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Wet-end properties of cationic graft terpolymerized polyacrylamides

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Abstract To improve the wet-end properties of linear-type copolymerized polyacrylamide (co-PAM), three types of cationic co-PAM were prepared by graft copolymerization, and their effects on the drainage, paper strength, and filler retention were investigated. Of the three synthesized terpolymers, dextrin-acrylamide-2-(dimethylamino)-ethylmethacrylate graft terpolymers (Dex-graft-(AM-DMAEMA)) moderately improved the wet-end properties compared with the other two graft terpolymers prepared. Notably, addition of 0.1% (on dry pulp) Dex-graft-(AM-DMAEMA) showed high filler retention of 78%. All of the prepared graft terpolymers showed equal or improved wet-end properties compared with acrylamide-2-(dimethylamino)ethylmethacrylate copolymer (AM-DMAEMA), which is a standard cationic co-PAM of similar molecular weight.

Key words Graft terpolymer · Cationic polymer · Polyacrylamide · Wet-end additive

Introduction

Polymers copolymerized with acrylamide and cationic or anionic monomers are called copolymerized polyacrylamides (co-PAMs) in paper industries. They are used as drainage aids, paper strength agents, and retention aids.¹ However, in order to have good performance as addi-

tives, co-PAMs of linear type with high charge density or high molecular weight are generally used. Recently, co-PAMs of branched cross-linking type have gained much attention.^{2,3} They can be synthesized using small amounts of cross-linking agents,^{4–6} which suggests the possibility of causing gelation of the polymers.

Graft copolymerization is effective in improving performance of the polymer. Through this process, co-PAMs of different type can be prepared. However, research reports on the preparation of wet-end additives by graft copolymerization are still scant.^{7,8}

In this study, graft copolymerization of acrylamide and cationic monomer to different saccharides was performed. The effectiveness of these polymers as wet-end additives was compared with acrylamide-2-(dimethylamino)ethylmethacrylate copolymer (AM-DMAEMA) of linear type.

Materials and methods

Materials

Acrylamide (AM) was recrystallized from benzene. 2-(Dimethylamino)-ethylmethacrylate (DMAEMA) was redistilled at reduced pressure prior to use. Water-soluble cyclodextrin (CD) was provided by Nihon Syokuhin Kako. Dextrin (Dex; mol. wt. 7.3×10^3) and hydroxyethylcellulose (HEC; mol. wt. 8.6×10^4 ; MS 1.0) were provided by Wako, Osaka, Japan. Other chemicals used were reagent grade. Bleached hardwood kraft pulp was beaten to 450 ml Canadian standard freeness (CSF). Kaolin clay was paper-making grade.

Polymer synthesis

CD, Dex (15.0 mmol as anhydroglucose unit), or HEC (7.5 mmol as anhydroglucose unit) was added to water (20 ml) in a flask with continuous stirring. A solution of monomer (75.0 mmol in water, 10 ml) neutralized with

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Table 1. Characterization of cationic copolymerized polyacrylamides (co-PAMs)

Sample	Yield (%)	Grafting (%)	DMAEMA composition in polymer (mol%)	$[\eta]$ (dL/g)	Molecular weight ($\times 10^5$)
AM-DMAEMA	84.9	–	8.6	–	5.8
CD-graft-(AM-DMAEMA)	71.1	378	6.1	2.29	3.8
Dex-graft-(AM-DMAEMA)	58.0	242	8.7	3.13	5.6
HEC-graft-(AM-DMAEMA)	45.9	241	4.8	2.24	4.9

DMAEMA, 2-(dimethylamino)-ethylmethacrylate; AM, acrylamide; CD, cyclodextrin; Dex, dextrin; HEC, hydroxyethylcellulose; $[\eta]$, intrinsic viscosity; L, liter

6N HNO₃ was added to the flask.^{9,10} The molar ratio of DMAEMA/AM was 1:9. The flask was then purged with nitrogen gas for 5 min. Ferrous ammonium sulfate hexahydrate (2.6×10^{-5} mol) and 30% hydrogen peroxide (2.6×10^{-3} mol) were added, and the mixture was kept at room temperature for 3 h with stirring (when using HEC, the mixture was kept at room temperature for 4 h).

The synthesized polymer was precipitated by dropping acetone into the polymer solution. The precipitate was soaked in methanol overnight, filtered, and dried at room temperature. AM-DMAEMA was synthesized by the method of Tanaka.¹¹

Polymer characterization

Cationic charge density was determined by colloid titration.¹¹ Grafting ratios were determined by the colloid titration and the Kjeldahl method. Intrinsic viscosity was measured in 1N NaNO₃ at 30°C.⁸ Molecular weight was measured by size-exclusion chromatography using a TSK gel G5000PWXL, and a series of polyethylene oxides (Tosoh) with different molecular weights ($2.6 \times 10^4 - 8.85 \times 10^5$). The eluant was an aqueous solution of 0.3M CH₃COOH and 0.3M CH₃COONa. The amounts of homopolymers were not determined.⁸ The results are listed in Table 1.

Polymer retention

The pulp slurry (0.6%) and a polymer solution (0.03%) were adjusted to pH 7 with dilute HCl or NaOH prior to measurement. Twenty milliliters of a 0.03% polymer solution was added to the 0.6% pulp slurry (200ml). After stirring for 30 min, the suspension was poured into a G2 glass filter. The amount of unretained polymer was determined by colloid titration of the filtrate. The polymer in the filtrate was subtracted from the initial amount of polymer added.¹²

Drainage measurement

The pulp slurry (1.2%) and polymer solution (0.03%) were adjusted to pH 7 with dilute HCl or NaOH prior to measurement. A designated amount of 0.03% polymer solution was added to the 1.2% pulp slurry (200ml). After stirring for 30 min, the mixed suspension was diluted to 1000 ml with water of pH 7, and the drainage was measured using a CSF tester.¹³

Table 2. Polymer retention of cationic co-PAMs

Sample	Polymer retention (%)
AM-DMAEMA	97.2
CD-graft-(AM-DMAEMA)	91.9
Dex-graft-(AM-DMAEMA)	96.1
HEC-graft-(AM-DMAEMA)	95.7

Polymers added 0.5% on dry weight of pulp

Making and testing of handsheets

A designated amount of 0.03% polymer solution was added to the 1.2% pulp slurry. After stirring for 5 min, handsheets were made according to JIS P 8209. Measurement of dry tensile strength was conducted according to JIS P 8112 after conditioning at 20°C and 65% RH for more than 24 h.

Retention of filler

Kaolin (0.9 g) was added to the 1.0% pulp slurry (300 ml), and then a designated amount of 0.03% polymer solution was added. After stirring for 60 min, handsheets were made as described above.¹⁴ The handsheets obtained were incinerated in a crucible to constant weight. Retention of filler was determined by subtracting the weight of ash from the added filler.

Results and discussion

Table 2 shows polymer retention on pulp fibers. For applications where polymers will be used as wet-end additives, it is necessary to have high polymer retention. Polymer retention at the 0.5% (on dry pulp) addition was 91.9%–97.2%. These retention values did not depend on the pH of pulp slurry in the pH range from 3 to 9. However, the retention value and the range were changeable according to the addition level and the ion concentration of the pulp slurry.

Figure 1 shows the drainage behavior of pulp slurry treated with each polymer. The CSF value of the pulp slurry treated with AM-DMAEMA was improved by approximately 90 ml for the 0.3% addition, but the CSF value at 0.5% decreased more than that for 0.3%. The cyclodextrin-acrylamide-2-(dimethylamino)ethylmethacrylate graft

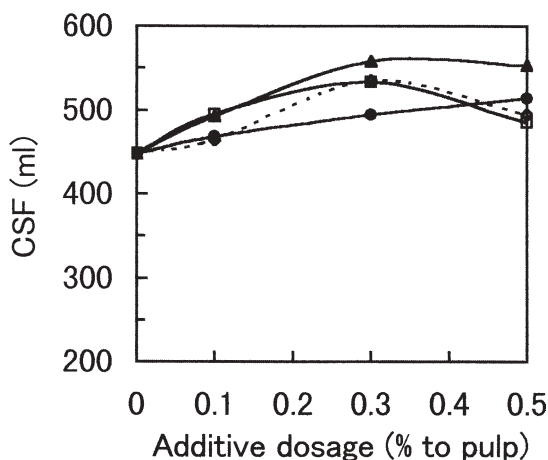


Fig. 1. Effect of cationic copolymerized polyacrylamides (co-PAMs) on pulp slurry drainage at pH 7, measured as Canadian Standard Freeness (CSF). *Dashed line with diamonds*, acrylamide-2-(dimethylamino)ethyl methacrylate (AM-DMAEMA) copolymer; *unfilled squares*, cyclodextrin-AM-DMAEMA graft terpolymer; *filled triangles*, dextrin-AM-DMAEMA graft terpolymer; *filled circles*, hydroxyethylcellulose-AM-DMAEMA graft terpolymer

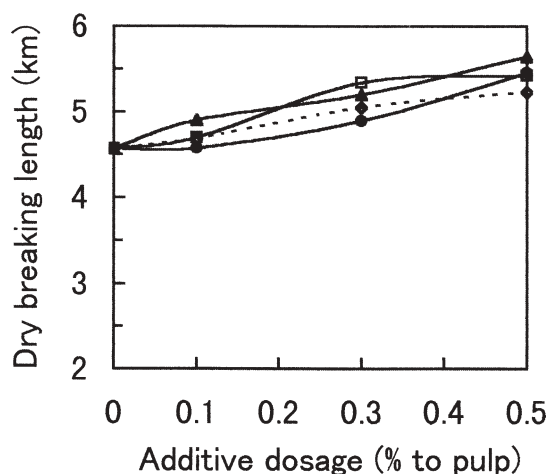


Fig. 2. Dry breaking length of bleached hardwood kraft pulp handsheets treated with cationic co-PAMs

terpolymer [CD-graft-(AM-DMAEMA)] showed drainage properties that were similar to those of AM-DMAEMA. On the other hand, the CSF value of the pulp slurry treated with Dex-graft-(AM-DMAEMA) was improved for 0.3% and 0.5% additions. Because this polymer has higher intrinsic viscosity compared with the other polymers, molecular size might be large.

Figure 2 shows the dry tensile strength of pulp sheets treated with each polymer. Generally, water-soluble polymers that have amide groups ($-\text{CONH}_2$) or hydroxyl groups ($-\text{OH}$) are effective in improving paper strength because they can combine pulp fibers through hydrogen bonding.¹⁵ Graft terpolymers synthesized in this study were suitable for this purpose. Dry tensile strength was improved with increasing additive dosage of the polymers, although those dry strength improvements were not so different from

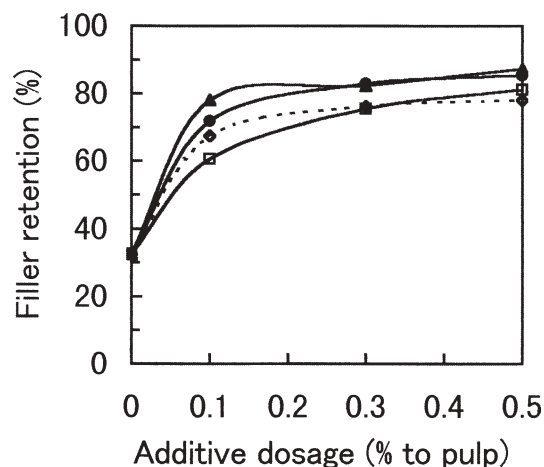


Fig. 3. Effect of cationic co-PAMs on filler retention. The filler was added 30% on dry weight of pulp

those of linear AM-DMAEMA. Pulp sheets treated with AM-DMAEMA showed an increase in dry tensile strength of 15% at 0.5% addition. Similarly, CD-graft-(AM-DMAEMA) and hydroxyethylcellulose-acrylamide-2-(dimethylamino)ethylmethacrylate graft terpolymer [HEC-graft-(AM-DMAEMA)] showed an increase in dry tensile strength of 19%. On the other hand, Dex-graft-(AM-DMAEMA) showed an increase of 23%. It is known that paper strength increases with increasing molecular weight of PAM.¹⁵ Link reported that the optimum strengthening effect for PAM occurred with a molecular weight of about 0.5 million.¹⁶ The molecular weight of cationic co-PAM synthesized in this study was indeed about 5×10^5 , and thus, the graft terpolymers synthesized had molecular weights necessary for improving paper strength.

Figure 3 shows the retention of filler on pulp sheets. Because fillers such as kaolin have negative surface charges in water, only part of them are retained on handsheets. In the case of no additive polymer, only 30% of the added filler was retained on handsheets. Therefore, it is necessary to add cationic polymers for sufficient retention of fillers on handsheets. The filler retention increased with increased dosage of polymers. AM-DMAEMA and CD-graft-(AM-DMAEMA) showed similar filler retention behavior. On the other hand, Dex-graft-(AM-DMAEMA) and HEC-graft-(AM-DMAEMA) showed higher filler retentions compared with the formers. Dex-graft-(AM-DMAEMA) showed filler retentions of 78% and 87% at the additive dosages of 0.1% and 0.5%, respectively. This polymer has a very large molecular size such that the filler might be more strongly retained on handsheets.

Conclusions

To improve the wet-end properties of cationic co-PAM of linear type, we synthesized three types of graft terpolymers and evaluated their performance. Synthesized graft terpolymers showed similar or superior wet-end properties com-

pared with AM-DMAEMA of linear type. In particular, Dex-graft-(AM-DMAEMA) moderately improved the wet-end properties compared with the other two graft terpolymers.

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