SPMC Technical Review

PM Series: Amphoteric Polyacrylamide to Improve Paperboard Manufacturing Processes

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1. Introduction

Recovered paper is widely used as a raw material for papermaking in the viewpoint of the environmental protection and efficient use of resources. The recovered paper accounts for approximately 65% of the total material consumption for paper and paperboard manufacture in Japan. The recovered paper contains various impurities such as calcium carbonate, resins (polyvinyl acetate, polyacrylic acid ester, etc.), and starch. These impurities cause various problems for the papermaking process. The pH range at headbox in paperboard manufacturing process often exceeds 6.5 and even approaches around 7.0 in some cases. For example, the presence of calcium carbonate increases the pH in the papermaking process. In this papermaking system, aluminum sulfate as a retention aid loses its ability[1)], resulting in decreasing paper strength and sizing effect. Increasing aluminum sulfate dosage can compensate for the decrease in the retention of wet-end additives; however, it causes many troubles such as increase in electrical conductivity of the papermaking system, formation of gypsum scale, generation of unpleasant smell originating from the degraded sulfate, and corrosion of the machine. Thus, it is preferable not to increase aluminum sulfate to overcome these issues. On the other hand, aluminum sulfate not only serves as a retention aid for the adsorption of wet-end additives but also enhances runnability by improving dewatering and cleaning up system through pitch control. Additionally, it is essential for rosin emulsion sizing agents to express the sizing effect. Therefore, it is difficult to decrease the dosage of aluminum sulfate.

Consequently, we developed the PM series as Papermaking Process Improvers, which are composed of novel amphoteric polyacrylamide (PAM). They can be used as wet-end additives to significantly reduce the aluminum sulfate dosage in paperboard manufacture with the presence of rosin emulsion sizing agents while maintaining the runnability and the quality of paperboard. This report presents newly developed PM series as papermaking wet-end additives, and properties of the amphoteric polyacrylamides.

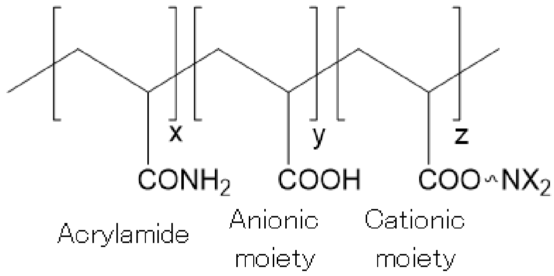
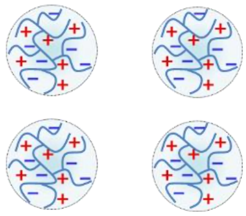
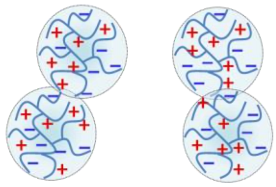
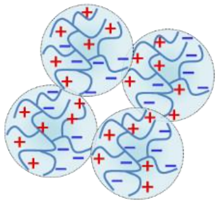


Figure 1. Molecular structure of amphoteric polyacrylamide

Table 1. Formation and properties of polyion complexes

Formation of polyion complexes	 Non-formation	 Weak	 Strong
Appearance of solution of amphoteric polyacrylamide			
Adsorption rate onto the pulp fiber (%)	72	90	95
Burst index ($kPa.m^2/g$)	2.81	2.96	2.75

2. Design of amphoteric polyacrylamides and their properties

The amphoteric polyacrylamide shown in Figure 1 is water-soluble polymer prepared via radical copolymerization of acrylamide, cationic monomers, and anionic monomers. It is a multifunctional papermaking chemical that enhances paper strength and runnability as a result of improved retention of fine fibers and water drainage. Thus far, improvements in amphoteric PAMs have been investigated and confirmed in their performances[2-5]. The following sections describe how the design of amphoteric PAMs affects the quality of paper and the runnability. The amphoteric PAMs can form polyion complexes (PICs) via electrostatic interactions between cationic moieties and anionic moieties. The degree of PIC formation varies depending on various factors such as the molecular weight of amphoteric PAMs, the ratio of cationic moieties and anionic moieties in the polymer, and the localization of ionic sites within the polymer. The formation of PICs increases apparent molecular weight, which can improve the adsorption of the PAMs onto the pulp. Table 1 describes the relationship between the adsorption rate of amphoteric PAMs onto the pulp and the paper strength under different degrees of formation of PICs. Stronger formation of PICs increases the adsorption of PAMs onto the pulp; however, excessive formation of PICs decreases burst index. The decrease in the burst index is mainly due to poor paper formation. Because the paper formation is significantly affected by the papermaking conditions, controlling the formation of PICs under these conditions is an important factor to consider in the design of amphoteric PAMs.

Figure 2 describes the relationship between the molecular weights of amphoteric PAMs and drainage rate, as well as press dewatering property. The vertical axis on the left represents the drainage rate measured by a Dynamic Drainage Jar Tester while the vertical axis on the right represents the water content (press dewatering property) after pressing wet web. The drainage improved as the molecular weights of the amphoteric PAMs become larger; however, the press dewatering property was worsened when the molecular weight exceeds a certain value. The cationic or anionic PAM of high molecular weight is used as the retention aid to improve the drainage and retention by flocculating pulp fibers to form the flocs. However, if the flocs are too large, it is difficult to remove entrapped water within the flocs, which results in poor dryness after the press dewatering section. The amphoteric PAMs with high molecular weights also exhibit the same behavior of poor press dewatering property due to the formation of large flocs. To enhance the runnability for papermaking machines, it is important to balance the drainage and the press dewatering and to optimize the molecular weights of amphoteric PAMs in the appropriate range.

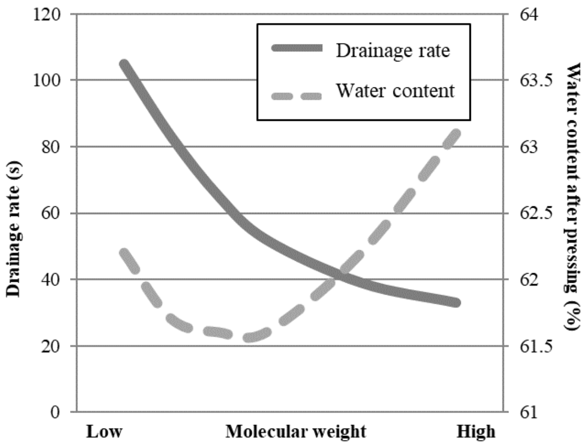


Figure 2. Effects of molecular weights of PAMs on drainage and press dewatering properties

The effect of cationicity (the amount of cationic moieties) on the sizing effect is illustrated in Figure 3. Increasing the cationicity in the amphoteric PAMs reduces the Cobb value (Water Absorptiveness), meaning that the sizing effect is improved. However, further improvement in the sizing effect was not observed when the cationicity exceeded a certain value. Moreover, utilization of amphoteric PAMs with excessive cationicity reversed the overall charge in the papermaking system, which deteriorates the retention. Therefore, it is also necessary to control the cationicity in a certain range. Furthermore, density (distribution) of cationic moieties within molecular chains of PAMs also influences the sizing effect. As shown in Figure 3 (marked as ★), it is noted that highly dense cationic moieties in the PAMs can inhibit the even adsorption of the sizing agents onto the pulp, which prevents the improvement of the sizing effect.

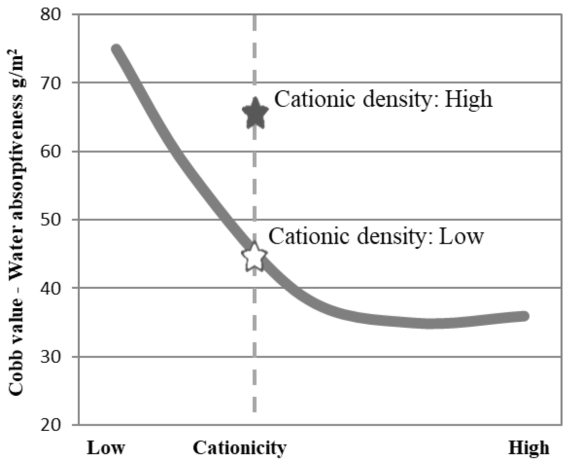


Figure 3. Effect of the cationicity in amphoteric PAMs on the sizing effect

3. Development of PM series as papermaking process improvers

To reduce the aluminum sulfate dosage in manufacturing paperboard in the presence of the rosin emulsion sizing agents, it is necessary to address the following issues

1. Decrease in sizing effect
2. Decrease in dewatering property
3. Increase in machine dirtiness

To overcome these issues, a novel wet-end additive PM7460 has been developed as a papermaking process improver by optimizing the design of amphoteric PAMs. The papermaking process improver was developed with new technologies to control the formation of PICs that differ from the conventional amphoteric PAMs. The properties of the papermaking process improver PM7460 are described in Table 2. PM7460 has higher cationicity, lower molecular weight than the conventional PAM.

Table 2. Properties of PM7460

	PM7460	Conventional PAM
Solid content (%)	20	20
Viscosity (mPa.s)	4000～10000	4000～10000
pH	2.5～4.5	2.5～4.5
Charge	Amphoteric	Amphoteric
Cationicity (index)	200	100
Anionicity (index)	100	100
Molecular weight (index)	50	100

Table 3 shows the results of evaluations of the papermaking in the presence of PM7460 or the conventional amphoteric PAM. The pulp slurry was prepared from OCC (old corrugated container). 3% or 0.5% aluminum sulfate, 0.5% paper strength additive, and 0.4% sizing agent versus the total pulp content were added to the pulp slurry. When the conventional PAM is used, reduction of the dosage of aluminum sulfate from 3% to 0.5% resulted in decrease of the paper strength (burst index) and the ash retention, and increase in the drainage time and the Cobb value. However, papermaking using PM7460 improved the sizing effect while retaining the paper strength and the drainage, although the dosage of aluminum sulfate was reduced to 0.5%.

Table 3. Results of evaluation of papermaking

Method	Paper strength additive/PM	Dosage[%]	Conventional PAM	Conventional PAM	PM7460
			0.5	0.5	0.5
	Aluminum sulfate	Dosage[%]	3	0.5	0.5
Runnability	Drainage time	[s]	30	78	37
Paper quality	Ash content in paper	[%]	11.5	10.9	11.6
	Burst index	[kPa.m^2/g]	2.73	2.55	2.78
	Cobb value	[g/m^2]	61	93	43
	Absorption rate of rosin	[%]	0.36	0.32	0.37

The improvement of sizing effect is explained via the result of adsorption rate of rosin. Papermaking with PM7460 did not decrease the adsorption rate of rosin, although the dosage of aluminum sulfate was significantly reduced. To investigate the distribution of rosin emulsion sizing agent, air-dried testpaper was analyzed using SEM (Scanning electron microscope, Table 4). Rosin emulsion sizing agent is observed as particles on pulp fibers because it does not melt by air-dry. The paper prepared with the conventional PAM showed that particles of rosin emulsion sizing agent were aggregated and observed at many positions (red circle in the figure). On the contrary, the image of the paper prepared with PM7460 shows uniformly distributed fine particles of rosin emulsion sizing agent with almost no aggregations. Utilization of PM7460 does not disrupt the adsorption of rosin emulsion sizing agents even though the aluminum sulfate is used at low dosage. Furthermore, it is considered that the good sizing effect is still retained as the result of suitable states and distribution of rosin emulsion sizing agent within paper.

The difference in the drainage rate when varying the dosage of aluminum sulfate is described in Figure 4. Compared to the conventional PAM, papermaking with PM7460 showed less impact on the water drainage upon changes in dosage of aluminum sulfate and still achieved good drainage rate without the presence of aluminum sulfate.

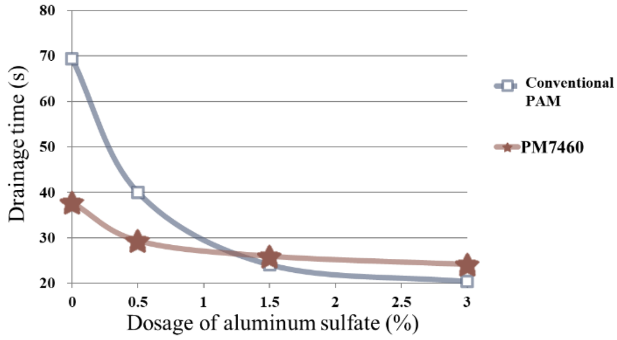
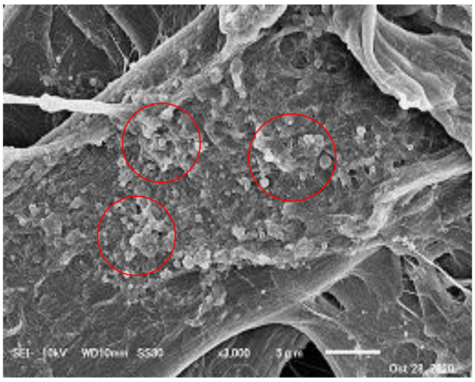
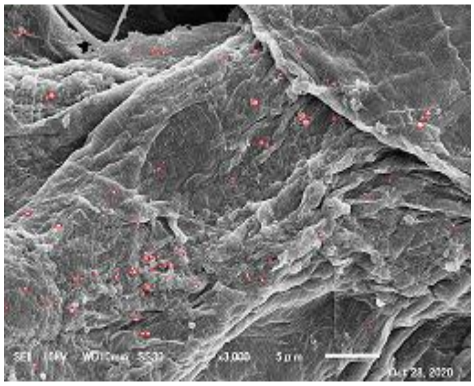


Figure 4. Evaluation of drainage

Figure 5 evaluates the press dewatering property by comparing the difference in water content of the wet web before and after the press section. Utilization with PM7460 resulted in lower water content after the press section (vertical axis) and improved press dewatering property . Moreover, the papermaking speed at the mill trial has been enhanced with the presence of PM7460, although the aluminum sulfate dosage is reduced.

Table 4. Distribution of particles of rosin emulsion agent

	Conventional PAM	PM7460
Dosage of aluminum sulfate	3.0%	0.5%
Adsorption of rosin	0.36%	0.37%
SEM images		

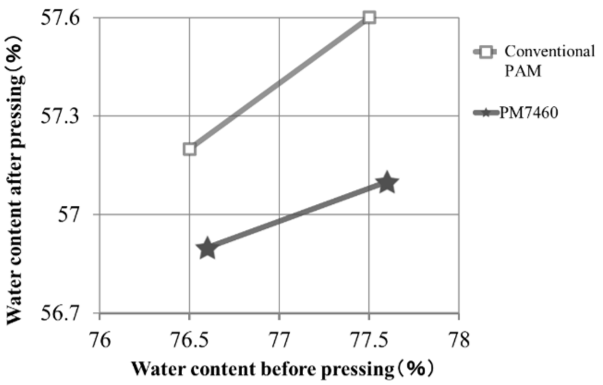


Figure 5. Evaluation of dewatering property

Lastly, the efficiency of PM7460 in clarification of papermaking system was evaluated (Table 5) by measuring turbidity and ionization degree of filtrate after addition of a certain dosage of each additive into de-inked pulp slurry, followed by the drainage process. The evaluation results of each additive, including aluminum sulfate, the conventional PAM as a dry strength additive, and cationic polymer as a coagulant, are compared to those of PM7460. The ionization degree represents the amount of anionic substances present in the filtrate from the pulp slurry. The turbidity represents the amount of colloidal components present in the filtrate. The addition of 0.1% PM7460 resulted the same ionization degree with addition of 0.5% aluminum sulfate (based on the pulp content). These results demonstrated the identical blocking efficiency of anionic substances under the above conditions. Furthermore, PM7460 resulted a better impact on reducing turbidity than aluminum sulfate.

Table 5. Evaluations of turbidity and ionization degree

Additives	Aluminum sulfate	Blank	Conventional PAM	PM7460	Coagulant
Dosage(%)	0.5	0	0.1	0.1	0.05
Ionization degree (meq/L)	-0.20	-0.23	-0.23	-0.20	-0.12
Turbidity (NTU)	60	500	40	15	25

4. Conclusion

PM7460 was developed as the papermaking process improver to decrease the dosage of aluminum sulfate in manufacturing paperboards, especially linerboard. Although the reduction of aluminum sulfate dosage causes various troubles to the paperboard-making processes and the paperboard quality, the utilization of PM7460 can solve these troubles such as decrease in sizing effect, poor dewatering property, and increase in machine dirtiness. These achievements can greatly contribute to stabilizing operations in papermaking, and further significantly contribute to the development of current papermaking companies.

＜References＞

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