

AKD Sizing Mechanism (IV)

- Effect of Polyelectrolytes -

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1. Introduction

One of the important problems sometimes encountered with alkaline sizing with AKD is the lack of off-dryer sizing, especially in the production of coated base and PPC paper. Although this is cause for only mild concern once a correlation was established between the degree of sizing obtained by oven curing for a proper time and temperature and that obtained by natural curing, this lack of sizing is detrimental for size press and other surface applications.

These problems have been overcome to a large extent by the introduction of various polymers at the wet-end. The efforts to enhance the AKD sizing efficiency are concentrated on the use of auxiliary polymers, which is often called AKD fixing agents or AKD curing promoters, as well as on synthesis of new sizing agent. The effects of the auxiliary polymers on AKD size degree have been postulated to be either promoting reactions between AKD and cellulosic hydroxyl groups in the sheet as a catalyst, or increasing AKD content in the sheet by polymers as retention agents. It has been well known that the addition of cationic polymers such as polyamidoamine-epichlorohydrin (PAE) resin, which is one of the wet-strength agents, to pulp suspension containing AKD emulsion enhances sizing features. The patent of Dumas is the first indication of sizing acceleration by auxiliary polymers, and Thorn *et al.* revealed that the auxiliary chemicals affect to the AKD curing rate to different degrees. Recently, Kondo and Makino show the specialized functional groups are effective on enhancing sizing efficiency of AKD.

In this paper, four types of polymers were synthesized as AKD sizing promoters and applied to the AKD sizing system. Effects of the sizing promoters on size degree were discussed. Special attention was being paid to what kind of cationic groups was the most effective on the development AKD sizing degree. Wet-strength and slip properties of resultant paper, which are the problems in AKD sized paper, are investigated. The

relationship between zeta potential and procedure of chemical addition were also discussed.

2. Experimental

Four kinds of polyelectrolytes (Polymers A-D) were polymerized and compared with a commercial product (Polymer E, polyamidoamine-epichlorohydrin (PAE) resin, Taekwang Chem. Co., Korea), which is commonly used in the AKD sizing system as a curing promoter. Highly branched cationic polyelectrolytes (Polymers B-D) containing various functional groups were prepared by the given method as described in the previous papers. The polymerized and commercial polymers were used as bulk products and as received, respectively, without further purification. Polymers used in this work are listed in Table 1.

The mixed bleached kraft pulp (HwBKP/SwBKP, 50/50, w/w) was refined to 450 mL of Canadian standard freeness (CSF) with Valley beater (AB Lorentzen & Wettre, Stockholm, Sweden). Handsheets were prepared from Noble and Wood square sheet former (Adirondack Machine Corp., New York, USA) according to Tappi Standard Test Method. A typical procedure for stock preparation is schematically depicted in Figure 1.

First-pass fines retention (FPFR) was obtained from the following method. Papermaking stock containing mixed pulp with coated broke and ground calcium carbonate (GCC) was placed into a dynamic drainage jar (DDJ) with a 200-mesh perforated screen and filled with water to make a total volume of 500 mL. After stirring the stock at 750 rpm for three minutes, chemicals and filler were added as described in Figure 1, and then 10 mL of the first drained effluent was discarded and 100 mL of the second was taken out. The second drained effluent was filtered and the weight of filtered solid was determined by gravimetry as a first pass fines retention (FPFR). The slurry of pulp and GCC without retention agent was drained until the drainage became clear. The weight of total drained solid was taken as a fines fraction. FPFR was calculated as a percentage of the fines fraction according to TAPPI Standard Method T261 pm-79.

Sizing degrees of handsheets were expressed as Stockigt sizing degrees. Zeta potentials of papermaking stocks were measured at 25°C by using a microelectrophoretic apparatus (Mobility Meter II, Paper Chem Lab. Inc., USA).

3. Results and Discussion

The effect of polymer types on size degree is shown in Figure 2. Four kinds of polymers are compared with commercial polymer (Polymer E in Table 1) used for size promoter. The size degrees of paper with two polymers (Polymers C and D) having cyclic secondary amine group are better than those of other polymers. This is coincident with the result of Kondo and Makino that the cyclic secondary amine group is effective in improving AKD sizing efficiency. Since the polymers C and D are almost same in terms of monomer composition and charge density except molecular configuration, it can be considered that the higher size degree may be due to the copolymer compositions.

The effect of the amount of cyclic secondary amine on Stockigt size degree is investigated as shown in Figure 3. Size degree gradually increases until the amount of cyclic secondary amine monomer reaches to 10 mol.% and goes to equilibrium. However, the amount of amine is fixed to 5 mol.% in this study because the cost of cyclic secondary amine is relatively expensive and the resultant size degree is considered to be enough. From the results of Figures 2 and 3, it can be considered that the cyclic secondary amine group plays a significant role in the development of AKD size degree.

There is a big difference in size degree between polymers C and D as also shown in Figure 2. The two polymers were prepared by the same polymerization condition in the same monomer compositions, and thus, are same polymers except molecular configurations. That is, the polymer C is a linear type while the polymer D is designed to highly branched one by using pentaerythritol triacrylate (PETA), a trifunctional polymerizable core compound. The PETA, which has three polymerizable units, can give many branches to polymer backbone. To investigate the effect of the molecular configuration of polymer on the size degree, PETA content in the polymerization system of polymer D is varied. Figure 4 illustrates the size degree and polymer viscosity are gradually increased as the amount of PETA increases. This indicates that the higher the degree of branch it is better to enhance the AKD size degree. However, PETA content keeps 5.0×10^{-4} mol.% in this experiment because the copolymer viscosity is not easy to handle when the PETA content becomes to higher.

A dependence of water contents remained in the handsheets on drying time at 125°C is shown in Figure 5. The water content is about 30% by 10 seconds drying, and then drastically decreases to a below 5%. Generally, the papermaking condition, which

produces a coated base paper for surface coating, only allows a very short drying time. This requires the development of size degree as fast as possible to obtain a proper surface properties in the size press. However, there is no proper relationship at drying conditions between mill-produced paper and laboratory handsheet. In a lot of papers concerning the development of AKD size degree, the drying times ranged from 3 to 10 minutes are considered to be too long to evaluate the size degree of base paper which will be subjected to surface coating. Therefore, in this paper, 50 seconds and 5 minutes are arbitrarily defined as the drying time of initial and cured size degrees, respectively.

Figure 6 shows the effects of drying time at 125°C on size degrees. The arrows at 50 second and 5 minutes in the Figure indicate the times for initial and cured size degrees, respectively, as described above. Since the polymer D is superior to other polymers in the development of AKD size degree (Figure 2), the highly branched polymer containing cyclic secondary amine group is compared with PAE resin (polymer E). The size degree of handsheet treated with polymer D is development just after drying, and increased linearly until the size degree goes to equilibrium at 150 seconds of drying time. The initial size degree with PAE resin is developed after 10 seconds drying and shows almost half values compared to polymer D. However, the size degrees show almost same values when the papers treated with polymers D and E allow enough time (5 minutes) to cure AKD. These results indicate that the highly branched polymer containing cyclic secondary amine group is the efficient size promoter in terms of not only initial size degree but also a speed of size development.

Figures 7 and 8 show the effects of the amounts of AKD and size promoter, respectively, on size degrees as a function of the polymer species. The initial size degrees determined at 50 seconds drying are increased in this experimental range as the amounts of AKD and size promoter increase. And the size degree of paper treated with polymer D is always higher than that with polymer E in terms of AKD and promoter dosage levels.

Papermaking condition has been changed from acidic to neutral pH, and furthermore, to an alkaline pH condition. The most important aspect of neutral/alkaline pHs allows the use of calcium carbonate, a relatively inexpensive and good quality filler. The advantages of this change which are often quoted are the reduced machinery corrosion and increased paper strength resulting from the increased fiber swelling obtained at higher pH. However, the development of AKD size degree is generally decreased as the pH of papermaking stock increases to the alkaline condition. A major reason for increasing the system pH is the higher filler loading level of calcium carbonate.

Figure 9 shows the dependence of system pH and size degrees on the amount of calcium carbonate as a function of polymer species. As shown in this Figure, the stock pH is increased up to 8.3 of pH as the amount of calcium carbonate increases to 34 wt.% on the weight of pulp, on the while, the size degrees are drastically decreased by increasing the addition level of calcium carbonate. One reason for decreasing the size degree at higher pH can be considered that the flocculating power of cationic polymer is decreased by alkaline conditions, because the quaternary cationic groups change to tertiary amine groups and thus, lose their cationic properties.

Figure 10 shows the effect of polymers on first-pass fines retention (FPFR) when the polymers as AKD size promoters are used together with or without retention aids. The FPFR treated with polymer D shows higher values than that with polymer E in the absence and presence of retention aids. Isogai *et al.* reported that the retention of AKD is one of the important factors of size development. If we assume the AKD retention is proportional to the amounts of fines retention, the result of Figure 10 implies that the polymer D having better retention power makes the higher size degree as a result of the higher retention. This is also good agreed with the results as described in our previous papers, which concern with the difference of flocculating power between linear and highly branched polymers.

To investigate the dependence of electrophoretic mobility of papermaking stock on the resultant size degree, the typical procedure for the stock preparation described in Figure 1 is varied to four procedures (Figure 11, Procedures I-IV). All procedures in this Figure consist of the same components and their dosage levels, but the addition points of individual component are different from one another. Only one case (Procedure I) can reaches to an isoelectric point by adding the retention aids, while the changes of the electrophoretic mobilities in the other three cases (Procedure II-IV) are negligible. Electrokinetics by measuring the electrophoretic mobilities have shown that the negative charge at the fiber surface decreases in a manner specific to the polymer and the paper stock. The quantity of retention aid required for an apparent isoelectric point to be reached is described as the cationic demand specific to the stock suspension. Horn and Linhart explained that the maximum flocculation is normally depends on the isoelectric point being reached.

Figure 12 compares the size degrees of handsheets, which are prepared according to the stock preparation procedures as described in Figure 11. The size degrees from Procedure I show the excellent results compared with Procedure II in both cases of polymer D and E. Combining this with the result of Figure 11 obviously indicates that

the sizing mechanism depends strongly on the AKD retention in the sheet.

Finally, the friction coefficients for both dynamic and static conditions are illustrated in Figure 13 as a function of polymer species. There are some reports that AKD tend to give a more slippery sheet than rosin-alum sized sheet. These characteristics of AKD have important restrictions for those converting operations where lower frictional resistance is undesirable. However, Figure 13 shows the handsheet sized by AKD with polymer D is less slippery than not only that of AKD but also blank one which is prepared handsheet in the absence of AKD and promoters. Marton reported that the presence of dialkylketone derived from the hydrolysis of AKD on the paper surface decreases the friction observed between contacting paper surfaces.