

AKD Sizing Mechanism (I)

- Effect of Water on AKD Reactivity -

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1. Introduction

Since alkyl ketene dimer (AKD) was introduced to the papermaking industry in the 1950s (1), AKD has been widely used as a neutral sizing agent. To elucidate the sizing mechanism, whether a beta-ketoester bond is formed between AKD and cellulose or AKD is physically trapped within the cellulose matrix has caused extensive debates. Formation of covalent ester bonds between AKD and hydroxyl groups in cellulose molecule has been reported as a major mechanism for the appearance of AKD sizing (1-6). Several evidences for the formation of beta-ketoester are as follows: a) an insoluble sheet was left when paper sized with AKD was put into cuprammonium solution which is a good solvent for cellulose (1); b) a certain amount of the size material was not solvent extractable and thus the sizing degree of paper remained after solvent extraction (2-4); c) a beta-ketoester was isolated from the reaction products of AKD with various cellulosic materials (5); and d) an IR absorption band due to carbonyl group of ester was detected in FTIR spectrum of AKD sized paper (6).

On the other hand, some reports (7-11) suggested that AKD may not react with cellulosic hydroxyl groups under the conditions of papermaking. Rohringer *et al.* (12) showed that no substantial amount of AKD reacted chemically with cellulose, and the formation of beta-ketoester was not critical for developing an efficient size degree. More recently, Isogai *et al.* (13) proposed, from the analyses of the extractives after cellulase treatment of AKD sized paper, that AKD and its hydrolyzed product (ketone) are physically trapped in the cellulose matrix. The attempts to detect any covalent bond formed between AKD and the hydroxyl group using model compounds were unsatisfactory due to the difficulty in the phase separation of the hydrophobic and hydrophilic reactants (8,12). No evidence for the formation of beta-ketoester was obtained from the neutral heterogeneous base-catalyzed reaction of octadecyl ketene

dimer with methyl alpha-D-glucopyranoside and also with cellulose pulp (12). In an acidic homogeneous condition (8), no reaction was also observed between tetradecyl ketene dimer and methyl beta-cellobioside.

The following two reports claimed the direct evidence. Nahm (5) reported the IR bands of the beta-ketoester from a base-catalyzed reaction system of AKD with various cellulosic materials in organic solvent. However, the reaction conditions were quite different from that of the actual papermaking process. Lindstrom *et al.* (6) presented, as a direct evidence, the IR absorption band due to beta-ketoester in a AKD sized paper, but it was unclear because of the poor resolution of ATR mode.

From the literature survey, the difficulty for detecting the direct evidence of beta-ketoester bond can be categorized by two reasons. The one is in making a proper reaction system similar to the papermaking process, and another is the detection limit of instruments. It is very difficult to detect considerable amounts of AKD that reacted with cellulose fibers in the paper sheets, because the amounts of AKD retained are usually below the detection limits of most techniques. Therefore, in this article, cellulose/AKD blends were prepared under various conditions where the water contents were strictly controlled, and the FTIR spectra were obtained from three components blend system (AKD/cellulose/water) to investigate whether the beta-ketoester formed or not.

2. Experimental

2-1. Materials

Alkyl ketene dimer (AKD) was provided as a wax from Nippon Oils Co., Ltd., Japan. Hydrolyzed AKD was prepared from AKD wax by hydrolytic treatment with 0.1N NaOH solution at 85°C for 20 hrs, followed by an acidification to pH 4 with 0.1N HCl solution. AKD and its hydrolyzed product used in this work were recrystallized from hexane repeatedly for three times, and confirmed by FTIR, ¹H-, and ¹³C-NMR. The cellulose sample used was a cotton linter with a degree of polymerization of 1200. HPLC-grade N,N-dimethylacetamide (DMAc) and N,N-dimethylformamide (DMF) were purchased from Aldrich Chem Co., Inc., and stored for more than one week over molecular sieves 3Å. Lithium chloride (LiCl, Aldrich Chem. Co., Inc.) was dried at 125°C for one week and stored in a desiccator. Other chemicals used in this work were commercial products of the highest available purity and used without further purification.

2-2. Preparation of the samples for FTIR study

In order to elucidate the effect of water in AKD-cellulose reaction, two types of reaction systems were prepared for the spectroscopic study; a reaction system containing water and a water-free system. The reaction system containing water was prepared by the mixing of two solutions of AKD in DMF and cellulose in LiCl/DMAc, which was referred to as cellulose/AKD blend.

LiCl/DMAc used as a common solvent for cellulose was prepared at a salt concentration of 5 wt.% by stirring a mixture of a proper amounts of LiCl and DMAc at room temperature. The cellulose sample was treated by a solvent exchange technique (14-16). The cellulose successively washed with water, methanol, and DMAc, was added to the LiCl/DMAc solution at room temperature so as to give an actual cellulose concentration of 1.0 wt.%. The cellulose fibers dissolved gradually in the solvent with continuous stirring over a few weeks. After stirring for 3 weeks, the viscous cellulose solution was filtered through a coarse fritted-glass funnel under high vacuum. AKD solution (1.0 wt.%) in DMF was prepared by stirring at 50°C over 3 hours.

The solutions of cellulose and AKD were mixed at 50°C in weight percent ratio of 80/20 (cellulose/AKD). The mixed solutions were stirred for at least one day and then poured into a circular glass tray with a flat bottom. By conditioning in a saturated moisture chamber for three days, the cellulose/AKD blends were slowly precipitated in a gel form because the moisture atmosphere acts as a coagulant. The gels were steeped for one day in water which was exchanged for fresh aliquots several times, and finally washed with tap water for at least three days to remove LiCl, DMAc and DMF from the blend (17). The washed sample, water-swollen cellulose/AKD blend gel, was then processed to pressing and heat treatment.

The water-free reaction system was prepared as follows. Cellulose homopolymer films were also prepared by the same coagulation method as described above and then, dried in an oven at 125°C for 6 hours. A stock solution of AKD (10 wt.%) was prepared by dissolving the AKD in chloroform to prepare cellulose films coated with AKD at completely dried condition. The dried cellulose homopolymer films were immersed into a AKD stock solution for 30 minutes, squeezed with Whatman No. 1 filter paper and finally air dried at room temperature.

2-3. Measurements

Perkin-Elmer SPECTRUM 2000 FTIR spectrophotometer was used for IR measurements in the transmission mode. Samples for the FTIR measurements were in the form of films. The wavenumber region ranged from 4000 to 400 cm^{-1} ; a total of 32 scans with a 1.0 cm^{-1} resolution were signal-averaged and stored. ^1H - and ^{13}C -NMR spectra were recorded on a Bruker AM-300 and AM-75 spectrometer, respectively. Deuterated chloroform was used as a solvent, and chemical shifts were referenced to tetramethylsilane.

2-4. Control of water content

In the preparation of cellulose/AKD blend gels with various water contents, the coagulated water-swollen blend gels were pressed by using a handsheet press according to Tappi Standard Method T205 sp-95. The pressing time of the handsheet press was varied to control the water content in the blend gels.

3. Results and Discussion

3-1. Reaction of AKD in the absence of water

Figure 1A shows FTIR spectra of AKD and its hydrolyzed product. The absorption bands at 1848 and 1722 cm^{-1} are assigned to C=O and C=C stretching vibrations, respectively, which appear at relatively higher wavenumbers than the ordinary bands because of a highly strained lactone ring (6,18). These two bands are completely disappeared by the hydrolysis of AKD, while a new band due to C=O stretching vibration of dialkylketone appears at 1707 cm^{-1} . AKD and its hydrolyzed product are also well assigned by ^1H - and ^{13}C -NMR spectra shown in Figures 1B and 1C, respectively.

The possibility of AKD to form beta-ketoester with cellulose is investigated using a water-free model system consisting of thin cellulose film soaked into the AKD stock solution (10% AKD in chloroform). Clear FTIR spectra were obtained. Figure 2 shows IR absorption bands of the cellulose films which are coated with AKD before and after heating. Two absorption bands at 1848 and 1722 cm^{-1} due to the carbonyl and the carbon-carbon double bond located at the lactone ring of AKD, respectively, are gradually decreased by heating at 125°C, and then completely disappeared after heating for 360 minutes. Instead, two new bands appeared at 1737 and 1714 cm^{-1} due to carbonyl stretching vibrations of beta-ketoester bonds and neighboring ketone carbonyls,

respectively (5). This result indicates that all of the AKD was capable of completely reacting with cellulose in the absence of water, and furthermore, in a neutral condition without catalyst.

3-2. Reaction of AKD in the presence of water

The effect of water on the reaction of AKD with cellulose has been investigated using water-swollen cellulose/AKD blend gels. Cellulose gel blended with AKD in the weight ratio of 80/20 was used as a model experiment of papermaking. The water-swollen blend gel (water content of 94%) is directly heated at 125°C between two pieces of teflon plates. IR spectra of the blend films after heating at 125°C are shown in Figure 3. No considerable amounts of beta-ketoesters are observed by heating the blend gels in the presence of excess water. A new absorption band at 1707 cm^{-1} with a shoulder (1700 cm^{-1}) may be due to carbonyl stretching vibration of dialkylketone in the hydrolyzed product of AKD (Figure 1A). This result indicates that AKD, in the presence of excess water, seems to be consumed exclusively by the reaction with water in cellulose matrix to form a ketone rather than to react with hydroxyl groups of cellulose.

Figure 3 also shows that a trace amount of AKD still remained after 60 minutes heating. Thereafter, no further changes in IR spectra of the blend films are detected by additional heating up to 600 minutes. The water content at 125°C of the blend gels is plotted in Figure 4 as a function of heating times. Figure 4 shows that water is completely removed from the blend by 60 minutes heating. Thus, the residual AKD can not react with cellulose to form a beta-ketoester despite of the absence of water after 60 minutes heating. This goes against the result of the previous section (Figure 2) whereby AKD completely reacted with cellulose in the absence of water. After 60 minutes heating, in the resultant water-free condition, the residual AKD does not react with cellulose, and also it can not be hydrolyzed due to the absence of water. No further reaction even in the water-free condition may be due to the steric hindrance from the hydrolyzed product of AKD. The steric hindrance seems to occur because the hydrolyzed product blocks the active sites of cellulose (hydroxyl groups), thus preventing the esterification reaction to proceed with the residual AKD.

3-3. Effect of water content on AKD reaction

The results of the previous experiments have indicated that AKD may completely

react with hydroxyl groups of cellulose to form beta-ketoester under the water-free condition, while almost all AKD may be converted to dialkylketone by hydrolysis reaction in the presence of excess water. However, in the latter case, the water content (94%) in the blend gel is much higher than that of the practical papermaking condition. The pressed wet web generally contains 60~70% of water in the papermaking process.

To investigate the effect of water content on the reaction of AKD, the water contents in the water-swollen blend gels were adjusted to 94%, 69%, 30%, and 7% by pressing in accordance with TAPPI Standard Method T205 sp-95. The blend gels having different water contents were then heated at 125°C for 50 seconds on a rotary drum dryer and the reaction was observed using FTIR spectroscopy.

Figure 5 shows the IR spectra of the cellulose/AKD blend (80/20, w/w) films after heating. Figure 5A shows that a small band appears at 1735 cm^{-1} due to ester bond between cellulose and AKD. The intensities of the band increase with decreasing water content. This indicates the lesser the water in the blend gels, the larger the amounts of beta-ketoester. This conclusion is also supported by the broad shoulder at 1717 cm^{-1} due to neighboring ketone carbonyl of beta-ketoester appearing at the lowest water content ((d) in Figure 5A). The two bands at 1735 and 1717 cm^{-1} were already assigned in Figure 2 as the absorption bands of the carbonyl stretching vibrations corresponding to beta-ketoester linkage and its neighboring ketone, respectively.

These results agrees with the report of Lindström *et al.* (3) which pointed out that only little chemical reaction takes place before the paper sheet is essentially dried. Although several researchers (2,6,19) presented that the formation of chemical covalent bond is a main mechanism of AKD sizing, their studies of AKD reaction were based on the results that AKD sized paper was heated for a long time in the absence of water. However, the condition of such a heating time in the absence of water can not exist in the papermaking system. More recently, Bottorff (20) reported more definitive evidences of the beta-ketoester formation using the solid state ^{13}C -NMR. In his work, however, AKD was applied to paper from solution and thus the effect of water on the reaction was omitted.

Figure 5B also shows another two absorption bands at 1707 and 1700 cm^{-1} resulting from AKD reaction with water. It was reported that AKD is hydrolyzed to the dialkylketone via an evolution of CO_2 gas from an unstable intermediate, beta-ketoacid (21). If so, the ketone carbonyl group of the dialkylketone has to show only one

absorption band at 1707 cm^{-1} . Spectra in Figures 5B and 3, however, exhibited two absorption bands at 1707 and 1700 cm^{-1} . The two bands indicate that another reaction product, in addition to the dialkylketone having carbonyl group, may exist in the hydrolyzed products of AKD. The band at 1707 cm^{-1} was already assigned in Figure 1A as carbonyl absorption of dialkylketone in the hydrolyzed product of AKD. Thus the band at 1700 cm^{-1} may be considered as carbonyl absorption from a beta-ketoacid. The absorption intensity at 1700 cm^{-1} is gradually increased with decreasing the water contents in the blend gels before heating (Figure 5B).

It is generally believed that the beta-ketoacid in the reaction of AKD may not be isolated because it is so unstable that it easily turns to a ketone through decarboxylation. However, some reports (10,22) rather indicated that the formed beta-ketoacid was significantly stable. These reports imply that there are at least two hydrolyzed products of AKD, e.g. ketone and beta-ketoacid, in the neutral condition.

Based on the experimental results, possible AKD reactions are schematically illustrated in Figure 6, which shows that the reaction products of AKD by heat treatments can be varied in the three components (cellulose/AKD/water) blend gels depending on their water contents.

4. Conclusions

The reactions of AKD with hydroxyl groups of cellulose are examined in the absence and presence of water using water-swollen blend gels (cellulose/AKD, 80/20, w/w) and cellulose films soaked into AKD solution (10 wt.% in chloroform). In this work, direct infra-red spectroscopic analysis proved that AKD reacts with cellulose as well as water depending on the water content in the blend.

AKD reacts competitively with cellulose and water. However, the reaction with water is predominant. In papermaking process, where a wet web after pressing contains 60~70% of water, most of AKD seems to be hydrolyzed to dialkylketone without a reaction with hydroxyl groups of cellulose to form beta-ketoester linkage during the drying process. Therefore, the presence of water can strongly influence on the mechanism of AKD reaction. A complete reaction scheme between AKD and cellulose in the papermaking system is proposed.

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