Journal of Korea TAPPI
Vol. 32. No. 5, 2000
Printed in Korea

Alkaline Sizing of Mechanical Pulp

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ABSTRACT

Alkaline Sizing behavior and mechanism of handsheets, which were prepared from thermomechanical pulp (TMP) with alkylketene dimer (AKD), were studied in terms of the conditions of the handsheet-making. AKD content in the TMP handsheets was increased with increasing of AKD addition level and the addition of a polyamideamine-epichlorohydrin resin (PAE) clearly enhanced AKD retention as well as the resultant sizing performance of TMP handsheets. Although drying of the AKD sized TMP webs at 20°C led to no or quite low sizing level, but TMP handsheets sized with AKD had higher sizing degrees with increasing of the temperature of heat treatment. Scanning electron microscopic observations of the AKD-sized TMP handsheets showed that AKD emulsion particles were present on pulp fiber surfaces independently without coagulation in the TMP handsheets dried at 20°C. Heat treatment of the AKD-sized handsheets resulted in disappearance of the AKD emulsion particles because of their melting and spreading. The addition of calcium carbonate filler to the TMP suspensions did not influence on AKD content in the TMP handsheets. Nevertheless, their sizing degrees clearly increased by the addition of $CaCO_3$ filler. Probably, AKD molecules adsorbed on the $CaCO_3$ filler particles contribute to the enhancement of sizing performance. Thus, AKD can give sizing features effectively to the TMP handsheets, when they are made under suitable conditions.

1. Introduction

Alkaline papermaking using calcium carbonate filler has become popular in printing and writing paper production. Recently, alkaline paper attached as advertisement to newspaper has often been returned to paper mills as waste paper mixed with newspaper by recycling. The use of recycled paper in newsprint production must be increased further or at least maintained at high level also in future. Thus, it may be necessary for newsprint production that the conventional acidic papermaking is somewhat shifted to neutral or alkaline papermaking systems in the near future.

Alkylketene dimer (AKD) is one of the typical alkaline sizes, and has been used as cationic emulsions in alkaline papermaking. The addition level of AKD at the wet-end is only 0.05-0.2% on dry weight of pulp. This effective sizing performance by AKD has

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been explained in terms of covalent bond formation between AKD molecules and hydroxyl groups of cellulose in pulp, which occurs during the thermal drying process in papermaking.[1-4] Recently, however, new sizing mechanisms other than the above covalent bond formation have been proposed for not only AKD but also other so-called "reactive sizes".[5-9]

Systematic data has not been published yet in scientific or technical journals on the applications of AKD sizing of mechanical pulps for producing newsprint production. But, it is well known that it is a little difficult to give sizing features effectively to mechanical pulps not only in alkaline but also in acidic sizing system. Larger surface areas of the mechanical pulp and/or great amounts of colloidal and dissolved anionic substances, *i.e.* anionic trash, present in the pulps may cause such ineffective sizing performance.

In this study, internal sizing of AKD with PAE was applied to a thermomechanical pulp. Handsheets were prepared under various conditions and then, their sizing degrees and retention values of size were measured in order to investigate the effects of papermaking conditions on sizing performance and size retention behavior for mechanical pulps. These informations shoud be helpful in improving sizing effect and predicting the sizing performance of high yield pulp.

2. Materials and Methods

2.1 Materials

Unbleached thermomechanical pulp (TMP), which was squeezed to solids content of about 17% in a paper mill was used as a never-dried high-yield pulp sample. The TMP pulp had a Canadian Standard Freeness of 205 mL. Commercial products of AKD emulsion and a polyamideamine-epichlorohydrin resin (PAE) were used. Ground calcium carbonate filler (P-50, Shiraishi Kogyo Co., Japan) was used in some cases for internal addition.

2.2 Handsheet making

To 0.15% TMP suspension, which contains $CaCO_3$ filler in some cases, known amounts of the AKD emulsion and PAE solution of 1% concentration were added in this sequence. Tap water was used to make handsheets. After stirring for 30 sec., the TMP suspension was subjected to making handsheets with basis weight of $60 g/m^2$ according to TAPPI Test Method.[10] Wet-pressed handsheets were dried at 20°C and 65% relative humidity for one day. Some of the once-dried handsheets were heated at 105°C for 20 min. in an oven, and then conditioned at 20°C and 65% relative humidity for another one day. In some experiments, the wet-pressed handsheets were dried using a rotary-drum dryer at 100°C for 2 min.

2.3 Analyses

Sizing level of handsheets was expressed as Stöckigt sizing degree.[11] AKD content in handsheets was determined by pyrolysis-gas chromatography.[12] About 0.5 mg of a handsheets sample was set in a small platinum pot for pyrolysis, and the sample was pyrolyzed at 500°C under a flow of He gas by a vertical microfurnace-type pyrolyzer, which was directly attached to a gas chromatograph (GC-14B, Shimadzu Co., Ltd., Japan) equipped with a capillary column of OV-1(30m × 25mm) and an FID detector. The column temperature was initially set at 200°C, and then was programmed to 300°C

at 5°C/min. Injection and detector temperatures were 250 and 280°C, respectively. The AKD contents in handsheets were calculated on the basis of peak areas due to three AKD components in the pyrolysis-gas chromatograms.[13] Aluminum and calcium contents in handsheets were measured by X-ray fluorescence analysis.[14] Surfaces of the handsheets were observed by field-emission-type scanning electron microscopy after Pt coating (S-4000, Hitachi, Co., Japan).

3. Results and Discussion

3.1 Effects of size addition level and heat treatment

Fig. 1 shows a typical pyrolysis-gas chromatogram of AKD-sized TMP handsheets. AKD content was determined on the basis of the three peaks due to AKD components. Compared with the pyrolysis-gas chromatograms of AKD-sized bleached kraft pulp handsheets, many peaks originating from lignin present in TMP were detected up to the retention time of 20 min.

Fig. 2 illustrates sizing degree and AKD content of TMP handsheets prepared with 0-0.4% (on dry weight of pulp) AKD and 0.1% (on dry weight of pulp) PAE. When the handsheets were dried at 20°C, they had no sizing feature up to 0.4% AKD addition level. On the other hand, after heating the handsheets at 105°C for 20 min., sizing features appeared on the handsheets prepared with AKD of more than 0.1% addition level. Because AKD-sized handsheets prepared from bleached kraft pulp have clear sizing features even after drying of the wet webs at 20°C, the result in Fig. 2 may be specific to the TMP handsheets. Sizing degrees after the heat treatment were changed drastically between the 0.1 and 0.2% AKD addition levels.

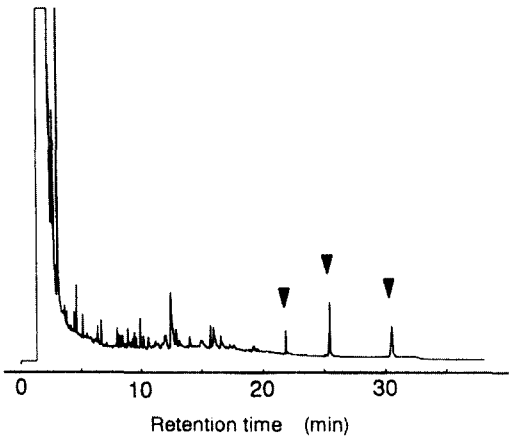

Fig. 1. Pyrolysis-gas chromatogram of AKD-sized TMP handsheet.

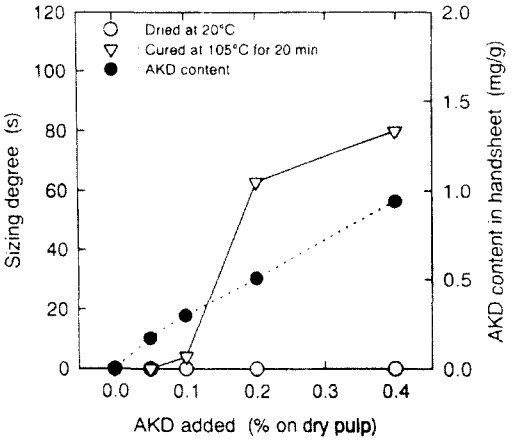

Fig. 2. Sizing degree and AKD content of TMP handsheets prepared with 0-0.4% AKD and 0.1% PAE.

AKD content in the TMP handsheets increased almost linearly with increasing of the AKD addition level. The main condition for good sizing is the efficient attachment of size to the pulp. However, as described later, AKD retention values (amount of AKD retained in handsheets / that of AKD added to pulp suspension) were clearly low; only about 34, 30, 26 and 24% at the AKD addition level of 0.05, 0.1, 0.2 and 0.4% (on dry

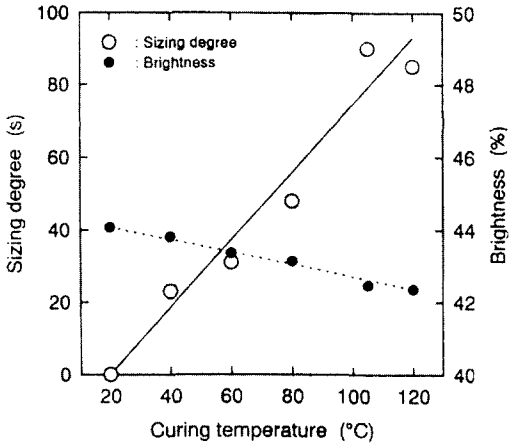

Fig. 3. Sizing degree and brightness of TMP handsheets prepared with 0.2% AKD and 0.1% PAE. Handsheets were heated at various temperatures for 20 min.

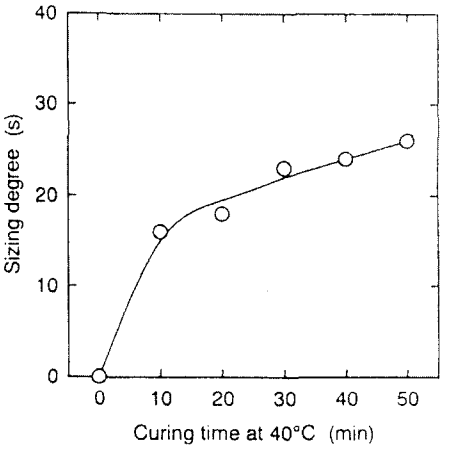

Fig. 4. Sizing degree of TMP handsheets prepared with 0.2% AKD and 0.1% PAE. Handsheets were heated at 40°C for various time.

weight of pulp), respectively. Because sizing degrees and AKD contents of TMP handsheets prepared with 0.2% AKD and 0.2% PAE were higher than those in Fig. 2, where the TMP handsheets were prepared with 0.1% PAE, the cationic polymer PAE behaved as a retention aid of AKD in the pulp suspensions. The PAE molecules are probably adsorbed on anionic sites of the AKD emulsion particles, which have amphoteric surface charges in pulp suspensions, and thus the cationic surface charges of the AKD emulsion particles are reinforced. Higher AKD retention values are then brought about by electrostatic interactions between the cationic charge-reinforced AKD emulsion particles and anionic pulp fiber surfaces in pulp suspensions, thus resulting in higher sizing degrees.[13] No sizing features appeared on the TMP handsheets prepared with 0.2% AKD and even 0.2% PAE, when they were dried at 20°C. The effects of heating temperature on sizing degree and brightness of the AKD-sized TMP handsheets were shown in Fig. 3, where 0.2% AKD and 0.1% PAE were used to make handsheets. Heating temperature greatly influenced the resultant sizing degree, and it increased almost linearly from 0 to about 90 sec. by heating the once-dried TMP handsheets to 105°C. Correspondingly, brightness of the TMP handsheets decreased linearly. Fig. 4 shows changes in sizing degree of the AKD-sized TMP handsheets by extending the heating time at 40°C up to 50 min. Sizing degree sharply increased within the first 10 min., and then increased gradually but steadily. Since subtle change in the TMP handsheet-making conditions have brought about the great difference in sizing degree as shown in Figs. 2-4, it may be difficult to control and obtain the high sizing level sensitively for AKD-sized paper prepared from mechanical pulps.

3.2 Different sizing characteristics between TMP and bleached kraft pulp

Sizing degree and AKD content of handsheets prepared from bleached hardwood kraft pulps having different freeness were

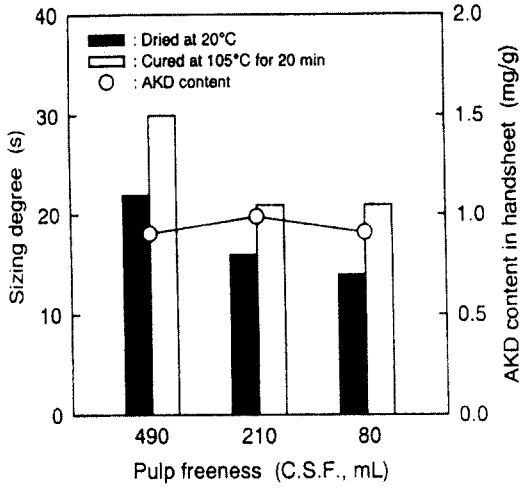

Fig. 5. Sizing degree and AKD content of handsheets prepared from bleached hardwood kraft pulp having various freeness values with 0.2% AKD and 0.1% PAE.

shown in Fig. 5, where 0.2% AKD and 0.1% PAE were used to make handsheets. Irrespective of the freeness value, AKD content in the handsheets was almost equal to each other among the three pulps. However, sizing degree gradually decreased with decreasing the freeness value of the pulp. This may be ascribed to a slight decrease in thickness of the handsheets and increase the content of fines according to decreasing of pulp freeness. It is known that St ckigt sizing degree is sensitively influenced by the paper thickness.[15] Although the TMP used in this study had 205 mL C.S.F., the TMP handsheets had different sizing patterns as well as AKD retention values from those for the handsheets prepared from the kraft pulp with 210 mL C.S.F. The AKD retention values for the TMP were about half of those for the kraft pulp, and the former handsheets had no sizing features whereas the latter ones had clearly high sizing level even after drying at 20°C. A large amount of anionic trash present in TMP may have resulted in such lower

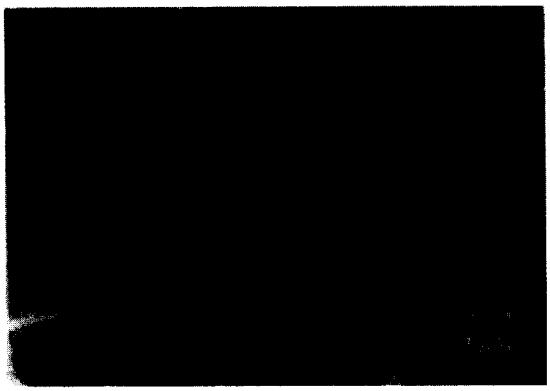

Fig. 6. Scanning electron microphotograph of AKD-sized TMP handsheet dried at 20°C.

AKD retention values than those for the bleached kraft pulp.

Surfaces of TMP handsheets prepared with 0.2% AKD and 0.1% PAE before and after the heat treatment at 105°C for 20 min. were observed by scanning electron microscopy (SEM). When the wet TMP webs were dried at 20°C, spherical AKD emulsion particles with 0.1-0.5 μm in diameter were present on pulp fiber surfaces in the TMP handsheet (Fig. 6). These AKD emulsion particles were observable also on AKD-sized kraft pulp handsheets dried at 20°C.[6-9] After the heat treatment, these AKD emulsion particles disappeared by melting and spreading over pulp fiber surfaces. The larger surface areas of the TMP handsheets may have resulted in their no sizing features after drying at 20°C.

3.3 Effects of $CaCO_3$ filler and pH of pulp suspension on sizing

Effect of the addition of $CaCO_3$ filler to TMP suspensions on sizing degree and AKD retention was studied in this section. Here, 0.2% AKD, 0.1% PAE and 0.5% aluminum sulfate were added in this sequence to the TMP suspension containing $CaCO_3$ filler. all

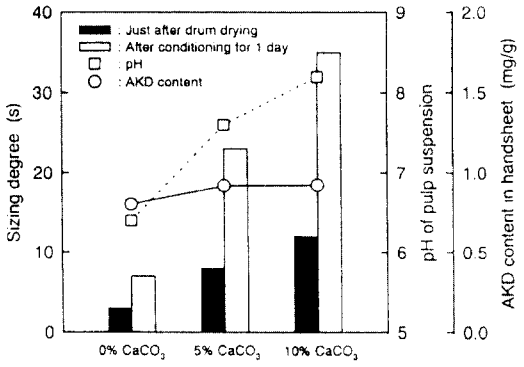

Fig. 7. Sizing degree and AKD content of TMP handsheets prepared from TMP suspension containing $CaCO_3$ filler with 0.2% AKD, 0.1% PAE and 0.5% $Al^2(SO^4)^3$. Handsheets were dried using a drum-dryer at 100°C for 2 min.

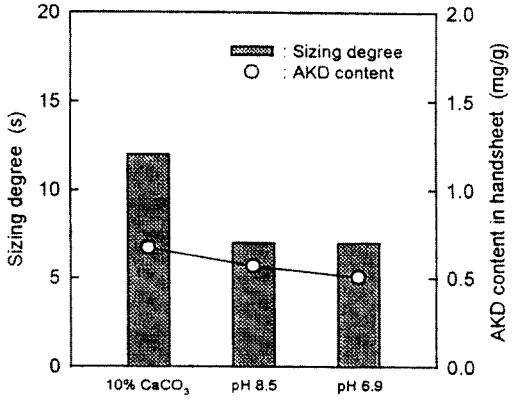

Fig. 8. Sizing degree and AKD content of TMP handsheets prepared under various pH values. Sizing degree was measured just after drum drying.

percentages are based on dry weight of the pulp. The wet TMP webs were dried using a rotary drum dryer at 100°C for 1min. and sizing degree of the TMP handsheets were measured just after the drum drying and after conditioning the handsheets at 20°C for 1 day. Aluminum content in the TMP handsheets was roughly constant (about 0.1mg/g) to the $CaCO_3$ addition level examined. Retention values of aluminum compounds origination from alum on the TMP handsheets were not influenced by $CaCO_3$ filler added. As shown in Fig. 7, sizing degrees of the TMP handsheets just after the drum drying were clearly lower than those after conditioning. This phenomenon of poor sizing just after drying of wet webs is well known in AKD sizing because the curing rate of AKD is rather slow. Sizing degree clearly increased with increasing the $CaCO_3$ addition level from 0 to 10% (on dry weight of pulp), even though AKD retention values were similar to each other among the three systems. This result shows that the presence of $CaCO_3$ filler in the TMP handsheets enhances sizing performance by some mechanisms other than the AKD retention. In a recent paper[16], it was stated that the sizing effect depended on the free surface energy of the filler; consequently, low surface energy(hydrophobic) talc and calcium carbonate should increase the sizing effect and the high surface energy kaolin clay should decrease the sizing effect. Since pH values of the TMP suspensions increased with increasing the $CaCO_3$ filler addition level (Fig. 7), the sizing behavior in Fig. 7 may be also explained in terms of the pH of TMP suspensions. As shown in Fig. 8, however, the pH of TMP suspensions had little influence on sizing degree of the TMP handsheets. Therefore, there may be some interactions between AKD and $CaCO_3$ filler, which enhance sizing performance in the TMP handsheets.

4. Conclusions

Alkaline sizing with AKD was applied to thermomechanical pulp, and the following conclusions were obtained.

1. AKD give poor sizing performance to TMP handsheets, but thermal drying is necessary for good sizing.
2. The addition of PAE to TMP suspensions enhances sizing performance, because higher AKD retention values can be achieved by the PAE addition.
3. Since sizing degree of the AKD-sized TMP handsheets is sensitively influenced by the various papermaking conditions, it seems to be difficult to adjust an aimed sizing level, especially in the range of slack sizing.
4. Each AKD emulsion particle are present independently without coagulation on pulp fiber surfaces, when the AKD-sized handsheets were dried at 20°C.
5. The presence of $CaCO_3$ filler in TMP handsheets enhances the resultant sizing degree, although it does not influence AKD retention.

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