

Study on the Preparation and Modification of Polyamide-Polyamine Epichlorohydrin (PAE) Resin

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ABSTRACT

We studied the synthesis process of PAE resin, and then blended carboxymethyl cellulose aqueous solution into PAE resin aqueous solution, so as to modify PAE resin, improve the performance of PAE resin, and reduce the cost of PAE resin. We discussed the effect of temperature, molar ratio, and holding time on the wet strength property of PAE resin; studied the modification process of PAE resin, and characterized PAE resin by IR spectroscopy; then studied the application performance of modified PAE resin. The results showed that, when the holding temperature was 70 °C, the molar ratio of Polyamide polyamine and epichlorohydrin was 1.2, and the holding time was 70 minutes; under these conditions the enhancement performance of modification PAE resin was optimal. When the proportion of carboxymethyl cellulose in modified PAE resin was 9%, and used this modified PAE resin by the dosage of 0.6%, compared to commercial PAE resin, modified PAE resin could improve the dry tensile index of paper hand sheet about 15%, the wet strength about 19%, the tear index 18%, and internal bond strength about 6%. What's more, the modified PAE resin was good for the drainage ability of the pulp by the dosage of 0.6%.

Key words: PAE resin, carboxymethyl cellulose, modification, wet strength, drainage ability

Introduction

Polyamide-Polyamine Epichlorohydrin (PAE) resin was placed in the market at the end of 1950s as an internal wet-strength agent for paper, and has widely been used in making tissue paper, paper towel, milk carton and others. PAE resin is one kind of water-soluble cationic thermosetting resin, with high wet strength, no free formaldehyde, and good water absorption. The mechanisms of wet-strength development of cellulose sheets prepared with PAE have been extensively studied, and the reinforcement and protection mechanisms have been proposed [1-2]. The former is the so-called holding mechanism between azetidinium groups of PAE and carboxyl groups of cellulose fibers, which are present as minor functional groups. The latter is the formation of water-insoluble PAE networks, which inhibit fiber-bond detachment of PAE-treated cellulose sheets re-wetted in water [3]. Even if PAE resin has so

many advantages in papermaking industry, it still has some shortcomings. For example, for some kinds of paper, PAE resin can not improve wet strength performance a lot, what's more the cost of PAE resin is much. In order to improve the wet strength performance of PAE resin, and make PAE resin better used in paper industry, many domestic and foreign experts began to modify PAE resin, such as poly-urea modification, chitosan grafted copolymer modification, acrylamide graft copolymer modification, styrene graft copolymer modification, acid aldehyde modification, etc [4-10]. Currently, domestic and foreign experts work on modifying PAE resin mainly from the following aspects: firstly, graft copolymer PAE resin with other chemicals to form a new polymerizable compound, so as to enhance the function of PAE resin or make PAE resin which has some new features; Secondly, under the same composition, change the synthesis conditions of conventional PAE resin in order to optimize the structure of PAE resin, and try to explore its new features or diversify its functions. Thirdly, modifying the PAE resin by blending with low-cost chemicals, so as to reduce the cost of

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PAE resin. In this paper, we studied the synthesis process of PAE resin, and then blended carboxymethyl cellulose aqueous solution into PAE resin aqueous solution, so as to modify PAE resin, improve the performance of PAE resin, and reduce the cost of PAE resin.

Experimental

Raw materials and reagents

A commercial hardwood and softwood bleached kraft pulp board (Jiang Su Paper Manufacturing Ltd., China). The main experimental chemicals were: adipic acid (AA), diethylenetriamine (DTEA), epichlorohydrin (EPI), carboxymethyl cellulose (CMC), etc. (They were all analytical grade.).

Experimental Methods

Synthesis process of Polyamide polyamine (PPA)

Added diethylenetriamine into the 500ml flask, used oil bath heated to 120°C, then added adipic acid into the flask under stirred conditions, continued heating to the temperature reached at 175°C, at this temperature kept for 4h and then stopped heating. Finally when the temperature of the polymer dropped to 100°C, diluted the polymer with boiled pure water to the concentration of 50%.

Synthesis process of PAE resin

Took a certain amount of the polyamide polyamine into 500ml flask, then diluted the polyamide polyamine with pure water to the concentration of 25%, and added slowly a certain amount of epichlorohydrin into the flask under stirred conditions, then heated to the predetermined temperature, and then stopped heating and started the time, in this process stirring should be continued, after holding to a certain time added the hydrochloric acid (concentration is about 50%) immediately into flask as soon as possible so as to adjust the pH to 3~4, then diluted the PAE resin solution with pure water to the concentration of 12.5%.

Preparation of modified PAE resin

Added the pre-configured sodium carboxymethyl cellulose solution (concentration is about 6%) with a certain proportion into the PAE resin solution (concentration is about 12.5%) to modify PAE resin, this process should occur under stirring.

Preparation of paper hand sheets

Mixed bleached softwood board with hardwood board according to the mass ratio with 4:1, and then beat to 45 °SR. Taking 2.5g slurry (on dry weight of pulp), added a certain amount of the modified PAE resin into the slurry to prepare paper hand sheets, then used hydraulic press and pressed the wet paper hand sheets for 2 minutes under the pressure of 0.5MPa, and then dried at 105° for 10 minutes, after moisture balance for 24 hours, measured the physical properties of the paper hand sheets according to the national standard of China.

Measurement of paper hand sheets wet strength

Cut the paper hand sheets into the width of 15 mm samples, then put the samples into a plate that equipped with water and soaked for

10 minutes, then took out gently and used filter paper to absorb the water on the surface of the samples, finally the samples were quickly used on tensile strength tester for testing wet strength.

Determination of the drainage effect

Took 2.0g dry pulp, stirred and diluted to 500ml, at this time added a certain amount of the modified PAE resin into the slurry, then placed the slurry into DDJ, and controlled stirrer speed at 750r·min⁻¹, then opened the folder and started the stopwatch at the same time, after collecting the 100ml filtrate, stopped timing immediately.

Results and discussion

The effect of holding temperature on the wet strength of PAE resin

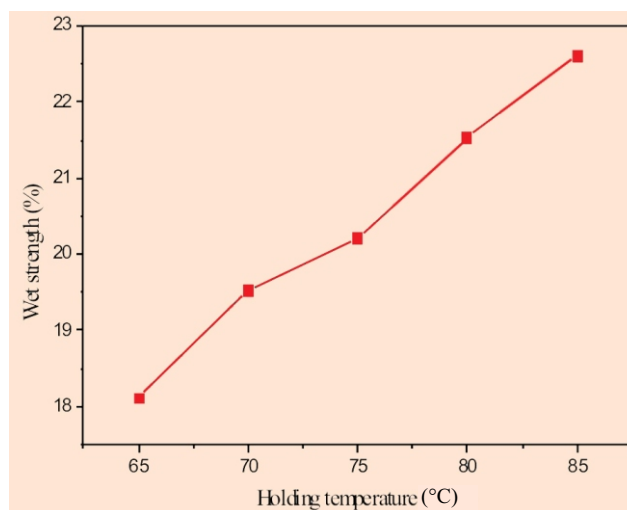


Fig. 1 The effect of holding temperature on the wet strength of PAE resin

The effect of holding temperature on wet strength of PAE resin is shown in Figure 1, it could be seen from Figure 1 that with the increase of holding temperature, the wet strength of PAE resin shows an increasing trend, but the holding temperature should not be too high. When the holding temperature was higher than 70°C, the viscosity of the product (PAE resin) was too large, which was easy to gel [11], in this condition substitution reaction mainly occurred between epichlorohydrin and polyamide polyamine (PPA). As we all know the product (PAE resin) should not only have a good wet strength performance, but also have a good stability. As described above, we chose the 70°C as the best holding temperature.

The effect of the molar ratio of epichlorohydrin and polyamide polyamine (PPA) on the wet strength of PAE resin

The molar ratio (polyamide polyamine and epichlorohydrin) was extremely important to synthesize PAE resin, which will directly affect the wet strength performance and stability of PAE resin product. It could be seen from Figure 2, with the increase of the molar ratio, the wet strength curve showed increase and then decrease trend. As we all knew the dosage of epichlorohydrin determined the ability of cross linked structure which was formed in the PAE resin molecules, when the ratio of the EPI / PPA was

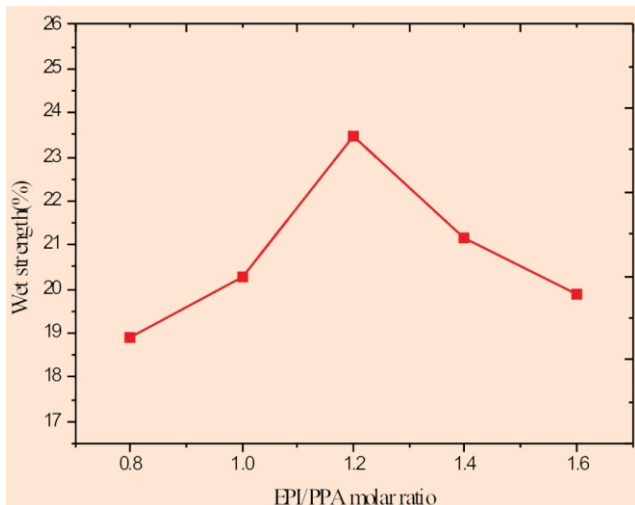


Fig. 2 The effect of the molar ratio of EPI and PPA on the wet strength of PAE resin

small, it would weaken the ability of cross linked structure, that was to say the ability of straight chain molecules turned into mesh structure had been weakened, thus the wet strength performance of PAE resin also had been weakened. When the ratio of the EPI / PPA had been increased, the wet strength performance of PAE resin also showed a downtrend. The reason could be the increasing degree of the cross linked structure, hindered the combination between PAE resin which with positively charge and the fibers which with negatively charge. To some extent, this negative effect reduced the retention of PAE resin on the fibers, and then the wet strength performance of PAE resin had been weakened. Taking the wet strength performance and stability of the product into consideration, we chose the molar ratio for 1.2.

The effect of holding time on the wet strength of PAE resin

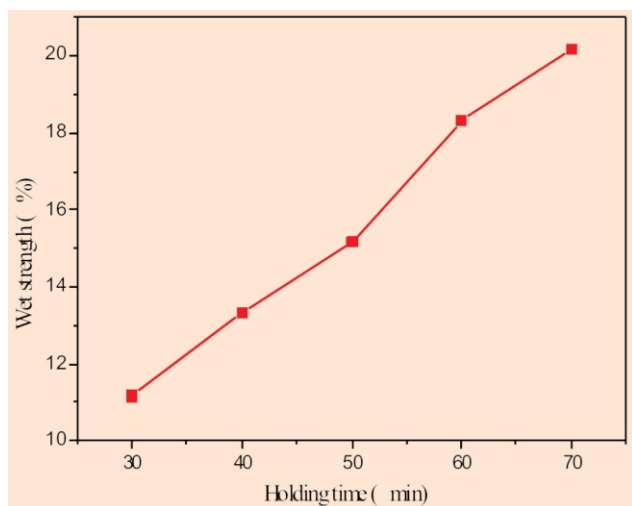


Fig.3 The effect of holding time on the wet strength of PAE resin

The effect of holding time on the wet strength of PAE resin was shown in Figure 3. It could be seen from the figure, with the increase of holding time, the wet strength performance of PAE resin also showed a trend of increase, it was found in the experiment the longer of the holding time, the product was easier to turn gel, which

was also very unfavorable during the synthesis process of PAE resin, but before the occurrence of the gel, the wet strength performance of PAE resin was constantly increasing with the increase of holding time. Thus, we could make up the low wet strength performance of PAE resin which caused by the low holding temperature through increased reaction holding time.

The effect of the proportion of carboxymethyl cellulose in modification of PAE resin on wet strength performance of modified PAE resin

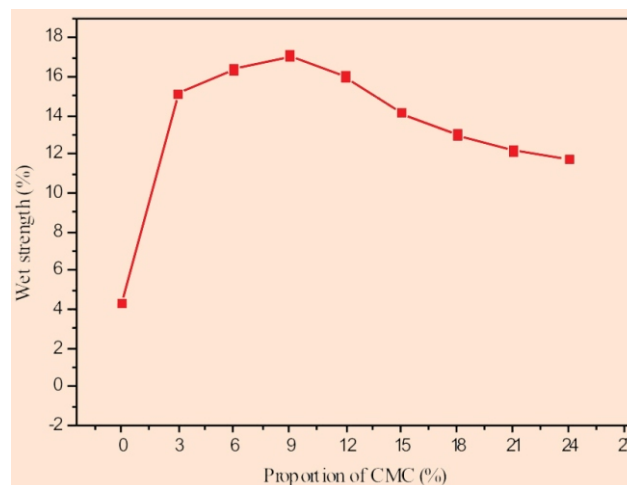


Fig.4 The effect of the proportion of carboxymethyl cellulose in modification of PAE resin on wet strength performance of modified PAE resin

When the modified PAE resin is used by the dosage of 1.0% (on dry weight of pulp), the effect of the proportion of carboxymethyl cellulose in modification of PAE resin on the wet strength performance was shown in Figure 4. It could see from Figure 4 that with the increase of the proportion of carboxymethyl cellulose in modification of PAE resin, originally the wet strength performance of modified PAE resin showed a growth trend, and when the proportion of carboxymethyl cellulose in modification of resin reached 9%, the wet strength performance of the modified PAE resin reached maximum. This was because the modified PAE resin contained both carboxyl groups (which provided by carboxymethyl cellulose) and azetidinium groups (provided by its own structure). During the subsequently drying process of the wet hand sheets, the carboxyl groups could combine with hydroxyl groups which on fiber superficial formed hydrogen bonds and the azetidinium groups could combine with fiber superficial carboxyl groups formed covalent bonds. Then, the former hydrogen bonds and the later covalent bonds would cooperate mutually. As a consequence, the wet strength of the hand sheets could be improved. However, in such a modified PAE resin molecular structure, it was existed the adsorption of carboxyl in the molecular chains, such inter-molecule adsorption not only made the carboxyl lose the activity, but also decreased the electropositive of PAE resin molecular, and affected its retention on the fibers. So when the proportion of carboxymethyl cellulose in the modification further increased, the wet strength performance of the modified PAE resin will be weakened instead. What's more, in terms of price, the cost of carboxymethyl cellulose (the concentration is 9%) was 2000 RMB · ton⁻¹, which was lower than the price of the commercial PAE resin (3600 RMB · ton⁻¹). So the addition of carboxymethyl into PAE resin, was conducive to the

reduction in the cost of PAE resin. In conclusion, the optimal carboxymethyl cellulose proportion in modified PAE resin was 9%.

The infrared spectrum of modified PAE resin

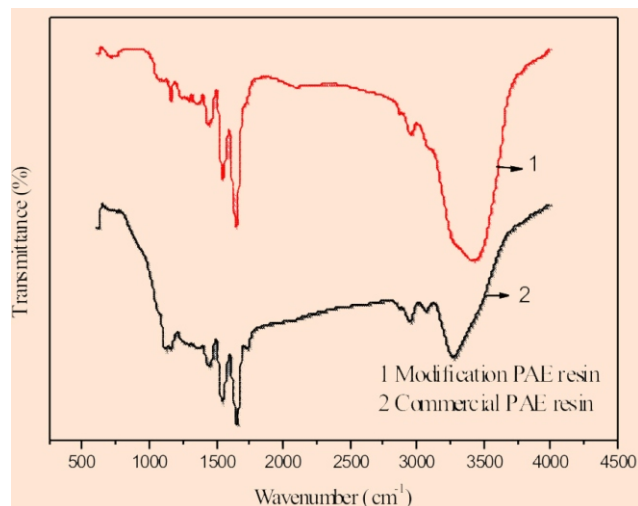


Fig.5 The infrared spectrum of modified PAE resin

The infrared spectrum of modified PAE resin (the proportion of carboxymethyl cellulose in the modification is 9%) was shown in Figure 5. From Figure 5, it could be seen that the absorption band at around $3750 \sim 3000 \text{ cm}^{-1}$ was attributed to N-H stretching vibration, the absorption band at around 1399 cm^{-1} was attributed to C-N stretching vibration, C-O stretching vibration occurred at 1250 cm^{-1} , the absorption band at around 1050 cm^{-1} was attributed to the breathing of azetidinium groups, and absorption band at around 930 cm^{-1} was O-H bending vibration. All of these evidences were related to the interaction between PAE and carboxymethyl cellulose. What's more from the Figure 5 we could prove that after modification the $\nu_{\text{N-H}}$, $\nu_{\text{O-H}}$ and $\nu_{\text{C=O}}$ absorption bands were much stronger than commercial PAE resin, these all phenomenon were attributed to there was a very strong synergistic action between PAE resin and carboxymethyl cellulose.

The effect of the dosage of modified PAE resin on the Zeta potential of slurry

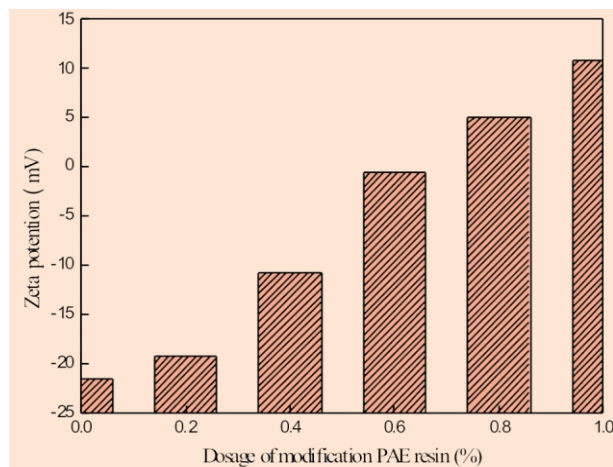


Fig.6 The effect of the dosage of modified PAE resin on the Zeta potential of slurry

The results of the Zeta potential of the slurry when modified PAE resin was added in different dosage were shown in Figure 6. It could be seen from Figure 6, with the increase of the dosage of modified PAE resin, the Zeta potential of the slurry also increased. That was because PAE resin was a cationic polymer. In addition, we could see from the Figure 6, when the dosage of modified PAE resin was 0.6% (on dry weight of pulp), the Zeta potential of the slurry was close to zero. Strazdins[12] and Anderson's[13] study showed that added cationic additives into the slurry system and when the Zeta potential of the slurry system became positive, which meant the adsorption of additives to fibers reduced dramatically, and influenced its further retention on the surface of fibers. In order to reduce the load of white water in papermaking and facilitate the subsequent recycling, we could know the optimum dosage of modified PAE resin was 0.6% (on dry weight of pulp).

In addition, from the Figure 6 we could also see that when the dosage of modified PAE resin was less than 0.2% (on dry weight of pulp), the variation tendency of the Zeta potential of the slurry was low, it could be because there was some negatively charged anionic trash in the slurry. When added modified PAE resin into the slurry, it could be consumed by the anionic firstly, when the modified PAE resin had finished capturing the anion trash, then it could deposit on the fibers' surface. Then, with the dosage of the modified PAE resin increased, an obvious increasing trend of Zeta potential of the slurry was shown in the figure.

The effect of the dosage of modified PAE resin on the drainage performance of the slurry

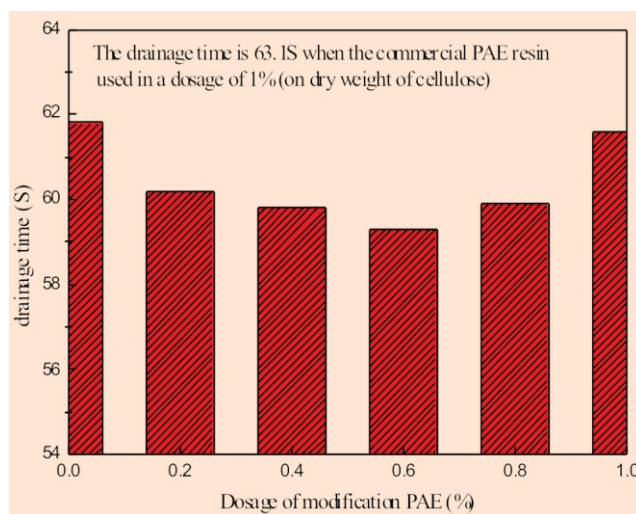


Fig.7 The effect of the dosage of modified PAE resin on the drainage performance of the slurry

In this study, the drainage time of the slurry was conducted under added different dosage of modified PAE. The results showed in Figure 7, due to the existing of carboxyl groups on the surface of fibers, the Zeta potential of the slurry showed negative, so it was conducive to the retention of short fibers after joining cationic additives. When the dosage of the modified PAE resin was less than 0.6% (on dry weight of cellulose), with the increase of the dosage of modified PAE resin, the drainage time of the slurry was on the decline; when the dosage of the modification PAE resin was more than 0.6% (on dry weight of cellulose), the drainage time of

the slurry began to increase. Because when the dosage of modified PAE resin was less, with the increase of the dosage of modified PAE resin, it could make much more fine fibers adsorbed by the long fibers, then formed a dense flocculate layer which could reduce the drainage resistance, so that the drainage time of the slurry decreased, when the dosage of the modification PAE was too high, the gap which weaved by large fibers was filled with a number of fine fibers, which formed a large and loose flocculate layer, which could increase the drainage resistance as well as the drainage time of the slurry. To some extent the drainage time could reflect the drainage performance of the slurry, so when the dosage of modified PAE resin was 0.6% (on dry weight of cellulose), the drainage performance of the slurry was optimal.

The study on the enhancement performance of modified PAE resin

Table .1 The enhancement performance of modified PAE resin

	Quantification (g.m ⁻²)	Tightness (g.cm ⁻³)	Dry tensile index (N.m.g. ⁻¹)	Tear index (m N.g.m ⁻²)	Internal bond strength (j.m ⁻²)	Wet strength (%)
Modified PAE resin	79.9	0.56	55.61	8.96	265.6	19.16
Commercial PAE resin	80.2	0.57	48.16	7.61	251.5	16.11

The comparison of the enhancement performance between modified PAE resin and commercial PAE resin was shown in Table 1. From Table 1, we could see the modified PAE resin was better than the commercial PAE resin in enhancement performance to paper hand sheets. When they were both used at the same dosage of 0.6% (on dry weight of pulp), compared with commercial PAE resin, modified PAE resin could further improve the paper hand sheets' dry tensile index about 15%, wet strength about 19%, tear index about 18%, and internal bond strength about 6%. Therefore, the modified PAE resin could replace commercial PAE resin as paper strengthening agents, and also compared with commercial PAE resin the cost was much lower.

Conclusion

When the holding temperature was 70 °C , the mole ratio of epichlorohydrin / polyamide polyamine was 1.2, the holding time was 70 min; in these conditions the enhancement performance of modified PAE resin was optimal.

When the proportion of carboxymethyl cellulose in modification of PAE resin was 9% and the dosage of modified PAE resin was 0.6%, compared with commercial PAE resin, it could further improve the paper hand sheets' dry tensile index about 15%, wet strength about 19%, tear index about 18%, and internal bond strength about 6%. At the same time, the drainage performance of the slurry was optimal.

The Modified PAE resin could replace commercial PAE resin as paper strengthening agents, and compared with the commercial PAE resin the cost is much lower.

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