J Wood Sci (2011) 57:34–39
DOI 10.1007/s10086-010-1136-z

ORIGINAL ARTICLE

**Hailan Jin · Takayuki Okayama · Ryota Arai
Hajime Ohtani**

Relationship between wettability and sizing degree of paper containing bulking agent

Received: January 15, 2010 / Accepted: May 31, 2010 / Published online: October 14, 2010

Abstract The addition of a bulking agent achieves the bulking of paper and increases the pore volume. In this study, the effect of adding bulking agents with various alkyl chain lengths (C_{14}, C_{18}, and C_{22}) on the bulk of paper, the sizing performance, and sheet wettability was evaluated. The bulking effect of a bulking agent with a short alkyl chain length (C_{14}) was large, and reduction in the sheet tensile strength was confirmed to be suppressed. Good sheet sizing performance was achieved when a bulking agent was used with an alkyl ketene dimer (AKD). When 0.1% or more of AKD was added, using a bulking agent with a shorter alkyl chain length increased the improvement in the sizing degree. Pyrolysis gas chromatography measurements of the amount of reacted AKD revealed that the addition of a bulking agent increased the AKD content of the sheet. The sheet contact angle measured by the two-liquid method tended to increase with increasing alkyl chain length. However, the sheet contact angle was not directly correlated with the Stöckigt sizing degree. By using 1% ferric chloride ($FeCl_3$) and 2% ammonium thiocyanate (NH_4SCN) aqueous solution, which are used for measuring the Stöckigt sizing degree, the time-dependent change in the contact angle on the paper sheet surface was measured to evaluate wettability. The Stöckigt sizing degree of paper sheets was found to be greatly influenced by the sheet wettability by NH_4SCN solution. In the case of 2% NH_4SCN aqueous solution, different samples exhibited large wettability differences. When 0.2% or less of AKD was added, the effect of the concentration on the contact angle was confirmed to be large at all NH_4SCN concentrations.

Key words Bulking agent · Stöckigt sizing degree · AKD · Contact angle · Wettability

H. Jin · T. Okayama (✉)
United Graduate School of Agricultural Science, Tokyo University of Agriculture and Technology, 3-5-8 Saiwai-cho, Fuchu, Tokyo 183-8509, Japan
Tel. +81-42-367-5725; Fax +81-42-334-5700
e-mail: okayama@cc.tuat.ac.jp

R. Arai
Faculty of Agriculture, Tokyo University of Agriculture and Technology, Tokyo 183-8509, Japan

H. Ohtani
Department of Materials Science and Engineering, Graduate School of Engineering, Nagoya Institute of Technology, Nagoya 466-8555, Japan

Introduction

Pulp fibers have both hydrophilic regions, due to hydroxyl groups, and hydrophobic regions, due to CH groups. Pulp fibers suspended in water are processed to form paper by filtering, pressing, and drying. Hydrogen bonds between cellulose fibers are the most important bonds in determining the strength of paper. The bond forming ability between cellulose fibers depends on the hydrophilicity of the fiber surfaces (i.e., their ability to form hydrogen bonds).[1]

In recent years, concerns regarding environmental problems have been growing; thus, the demand for bulkier and lighter paper is increasing. In paper bulking during the paper manufacturing process, the pore volume of paper is increased by adding a compound that coats the surface of pulp fibers and inhibits the formation of hydrogen bonds between the fibers. Recently, numerous bulking agents have been developed, and the level of paper bulking on the addition of these bulking agents has been investigated. Paper bulking by the addition of a bulking agent improves paper properties, including improved opacity, improved softness and texture, and improved printability due to improved smoothness. In addition, the amount of raw pulp used can be reduced, thus reducing costs.

Asakura and Isogai[2] have reported that some cationic diamide salts prepared from higher fatty acids and diethylene triamine are effective in decreasing the sheet density and tensile strength of paper. No sizing performance of paper was observed by the addition of diamide salt prepared from isostearic acid. Noda et al.[3] revealed that the drainage resistance of pulp slurries is decreased by the addition of di(oleamidoethyl)ammonium formic acid salt (DOFAS) because of partial coverage by hydrophobic

DOFAS molecules of hydrophilic pulp fiber surfaces. In our previous article,[4] changes in sheet density, tensile strength, and sizing degree of paper were investigated in terms of the addition of bulking agents and alkyl ketene dimer (AKD).

In this study, changes in paper sheet properties resulting from the addition of bulking agents, which were mainly synthesized from fatty acids with three different alkyl chain lengths (C_{14}, C_{18}, and C_{22}), were investigated. In addition, changes in the sizing performance and the wetting properties were evaluated when a bulking agent was added under neutral papermaking conditions, in which AKD was used as the sizing agent.

Experiment

Preparation of handsheets and measurement of various properties

Commercial hardwood bleached kraft pulp was used as the pulp sample. It was beaten to a freeness of 430 ml (Canadian standard freeness) with a beater to prepare the handsheets. Bulking agents having alkyl groups with various chain lengths were used as the bulking agent (Table 1), and an alkyl ketene dimer (Arakawa Chemical Industries, K-903-20) was used as the sizing agent. The pulp concentration was adjusted to 2%, and bulking agent and AKD were added. The prepared pulp sample was diluted, and handsheets for testing were prepared according to JIS P 8222. Pressing was performed at 350 kPa for 3 min. The sheets were dried at 105°C for 2 min and conditioned under standard conditions (23°C and 50% RH) before measurement.

In addition to the density of the handsheets, various properties including tensile strength and zero-span tensile strength were measured according to JIS standards. The Stöckigt sizing test was used to evaluate the sizing degree of sheets.[5] The average value for two sides of paper was calculated by measurements performed on each side of three test pieces. To measure the pore distribution of sheets, a mercury porosimeter (Auto Pore IV 9500, Micromeritics, Shimadzu) was used, and the mercury intrusion method was followed.[6]

Measurement of bulking agent and AKD retentions in sheets

The retention of the bulking agent was measured as reported previously.[7] Chloroform was used as the extraction solvent, and the Soxhlet extraction method was used.

The AKD retention in a sheet was quantified by pyrolysis gas chromatography (Py-GC) using about 1 mg of sheet paper.[8] A GC 4000 (GL Sciences) was used for gas chromatography, and a Frontier Lab PY-2010SL was used as the pyrolysis system. The pyrolysis temperature was 500°C and the Py-GC oven temperature was increased from 50° to 300°C at a rate of 15°C/min. A Frontier Lab Ultra Alloy$^+$-5 (5% diphenyl–95% dimethyl polysiloxane, 30 m × 0.25 mm i.d., 0.25 μm film) was used as the separation column, and a hydrogen flame ionization detector was used for detection and recording. The AKD content of a sheet was evaluated based on the peak area of the corresponding component in the observed pyrogram.

Evaluation of sheet wettability by the two-liquid method

The wettability was evaluated by the two-liquid method using five alkanes. In this method, the contact angle of a water droplet on a sheet surface was measured in an alkane.[9] A contact angle meter (CA-D, Kyowa Interface Science) was used to measure the contact angles.

Measurement of dynamic contact angle on paper sheet surface

The contact angle of droplets on the sheet surface was measured with 1% ferric chloride ($FeCl_3$) aqueous solution and 2% ammonium thiocyanate (NH_4SCN) aqueous solution, which are used in the Stöckigt sizing test,[5] and with deionized water. In addition, the contact angle was measured for 1% and 3% NH_4SCN aqueous solutions. Photographs of droplets on the sheet surface were taken from the side with a Nikon D3 digital single-lens reflex camera (Nikon, Japan). The shooting intervals were at 9–12 frames/s and the shooting time was 60 s. The average value was calculated by four determinations on the glossy side of test pieces.

Results and discussion

Changes in various properties and pore structure due to different alkyl chain lengths of bulking agents

The sheet density was reduced when any bulking agent was added. In conjunction with this, a decrease in the tensile strength was observed. When AKD and 0.8% bulking agent were used in combination, bulking agents with shorter alkyl chain lengths were found to have greater bulking effects (Table 2). The sheet density decreased slightly even when

Table 1. Properties of bulking agents

	Chain length of alkyl substituent	Melting point (°C)	pH	Surface tension (Nm/m^2)	Particle size (μm)
A	14	75, 90	6.2	40.9	4.45
C	18	78	6.6	62.0	4.77
E	22	91, 106	6.7	40.6	6.15

Table 2. Effects of addition of bulking agents on sheet density, tensile index, and pore diameter of handsheets

Addition[a]	Sheet density (g/cm^3)	Tensile index (Nm/g)	Chloroform extractive content (mg/g)	Retention of Chloroform Extractives (%)	Average pore diameter[b] (μm)
Control	0.67	46.3	–	–	5.3
A	0.62	38.0	4.30	53.7	3.4
C	0.64	38.3	4.88	60.9	2.7
E	0.65	32.4	5.63	70.3	2.3
AKD	0.66	46.2	–	–	3.3
A + AKD	0.62	33.6	4.32	55.1	3.5
C + AKD	0.62	35.7	4.71	58.7	4.3
E + AKD	0.63	32.6	5.53	69.6	6.0

[a] Bulking agents added at 0.8%; AKD added at 0.1%
[b] By mercury intrusion method

AKD was added in combination with A, C, and E. Thus, the shorter the alkyl chain length is, the greater the bulking effect is even when AKD is added in combination. In addition, the tensile strength tended to decrease with increased bulking. However, when a bulking agent was added with no AKD, bulking agent A, which had the greatest bulking effect, suppressed the reduction in the tensile strength to a certain degree. Thus, bulking agent A has a good bulking effect while suppressing the reduction in the bonding strength between fibers to some extent. This was also confirmed in the previously reported interfiber bonding evaluation using the same Page equation.[7,10,11]

The bulking effect is mainly determined by the bulking agent content of sheets. Therefore, retention of the bulking agent in the sheet was measured by chloroform extraction. In all cases where only a bulking agent was used and AKD and a bulking agent were used in combination, bulking agents with longer alkyl chain lengths had higher retentions (Table 2). This is considered to be due to bulking agents with longer alkyl chains having larger particle sizes so that they are sterically bulkier in pulp suspensions; consequently, the fixed amount is increased. However, a strong correlation between the fixed amount and the bulking effect was not observed.

The average pore diameter of a sheet decreased when bulking agent alone was added, and the average pore diameter decreased with increasing alkyl chain length (Table 2). When AKD alone was added, the average pore diameter of the sheets also decreased. However, when AKD was used in combination with a bulking agent, the average pore diameter increased compared with that found on the addition of AKD alone, and it tended to increase with increasing alkyl chain length. However, the increase in the sheet pore volume on the addition of a bulking agent is not necessarily closely related to the alkyl chain length.

Effect on sizing performance

Figure 1 shows the amount of added AKD and the AKD content of the sheet measured by Py-GC. When a bulking agent was used with AKD, the AKD content of the sheet increased. In all cases, the AKD retention increased on the addition of a bulking agent. In this experiment, AKD was added after the addition of the bulking agent; therefore, the bulking agent may function as an additional retention site for AKD.

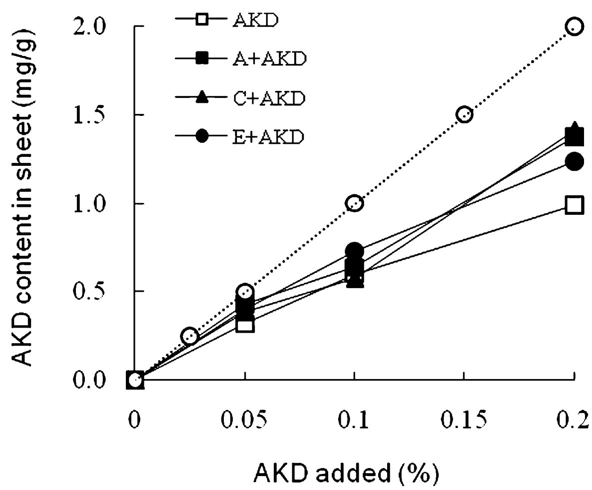

Fig. 1. Alkyl ketene dimer (*AKD*) content in handsheets as determined by pyrolysis gas chromatography. Bulking agents A, C, and E were added at 0.8%. *Broken line*, calibration curve; *solid line*, observed relationship

However, the sizing degree of the sheet was not always consistent with the AKD content results (Fig. 2). Specifically, when 0.05% of AKD was added, the sheet with the lowest AKD retention, to which only AKD had been added, exhibited good sizing performance. Accordingly, when 0.05% of AKD was added, the bulking agents increased the AKD retention, but they may have suppressed the sizing performance. When 0.1% or more of AKD was added, the sizing performance improved with increasing AKD content. When 0.1% of AKD and 0.8% of bulking agent were added together, the sizing degrees of sheets were 23.5, 25.7, and 24.2 s for A, C, and E, respectively. Thus, they displayed similar sizing performances as that when only 0.2% of AKD was added (26 s). When a bulking agent is used in combination with AKD, a good sizing performance is achieved as

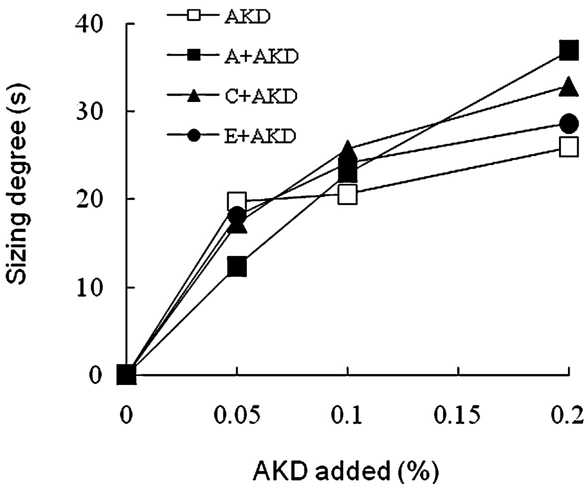

Fig. 2. Relationship between AKD addition and sizing degree of handsheets prepared by adding AKD with bulking agent A, C, or E added at 0.8%

well as a bulking effect, even when a small amount of AKD is added.

When the amount of AKD that was added was increased up to 0.2%, bulking agents with shorter alkyl chain lengths exhibited better sizing performances. On the other hand, when 0.2% of AKD was added, the AKD content of the sheet increased from 0.99 mg/g (when only AKD was added) to 1.37, 1.41, and 1.24 mg/g when A, C, and E were also added, respectively (Fig. 1). Accordingly, not only the AKD content but also the interactions among the bulking agent, AKD, and pulp fibers contributed to the sizing performance. When the AKD content of the sheet was lower than about 0.4 mg/g, longer alkyl chain lengths gave better sheet sizing performances. When the AKD content was higher than about 1 mg/g, shorter alkyl chain lengths gave better AKD sizing performances.

Evaluation of sheet wettability

Matsunaga and Ikada[9] made it possible to measure the solid surface free energy by the two-liquid method. In the two-liquid method, the contact angle of a polar liquid such as water is measured by immersing a solid with a high surface energy, such as cellulose or hydrophilic polymer, in a saturated hydrocarbon.

In this present study, each component of the sheet surface free energy was calculated from the respective contact angles in five alkanes (Table 3). When a bulking agent alone was added, longer alkyl chain lengths gave larger dispersion component of the sheet surface free energy (γ_S^d) and almost no change in polar component of the sheet surface free energy (γ_S^p). Thus, increasing the number of alkyl chain carbon atoms in the bulking agent does not affect γ_S^p of a sheet. On the other hand, when used in combination with AKD, γ_S^p decreased with increasing alkyl chain length. Thus, longer alkyl chain lengths generate more interaction with AKD, reducing γ_S^p. In the case of a reactive sizing agent such as AKD, the acid–base interaction with water is thought to

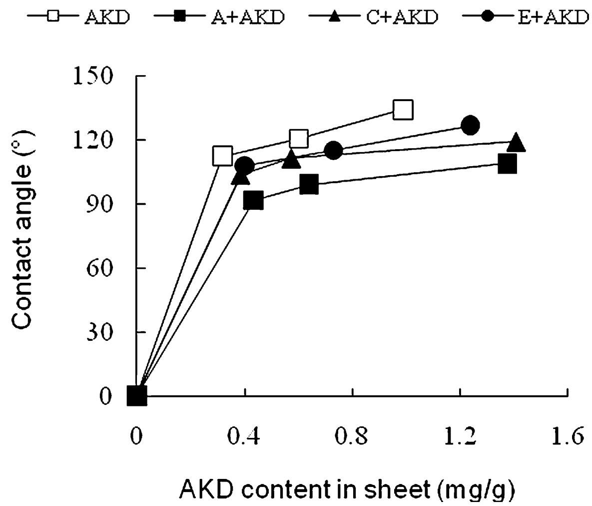

Fig. 3. Relationship between AKD content in handsheets and contact angles with *n*-hexane. Bulking agents A, C, and E were added at 0.8% and the contact angle with *n*-hexane was measured at a contact time of 30 s

Table 3. Surface energy parameters (in mJ/m^2) of AKD-sized handsheets

Addition[a]	γ_S^d	γ_S^p	γ
A	3.3	37.4	40.7
C	39.5	39.0	78.6
E	124.7	33.5	158.2
AKD	83.7	1.5	85.2
A + AKD	70.6	8.9	79.4
C + AKD	165.3	3.0	168.3
E + AKD	104.1	0.9	105.0

γ, surface free energy of sheet
[a] Bulking agents added at 0.8%; AKD added at 0.1%

be suppressed by the sizing agent coating the cellulose surface. As a result, the fibers become hydrophobic and good sheet sizing performance is realized. In all cases, good sizing performance was achieved without affecting the sizing effect of AKD.

Figure 3 shows the relationship between the AKD content of the sheet and the contact angle by the two-liquid method. In all cases, the sheet contact angle increased with increasing amounts of added AKD. This is consistent with the results of Yoshinaga et al.[12] Larger contact angles were observed when AKD alone was added than when AKD and a bulking agent were added. In addition, bulking agents with longer alkyl chain lengths produced sheets with larger contact angles. The addition of a bulking agent provides some hydrophilicity to a sheet; as a result, the contact angle is reduced. Furthermore, a longer alkyl chain length increases the hydrophobicity, so that sheets with larger contact angles were formed. Measuring the sheet contact angle by the two-liquid method evaluates the sheet surface free energy without considering the effects of spreading pressure on the sheet and water permeation into the sheet; consequently, a direct correlation with the Stöckigt sizing degree was not observed.

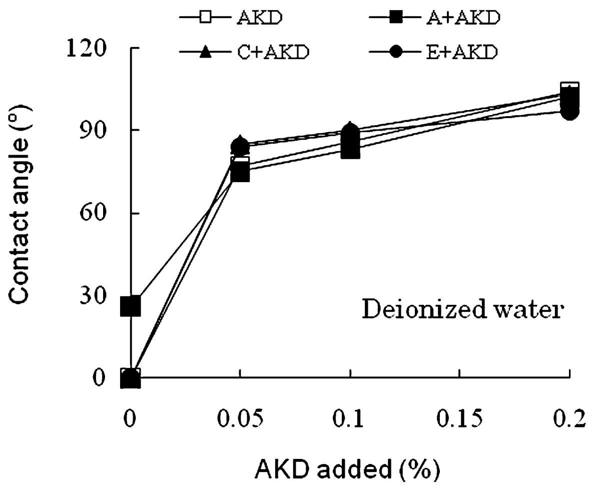

Fig. 4. Relationship between AKD addition in handsheets and contact angles with water. Bulking agents A, C, and E were added at 0.8% and the contact angle with water was measured at a contact time of 60 s

Evaluation of Stöckigt sizing degree and contact angle on sheet

In the past, paper wettability was evaluated by measuring the contact angle.[13] Measurement of the dynamic contact angle change over extremely short times when paper is in contact with water was performed by Okayama et al.[14–16]

The measurement results of the Stöckigt sizing degree of a sheet suggest that the sheet wettability might have changed when a bulking agent and AKD were added in combination, (Figs. 1 and 2). Therefore, the contact angle change on the sheet surface was measured for 1% $FeCl_3$ and 2% NH_4SCN (used for measuring the Stöckigt sizing degree) and deionized water. The surface tensions of 1% $FeCl_3$ and 2% NH_4SCN were 64.0 and 56.0 Nm/m, respectively.

Figure 4 shows that all the contact angles of water exhibited similar trends and are not affected greatly by the addition of bulking agent and AKD. On the other hand, the contact angle of $FeCl_3$ and that of NH_4SCN on the sheet surface displayed different trends depending on the kind of bulking agent used (Fig. 5). Sheets to which C + AKD or E + AKD had been added exhibited a large contact angle for 1% $FeCl_3$, and the sheet to which only AKD had been added had a smaller contact angle. In all cases, the change in the contact angle for 1% $FeCl_3$ with the amount of AKD added exhibited similar trends. However, the addition of A + AKD exhibited a different trend of contact angle for 2% NH_4SCN than those of C + AKD and E + AKD. This trend is similar to the change in the Stöckigt sizing degree of the sheet. Accordingly, the present Stöckigt sizing degree is assumed to be largely influenced by the sheet wettability with $FeCl_3$ and NH_4SCN (particularly by the wettability with NH_4SCN).

When 0.05% of AKD was added, the contact angle of 2% NH_4SCN on the sheet surface with added A + AKD was markedly lower than those with C + AKD or E + AKD (Fig. 5). This indicates that the wettability, by NH_4SCN, of the sheet with added A + AKD was large. Because not much difference was observed with the AKD content of the sheet,

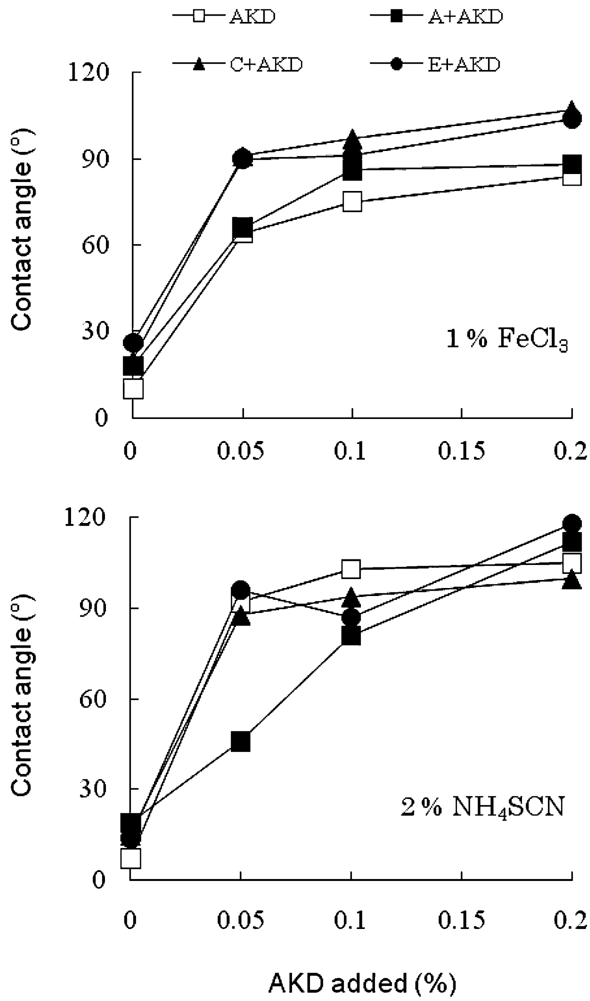

Fig. 5. Relationship between AKD addition in handsheets and contact angles with 1% $FeCl_3$ and 2% NH_4SCN. Bulking agents A, C, and E were added at 0.8% and the contact angles with 1% $FeCl_3$ and 2% NH_4SCN were measured at a contact time of 60 s

it is considered that the NH_4SCN wettability of the sheet with added A + AKD contributed to the low sizing degree.

On the other hand, when 0.1% or more AKD was added, no significant effect was observed on the sheet contact angle. When 0.1% of AKD was added, the AKD content of the sheet changed very little. Thus, there was not much difference in the sizing degree of sheets in the range of 20–25 s. When the additive rate of AKD was 0.2%, the AKD content of the sheet increased markedly due to the addition of a bulking agent. The change in the contact angle depended mainly on the AKD content. In the case of C + AKD for the highest AKD content, the NH_4SCN wettability was relatively high. As a result, A + AKD is considered to have the highest sizing performance.

Figure 6 shows the contact angles for two different NH_4SCN concentrations. In the case of 1% NH_4SCN, A + AKD had similar contact angles to those of the other cases, and similar wettabilities were also measured. However, lower wettabilities were obtained when the NH_4SCN concentration was 3%. Thus, the difference in wettability among respective samples was small for 1% NH_4SCN. In

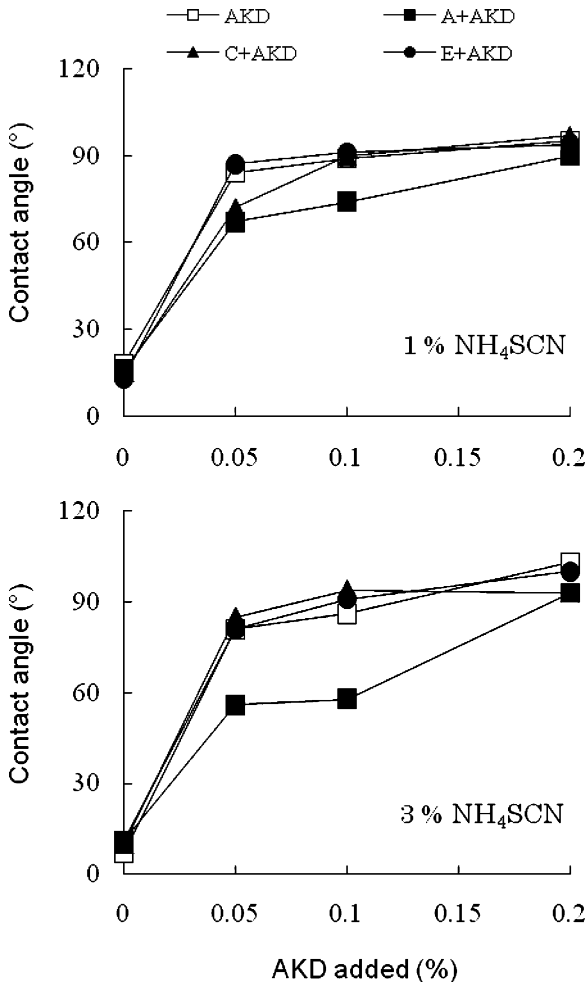

Fig. 6. Relationship between AKD addition in handsheets and contact angles with 1% and 3% NH_4SCN. Bulking agents A, C, and E were added at 0.8% and the contact angles with 1% and 3% NH_4SCN were measured at a contact time of 60 s

addition, for all concentrations of NH_4SCN, the contact angles when 0.2% of AKD was added were very similar. Thus, when 0.2% or lower AKD is added, the effect on the contact angle of NH_4SCN was found to be high.

Conclusions

Bulking agents with shorter alkyl chain lengths have higher bulking effects. In addition, it was found that a bulking agent with an alkyl chain length of C_{14}, which has a high bulking effect, suppressed the reduction in paper strength.

Py-GC measurements revealed that the addition of a bulking agent increased the amount of AKD fixed in the sheet. When the amount of added AKD was increased to 0.2%, a bulking agent with a short alkyl chain length improved the paper sizing performance.

When AKD and a bulking agent were added together, the sheet contact angle, measured by the two-liquid method, tended to increase with increasing alkyl chain length. Lowering of γ_S^p of a sheet was also confirmed.

The measurement of the Stöckigt sizing degree was found to be greatly influenced by the sheet wettability for 2% NH_4SCN. In addition, when 0.2% or lower AKD was added, the effect of the concentration on the contact angle became high at all NH_4SCN concentrations.

References

1. Robinson JV (1980) Fiber bonding. In: Casey JP (ed) Pulp and paper chemistry and chemical technology, vol 2. Wiley, New York, pp 915–963
2. Asakura K, Isogai A (2003) Effects of internal addition of fatty acid diamide salts on sheet properties. Nordic Pulp Pap Res J 18:188–193
3. Noda T, Enomae T, Isogai A, Okuda T (2005) The effects of di(oleamidoethyl)ammonium salt addition at the wet-end on drainage and sheet properties. Nordic Pulp Pap Res J 20: 430–435
4. Jin H, Okayama T, Ohtani H (2010) Influence of addition of bulking promoter on AKD-sizing performance. J Wood Sci 56:127–132
5. JSA (2004) JIS P 8122 Paper and board – Determination of sizing – Stöckigt method
6. Japan TAPPI (2000) Pulp and paper testing method no. 48: paper – determination of pore volume distribution by mercury intrusion porosimetry
7. Jin H, Okayama T (2009) Effects of internal addition of bulking promoter on low-density and porous structure of handsheet (in Japanese). Sen'i Gakkaishi 65:139–145
8. Yano T, Ohtani H, Tsuge S, Obokata T (1992) Determination of neutral sizing agents in paper by pyrolysis-gas chromatography. Analyst 117:849–852
9. Matsunaga T, Ikada Y (1981) Dispersive component of surface free energy of hydrophilic polymers. J Colloid Interface Sci 84: 8–13
10. Page DH (1969) A theory for the tensile strength of paper. Tappi 52:674–681
11. Cildir H, Howarth P (1972) The effect of re-use on paper strength. Pap Technol 13:333–335
12. Yoshinaga N, Okayama T, Oye R, Sawatari A (1993) Effect of various treatments on wettability of pulp fiber (in Japanese). Sen'i Gakkaishi 49:493–499
13. Dunstan D, White LR (1986) A capillary pressure method for measurement of contact angles in powders and porous media. J Colloid Interface Sci 111:60–64
14. Okayama T, Kimura S, Oye R (1985) Measurement of dynamic wettability of paper surface (in Japanese). Japan Tappi J 39:1157–1163
15. Okayama T. Ochi T, Oye R (1987) Measurement of dynamic wettability of paper surface. Part 2 (in Japanese). Japan Tappi J 41:515–522
16. Ochi T, Okayama T, Oye R (1988) Measurement of dynamic wettability of paper surface. Part 3 (in Japanese). Japan Tappi J 42:579–586