

# Synthesis and Application of a Cationic Polyacrylamide Dry Strength Agent with Anionic Content

Guangyan Wang and Yi Jing\*

A new net-cationic polyacrylamide dry strength agent was synthesized through free radical polymerization using acrylamide (AM), itaconic acid (IA), N,N-dimethylacrylamide (F), and sodium methallyl sulfonate (T). Ethylene diamine tetraacetic acid was used as a chelating agent; dimethylaminoethyl methacrylate methyl chloride (DMC) solution was used as a cationic monomer, and ammonium persulfate (APS) was used as an initiator. Orthogonal design and single-factor experiments were utilized to study the effect of many factors, such as reaction time, the ratio of monomers, and the dosage of APS and DMC on the cationic polyacrylamide. The synthesized products were characterized by Fourier transform infrared spectroscopy (FTIR), gel permeation chromatography (GPC), particle charge detector (PCD), and zeta potential analysis. The results showed that the optimum conditions were as follows: optimal monomer proportion:  $m(\text{AM}):m(\text{IA}):m(\text{T}):m(\text{F}) = 23.79:2.39:0.21:0.32$ ;  $w(\text{DMC}) = 28\%$ ;  $w(\text{APS}) = 1.0\%$ , reaction time was 3 hours, reaction temperature was 93 °C, stirring speed was 130 rpm, and reaction pH value was 3.0. The solid content of the polymer was 21.2%. By adding the cationic polyacrylamide to old corrugated container pulp, the tensile index increased by 29.7% and the burst index increased by 66.1%, displaying the obvious enhancement of the paper.

*Keywords:* Cationic polyacrylamide; Dry strength agent; Synthesis; Applications

*Contact information:* Jiangsu Provincial Key Lab of Pulp and Paper Science and Technology, Nanjing Forestry University, Nanjing Jiangsu, 210037, P.R .China; \*Corresponding author: jingyi@nifu.com.cn

## INTRODUCTION

Secondary fibers have received more attention by countries around the world because they are a paper resource that contributes to both economic and social benefits (Zhu 2010). With living standards improving and the rapid growth of the industrial economy, the packaging industry has higher requirements regarding the quality of corrugated base paper. The following methods are commonly used to improve the quality of corrugated base paper. One method is to optimize the quality of the waste paper or choose good quality paper by using imported old corrugated container to replace or partly replace domestic ordinary paper. This technique is limited by costs and sources of old corrugated container. A second method is to add a small amount of grass or better secondary fiber pulp to improve the quality of corrugated base paper. A third method is to use chemical agents that have lower costs to affect the fiber's strength. Studies have shown that using chemical agents is a good technique (Chen *et al.* 1998). Adding a polyelectrolyte, such as cationic polyacrylamide, to improve fiber combination is a promising technique (Hubbe 2006).

Polyacrylamide is widely used in various fields because of its molecular structure characteristics and its many varieties. It is also one of the most widely used products in

the synthesis of water-soluble polymers and has been referred to as a “universal additive” by Fang *et al.* (2006). The papermaking industry is a large consumer of polyacrylamide, which is mostly used for dry strength improvement, filler retention, and the clarifying of whitewater (Zhou 2010). Cationic polyacrylamide in particular has an advantage in that it has a positive charge, which makes the addition of a precipitation agent such as aluminum sulfate unnecessary when used in the production of paper.

This study used sodium methallyl sulfonate, itaconic acid, N,N-dimethylacrylamide, and sodium methallyl sulfonate as monomers to synthesize a quaternary copolymer. Some of the monomers are low-cost and contribute special properties to the polymer. For example, itaconic acid can make the polymer more easy to degrade (Gu *et al.* 2011). This copolymer was then applied to papermaking, and its effects on paper strength were studied. Finally, the synthetic products were characterized using some advanced characterization methods.

## EXPERIMENTAL

### Materials

Acrylamide was purchased from Guoyao Chemical Co., Ltd., China. Itaconic acid was obtained as an industrial product, in white powder form, from Tianjin Chemical Industry Group (China). Dimethylaminoethyl methacrylate methyl chloride (DMC, 75%) was of chemical grade, applied by Aladdin Industrial Corporation. N,N-dimethylacrylamide and sodium methallyl sulfonate was obtained from Panya Chemical Co., Ltd. Ammonium persulfate, sodium hydroxide, sodium sulfite anhydrous, methanol, and ethylenediamine tetraacetic were all of analytical grade.

### Methods

#### *Synthesis of CPAM dispersion*

Varying quantities of monomers (AM and N,N-dimethylacrylamide), itaconic acid, and sodium methallyl sulfonate were added to a 250-mL four-neck separable flask equipped with an anchor-like paddle stirrer, a feeder, a thermometer, and a nitrogen inlet tube. The concentration of reactants was controlled at 25%. The reaction pH was 3.0. The stirring speed was set to 130 rpm. After purging with N<sub>2</sub> for 30 min in a water bath, heating was begun. When the temperature reached 59 °C, part of the APS was added to the flask to initiate the monomers for the first time. One hour later, the rest of the monomer was added to the flask. When the temperature reached 93 °C, the rest of the APS was added to initiate the monomers a second time, and the reaction continued until the viscosity of the polymer reached the target. Then, sodium hydroxide solution was used to adjust the pH to 6.8, and the reaction was halted.

#### *FTIR analysis*

FTIR analysis was carried out with an FTIR-650 instrument from Thermo Nicolet. The copolymer was purified through the following procedures: the copolymer solution was washed with a large quantity of a 41% methanol aqueous solution. This operation was repeated several times to remove the unreacted monomers and inorganic salts. Then, the copolymer was dried to a constant weight at 40 °C under vacuum. The dried sample was detected by FTIR-650.

*Particle charge detector analysis (PCD)*

The charge density of the polymer was measured using a Müttek PCD-03 instrument from the BTG company. The specific method was as follows: the polymer was diluted to a 0.01% concentration and placed in a 10-mL PCD plastic measuring pool with a pipette. Then, it was titrated by the Sodium Polystyrene Sulfonate (Pes-Na) until the endpoint was reached.

*Gel permeation chromatography (GPC)*

The molecular weight of the CPAM dispersion was measured by HPLC1515 according to China national standards, GB12005-1989.

*Zeta potential analysis*

The zeta potential of the waste paper pulp was measured according to China national standard GB/T24993-2010. Then, 0.5% CPAM polymer solution was added to the pulp, which was stirred until it became uniform, at which time the pulp's zeta potential was measured again.

*Analysis of paper properties*

The basis weight of the paper was measured according to China national standard GB/T451.2-1989. The basis weight was 80 g/m<sup>2</sup>, and the drying temperature was 105 °C. The tensile strength and burst strength of paper were measured according to China national standards GB/T453-1989 and GB/T454-1989, respectively (Shi *et al.* 2010).

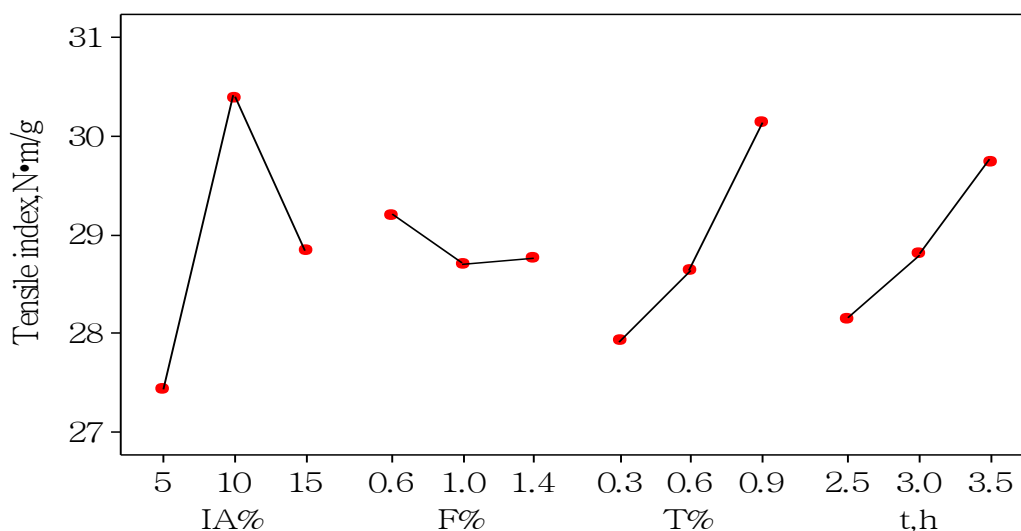
**RESULTS AND DISCUSSION****Orthogonal and Single-Factor Experimental Designs**

Reaction time, temperature, and material proportions are basic factors for CPAM synthesis. Therefore, to study the influence of the synthetic process on the polymer, an orthogonal experimental design was applied. Here, the % values represent the ratio of other monomers to the AM. Table 1 shows the results of reaction time and dosage of every monomer on the polymer's effects on paper strength properties, especially the tensile and burst strengths.

**Table 1.** Results of the Orthogonal Experiments

NO.	Dosage of itaconic acid /%	Dosage of N,N-dimethylacrylamide/ %	Dosage of sodium methallyl sulfonate /%	Reaction time/h	Tensile index/ N•m/g	Burst index/ kPa•m <sup>2</sup> /g
1	5	0.6	0.3	2.5	26.0	1.938
2	5	1.0	0.6	3.0	26.9	1.764
3	5	1.4	0.9	3.5	29.4	1.893
4	10	0.6	0.6	3.5	31.3	2.125
5	10	1.0	0.9	2.5	30.7	1.879
6	10	1.4	0.3	3.0	29.2	2.010
7	15	0.6	0.9	3.0	30.3	1.764
8	15	1.0	0.3	3.5	28.5	1.749
9	15	1.4	0.6	2.5	27.7	1.760

The data were then analyzed by range analysis. Table 2 and Table 3 show the effects of factors on the tensile and burst indices.

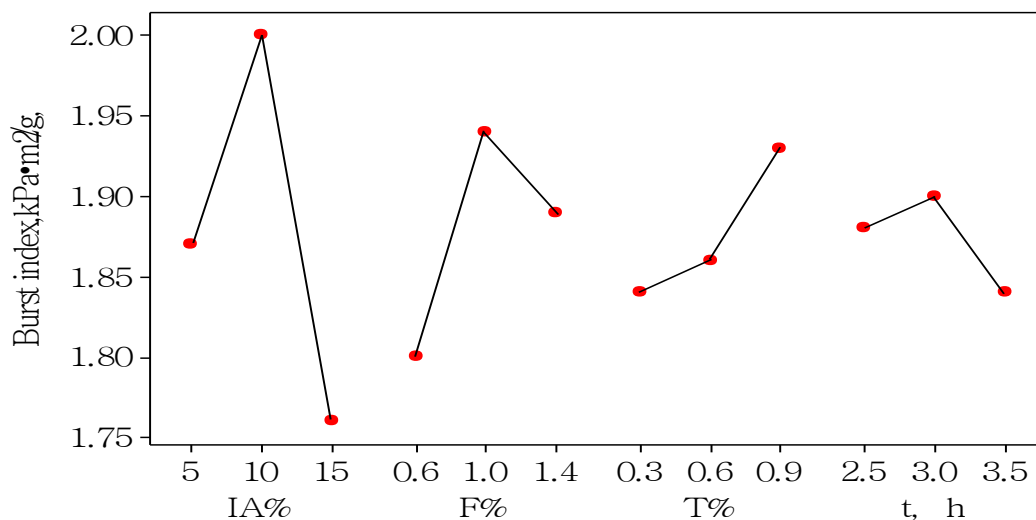


**Fig. 1.** Effect of factors on tensile index. IA% represents the dosage of itaconic acid, F% represents the dosage of N,N-dimethylacrylamide, T% represents the dosage of sodium methallyl sulfonate, and t represents the reaction time. All dosages are relative to the dosage of acrylamide.

According to Fig. 1, monomers dosage had an effect on the tensile index of the paper. That is to say, the proportional monomer composition affected the polymer's properties. Additionally, various factors exhibited different effects. The sequence is as follows: dosage of itaconic acid > dosage of sodium methallyl sulfonate > reaction time > dosage of N,N-dimethylacrylamide. Therefore, for the tensile index, the optimal dosage of monomer was as follows: itaconic acid: 10%, sodium methallyl sulfonate: 0.9%, N,N-dimethylacrylamide: 0.6%, and reaction time: 3.5 h.

From Fig. 1 it is apparent that the performance of the additives increased with increases of itaconic acid and methallyl sulfonate, both of which are anionic monomers. The two monomers contribute an anionic carboxyl group and sulfonic acid group, respectively. Because the use of the cationic monomer (DMC), the prepared polymers also contained the cationic quaternary ammonium salt group, which was present in greater quantity. So the polymer can be regarded as an amphoteric polymer having an excess of positively charged groups (Xu *et al.* 2009). Past research has shown that such amphoteric polymers can be effective as dry-strength agents for paper (Song *et al.* 2006).

Compared with Fig. 1, Fig. 2 shows that monomer dosage had different effects on the burst index than it did on the tensile index. The sequence is as follows: dosage of itaconic acid > dosage of N,N-dimethylacrylamide > dosage of sodium methallyl sulfonate > reaction time. For the burst index, the optimal dosage of monomer is as follows: itaconic acid: 10%, sodium methallyl sulfonate: 0.9%, N,N-dimethylacrylamide: 1.0%, and reaction time: 3.0 h. Again it is apparent that IA had more influence on the polymer's performance than any of the other three factors.



**Fig. 2.** Effect of factors on burst index. Abbreviations are the same as in Fig. 1.

To further determine the optimal proportion of monomers, different polymers were synthesized according to the above results. The polymers were then added to the pulp, and their effects on paper strength were compared. The results are shown in Table 2.

**Table 2.** Optimum Experimental Conditions and the Paper Strength Indices

	Tensile index/ N·m/g	Burst index/ kPa·m <sup>2</sup> /g	Parameters of two polymers
Tensile optimization	30.9	2.160	IA:10%
			F: 0.6%, T: 0.9%
			t:3.5h
Burst optimization	31.2	2.177	IA:10% F:1.0%, T:0.9% t:3.0h
Blank experiment	24.7	1.236	Without adding strength agent

Finally, by comparing the polymers synthesized under different conditions, the proportions of monomers and reaction time were chosen as follows:

$$w(\text{AM}):w(\text{IA}):w(\text{T}):w(\text{F})=100:10:0.9:1.0;$$

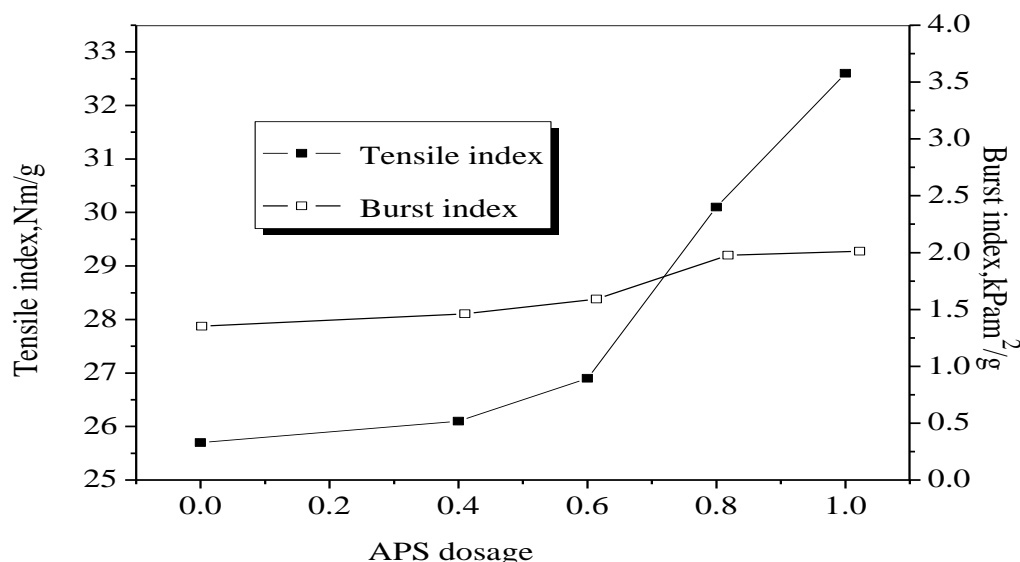
$$m(\text{AM}):m(\text{IA}):m(\text{T}):m(\text{F})=23.79:2.39:0.21:0.32;$$

Reaction time=3 h.

### The Influence of Ammonium Persulfate (APS) Dosage on the Polymer

As can be seen from Fig. 3, with increasing ammonium persulfate (APS) dosage, the tensile and burst strengths of the paper also increased. When the dosage of APS reached 1%, the tensile and burst strengths both reached a maximum. If the dosage of

APS is further increased, the polymer emulsion will turn into a gel-like substance, which is called hydrogel.



**Fig. 3.** Dosage of ammonium persulfate (APS) with polymer properties

Preliminary work showed that hydrogels prepared in this manner could only swell in water but not dissolve. Furthermore, the prepared hydrogels did not contribute to the paper's strength. The reasons for these results are as follows: when the dosage of the initiator is small, part of the monomer did not take part in the reaction because of the lack of free radicals; that is to say, the rate of conversion of all the monomers was low. At this point, the polymer's molecular weight was small and it had almost no effect on paper. When the dosage of the initiator was increased, the concentration of the initiator increased along with the number of radicals formed initially, so the probability of particle collision increased too, which led to a bigger particle size and higher conversion rate (Maxwell *et al.* 1987). When the dosage of the initiator reached a certain degree, increasing of the APS's dosage became counterproductive. The reasons are as follows: with increasing initiator concentration, the number of free radicals became excessive; these free radicals can cause reactant particles concentrated in one place to instantaneously cause agglomeration, deteriorating the stability of the reactant and increasing the rate of termination. Therefore, the average molecular weight of the polymer decreased, thus reducing the polymer's enhancement of the paper strength.

### **Influence of Methacryloyloxyethyl Trimethyl Ammonium Chloride (DMC) Dosage on the Polymer**

As can be seen from Fig. 4, the burst strength of the paper increased with the increase in DMC's dosage, while the tensile strength decreased at first and then increased dramatically with the increase in DMC's dosage. When the dosage of DMC reached 28%, the tensile strength and burst strength both reached a maximum. The reasons are as follows: when the dosage of DMC increased, the charge density of the polymer increased too; the pulp fiber is negatively charged, so the electrostatic adsorption between the

polymer and the pulp fiber was enhanced. At the same time, the adhesion effect of cationic polymers themselves can absorb fibers easily, therefore, increasing the strength of the paper. However, DMC is a hydrophilic substance, and when the dosage is too large, it reduces the viscosity of the polymer as well as the molecular weight. It is thus difficult to synthesize a polymer that has an enhancement effect on the paper. On the other hand, excessive cations can easily lead to flocculation, which leads to an uneven distribution of fibers in the pulp, as well as a reduction in the strength of the paper (Espy 2001; Kim 2004; Luo *et al.* 2002; Zhu 2005).

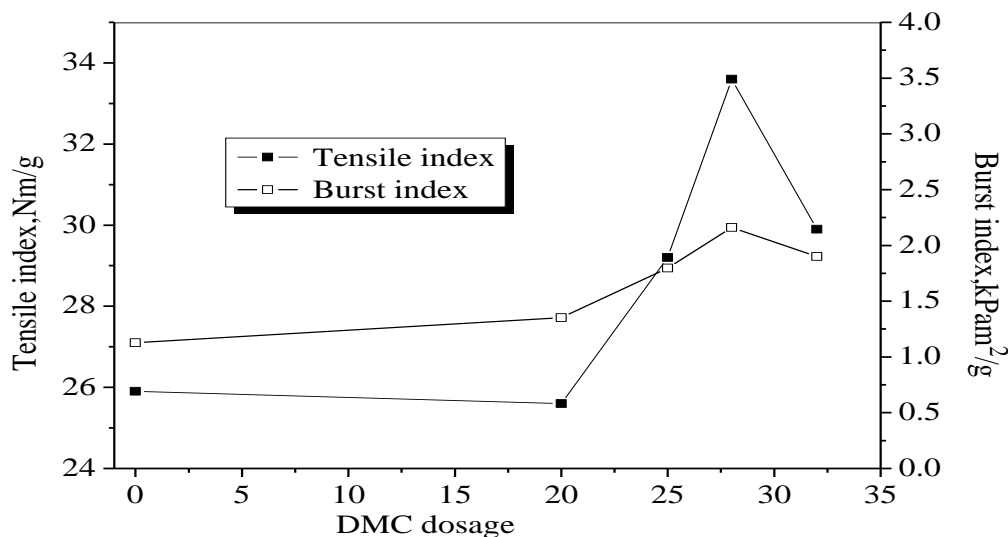


Fig. 4. Dosage of dimethylaminoethyl methacrylate methyl chloride (DMC) on polymer properties

### FTIR Analysis of CPAM Dispersion

The FTIR spectrum of the synthesized CPAM dispersion is shown in Fig. 5.

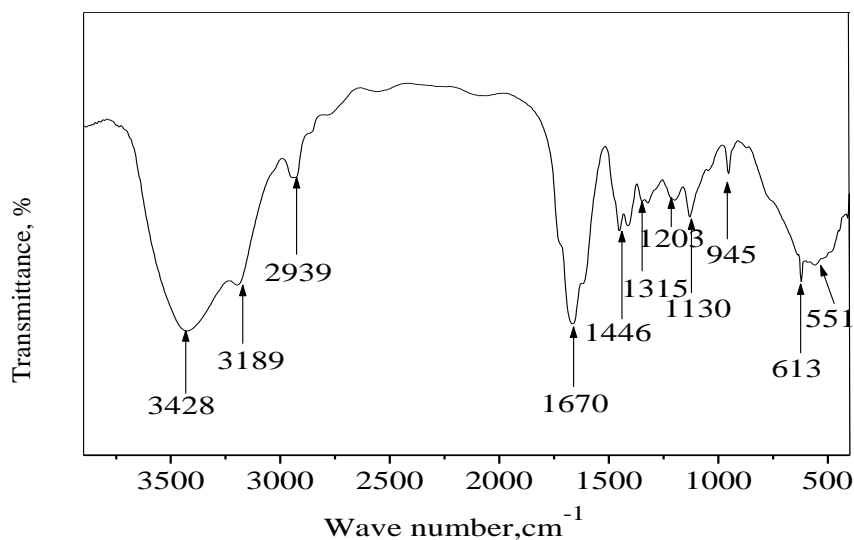


Fig. 5. IR spectrum of the polymer

The peak at  $3428\text{ cm}^{-1}$  is strong and wide and is attributed to the stretching vibration of associated O-H groups. The peak at  $3189\text{ cm}^{-1}$  is weak and pointed and is attributed to the stretching vibration of N-H from acrylamide. The peak at  $2939\text{ cm}^{-1}$  is attributed to the stretching vibration of C-H from methyl, while the methyl comes from the methylallyl sulfonate. The peaks between  $1315$  and  $1446\text{ cm}^{-1}$  and  $1203$  and  $1315\text{ cm}^{-1}$  are split into twin peaks, which shows the existence of the accompanying dimethyl and trimethyl that come from N,N-dimethyl acrylamide and DMC. The absorption peak at  $1670\text{ cm}^{-1}$  is strong and sharp and is attributed to the carbonyl (C=O) of the carboxyl group. The peak located at  $1130\text{ cm}^{-1}$  is attributed to the stretching vibration of C-O from the ester base. The peak at  $945\text{ cm}^{-1}$  is attributed to C=C stretching vibration. FTIR analysis shows that all monomers were involved in the polymerization reaction.

### Physical Properties

Under the optimal reaction conditions, the CPAM dispersion was synthesized with high charge density, high molecular weight, good solubility, and excellent stability. The properties of CPAM are listed in Table 3.

**Table 3.** Physical Properties of CPAM Dispersion

Items	Testing results
Appearance	Light yellow liquid
Solids content (%)	21.2%
Dissolvability	Dissolved quickly in water
pH value	6.9
Apparent viscosity(cp)	7200~7450
Charge density[eq/g]	$1.47 \times 10^{-4}$
Relative molecular weight (g/mol)	$2.6 \times 10^5$
Stability	No charge in 3 months

### Influence of the Polymer on the Zeta Potential of Domestic Old Corrugated Container (OCC) Pulp

The zeta potential of old corrugated container pulp was measured before and after adding the polymer. The results were as follows: the zeta potential of the OCC pulp changed from  $-49.6\text{ mv}$  to  $-33.9\text{ mv}$  with the addition of 0.5% polymer solution. That is, adding polymer emulsion reduced the value of the zeta potential because the cationic polyacrylamide is a polyelectrolyte with positive charge; when added into the pulp, it was adsorbed on the fiber, so that the zeta potential of the slurry declined.

### CONCLUSIONS

1. Through orthogonal and single-factor experiments, the best synthesized conditions to achieve increased dry strength were found to be as follows: a proportion of monomers of m(acrylamide):m(itaconic acid):m(sodium methallyl sulfonate):m(N,N-dimethyl-acrylamide) equal to 23.79:2.39:0.21:0.32 and dosages of dimethylaminoethyl methacrylate methyl chloride and ammonium persulfate of 28% and 1%, respectively. The reaction time was 3 h, reaction temperature was  $93\text{ }^{\circ}\text{C}$ , speed of stirring was 130 rpm,



and reaction pH value was 3.0. The orthogonal experiments showed that in addition to the acrylamide, the dosage of itaconic acid had the biggest influence on the synthesis of the polymer emulsion. Through single-factor experiments, it is now known that the dosages of dimethylaminoethyl methacrylate methyl chloride and ammonium persulfate have a close relationship with enhancement effects of the polymer.

2. It is easier to control the reaction by adding the initiator to the reactant at two times rather than once. Also, the stability of the resulting synthetic polymer is better. The polymer not only enhances paper but can also reduce the negative zeta potential of pulp. From the FTIR spectra, it is apparent that the polymer emulsion was synthesized by copolymerization involving all monomers rather than the separate homopolymerization of each of the monomers by itself.
3. Under the optimum reaction conditions, the relative molecular mass of the synthetic polymer emulsion was  $2.6 \times 10^5$  g/mol, the charge density was  $1.47 \times 10^{-4}$  [eq/g], and the apparent viscosity ranged from 7200 to 7450 cp. The product exhibited good solubility and stability.

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