Synthesis and Applications of Polyacrylamide Derivatives in the Wet End of Papermaking (Part II. Reactive N-chloropolyacrylamide)

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Abstract: N-chloropolyacrylamide (N-Cl-PAM) obtained from the N-chlorination of the Hofmann reaction of polyacrylamide is easily transferred to the amino group, even with a reaction temperature as low as 0 °C. In this study we investigated how the N-chlorination of polyacrylamide with a low reaction temperature, under low alkaline conditions to avoid the N-chloroamide group forming the amino group (Hofmann reaction), obtained high conversions of the reactive N-chloroamide group. N-Cl-PAM is a highly reactive polymer that easily promotes paper strength. It reacts with the cellulose's hydroxyl and carboxyl groups to form covalent bonds establishing a strong bond between agents and fibers. The established networks of the strengthening agents increase the quantity and quality of the hydrogen bond structures, and therefore the molecule bonding arrangement. It has better properties than anionic and cationic wet end additives for the improvement of paper strength.

Keywords: N-chloropolyacrylamide, Hofmann reaction, Carboxyl group, Amino group, Wet end, Paper strength, Covalent bond, Recyclewaste paper.

Introduction

Many different types of water-soluble polymers are used in the paper industry for improving drainage, fines or filler retention, paper strength improvement, etc. The most commonly used polymers are classified as anionic and cationic types. Although anionic polymers have been widely used, their adsorption by the fiber surface was said to be usually less than 60% even in a system containing cationic alum. Therefore, papermakers have recently become more aware of cationic polymers that are expected to adsorb efficiently onto the negatively charged pulp fibers.

Cationic polyacrylamide (C-PAM) contains various reactive units prepared by Hofmann degradation. Those C-PAM contained 5-7 meq/g of cationic ions. Handsheet with 0.5% C-PAM addition showed an increase in paper strength of about 25% [1].

There are three steps to the Hofmann reaction, as follows:

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\begin{align*}
\text{R-CO\text{NH}_2} & \xrightarrow{\text{0Cl}} \text{R-CO\tilde{\text{N}}C\text{I}} \rightarrow [\text{R-N=C=O}] \xrightarrow{\text{0Cl}} \text{R-NH}_2 \quad (1) \\
\text{II} & \quad [\text{III}] & \quad [\text{IV}]
\end{align*}
\]

Generally, low-molecular weight carbamoyl derivatives, carbamoyl ethylated starch or carbamoyl ethylated polyvinyl alcohol etc., in the low temperature range of 0 - 5 °C proceeds N-chlorination (I to II) of the Hofmann reaction, and then the reaction temperature must be raised to 80 - 90 °C to form the amino group (II to IV) by hydrolysis [2]. But Tanaka and Senju [3] found the reaction rate of PAM with the Hofmann reaction was one hundred times faster than the low molecular weight carbamoyl derivatives. PAM easily formed the amino group, even with a reaction temperature as low as 0 °C. The purpose of this study is to keep proceeding N-chlorination of PAM to maintain a high conversion of the N-chloroamide group (\(-\text{CO\tilde{\text{N}}CI}\), but not the amino group (Hofmann reaction). The effect of reaction temperature and reactant concentration were studied to find the optimum conditions for the N-chlorination of PAM.

Pulping wood as a raw material for papermaking is in short supply in Taiwan, so large amounts of waste paper (recycled material) are used in the local papermaking process. Demand for waste paper as a raw material is increasing rapidly. In Taiwan, in the last ten years, the amount of waste pa-
paper feedstock was about 75% of the total amount of local paper production feedstock [4]. These fibers from the recycled waste paper feedstock are short and thin. Such a large percentage of waste paper as pulp feedstock increases fines in the wet end of the process. Fines result in bad paper formation in the end product, and reduce paper strength. As a result the "wet web" of the production run before entering the dryer is easily broken, causing costly disruption in production. Adding paperstrength agents to the "wet end" of the papermaking process will increase paper strength and reduce the incidence of production breakdowns.

Paper strength is dependent on the strength of individual fibers, the strength of interfiber bonds, the number of bonds (bond area) and the distribution of fibers and bonds (formation). Fiber to fiber bonds are usually weaker than the strength of individual fibers until the latter became the limiting factor in a well bonded sheet [5]. Mechanical entanglement leading to fiber flocculation in the wet end of papermaking is a first step in a long chain of forming the stable network of fibers. One consequence of beating is the increased fibrillation of the fiber surface, enhancing the probability of entanglement and producing a great number of microfibrils capable of actively contributing to the formation of additional fiber-fiber bonds. Various forces may participate in fiber-to-fiber bond formation, the most important being that of hydrogen bond formation, although other forces such as covalent, ionic (electrostatic) and van der Waal's forces also be operative [6].

There are several ways, in papermaking practice, to increase sheet strength. In the work described here, various strength agents containing N-chlorination of polyacrylamide (PAM), polydimethylallyl ammonium chloride (PDMDAAC), and mixed agents are synthesized, and their paper strength increase are studied.

### Experimental

#### 1. Materials

(1) PAM was supplied by the Nacalai Tesque Company of Japan (the degree of PAM was 33,000). The nitrogen content of PAM was 80.6% (determined by the Kjeldahl method [7]).

(2) Preparation of PAM

Acrylamide was twice crystallized using chloroform. In the free radical chain polymerization of acrylamide, potassium persulfate was used as an initiator and isopropyl alcohol as a chain transfer agent. Acrylamide monomer solution introduced nitrogen to remove traces of oxygen in the ampoule. The polymerization of acrylamide was performed at 50 °C for two hours, and the molecular weight of PAM was determined by gel permeation chromatography (GPC). For GPC analysis, the pre-column was Shodex OHpak SB-800P and the GPC column was Shodex OHpak SB-80M. The standard for determination of the molecular weight was polyethylene glycol (PEG) (Mw: 885000, 95000, 7100, 960).

(3) Preparation and analysis of N-Cl-PAM

After cooling, an aqueous solution of 20 mL sodium hypochlorite and 20 mL sodium hydroxide solution was added to an ampoule which was kept in a thermostatic bath at 0 °C. 20 mL of 0.1% aqueous PAM solution was added to the ampoule for a period of 3 minutes.

After a given time, a reaction solution of 2-3g was diluted with cooled water to 200 mL. The diluted solution was separated into four beakers of 50 mL.

The analysis methods of the products were obtained by the following steps: (i) Total chlorine (T-Cl) content (the sum of the amount of hypochlorite and N-chloroamide group) was determined by Iodine titration [8]. To the above diluted 50 mL solution was added 10% KI (10 mL) and 0.1 N H2SO4 (10 mL). After the mixed solution was placed in a dark site for 10 minutes, it was titrated with 0.02 N sodium thiosulfate to determine the T-Cl content. (ii) There was used 2% ethyl malonate solution [9] to erase free chlorine in the 50 mL diluted solution, and it was titrated by iodine titration to determine the amount of the N-chloroamide (N-Cl) group. (iii) The amino group was determined by colloid titration [11, 12]. The 50 mL diluted solution was acidified with 0.1 N HCl to about pH 6.5. One or two drops of 10% KI were added, plus a small amount of sodium sulfite powder to erase the hypochlorite and N-Cl group in the solution. 20 mL of the above solution was diluted to 100 mL, and 0.1 N HCl was added to bring the solution to pH 2. Then two drops of 0.1% TBO (toluidine blue O) were added as an indicator. After shaking for a few seconds, 1x10⁻³ N PVSK (potassium polynvinyl sulfate) solution was added to determine the amino group content. (iv) The carboxyl group was also determined by colloid titration. The 20 mL solution was diluted to 100 mL after adding one or two drops of 10% KI and a small amount of sodium sulfite powder. 0.5 N NaOH was added to bring the solution to a pH of 11.5-12. Ten mL of 1x10⁻³ N MGCH (methyl glycol chitosan) added, and the TBO was added as an indicator. The excess MGCH was used with back titration of 1x10⁻³ N PVSK to determine the amount of the carboxyl group.