Effect of Alkylketene Dimer Treatments on Water Repellency of Various Organic and Inorganic Materials

Akira Isogai

Graduate School of Agricultural and Life Science, The University of Tokyo,
1-1-1, Yayoi, Bunkyo-ku, Tokyo 113-8657, Japan

Abstract: An AKD emulsion size was treated to various organic and inorganic materials suspended in water, and the levels of water repellency were evaluated by observing water droplets put on the AKD-treated materials. Barium oxide, bleached kraft pulp, celite, glass wool, calcium carbonate, microcrystalline cellulose powder, talc and titanium dioxide turned to have clear water repellency by the AKD treatment more efficiently than alum-emulsion rosin size treatments. The water repellency of these AKD-treated materials was maintained after extraction with chloroform at 70°C for 1 day, but completely disappeared by extraction with 1% aqueous Tween 80 at 20°C for 1 day. On the other hand, active carbon, bentonite, silica gel and white carbon had no water repellency even by the same AKD treatment. The appearance of water repellency depended on neither chemical structures nor particle sizes of the materials, but there was an inverse correlation between their specific surface areas and the levels of water repellency. Namely, water repellency appeared on the material at 0.4% AKD addition level, when its specific surface area was lower than about 15 m²/g.

(Received 5 August, 2000; Accepted 18 October, 2000)

1. Introduction

It is well known that alkylketene dimers (AKD) can give water repellency to paper more efficiently than the other so-called non-reactive sizes such as rosin sizes. This efficient paper sizing by AKD has been explained in terms of covalent bond formation between cellulose hydroxyl groups and AKD molecules in paper under thermal drying process of papermaking [1]. Solid-state ¹³C-NMR analysis of handsheets prepared with ¹³C-labeled AKD [2] and the behavior of extraction resistance of size components in AKD-sized papers by organic solvents [3,4] supported this hypothesis.

On the other hand, the author proved on the basis of detailed solid-state ¹³C-NMR analysis of cellulase-treated residues of ¹³C-labeled AKD-sized handsheets and extraction experiments with either chloroform or 1% aqueous Tween 80 that most size components are present as the original AKD or hydrolyzed AKD (ketones) molecules in AKD-sized paper without forming covalent bonds with cellulose hydroxyl groups [5]. Furthermore, the reason why the chemical structure of AKD instead of hydrolyzed AKD (ketones) was necessary at the wet-end addition for efficient paper sizing was explainable in terms of the partly hydrophilic characteristic of AKD.

Namely, when ketone emulsions were added to pulp suspensions, ketone molecules formed large coagulants in pulp fiber matrix during couching, pressing and drying processes of the wet webs owing to greatly hydrophobic characteristic of the ketone molecules. In contrast, when AKD emulsions are added to pulp suspensions, partly hydrophilic or surfactant-like AKD molecules bring about evenly distributed states of the size emulsion particles on hydrophilic pulp fiber surfaces in papermaking process, where water is always present. After homogeneous distributions of AKD emulsion particles on pulp fibers are achieved by the AKD

Fig. 1 Possible reactions between AKD and hydroxyl groups of organic and inorganic materials.

molecules, hydrolysis to ketones then enhances sizing performance, because ketones are more hydrophobic than AKD [6]. Possible reactions between AKD and hydroxyl groups are shown in Fig. 1 [7].

On the basis of the above hypothesis, AKD may efficiently give water repellency to not only cellulosic materials but also other inorganic materials, which have no hydroxyl groups. In this study, therefore, an AKD emulsion size was treated to various organic and inorganic materials suspended in water. Then, water repellency behavior of these AKD-treated materials was studied in terms of chemical structures, specific surface areas, particle sizes and ζ -potentials of the tested materials in order to elucidate the developing mechanism of water repellency by AKD. Furthermore, from practical viewpoints, development of water repellency of inorganic materials is significant for composite materials consisting of the inorganic compounds and pulp fibers.

2. Experimental

2.1 Materials

Active carbon powder, aluminum hydroxide, bentonite, celite, corn starch, microcrystalline cellulose powder, glass wool and polyvinyl alcohol were commercial products of laboratory grades (Wako Chemicals Co., Japan). Clay, precipitated calcium carbonate, talc, titanium dioxide and white carbon were commercial papermaking fillers for the internal addition. Silica gel was a column- chromatographic grade (Wako Chemicals Co., Japan). The AKD emulsion used was a commercial product (12% AKD content), which was dispersed with a cationic starch (AS-202, Japan PMC Co. Japan). The emulsion rosin size dispersed with a styrene-acrylic acid-type copolymer (50% rosin acid content) was also a commercial product (AL-120, Japan PMC Co. Japan).

2.2 Preparation of AKD-sized materials

One of the above materials (2 g) was suspended in tap water (200 mL) with continuous stirring, and then 0.4% (on dry weight of the material) AKD was added to the suspension. After stirring for 1 min, the mixture was filtered on a Buchner funnel of 4.5 cm in diameter without suction. The wet mat thus formed was picked up with the attached filter paper, and dried at 105°C for 30 min in an oven. After conditioning at 20°C and 65% relative humidity for more than 4 h, water-repellency of the mat was evaluated by putting water droplets on the mat. As a comparison, an aluminum sulfate solution and the emulsion rosin size were treated to some

materials in a similar manner to the AKD treatment.

2.3 Extractions of size components from the AKD-sized materials

Size components in the above AKD-treated and once-dried materials were extracted with chloroform at 70°C or 1% aqueous Tween 80 at 20°C for 1 day. During this extraction, the mat form of the AKD-treated materials crumbled into powders or fibers. After the chloroform extraction, the residual chloroform was removed from the material by filtration on a Buchner funnel, and the mat formed was washed successively with acetone and water followed by heating with the attached filter paper at 105°C for 30 min in an oven. After the 1% Tween 80 extraction, the extracted material was washed thoroughly with water on a Buchner funnel, and the mat formed was heated with the attached filter paper at 105°C for 30 min in an oven.

2.4 Measurements

ζ -Potentials, particle sizes and their distributions of the materials were measured in tap water at 25°C using a laser-doppler-electrophoresis-type zeta meter equipped with a photon correlation spectroscopy-type particle size meter (Zetasizer 3000, Malvern Instruments Ltd., UK). Specific surface areas of the materials were measured by the nitrogen-adsorption method on the basis of the BET theory after vacuum drying at 40°C for 1 day (OMNI SORP 100CX, Coulter Co., USA). Water-repellency of the materials was evaluated by observing water droplets (about 0.04 mL) put on the mat using a micro syringe. A stereo-microscope (BX50, Olympus Co., Japan) was used for the observation.

3. Results and discussion

3.1 Water repellency behavior of AKD-treated materials

Table 1 shows representative chemical formulae, specific surface areas, average particle sizes and ζ -potentials of the inorganic and organic materials used for the AKD treatments. Some of the materials have hydroxyl groups. Fiber sizes of bleached hardwood kraft pulp, glass wool and cellulose powder were measured by optical microscopy, because their shapes were inadequate to the apparatus for measuring zeta potentials and particle sizes. Most of the materials in Table 1 had negative ζ -potentials. In this study, retention values of AKD on the materials were not measured.

Table 2 summarizes the results of water repellency of the AKD-treated materials, and those after the chloroform

Table 1 Basic properties of inorganic and organic materials used for AKD treatment.

Sample	Representative chemical formula	Specific surface area (m ² /g)	Particle size (μm)	ζ-potential (mV)
A	Activated carbon	C	1.53	-18.8
B	Aluminum hydroxide	Al(OH) ₃	3.70	-20.3
C	Barium oxide	BaO	1.44	+5.6
D	Bentonite	AlSiMgNa(OH)	2.89	-18.1
E	Bleached kraft pulp	[C ₆ H ₇ O ₂ (OH) ₃] _n	ca. 20 × 1000	n.d.
F	Celite	MgF ₂	9.03	-31.2
G	Clay	Al ₂ O ₃ •2SiO ₂ •2H ₂ O	1.31	-22.4
H	Corn starch	[C ₆ H ₇ O ₂ (OH) ₃] _n	9.96	-2.8
I	Glass wool	SiO ₂	ca. 5 × 3000	n.d. ^{a)}
J	Calcium carbonate	CaCO ₃	2.56	-13.0
K	Cellulose powder	[C ₆ H ₇ O ₂ (OH) ₃] _n	ca. 17 × 250	-5.9
L	Polyvinyl alcohol	[C ₂ H ₃ (OH)] _n	n.d.	n.d. ^{a)}
M	Silica gel	SiO ₂	1.28	-19.5
N	Talc	3MgO•4SiO ₂ •H ₂ O	4.55	-21.7
O	Titanium dioxide	TiO ₂	2.03	-9.5
P	White carbon	SiO ₂	2.47	-20.8

a) n.d.: Not determined.

Table 2 Water repellency of AKD-treated materials, and that after CHCl₃ or Tween 80 extraction.

Sample	Before extraction	After extraction with	
		CHCl ₃	1% Tween 80
A	Activated carbon	—	
B	Aluminum hydroxide	+	
C	Barium oxide	++	—
D	Bentonite	—	
E	Bleached kraft pulp	++	—
F	Celite	++	—
G	Clay	+	
H	Corn starch	+	
I	Glass wool	++	—
J	Ground calcium carbonate	++	—
K	Microcrystalline cellulose	++	—
L	Polyvinyl alcohol	±	
M	Silica gel	—	
N	Talc	++	—
O	Titanium dioxide	++	—
P	White carbon	—	

++: Contact angle is in the range of 90-180° for more than 1 min.

+: Contact angle is in the range of 30-90° for more than 1 min.

±: Low but detectable water repellency.

—: No water repellency.

Fig. 2 Optical microphotographs of AKD-treated glass wool, on which a water droplet was dropped. A: AKD-treated glass wool, B: after CHCl_3 extraction, and C: after 1% Tween 80 extraction.

Fig. 3 Optical microphotographs of AKD-treated microcrystalline cellulose powder, on which a water droplet was dropped. A: AKD-treated cellulose powder, B: after CHCl_3 extraction, and C: after 1% Tween 80 extraction.

or 1% Tween 80 extraction. Barium oxide, bleached hardwood kraft pulp, celite, glass wool, calcium carbonate, microcrystalline cellulose powder, talc and titanium dioxide had high water repellency by the AKD treatment. Apparent contact angles of the water droplets on these materials were in the range of $90\text{--}180^\circ$ for more than 1 min. On the other hand, active carbon, bentonite, silica gel and white carbon had no water repellency. When the addition level of AKD increased to more than 4% on dry weight of these four materials, it was ten times as much as that in Table 2, water repellency was detected on the AKD-treated materials. Polyvinyl alcohol had detectable water repellency, but contact angles of the water droplets were less than 30° (Table 2). Thus, the levels of water repellency were various among the AKD-treated materials. Some of the AKD-treated inorganic materials, which showed high levels of water repellency, had no hydroxyl groups. Thus, the presence of hydroxyl groups in the material was not necessary for the appearance of water repellency by the AKD treatment.

As a comparison, aluminum sulfate and the emulsion rosin size were treated to bleached kraft pulp, celite, glass

wool, microcrystalline cellulose powder, talc and titanium dioxide in a similar manner to the AKD treatment. The amount of aluminum sulfate added was fixed to 1% on dry weight of the material. Clear water repellency was observed on the rosin-treated materials at the rosin size addition level of more than 1.2%, whereas no or quite low water repellency was observed at the rosin size addition level of less than 1%. Thus, the AKD emulsion size gave water repellency to not only cellulosic fibers but also such inorganic materials more efficiently than the emulsion rosin size.

3.2 Water repellency of the AKD-treated materials after extraction

The AKD-treated materials with clear water repellency were subjected to the extraction with either chloroform or 1% aqueous Tween 80. The levels of water repellency were maintained for all the AKD-treated materials tested even after the chloroform extraction. However, water repellency of these materials completely disappeared, when they were stirred in 1% aqueous Tween 80 at 20°C for 1 day. Optical microphotographs of some examples are shown in Figs. 2-5: glass wool, microcrystalline cellulose powder, bleached hardwood

Fig. 4 Optical microphotographs of AKD-treated hardwood bleached kraft pulp, on which a water droplet was dropped. A: AKD-treated hardwood bleached kraft pulp, B: after CHCl_3 extraction, and C: after 1% Tween 80 extraction.

Fig. 5 Optical microphotographs of AKD-treated calcium carbonate filler, on which a water droplet was dropped. A: AKD-treated calcium carbonate filler, B: after CHCl_3 extraction, and C: after 1% Tween 80 extraction.

kraft pulp and calcium carbonate. Diameters of water droplets in Figs. 2A-5A were about 2 mm. Other barium oxide, celite, talc and titanium dioxide had quite similar behavior of water repellency before and after the extractions. Thus, irrespective of cellulosic or inorganic materials, the AKD components, which contributed to the appearance of water repellency, can be removed from the AKD-treated materials by the Tween 80 extraction similarly to the results of extractions of AKD-sized handsheets [5].

It was proved in one of the previous papers that, even if covalent bonds between AKD and cellulose hydroxyl groups were present, the β -ketoester bonds were stable without cleavage during the 1% Tween 80 treatment at 80°C for 1 day [7]. Therefore, AKD and hydrolyzed AKD (ketones) are present without covalent bonds in not only cellulosic materials but also such inorganic materials, and thus extractable by the Tween 80 treatment. Probably both hydrogen bond and van der Waals interactions are present between the material and AKD components. Since a cationic starch was present in the AKD emulsion as a stabilizer, the starch may play some roles as a mediator in the interactions between the

materials and AKD components.

3.3 Factors influencing water repellency of the AKD-treated materials

The relationship between the level of water repellency and characteristics of the materials treated with AKD are studied in this section. Barium oxide, celite, glass wool, calcium carbonate and titanium dioxide, which had high levels of water repellency by the AKD treatment, had no hydroxyl groups in their chemical structures (Tables 1 and 2). Thus, the presence of hydroxyl groups or the possibility for the material to form covalent bonds with AKD molecules is not necessary for the appearance of water repellency. Especially glass wool, silica gel and white carbon have the same chemical structures, SiO_2 . However, the behavior of water repellency of these materials by the AKD treatment was opposite between glass wool and the other two. Thus, the appearance of water repellency does not depend on chemical structures of the materials. Furthermore, neither particle sizes nor ζ -potentials of the materials affected the resultant water repellency.

On the other hand, specific surface areas of the materials seemed to influence their behavior of water

Fig. 6 Relationships between logarithmic values of the specific surface areas of the tested materials and their water repellency levels after the AKD treatment. Alphabets correspond to those in Tables 1 and 2.

repellency. Fig. 6 shows the relationship between the levels of water repellency and logarithmic values of specific surface areas of the materials. Because the specific surface areas were determined by the nitrogen adsorption method under dry conditions, some water-swollen materials such as bentonite, silica gel, corn starch and cellulosic materials may have given smaller values than those in water. Nevertheless, there still was an inverse correlation between the levels of water repellency and logarithmic values of specific surface areas. Water repellency appeared on the AKD-treated material, when its specific surface area was lower than about $15 \text{ m}^2/\text{g}$ (about 3 as the logarithmic value in Fig. 6). Therefore, specific surface areas of the materials may govern their resultant water repellency in the AKD treatment, rather than their particle sizes, ζ -potentials or chemical structures, if the retention values of AKD on the AKD-treated materials are assumed to be roughly equal among them. In the case of materials with larger specific surface areas, the AKD components may spread into pores of the materials by the heating, thus resulting

in lower coverage ratios with the size components on the surface [7].

4. Conclusions

When 0.4% AKD was added to barium oxide, bleached kraft pulp, celite, glass wool, calcium carbonate, microcrystalline cellulose powder, talc and titanium dioxide suspended in water, they turned to have high levels of water repellency. When emulsion rosin size was used, addition levels of more than 1.2% were required to give water repellency to these materials. Thus, AKD can bestow water repellency on not only cellulosic materials but also some inorganic materials more efficiently than the emulsion rosin size. The water repellency of these AKD-treated materials was maintained after the chloroform extraction, but completely disappeared by the 1% aqueous Tween 80 extraction. On the other hand, active carbon, bentonite, silica gel and white carbon had no water repellency even by the AKD treatment. The appearance of water repellency depended on neither chemical structures nor particle sizes of the materials, but there was an inverse correlation between their specific surface areas and the appearance of water repellency.

References

1. J. W. Davis, W. H. Roberson, and C. A. Weisgerber, *Tappi J.*, **39**(1), 21 (1956).
2. K. J. Bottorff, *Tappi J.*, **77**(4), 105 (1994).
3. T. Lindström and H. O'Brian, *Nordic Pulp Paper Res. J.*, **6**, 34 (1986).
4. J. C. Roberts and D. N. Garner, *Tappi J.*, **68**(4), 118 (1985).
5. A. Isogai, *J. Pulp and Paper Sci.*, **25**, 251 (1999).
6. A. Isogai, Proc. 52nd Appita Annual Meeting, Brisbane, May, Vol. 1, p. 71 (1998).
7. A. Isogai, *J. Pulp Paper Sci.*, **26**, 330 (2000).
8. W. J. Bartz, M. E. Darroch, and R. L. Kurrle, *Tappi J.*, **77**(12), 129 (1994).