

## Research Article

# Effects of AKD Sizing on the Morphology and Pore Distribution Properties of OCC Fibers

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Changes of the morphology and pore structure of old corrugated container (OCC) fibers during an alkyl ketene dimer (AKD) sizing process were studied. The resulting samples were characterized by scanning electron microscopy (SEM), atomic force microscopy (AFM), contact angle, and BET surface area analysis. The length of fibers had obvious influence on the AKD sizing effect, and the length of fibers ranged from 100 to 200 meshes showed the best sizing performance. The surface roughness of 0.3% AKD sizing OCC fibers decreased from 27.949 nm to 12.811 nm. Compared with the control sample, the pore volume of fibers sized with 0.1% AKD decreased 4.3% when the average pore diameter was fixed at 2.4~3.0 nm. And when the usage of AKD increased to 0.3% and 0.5%, the pore volume decreased 1.4% and 6.3% accordingly. The decrease in the pore volume of AKD-sized fiber indicated the penetration and deposition of dispersed particles of AKD in the fiber lumens.

## 1. Introduction

In recent years, papermaking industry has made rapid progress along with the development of China's economy, and recycled fiber has become an extremely important raw material because of its low pulping cost, energy saving, environment protection, circulating use, and other advantages [1].

Old corrugated container (OCC), as an environmental friendly packaging material, is one of the main sources of recycled fibers, with a high degree of recycling for many years. OCC is mainly composed of used unbleached kraft pulp, bleached kraft pulp, hardwood semichemical pulp, and grass pulp. The fibers irreversibly change their structure;

both the tensile strength and the water retention value of fibers decreased upon recycling [2].

Many researches have been studying on recycling of fibers from different points; it was found that fibrils and other bonding sites are not fully rehydrated when the dried fiber is repulped, which reduces their ability of the fiber, which is consistent with the decreased ability of the fiber to hold water; this is called hornification [3]. Several authors considered the different fiber structure changes affecting the amount of water that fibers hold within the walls and the tendency to be stiffer, including irreversible pore closure [4], microfibril aggregation or coalescence [5], combination of rearrangement of cellulose [6], crosslinking between cellulose

and hemicelluloses [7], crystallization [8], and hemicellulose removal [9]. However, the mechanism for hornification has still not been completely understood.

Internal sizing is a widely used process in papermaking to reduce the rate of liquid penetration into a paper. The traditional method of sizing is using acid sizing (rosin sizes and aluminium sulfate) as sizing agents. However, with the wide application of calcium carbonate (ground calcium carbonate (GCC) and precipitated calcium carbonate (PCC)) used in papermaking, neutral or alkaline sizing has been a widespread use and highly regarded owing to economic reasons and paper storage durability and avoided the corrosive action to approaching system or paper machine caused by aluminium ion [10].

Alkyl ketene dimer (AKD) is a common commercial chemical that is classified as nonhazardous (under OSHA regulations); the chemical structure of AKD is shown in Figure 1 [11]. In a drying process, AKD particles form  $\beta$ -ketoester bonds with cellulose. As a result, the hydrophobic groups become aligned and the surface free energy is reduced. A reduction in hydrogen-bonding potential implies a reduction in the hydrophilicity of the fiber, which is consistent with the decreased ability of fiber to hold water.

Therefore, it can be concluded that AKD might play an important role in the swelling properties or hornification of fiber. In recent years, many research results about the hydrophobic interaction of AKD on original fibers have been published [12, 13]. In general, it is believed that AKD reacts with cellulose fiber and forms a  $\beta$ -keto ester bond, hence making paper hydrophobic [14]. But there was little attention given to the influences on recycled fiber swelling properties, hornification, and morphology of AKD. In fact, original and recycled fibers had been significantly different in sizing and swelling ability, zeta potential, filler distribution, chemical agent content, and other aspects; further research is needed to inhibit hornification and improve the recycling performance of recycled fiber.

In this study, we observe the effect of AKD sizing on the morphology of OCC fiber. The factors influencing this study such as the surface contact angle and BET analysis of AKD-sized OCC fiber were also investigated.

## 2. Experimental

### 2.1. Materials

**2.1.1. Raw Materials.** AKD sizing emulsion was supplied by Tianma Specialty Chemicals (1865, China), the solid content was 13.2%, and its mean diameter was determined to be 0.5  $\mu\text{m}$  using a Laser Diffraction Particle Size Analyzer (MS2000MU, Malvern, Worcestershire, UK).

OCC fiber made in China was torn into pieces of about 25  $\times$  25 mm in size and soaked in water for 12 h at room temperature, then slurried with a slusher (N-197VT, Adirondack Machine Corporation, USA) at a beating degree of 38°SR.

**2.1.2. Classification of OCC Fibers.** OCC fibers were classified by the Bauer-McNett Classifier according to the Tappi T 233 cm-06 standard: mesh of sieves: 30, 50, 100, and 200.

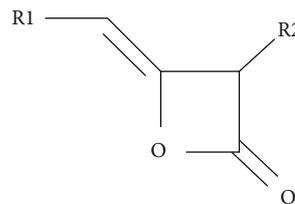


FIGURE 1: Chemical structure of AKD. R1 and R2 represent straight chains of lengths varying between 16 and 18 atoms.

**2.1.3. Preparation of Handsheets.** From a beaten pulp, a fiber suspension with a fiber consistency of 0.15% was prepared, and 0.1%, 0.2%, 0.3%, 0.4%, or 0.5% of AKD (based on dry weight of pulp) was added to the pulp suspensions with continuous stirring at 6,000 revolutions. The samples were identified as A1, A2, A3, A4, and A5 according to the AKD level employed in preparation. The control sample (no AKD added) was designated as Sample C. Then, the mixture was subjected to the preparation of handsheets with a basis weight of 80 g/m<sup>2</sup> on a handsheet machine (RK3-KWTjul, Vorchdorf, Austria) with the Rapid-Köthen method according to the GB/T 24214-2009 standard.

**2.1.4. Scanning Electron Microscopy (SEM) Analysis.** Morphologies of the handsheet surfaces were examined with a scanning electron microscope (SEM S3700, Hitachi, Japan) operating at an accelerating voltage of 15 kV. Before observation, the samples were coated with gold using a vacuum sputter coater.

**2.1.5. Atomic Force Microscopy (AFM) Analysis.** AFM images were recorded at room temperature on a MultiMode NanoScope IIIA (Digital Instruments, Santa Barbara, CA) operating in a tapping model.

**2.1.6. Determination of Pore Distribution.** A pore size distribution detector ASAP2010M (Micromeritics, USA) was used for the structural analyses of the fiber pores. High-purity N<sub>2</sub> was used as an adsorbate, and the adsorption-desorption of high-purity N<sub>2</sub> was determined at 77 K in a liquid nitrogen trap using a static volumetric method.

**2.1.7. Contact Angle Measurements.** Contact angles with distilled water on the paper were measured with an OCA Data Physics Instruments GmbH equipment.

**2.1.8. Water Absorption Measurements.** Water absorption of handsheets was measured according to the GB/T 1540-2002 standard.

All experiments were run in triplicate with the relative standard deviations (RSD) of about 5%.

## 3. Results and Discussion

**3.1. SEM Imaging of Sized and Unsized Handsheets.** Figure 2 presents the images of the surface morphology of unsized and sized handsheets. It was found that unsized fiber shows smooth image contours and crisp edges. As a result of AKD sizing, white membrane materials cover most of the surface

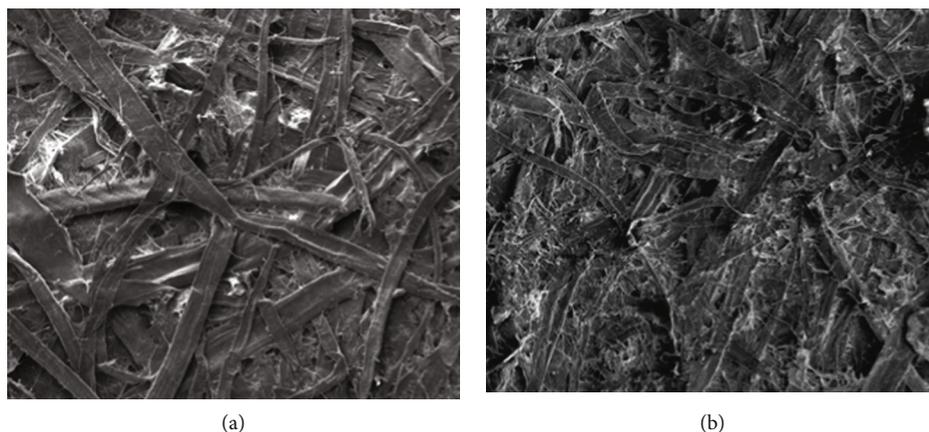


FIGURE 2: SEM images of unsized and sized handsheets: (a) unsized handsheet and (b) sized handsheet (the dosage of AKD was 0.3%).

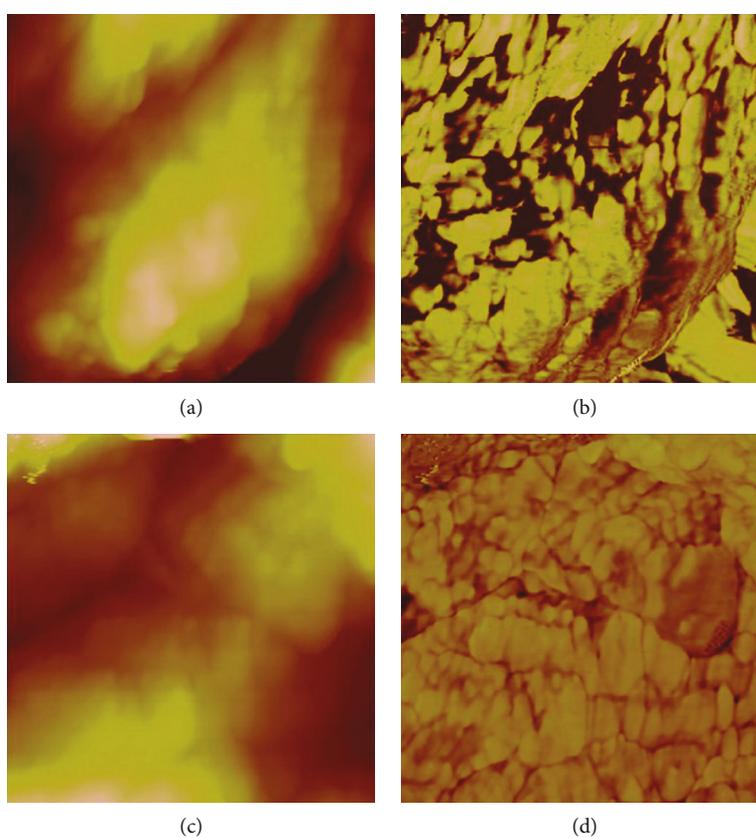


FIGURE 3: AFM images of unsized and sized handsheet: (a, c) unsized handsheet, (b, d) sized handsheet (the dosage of AKD was 0.3%), (a, b) height image, and (c, d) phase image.

and of gaps of fibers; the hydrophobic polymer film on the surface of the handsheet was formed [15].

**3.2. AFM Imaging of Sized and Unsized Handsheets.** Figure 3 shows the different AFM images of unsized and sized handsheet (scan range  $1\ \mu\text{m} \times 1\ \mu\text{m}$ ). In Figure 3(a), many folds and grooves were found on the surface of the unsized handsheet, resulting in an increase in surface roughness ( $R_q = 27.949\ \text{nm}$ ). Compared with Figure 3(a), the surface roughness of the sized handsheet decreased because of the form of the AKD film on the surface of the handsheet, and

the  $R_q$  has fallen by a shocking 54% down to  $12.811\ \text{nm}$ . Generally, the white and black areas in the phase image varied with the surface properties of samples reflecting all sorts of things, including soft and hard degree, elasticity, hydrophily, and adhesion. In a previous study, it was found that a dark area has a higher hydrophily; on the contrary, a bright area reflects strong hydrophobicity [16]. The dark area in Figure 3(d) indicated the existence of hydrophilic cellulose, and there are two reasons for the bright area in Figure 3(d): the hydrophobic film formed by AKD emulsion and amorphous lignin exist in OCC fibers.

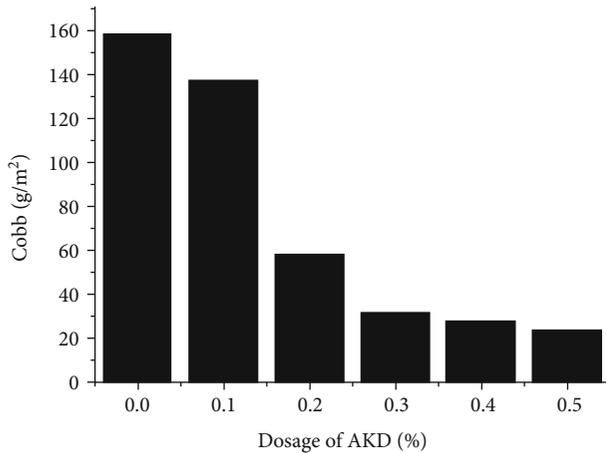


FIGURE 4: Changes of Cobb with different dosages of AKD.

**3.3. Sizing Degree of Handsheets.** The changes of Cobb with different dosages of AKD are shown in Figure 4. With AKD added, the hydrophobicity of the handsheets was dramatically increased. However, when the dosage of AKD reached to 0.3%, the hydrophobicity of handsheets cannot obviously be improved; the result prompts us that it is important to investigate the best dosage of AKD in a certain system. In engineering applications, excessive high dosage of AKD can lead to a high cost of production and slip phenomenon because of the lower friction coefficient of paper. More seriously, AKD particles in white water may be hydrolyzed to produce double alkyl ketone which can cause precipitation of the suspension and make a deposition problem on the net, blanket, dryer, and calendar rolls. This process ultimately results in papersheet breaks and holes or spots on the surface of papersheet. Therefore, an urgent problem faced by the researchers in papermaking is how to avoid excessive use of AKD emulsion.

**3.4. Effects of Fiber Length on Sizing Degree.** An interesting thing can be found in Figure 5 that the sizing degrees of OCC fibers have a significant relationship with their length; the length of fibers ranged from 100 to 200 meshes showing the best sizing performance. The main reason given for this is that uniform handsheets get higher a retention ratio of AKD particles. Though short fibers are helpful for AKD retention, AKD holds on fines' lose easily with the fines losing on wire section, but longer fiber length could be related to the reduction in the AKD particle retention ratio because of the cracks between long fibers. In a word, a suitable length is an important factor of improving the hydrophobic property of AKD sizing OCC fibers [17].

**3.5. Effects of AKD Sizing on Contact Angles.** Sharma et al. established the well-regarded Young's equation which defines the balances of forces caused by a wet drop on a dry surface [18]. Young's equation gives the following relation:

$$\cos\theta = \frac{\gamma_{sg} - \gamma_{sl}}{\gamma_{gl}} \quad (1)$$

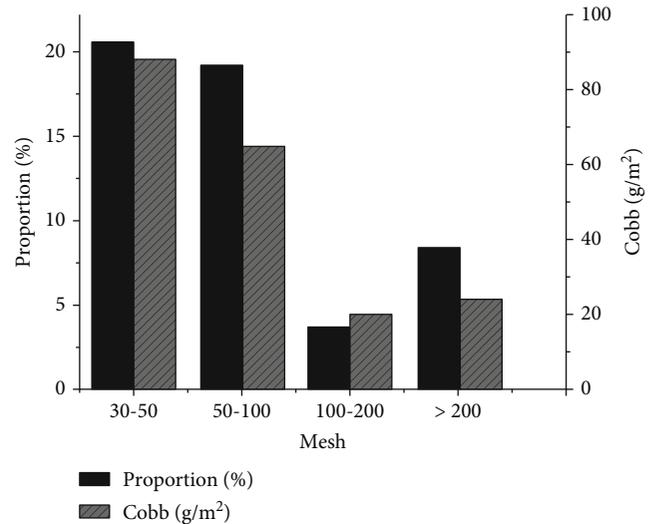


FIGURE 5: Effects of fiber length on sizing degree (the dosage of AKD was 0.3%).

where  $\gamma_{sl}$ ,  $\gamma_{gl}$ , and  $\gamma_{sg}$  are the interfacial tensions between the solid and liquid, the gas and liquid, and the solid and gas, respectively. The equilibrium contact angle is denoted by  $\theta$ .

Figure 6 shows the comparison of Samples C and A2 at the time of contact (5 s). As can be seen in Figure 6(a), on the surface of unsized handsheet, the water contact angle approached zero, which indicated that unsized OCC fibers had good surface wettability. However, the fibers sized by 0.2% AKD (Sample A2) showed a good hydrophobic property at the time of contact (5 s). The contact angle is related to the contact time of aqueous solutions with paper during printing and other applications (contact time in milliseconds). Therefore, it is very important to study the relationship the contact angle and contact time [19].

Table 1 shows that with the increasing time, the contact angle of different samples showed a decreasing trend. Besides that, there is an obvious decrease in that of the group with lower sizing degree (Sample A1). In other words, a bigger contact angle shows better sizing stability.

**3.6. Effects of AKD Sizing on Porous Structure of OCC Fiber.** As shown in Figure 7, the effects of AKD sizing on the porous structure of OCC fibers were evaluated. The dosage of AKD used in the sizing procedure significantly influenced the pore characteristic of OCC fibers. It was found that the pore volume of fibers decreased with the increase in the dosage of AKD. The corresponding pore volume was at maximum when the average pore diameter was 2.4~3.0 nm. Compared with the control sample, the pore volume of fibers sized with 0.1% AKD decreased 4.3% when the average pore diameter was fixed at 2.4~3.0 nm. And when the usage of AKD increased to 0.3% and 0.5%, the pore volume decreased to 1.4% and 6.3% accordingly. The decrease in the pore volume of AKD-sized fiber indicated the penetration and deposition of dispersed particles of AKD in the fiber lumens.



FIGURE 6: Contact angle of unsized and AKD-sized papers (contact time = 5 s): (a) Sample C, no AKD added; (b) Sample A2, 0.2% AKD added.

TABLE 1: Contact angle behavior of different papers at different contact times.

Sample	5 s	10 s	20 s	30 s	40 s
A1	 88.4°	 86.2°	 80.9°	 76.5°	 65.8°
A3	 116.2°	 115.3°	 113.0°	 112.5°	 111.4°
A5	 125.7°	 120.8°	 119.3°	 118.2°	 116.5°

A1: 0.1% AKD added; A3: 0.3% AKD added; A5: 0.5% AKD added.

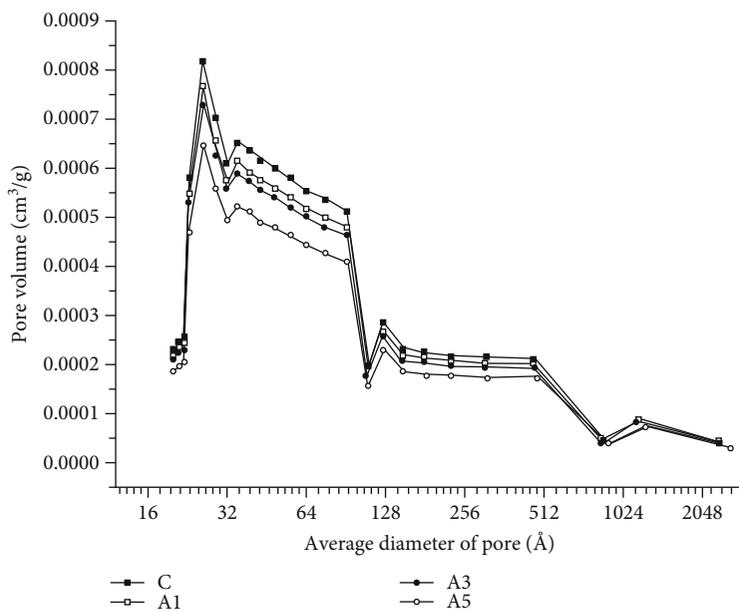


FIGURE 7: Pore size distribution of unsized and AKD-sized OCC fibers: C—no AKD added; A1—0.1% AKD added; A3—0.3% AKD added; A5—0.5% AKD added.

## 4. Conclusions

AKD is widely used as an internal sizing agent in papermaking to increase paper hydrophobicity. The smoothness of fiber further increased after AKD sizing. The length of fibers had obvious influence on the AKD sizing effect. In this paper, the length of fibers ranged from 100 to 200 meshes showing the best sizing performance. The surface morphology of OCC fibers is drastically changed after AKD sizing. The surface roughness of 0.3% AKD sizing OCC fibers decreased from 27.949 nm to 12.811 nm compared with the control sample. The pore volume of AKD-sized fiber decreased with the increase in the AKD emulsion additional level indicating the penetration and deposition of dispersed particles of AKD in the fiber lumens. The evidence suggests that AKD sizing will have important influence on not only the hydrophobic property but also the great factors of the hornification or swelling ability of OCC fibers during recycling.

## Data Availability

The data used to support the findings of this study are included within the article.

## Conflicts of Interest

The authors declare that they have no conflicts of interest.

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