J Wood Sci (2010) 56:127–132
DOI 10.1007/s10086-009-1077-6

ORIGINAL ARTICLE

Hailan Jin · Takayuki Okayama · Hajime Ohtani

Influence of addition of bulking promoter on AKD-sizing performance

Received: June 10, 2009 / Accepted: August 26, 2009 / Published online: January 2, 2010

Abstract Paper density, tensile index, sizing degree, and other properties of the handsheets were measured in term of addition level of bulking promoters and alkyl ketene dimer (AKD). Bulking promoters had clear bulking effects, and in subsequent addition of the AKD, the sheet density was further decreased slightly. Although the density of the handsheet decreased from 0.64 to 0.61 g/cm^3 when 0.2% AKD was added with the 0.8% bulking promoter, tensile strength decreased from 20.3 to 19.8 Nm/g. The addition of AKD led to suppression of the decrease in the tensile index. The bulking promoter may also have potential to give sizing effects to the paper sheet as well as the increase in paper thickness. When 0.05% AKD was added together with 0.8% of bulking promoter, the sizing degree of the handsheet was 25.6 seconds, and it was almost the same, 27.3 seconds, as the addition of 0.1% AKD only. AKD retention in the handsheet was determined by pyrolysis-gas chromatography (Py-GC). The addition of the bulking promoter contributed to AKD retention in the handsheet regardless of the sizing degree. Wetting characteristics of the handsheet were determined by contact angle measurements. Surface free energy, γ_s, of the handsheet as calculated from the contact angle decreased as the level of AKD addition increased.

Key words Bulking promoter · Alkyl ketene dimer · Sizing performance · Surface free energy

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

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

Introduction

In recent years, it has become necessary to effectively use resources and to conserve forest resources. Consequently, the need to recycle materials has also been emphasized. In the paper industry, there is increasing demand for bulky paper that has similar qualities as conventional paper. A paper bulking promoter is a chemical that can produce a bulking effect by altering the surface properties of pulp fibers. However, the addition of a bulking promoter often reduces the effectiveness of the sizing agents that are concurrently used. Consequently, the kinds of paper in which bulking promoters can be used have been limited. There are presently numerous bulking promoters that can maintain or enhance sizing performance.

After the paper industry made a decisive change from acid papermaking to neutral papermaking, alkyl ketene dimer (AKD) was frequently used as a neutral sizing agent. Particles of AKD generally melt, spread, and are fixed in a sheet by heat treatment during the drying process of paper manufacturing. In this process, sizing agent particles form β-ketoester bonds with cellulose. As a result, the hydrophobic groups become aligned and the surface free energy is reduced. Thus, this mechanism is known to be necessary for achieving sizing. Another important reaction of AKD during papermaking is a hydrolysis reaction with water. The initial AKD hydrolysis forms an unstable β-keto acid, and a ketone is formed in the subsequent decarboxylation. This ketone does not react with acidic hydroxyl groups so that it does not contribute to sizing. However, some researchers claim that the ketone does exert an influence on sizing.[1]

This present study evaluates and discusses the change in paper sizing performance when a bulking promoter is added. This study was conducted under neutral papermaking conditions by using an AKD. In addition, the sheet wettability was evaluated by measuring contact angles on the sheet surface using the two-liquid method. The surface free energy was then calculated. The relationship between the sheet bulking effect and sizing performance is discussed.

Table 1. Properties of bulking promoters

Type of bulking promoter	Melting point (°C)	pH (0.5%)	Surface tension (0.1%) (Nm/m)	Particle size (μm)
A Fatty acid amide amine	89	6.0	44.1	6.15
B Fatty acid diamide	57	4.9	20.0	9.29

Experimental methods

Samples

Bleached hardwood kraft pulp was used, and the pulp was beaten to a freeness of 500 ml CSF (Canadian standard freeness) with a beater. A fatty acid amide amine (A) or a fatty acid diamide (B), which have different chemical structures, were used as the bulking promoters (Table 1). The concentration of the beaten pulp was adjusted to 2%; then, 0%, 0.4%, 0.8%, or 1.2% bulking promoter (with respect to the weight of the oven-dry pulp) was added, and 0.05%, 0.1%, or 0.2% AKD (Arakawa Chemical Industries; K-903-20) was added. AKD was added 1 min after the addition of the bulking promoter. Handsheets with a basis weight of 60 g/m^2 were prepared according to JIS P 8222. Wet test sheets were pressed at 350 kPa for 3 min. The sheets were dried in a forced air circulation oven at 105°C for 2 min. The dried sheets were conditioned with air circulation at 23°C and 50% RH for 24 h.

Measurements

In addition to the density of the handsheets, various physical properties (such as tensile index and zero-span tensile index) were measured according to JIS standards. The Stöckigt sizing test was used to evaluate the degree of sheet sizing.[2]

Measurement of sheet pore structure by mercury intrusion method

A mercury porosimeter (Auto Pore IV 9500; Micromeritics Instrument) was used to measure the sheet pore structure. According to the principle of mercury intrusion method, the volume of mercury that is pressed into the pores of a paper sample is automatically measured as a function of the applied pressure. The basic principle is based on the Kelvin equation, which involves the pore radius r, mercury surface tension δ, contact angle θ, and pressure P.

$$P = -\frac{2\delta\cos\theta}{r} \quad (1)$$

Here, $\delta = 480$ dyn/cm, $\theta = 140°$, and the applied pressure P is used to obtain the pore radius. Thus, the pore volume and pore distribution curve, which are related to the pore radius r, can be determined.[3]

Evaluation of solid surface free energy by two-liquid method

The sheet wettability was evaluated by using five alkanes by the two-liquid method. The contact angle of a water droplet on a sheet surface was measured in an alkane.[4] A contact angle meter (CA-D; Kyowa Interface Science) was used to measure the contact angles.

Measurement of AKD retention by pyrolysis gas chromatography (Py-GC)

The AKD content in a ca. 2 mg sheet when a bulking promoter was added was quantified by pyrolysis gas chromatography (Py-GC).[5] A GC 4000 (GL Sciences) was used for gas chromatography and a Frontier Lab PY-2010SL was used as the pyrolysis apparatus. The pyrolysis temperature was 500ºC and the Py-GC oven temperature was increased from 50 to 300ºC at a rate of 10ºC/min. 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 flame ionization detector was used for detection and recording. Helium gas was used as the carrier gas; it had flow rates of 50 ml/min inside the pyrolizer and of 1 ml/min inside the separation column, and the split ratio was 50:1. Interface temperature was 320ºC and inlet temperature was 300ºC. It was confirmed that no peak was detected by the Py-GC when only bulking promoter was added. Therefore, the AKD content in a sheet was evaluated based on the peak area of Py-GC.

Results and discussion

Bulking of sheet and changes in tensile index and pore structure

When 0.1% AKD was added and the amount of bulking promoter A was increased, the bulking effect was shown, and the tensile index decreased. When 1.2% bulking promoter A was added, the sheet density decreased from 0.65 to 0.62 g/cm^3, and the tensile index drastically decreased from 34.7 to 16 Nm/g. The decrease in tensile strength by addition of bulking promoter was in agreement with the results reported in our previous paper.[6]

Figure 1 shows the relationship between the density and the tensile index of handsheets prepared by adding 0.8% bulking promoter A and varying the amount of AKD. When 0.8% bulking promoter was added and the amount of AKD was increased, the sheet density decreased further. On the other hand, there was only a small reduction in the tensile index. When 0.2% AKD was added in addition to the bulking promoter, the sheet density decreased from 0.64 to 0.61 g/cm^3, and the tensile index changed only slightly, from 20.3 to 19.8 Nm/g. Thus, sheet density can be decreased while suppressing a reduction in the tensile index by increasing the amount of AKD while using a suitable amount of bulking promoter A.

On the other hand, decrease in sheet density by addition of bulking promoter B and the accompanying reduction in sheet tensile index were also confirmed. The decrease in tensile strength of the sheet was dependent on decrease in interfiber bonding strength by the Page equation.[6]

The addition of bulking promoter A or B increased the sheet pore volume (Table 2). Only a small change was observed in the sheet pore volume with the addition of 0.1% AKD alone. However, the addition of AKD after the addition of a bulking promoter further increased the pore volume of the sheet.

In the distribution of sheet pore diameters, the peak was broadened to larger pore diameters on the addition of a bulking promoter or the addition of both AKD and a bulking promoter relative to the peak for sheet pore diameters of 1–20 μm that were observed before the addition; the peak became larger (Fig. 2). Very little change in the distribution of sheet pore diameter was observed by the addition of only AKD.

Bulking and sizing performance

Even the addition of only bulking promoter A provided an adequate sheet sizing performance (Table 2). The addition of 0.1% AKD only expressed a sheet sizing degree of 27.3 seconds (s). On the other hand, a high sizing performance with a sizing degree of 32.6 s was achieved when 0.8% bulking promoter A and 0.1% AKD were added. Thus, the sheet sizing performance was confirmed to improve. In the case of bulking promoter B, on the other hand, no sizing performance was measured either in the presence or absence of added AKD.

Figure 3 shows the effects of adding AKD on the sheet density and the Stöckigt sizing degree, when the amount of bulking promoter A was 0.8%. The sheet density decreased with an increase in the amount of AKD. When only AKD was added, no effect on the sizing performance was observed if the amount was less than 0.05%. However, when the amount was higher than 0.1%, the Stöckigt sizing degree tended to increase. When the amount of AKD was increased in the presence of the bulking promoter A, an improved sizing performance was observed even at a low level of AKD. The Stöckigt sizing degree increased with an increase in the amount of AKD. When 0.05% AKD was used in combination with 0.8% A, a sizing performance was

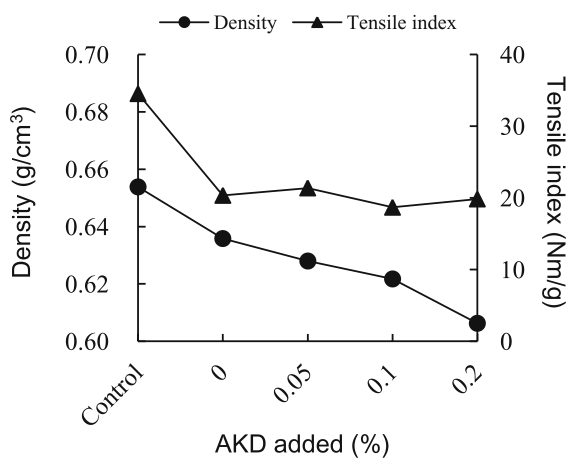

Fig. 1. Effects of alkyl ketene dimer (*AKD*) addition on handsheet density and tensile index. Bulking promoter A was added at 0.8%

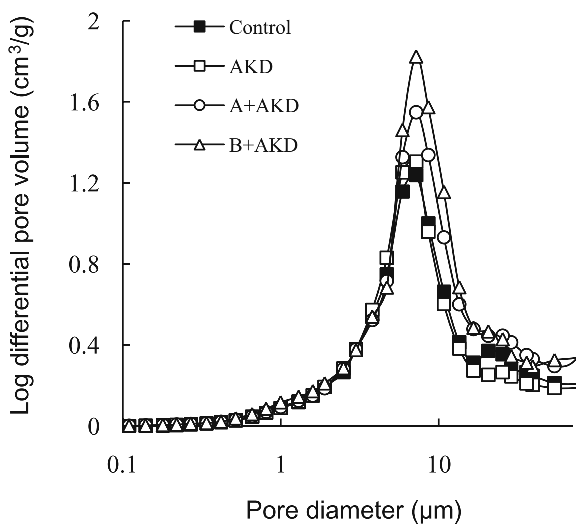

Fig. 2. Effects of addition of bulking promoters and AKD on pore diameter of handsheets. A, B, 0.8% added; AKD, 0.1% added

Table 2. Effects of addition of bulking promoters on physical properties and pore structure of handsheet

Addition[a]	Density (g/cm^3)	Tensile index (Nm/g)	Sizing degree (s)	Pore intrusion volume (cm^3/g)
Control	0.65	34.5	0	1.08
A	0.64	20.3	7.6	1.22
B	0.58	21.3	0	1.30
AKD	0.65	34.7	27.3	1.05
A + AKD	0.62	18.7	32.6	1.44
B + AKD	0.58	20.3	0	1.44

[a] A, B added at 0.8%; AKD added at 0.1%

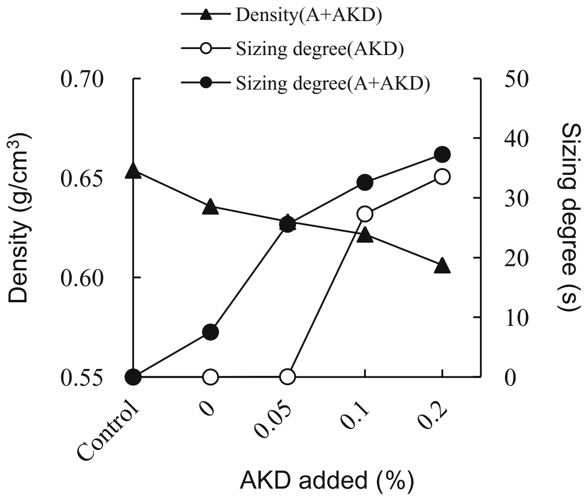

Fig. 3. Effects of AKD addition on handsheet density and Stöckigt sizing degree. A, 0.8% added

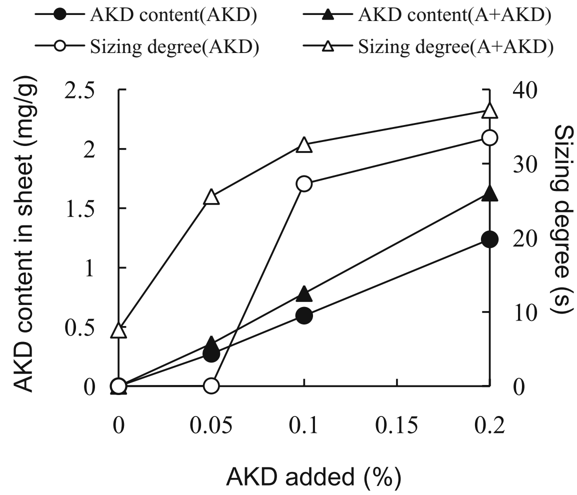

Fig. 5. Relationship between AKD contents by determined Py-GC and sizing degree of handsheets. A, 0.8% added

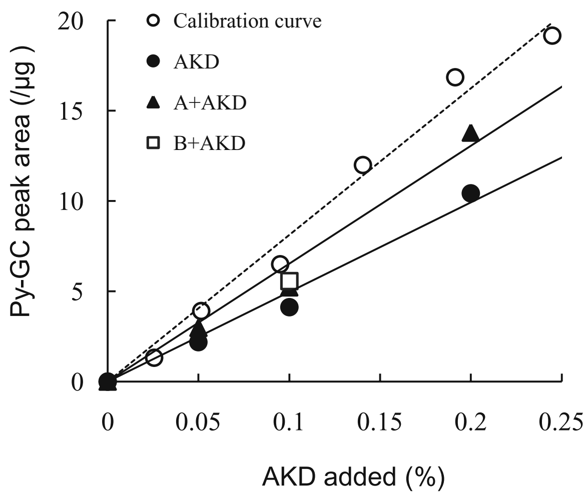

Fig. 4. AKD retention of handsheets determined by pyrolysis-gas chromatography (*Py-GC*). A, B, 0.8% added

expressed comparable to that when only 0.1% AKD was added. This result thus implies that a sheet with good sizing performance can be prepared, while achieving a bulking effect, by the addition of only a small amount of AKD.

Retention of AKD and sizing performance

Figure 4 shows the relationship between the amount of AKD and the peak area of AKD, which was measured by Py-GC. When AKD was added in combination with bulking promoter A, a higher retention of AKD was realized. When only AKD was added, the retention was 50%–65%. On the other hand, when both bulking promoter A and AKD were added, the retention was 70%–85%. It is conjectured that the retention of AKD was increased by adding a bulking promoter and that this contributed to the improvement in the sizing performance. On the other hand, when 0.1% AKD was added in combination with bulking promoter B, which had no sizing effect, the retention of AKD was about 70%, which is comparable to the case of bulking promoter A. The results show that bulking promoter A does not disturb the interaction between the pulp fibers and AKD and it results in a good sheet sizing performance. In the case of bulking promoter B, the sizing performance was reduced, although AKD was still retained in the sheet.

Figure 5 shows the relationship between the AKD content in a sheet and the sizing performance. In all cases, the AKD content in a sheet increased with an increase in the amount of AKD. When only AKD was added, the sizing performance increased with an increase in the amount. When the amount was increased from 0.1% to 0.2%, the Stöckigt sizing degree increased slightly, from 27.3 to 33.5 s, although the AKD content increased drastically from 0.59 to 1.24 mg/g. On the other hand, when only 0.05% AKD was added, no sheet sizing performance was realized, although the sheet contained 0.27 mg/g AKD. This result suggests that more than a certain amount of AKD must be distributed in the sheet to have an effect on sizing performance. When AKD was added in combination with bulking promoter A, the AKD content was higher than when only AKD was added. Good sizing performance was realized when the amount of AKD was 0.05%. Thus, the combined use of bulking promoter and AKD is considered to be effective for improving sheet sizing performance.

Evaluation of sheet sizing performance and wettability

"Wetting" is the process in which a liquid contacts a gas-adsorbed solid surface and the surface is covered by the liquid. As a result, the solid–gas interface is replaced by a solid–liquid interface. When solid/liquid/gas phases are in equilibrium, Young's equation is valid:

$$\gamma_S = \gamma_{SL} + \gamma_L \cos\theta \tag{2}$$

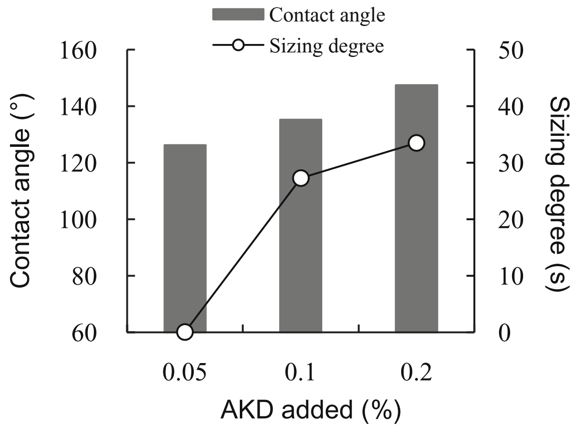

Fig. 6. Effects of AKD addition on handsheet contact angles and sizing degree. Contact angle, with *n*-hexane at 30 s contact time

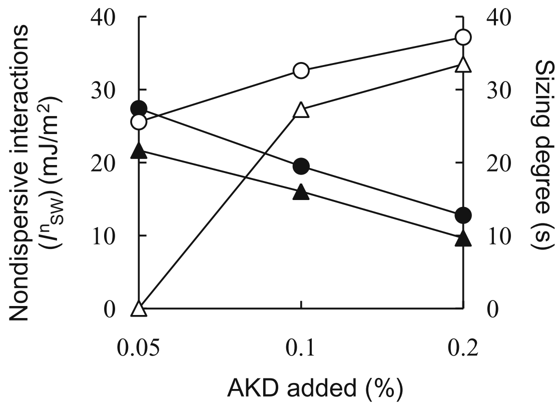

Fig. 7. Relationship between nondispersive interaction (I^{n}_{sw}) and sizing degree of handsheets prepared from addition of AKD. A, 0.8% added). *Triangles*, AKD; *circles*, A + AKD. *Closed symbols*, I^{n}_{sw}; *open symbols*, sizing degree

Here, γ_S is the surface free energy of solid, γ_{SL} is the free energy of the solid–liquid interface, γ_L is the surface free energy of the liquid, and θ is the contact angle.

Tamai et al.[7] have proposed a method for measuring the contact angle by immersing a solid in a liquid. Matsunaga and Ikada[4] 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 a hydrophilic polymer, into a saturated hydrocarbon.

$$\gamma_W - \gamma_H + \gamma_{WH}\cos\theta = 2\left(\sqrt{\gamma^d_W} - \sqrt{\gamma_H}\right)\sqrt{\gamma^d_S} + I^n_{SW} \quad (3)$$

where γ_W is the surface tension of the wetting liquid, γ_H is surface tension of a saturated hydrocarbon, γ_{WH} is interface tension between the wetting liquid and the saturated hydrocarbon, θ is the contact angle of the wetting liquid on the solid immersed in a saturated hydrocarbon, γ^d_W is the dispersion component of the wetting liquid surface tension, γ^d_S is the dispersion component of the solid surface free energy, I^n_{sw} is all nondispersive interactions, which are equal to $2(\gamma^p_S \cdot \gamma^p_W)^{1/2}$, and γ^p_S is the polar component of the solid surface free energy.

Here, a linear relationship is obtained when $\gamma_W - \gamma_H + \gamma_{WH}\cos\theta$ is plotted against $2\{(\gamma^d_W)^{1/2} - (\gamma_H)^{1/2}\}$. I^n_{sw} and $(\gamma^d_S)^{1/2}$ are obtained as intercept and slope of the resulting straight line, respectively.

In this study, the contact angle of water on the sheet surface was measured in a saturated hydrocarbon solution by the two-liquid method. Each component of the sheet surface free energy was calculated from Eq. 3, and the relationship with sizing performance is discussed.

The contact angle tends to increase with an increase in the amount of AKD, and the results agree with the increase in the Stöckigt sizing degree when more than 0.1% AKD was added (Fig. 6). When 0.05% AKD was added, very little sheet sizing effect was observed. However, the contact angle by the two-liquid method was 126°. Thus, it was found that even when the amount is insufficient to realize the sizing performance of AKD, only some hydrophobicity could be produced in a sheet.

Table 3. Surface energy parameters of AKD sizing handsheets

	AKD addition (%)	γ^d_S (mJ/m²)	γ^p_S (mJ/m²)	γ (mJ/m²)
AKD	0.05	31	2.3	33
	0.1	28	1.3	29
	0.2	6	0.5	6
A + AKD[a]	0.05	153	3.7	156
	0.1	149	1.9	150
	0.2	45	0.8	46

Table 3 shows the calculated values for each component of the surface free energy of sheets with added bulking promoter A and AKD. Each component of the surface free energy for sheets tends to decrease with an increase in the amount of AKD. Figure 7 shows the relationships between all nondispersive interactions I^n_{sw} and the sizing performance. In the case of a reactive sizing agent such as AKD, the sheet sizing performance is realized by coating the cellulose surface with AKD. This step reduces the acid–base interactions with water and the surface energy and generates hydrophobicity. The reduction in I^n_{sw} that accompanies the increase in sizing degree indicates the reduction of hydrophilicity. These results are consistent with the paper sizing principle. When bulking promoter A and AKD were used in combination, an increase in the Stöckigt sizing degree and a decrease in I^n_{sw} were observed with an increase in the amount of AKD. The addition of bulking promoter A realized a good sheet sizing performance without affecting the sizing effect of AKD.

In the case of bulking promoter B, the sizing performance could not be realized at all, although the contact angle was measured to be 109° by the two-liquid method (Fig. 8). As shown in Fig. 4, when bulking promoter B and AKD were used in combination, about 70% of AKD was fixed in the sheet. It is conjectured that the pulp fiber surface

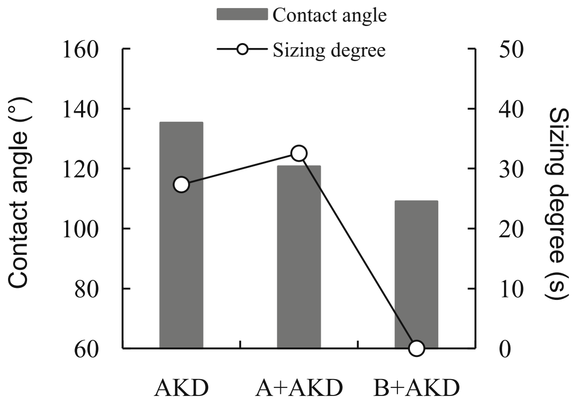

Fig. 8. Effects of addition of bulking promoters and AKD on handsheet contact angles and sizing degree. Contact angle, with *n*-hexane at 30 s contact time; A, B, 0.8% added; AKD, 0.1% added

was covered with bulking promoter B and thus the sizing performance of AKD was suppressed.

Conclusions

A bulking promoter was added in neutral papermaking with the use of an AKD. The relationship between the bulking of paper and sizing performance was investigated, and the following results were obtained.

The addition of a bulking promoter reduced the sheet density. In addition, further bulking occurs by increasing the amount of AKD; thus, an increase in the pore volume of the sheet was confirmed.

One of the bulking promoters provided a slight sheet sizing performance by its addition and improved the sizing performance further in combination with AKD. In this case, the retention of AKD was confirmed to be improved by the addition of the bulking promoter. The improvement in the sheet sizing performance is presumed to be related to the increased AKD retention caused by the bulking promoter and the effect of improved sheet hydrophobicity.

An increase in the sheet contact angle and a decrease in surface free energy resulting from the addition of AKD were confirmed, and an increase in sheet hydrophobicity was observed. One of the bulking promoters provides a high sheet sizing performance, although the AKD content was similar in the bulky sheet. On the other hand, the other bulking promoter prevented the sizing performance, although AKD was still retained in the bulky sheet.

Pyrolysis gas chromatography measurements revealed that the addition of a bulking promoter would increase AKD retention.

References

1. Taniguchi R, Isogai A, Onabe F, Usuda M (1993) Sizing mechanism of alkylketene dimmers. Part 3. Appearance of sizing features of AKD-sized sheets. Nord Pulp Pap Res J 8:352–357
2. JSA (2004) JIS P 8122: Paper and board – Determination of sizing – Stöckigt method
3. Japan TAPPI (2000) Pulp and paper testing method No. 48: Paper – Determination of pore volume distribution by mercury intrusion porosimetry
4. Matsunaga T, Ikada Y (1981) Dispersive component of surface free energy of hydrophilic polymers. J. Colloid Interface Sci 84:8–13
5. Yano T, Ohtani H, Tsuge S, Obokata T (1992) Determination of neutral sizing agents in paper by pyrolysis-gas chromatography. Analyst 117:849–852
6. 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
7. Tamai Y, Makuuchi K, Suzuki M (1967) Experimental analysis of interfacial forces at the plane surface of solids. J Phys Chem 71:4176–4179