STUDY ON THE REACTION OF ALKYL KETENE DIMER (AKD) AND CELLULOSE FIBER

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A cellulose homogeneous system was prepared by dissolving cellulose fibre in an 8.0 wt% LiCl/DMAC solution. AKD was reacted with the cellulose under the homogeneous system and a heterogeneous system, respectively. The reaction products were characterized by Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), thermogravimetric analysis (TGA), differential thermal analysis (DTA), and Wide-angle X-ray diffraction (WXRD). The results indicated that hydrogen bonds between cellulose molecules were disrupted under homogeneous conditions. The activity and accessibility to the reagent of hydroxyl groups were enhanced so that the β-keto ester bonds between AKD and cellulose were generated. However, the activity and accessibility of hydroxyl protons of the anhydroglucose units were not highly reactive under heterogeneous conditions. Moreover, cellulose itself was heterogeneous in nature, as different parts of its constituent fibrils displayed very hard accessibilities to the reagent. The β-keto ester bonds were not detected in the reaction products. Thus, the reaction between AKD and cellulose was difficult to achieve under heterogeneous conditions. In the sizing process, the reaction of cellulose should not simply be regarded as being that of a trihydric alcohol that is similar in its chemistry to sugars having three hydroxyl groups. Thus, the controversy about the sizing mechanism of AKD still remains unresolved.

Keywords: AKD; Cellulose; Homogeneous system; Heterogeneous system; Sizing mechanism

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INTRODUCTION

The synthetic sizing agent AKD is one of the most widely used sizing systems in neutral/alkaline papermaking (Kardecemir et al. 2005). But the sizing mechanism and the interaction between cellulose and AKD are still not fully understood. The mechanism of AKD sizing is believed to occur by a three-step mechanism involving (1) the retention of the AKD particles on the pulp fibers, (2) the spreading of the AKD particle to a monolayer thickness film, and (3) the generation of β-keto ester involving a covalent cellulose-AKD bond. These alkaline sizing agents become chemically bound to the cellulose fibers with hydrophobic chains pointing outward, producing a water repellent surface. It has been proposed that the β-keto ester bond plays a major role in the sizing process (Garnier et al. 1998; Brotorff 1994; Marton 1990; Ödberg et al. 1987; Roberts et al. 1985). However, some scholars have claimed that this chemical bond is not responsible for paper sizing, and they have raised doubts about the above-mentioned mechanism (Isogai et al. 1992; Rohringer et al. 1985).
Cellulose can be characterized as a high molecular weight homopolymer of β-1,4-linked anhydro-D-glucose units in which every unit is corkscrewed by a 180° angle with respect to its neighbors on the same chain. In nature, cellulose does not occur as an isolated individual molecule. Typically, approximately 36 individual cellulose molecules, as they are biosynthesized, assemble together into larger units known as elementary fibrils, which pack into larger units called microfibrils, and these in turn become assembled into the cellulose fibers. The molecular structure of cellulose suggests that it is a linear-chain polymer with a large number of hydroxyl groups. The degree of linearity enables the molecules to approach together. Thus, cellulose has a high cohesive energy that is greatly enhanced by the fact that the hydroxyl groups are capable of forming extensive hydrogen bond networks between the chains and within the chains. Thus, the physical properties and the chemical reactivity of fibrous cellulose are not only influenced by the chemical constitution of the cellulose molecules but are also determined by the supramolecular structure of cellulose, i.e. the overall arrangement of chain molecules in a fibre (Roy et al. 2009; Viëtor et al. 2000).

The reactions of cellulose nearly always take place under heterogeneous conditions because of its high degree of crystallinity and insolubility in commonly used solvents. The accessibility of reagents to the functional groups of cellulose may be restricted due to the complex physical structure. Moreover, cellulose itself is heterogeneous in nature, as different parts of its constituent fibrils display very different accessibilities to the reagent. So, the reaction of cellulose should not simply be regarded as being that of a trihydric alcohol that is similar in its chemistry to sugars having three hydroxyl groups (Wang et al. 2007; Zhao et al. 2006).

Lithium chloride/N,N-dimethylacetamide (LiCl/DMAc) is one of the most efficient solvent system for cellulose (Potthast et al. 2002). The mechanism of dissolution (Fig. 1) involves hydrogen bonding of the hydroxyl protons of cellulose with the chloride ion, which is in turn associated with the Li+(DMAc) macrocation complex.

![Fig. 1. Mechanism for the dissolution of cellulose in the LiCl/DMAc solvent system](image-url)
The resulting charge-charge repulsions or a bulking effect would tend to allow further solvent penetration into the polymer structure (McCormick et al. 1985). LiCl/DMAc dissolves cellulose with high molecular weight (>10^6) molecularly at the ambient temperature without noticeable degradation. This feature makes the solvent system suitable for the processing, characterization, or derivatization of cellulose (Matsumoto et al. 2001; Ishii et al. 2008, Ishii et al. 2006, Benoit et al. 2007; El Seoud et al. 2000). Based on their work, in this study, we investigated whether the reaction between cellulose and AKD could take place. Also, we studied the reaction under homogeneous and heterogeneous conditions, respectively.

EXPERIMENTAL

Chemicals and Instruments

Commercial bleached kraft pulps prepared from hardwood (poplar) were used as cellulose samples. Purities of AKD was more than 90%, the ratio of C18/C16 was 40%:60%, the melting point was 50 °C. Lithium chloride, N,N-dimethylacetamide, potassium permanganate, and toluene were commercially available and used without further purification.

Fourier transform infrared (FTIR) spectra were recorded using a TENSOR27 FTIR spectrometer in the range of 4500 to 400 cm\(^{-1}\). The phase transformation analysis of the samples was conducted by Wide-angle X-ray diffraction (WXRD) using an X-ray diffractometer (D/max-2500/PC, Rigaku Co. Ltd., Tokyo) with CuKα radiation (40 kV, 60 mA) in the 2θ = 5° to 60° range. SEM images were observed on a JSM-6700F scanning microscope. The samples were coated with a thin layer of gold under vacuum before examination. Thermogravimetric (TG) analysis and differential thermal analysis (DTA) of the samples were carried out on a Pyris Diamond TG/DTA analyzer (STA449C/3/F, German). The TG/DTA analyses were performed with a sample weight of 14.2 mg, a heating rate of 10 °C/min, and flowing nitrogen (20 mL/min).

Reaction of Cellulose and AKD under Homogeneous Conditions

5 g of pulp was preswelled in 150 mL DMAc at 160 °C for 0.5 h. 15 mg potassium permanganate was added to the mixture as the active agent. Then the mixture was filtered to obtain the preswelled cellulose. Stock solution of LiCl in DMAc (8 %, w/w) was prepared by dissolving 7.4 g LiCl in 100 mL DMAc in a 250 mL Schott bottle. The bottle was immediately sealed to prevent moisture absorption. The mixture was stirred for 24 h until the salt appeared to be completely dissolved.

LiCl/DMAc solvent and preswelled cellulose were added to a three-necked flask equipped with a thermometer and magnetic stirrer under nitrogen atmosphere. The mixture was stirred at 100 °C for 2 h to obtain the cellulose solution; 5 g AKD was added to the cellulose solution obtained above and stirred at 100 °C for 2 h. Finally, the solution was placed under vacuum for 24 h at room temperature to obtain the casting solution.

The membranes were prepared by a phase inversion technique. The casting solution was cast on a glass plate using a doctor blade. The glass plate was quickly immersed in the gelation bath. Membrane sheets were subsequently stored in water for 24
h to remove the residual LiCl/DMAc completely to obtain the membrane. Then the composite membrane sheets were soaked in toluene to remove the unreacted AKD.

**Reaction of Cellulose and AKD under Heterogeneous Conditions**

5 g cellulose was ground with a grinder. 50 g AKD was melted at 80 °C. Then these two materials were added in three-necked flask equipped with a thermometer and magnetic stirrer under nitrogen atmosphere. The mixture was stirred at 100 °C for 12 h. Then the mixture was cooled to room temperature. The resulting mixture was soaked in toluene to remove the unreacted AKD.

**RESULTS AND DISCUSSION**

Figure 2 shows the FTIR spectra of the membrane prepared under the homogeneous conditions. Curve 1 is the spectrum of the cellulose membrane, whereas curve 2 is the spectrum of the composite membrane prepared by the reaction product of cellulose and AKD. As can be seen from the figure, the two spectra both showed the O–H stretching vibration of hydroxyl at 3406 cm⁻¹ and the characteristic absorption peak of C=O at 1063 cm⁻¹. In addition, the spectra also showed the characteristic absorption peaks of regenerated cellulose at 898 cm⁻¹ and 1159 cm⁻¹. This indicated that the cellulose was dissolved in LiCl/DMAc without degradation. Thus, the cellulose was restored to its molecular structure by regeneration. However, in curve 2, the characteristic absorption peak of β-keto ester at 1703 cm⁻¹ show that the lactone ring reacted with hydroxyl groups. The absorption peak at 721 cm⁻¹ indicated that the molecular structure of the composite membrane contains four CH₂ groups at least.

![Fig. 2. The FTIR spectra of reaction products under homogeneous conditions](image-url)
There was no absorption peak of lactone ring at 1840 cm\(^{-1}\). This indicated that unreacted AKD was removed from the composite membrane completely. Therefore, in the spectra of composite membrane, the emergence of new peaks at 1703 cm\(^{-1}\) and 721 cm\(^{-1}\) was due to the reaction products of AKD and cellulose.

Figure 3 shows the FTIR spectra of the product under the heterogeneous conditions. Curve 1 is the spectrum of cellulose, whereas curve 2 is the spectrum of the reaction products of cellulose and AKD. As can be seen from the figure, these two spectra are basically the same. They both show the O–H stretching vibration of hydroxy at 3408 cm\(^{-1}\), the characteristic absorption peak of C–O at 1059 cm\(^{-1}\), and the C–H bending vibration of CH-O at 1430 cm\(^{-1}\), and so on. It was important that there was no absorption peak of β-keto ester near 1703 cm\(^{-1}\). This indicated that there was no detectable amount of β-keto ester in the reaction products.

In summary, the crystalline region of cellulose was destroyed under the homogeneous conditions. Intramolecular and intermolecular hydrogen bonds were all disrupted. So, the activity and accessibility of hydroxy to the reagent were enhanced. AKD could react with cellulose under these conditions. But under heterogeneous conditions the reactivity of these three hydroxyl groups was restricted. The penetration of reagents was thereby restricted to the disordered regions.

In the sizing process during papermaking, AKD is emulsified with cationic starch. The emulsion is retained on the surface of the paper, and it becomes spread out on the surface during drying. This process occurs in a complex manner under heterogeneous conditions. Therefore, we considered that cellulose could not react with AKD under ideal experimental heterogeneous conditions. The reactivity of the cellulose and AKD was also not high during the sizing process. There was not enough β-keto ester present to account for the role of AKD in sizing. Previously, some scholars had detected the β-keto ester in paper sized by AKD emulsion. It is possible, however, that the detected β-keto ester was the reaction product of AKD and cationic starch.

**Fig. 3.** FTIR spectra of reaction products under heterogeneous conditions
The SEM images of the reaction products are shown in Fig. 4. As can be seen in Fig. 4(a), the surface of cellulose membrane prepared under homogeneous conditions had some circular debris. The main reason for the forming of the debris was that the solvent in the casting solution could exchange with the water in the coagulation bath during the film-forming process. Figure 4(b) shows the membrane prepared by reaction products of AKD and cellulose under homogeneous conditions. It can be seen that there were many granular features within the size range of about 10 to 100 µm. Because the solvent and the unreacted AKD had been removed completely, the granular substances were considered to be a result of phase separation involving the reaction product, β-keto ester, of cellulose and AKD. The β-keto ester function was also confirmed by FTIR analysis (Fig. 2). Figures 4 (c) and (d) show SEM images of fiber ground by physical method and the fiber that had been reacted with AKD under heterogeneous conditions respectively. As can be seen from these two figures, the cell wall of the fiber surface was destroyed as a result of the physical grinding method. There were a great quantity of fissures on the surface of the fiber. Figure 4 (d) shows that the structure of fiber surface did not change significantly compared with Fig. 4 (c). There were no granular substances on the surface of the fiber. This indicated that AKD did not react with cellulose. Therefore, there was no β-keto ester attached on the surface of fiber.

Fig. 4. SEM images of reaction products
The molecular structure of cellulose is a linear-chain polymer with a large number of hydroxyl groups. The degree of linearity enables the molecules to approach together. These behaviors are responsible for the stiff and straight chain nature of the cellulose molecules as well as the cause of the considerable tendency of the chains to organize in parallel arrangements into crystallites and crystallite strands. As can be seen from Fig. 5, the wide-angle X-ray diffraction patterns of cellulose membrane (a) showed the characteristic crystalline peaks at $\theta=21.59^\circ$ and $23.50^\circ$. These peaks correspond to the cellulose I crystal, indicating the cellulose membrane recovered the cellulose I crystalline form by recrystallization. However, the characteristic crystalline peaks at $23.50^\circ$ disappeared in the composite membrane (b), which indicated that AKD reacted with cellulose under homogeneous conditions. The reaction products destroyed the original crystalline structure of cellulose; therefore, the cellulose molecules could not completely reform their highly regular arrangement of hydrogen bonds.

![Graph showing WXRD patterns](image)

**Fig. 5.** Wide-angle X-ray diffraction (WXRD) of reaction products under homogeneous conditions

Figure 6 shows the WXRD of cellulose under heterogeneous conditions. The two curves both show the characteristic crystalline peaks at $\theta=15.38^\circ$ and $22.84^\circ$. Thus the sample was identified as the cellulose I crystal. The two curves were exactly the same. This showed that the crystalline structure of cellulose molecules was not destroyed, i.e. cellulose did not react with AKD under the heterogeneous conditions.

Figure 7 shows the TG and DTA curves of membranes prepared under homogeneous conditions. As can be seen from the TG curves of cellulose (curve 1), at the low temperature, 4.02 wt% in weight loss was observed owing to slight dehydration. However, the composite membrane (curve 2) did not have any weight loss. The pure cellulose membrane had a high hydrophilicity that could absorb moisture from the surrounding air.
In the composite membrane, long chain hydrophobic alkyl of β-keto ester arranging outward resulted in the water resistance. Therefore, weight loss of the cellulose membrane was observed at low temperature. On further heating there was a sharp weight loss, and the decomposition occurred at 290 °C both for cellulose membrane and composite membrane, with about 63.25 wt% and 67.54 wt% in weight loss, respectively. Thermopositive peaks of cellulose membrane and composite membrane occurred at 665.5 °C and 568 °C respectively. These thermopositive peaks were caused with some reactions of cellulose. An endothermic peak of composite membrane occurred at 710 °C due to decomposition or cracking reactions. This process was accompanied by a 3.35 wt % in weight loss. The decomposition reaction of β-keto ester at the higher temperature can account for the weight loss.

![Graph of WXRD](image)

**Fig. 6.** The WXRD of reaction products under heterogeneous conditions

Figure 8 shows the TG and DTA curves of fiber under heterogeneous conditions. As can be seen from the figure, these two curves were the same. The decomposition temperature occurred at 270 °C, with about 82.9 wt% and 79.44 wt% in weight loss respectively. This thermopositive peak at about 360 °C was caused by some cracking reactions of cellulose. This thermopositive peak at about 670 °C without any weight loss was caused by intramolecular rearrangement. In addition, there was no endothermic peak at high temperature in curve 2. This indicated that there was no detectable β-keto ester. If there was β-keto ester in the reaction products, the cracking reaction of β-keto ester could be happening at high temperature. There should be endothermic peak at the high temperature in curve 2.
Fig. 7. The thermograms of reaction products at homogeneous conditions

Fig. 8. The thermograms of reaction products at heterogeneous conditions
CONCLUSIONS

The reaction between AKD and cellulose under homogeneous and heterogeneous systems, respectively, was studied. The reaction products were characterized by FTIR, SEM, TGA-DTA, and WXRD. The following results were obtained.

1. The crystalline region of cellulose was destroyed under homogeneous conditions. Intramolecular and intermolecular hydrogen bonds were all disrupted. The hydroxyl groups were able to react with AKD to generate \( \beta \)-keto ester bonds.

2. Under heterogeneous conditions, the activity and accessibility of free hydroxyl groups on glucose-based rings were restricted. There was no \( \beta \)-keto ester detected in the reaction products. This proved that the reaction between cellulose and AKD would happen only under certain reaction conditions. It was difficult to achieve a significant degree of reaction under the heterogeneous conditions.

3. The viewpoint that the \( \beta \)-keto ester generated by the reaction between AKD and the hydroxyl groups of cellulose at a fiber surface plays an important role in the sizing process remains without strong supporting evidence.

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REFERENCES CITED


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Song et al. (201#). “AKD reaction mechanism,” BioResources 7(1), 652-662.