS

^{b)}Calculated from a Huggins plot, measured at 25°C

^{c)}Solution with 20% polymer, measured at 25°C

^{d)}Solution with 10% polymer, measured at 25°C

age time for initial 100 ml drain was measured. Hand-sheets were conditioned under 23°C and 50 % RH for 24 hours and then their properties were determined.

2.7 Retention yield of amphoteric PAM

Nitrogen in handsheet was measured by total nitrogen analyzer by Mitsubishi Chemical Analytic Co. The retention yield of amphoteric PAM was calculated by subtracting nitrogen content in bank sheet, which was prepared without PAM addition, from that of tested sheet.

3. Result and discussion

3.1 Characteristics of amphoteric PAM

3.1.1 Structure

Fig. 1 shows a relationship between the weight-average molecular weight (M_w) measured with GPC-MALS and radius of gyration (R_g). GPC-MALS can give R_g on every molecular weight level, and by analyzing those data, the degree of branching in polymer can be determined⁸⁾. If two polymers have the same R_g and are different in molecular weight like IV, II and VI, one of higher molecular weight is more highly branched than the other. If two polymers have the same molecular weight and are different in the R_g like III and VI, one of less R_g is more highly branched. By analyzing those data, it was found that samples I ~ III had almost the same kind of branched structure. The field in Fig. 1 can be divided to three areas which correspond to three types of molecular structures, linear, low branched and high branched respectively. IV has a linear structure. I ~ III have a low branched structure. V ~ VI have a highly branched structure. Fig. 2 illustrates images of those structures in which locations of ionic groups are schematically presented.

3.1.2 Viscosity of aqueous solution

Samples IV, II and VI, which had the same degree of R_g

Fig. 1 Molecular weight (M_w) vs radius of gyration (R_g) of amphoteric PAM

Fig. 2 Schematic illustration of amphoteric PAM

determined by GPC-MALS, were compared with each other in their viscosity of aqueous solution. VI that was of a linear structure had an extremely high viscosity that could not be determined in a normal solid consistency range. When the degree of branching in polymer increased like from I that was of low branch to II that was highly branched, its viscosity went down as listed in Table 1. Amphoteric PAM based dry strength resins sold in the market have physical properties (molecular weight, degree of branching, radius of gyration and viscosity of aqueous solution) similar to those of sample I that was of low branch. Amphoteric PAM like II and III, which has high molecular weight with low degree of branching and which, in other words, has large R_g , has high solution viscosity and is difficult for practical applications. VI that was highly branched had the same level of solution viscosity to that of I. It suggested that by increasing the degree of branching, amphoteric PAM of large R_g could have solution viscosity practically applicable.

3.2 Evaluation of amphoteric PAM as dry strength resin

3.2.1 Drainage rate test

The effect on drainage is shown in Table 2 and Fig. 3. By comparing I, II and III with each other, all of which

Fig. 3 Effect of amphoteric PAM on drainage time
pulp : WCB, electro-conductivity : 150 mS/m, ph : 7.0, alum : 1 %

Table 2 Properties of handsheet and retention of PAM

PAM	Drainage (s.)	Dry burst index (kPa·m ² /g)	Sheet formation index	PAM retention (%)
I	12.9	3.35	88.3	44.9
II	11.3	3.39	89.7	47.3
III	8.9	3.43	92.6	49.8
IV	5.7	3.34	97.5	53.8
V	13.6	3.41	86.2	49.1
VI	10.7	3.55	89.3	58.9

had a low branched structure, it was found that drainage improved along with larger Rg though its molecular weight was also larger. The same trend was found with those of high branched structure (V and VI). When IV, II and VI which had nearly the same Rg were compared each other, IV that was of linear structure was the best and the other two were almost the same level. When they were compared at the same molecular weight basis such as I to IV, II to V and III to VI, ones of low branched or linear structure gave better drainage. The ranking of drainage quality among the samples corresponded to their intrinsic viscosity, neither to their Rg nor to their molecular weight as shown in Table 1. Intrinsic viscosity represents the volume occupied by a unit weight of polymer in solution as indicated by its unit dL/g. A higher intrinsic viscosity means that polymer chains entangle each other at a higher level, compared at the same polymer consistency. Therefore, amphoteric PAM of high intrinsic viscosity still maintains entanglement of its polymer chains even after being mixed to pulp slurry and will be able to coagulate pulp and improve drainage.

3.2.2 Dry strength and retention of amphoteric PAM

Dry strength of handsheets are summarized in Fig. 4. Among amphoteric PAMs I ~ III which had a similar structure, one that had larger Rg, which was equivalent to higher molecular weight, had better strength. The same trend was observed with V and VI. Among amphoteric PAMs IV, II and VI, which had the same Rg but were different in their molecular weight, one of higher molecular weight that meant more branched had better strength. The same trend was found with I and V. As six amphoteric PAM polymers studied in our experiment had the same ionic composition, they proved that the difference in the polymer structure affected dry burst strength. In general, the strength was dependent on retention yield of amphoteric PAM as shown in Fig. 5. Their retention was improved by increasing molecular weight and degree of branching, and their sheet strength increased accordingly. Polymer IV, which had a linear structure and large Rg,

Fig. 4 Effect of amphoteric PAM on dry burst strength pulp : WCB, electro-conductivity : 150 mS/m, ph : 7.0, alum : 1 %

Fig. 5 Plots of Dry burst strength vs retention of amphoteric PAM

could coagulate fiber and fine more than others, and large coagulated flocks of fibers and fines were retained physically in sheet. Though the retention yield of that polymer was high, sheet formation was disturbed by the flocks and resulted in poor strength. Polymers that had large Rg by

branching did not deteriorate sheet formation.

3.2.3 Effect of larger molecular weight and higher degree of branching

How larger molecular weight and higher degree of branching affected on improving sheet strength was evaluated using amphoteric PAM samples I, II and V (see Fig. 6). I and II had the same kind of molecular structure and II had larger molecular weight than I. By increasing molecular weight, number of ionic groups in one polymer chain, which worked as retention sites, increased. As the Rg became larger, the chance of contacting pulp also increased. Therefore, sample II was less influenced by impurities, such as anionic trash that would hinder its retention, and its retention was improved. II and V had the same molecular weight and V was more branched than II. As the number of ionic groups in a molecular chain was the same, V that was highly branched had less Rg than II. So, ionic groups in V were more densely packed than II. The difference in the density of ionic groups could be measured by zeta-potential. Their zeta-potentials in sodium chloride solution on which concentration was 10 mM were listed in Table 3. Though II and V had the same molecular weight and ionic property, V that was highly branched gave a larger zeta-potential. The higher density of ionic groups surely contributed to better retention of amphoteric PAM to pulp.

Fig. 6 Effect of molecular weight and structure change on the ionic character of amphoteric PAM

Table 3 Zeta-potential of amphoteric PAM

Sample	Zeta-potential ^{a)} (mV)
II	+5.9
V	+9.3

^{a)} Measured in 10 mM NaCl solution, at pH 3.5

3.2.4 Formation of poly-ionic complex

It is known that amphoteric PAM that has anionic and cationic groups within itself is able to form poly-ionic complexes among them. It was expected that poly-ionic complex of amphoteric PAM would behave differently, dependent on its degree of branching like observed in zeta-potential. Amphoteric PAM solutions of which electro-conductivity was adjusted to 150 mS/m by adding $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ were prepared. Their light transmittance was measured as a function of pH, which was shown in Fig. 7. In the ranges where light transmittance was low, amphoteric PAM formed poly-ionic complexes and its solution got milky. V that was highly branched did it in a wider range than II. The solutions were further adjusted to electro-conductivity of 650 mS/m by adding $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$. Then, II that was less branched could not form poly-ionic complex as electro-static force between ionic groups was shielded by the presence of inorganic salt abundant in the solution. On the other hand, V that was highly branched could form the complex even in the solution of high electro-conductivity. It was concluded that highly branched amphoteric PAM was less influenced with shielding effect by inorganic salt on its electro-static force as it had ionic groups in higher density.

When a lot of inorganic salt is present in water, packing ionic groups in high density by branching will increase effective charge of polymer and help form ionic complexes. Therefore, highly branched amphoteric PAM will work effectively to increase dry strength in a paper-making condition where electro-conductivity is high. The effect on dry strength with different electro-conductivities, 150, 350 and 550 mS/m respectively, which were controlled by $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, was determined with samples II and V, and was summarized in Fig. 8. Their dosage was 0.5%. Though sheet strengths were declined with in-

Fig. 7 Light transmittance change of amphoteric PAM solution as function of pH

Fig. 8 Effect of electro-conductivity on paper strength

creasing electro-conductivity, their losses were far smaller in V than in II.

4. Conclusion

How the structure of amphoteric PAM affected on its dry strength was investigated. Several amphoteric PAMs were synthesized which contained the same amount of ionic monomers and were different in radius of gyration, molecular weight and degree of branching. By introducing branched structure, amphoteric PAM could be of large molecular weight and have large R_g without increasing its solution viscosity. By increasing the degree of branching, amphoteric PAM which had high molecular weight and also had large R_g (sample VI) would be applicable in use though it was believed to be impossible.

It was found that by controlling amphoteric PAM's structure, its ability as dry strength resin could be improved. Our findings are summarized as below.

- 1) Increasing molecular weight with maintaining the same molecular structure which means to increase molecular weight as well as R_g , number of retention sites (ionic groups) in one molecular chain will in-

crease. As the R_g also gets larger, the retention of amphoteric PAM on pulp will improve. Improved retention results in better dry strength.

- 2) Increasing the degree of branching at the same molecular weight (higher branching)

The density of ionic groups in polymer chain will increase and its retention on pulp will be improved. Improved retention results in better dry strength. High density of ionic groups make polymer less influential to shielding effect by inorganic ions and help form poly-ionic complexes. As a result, it works in a paper-making condition in which electro-conductivity is relatively high.

- 3) Increasing branching and molecular weight at the same time

By the synergistic effect with 1) and 2), the best result will be obtained.

The environment in paper making will become less and less favorable to wet end chemicals, one of which is dry strength resin. We will do our best to supply chemicals of fine function applicable for future paper making.

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