

AKD Sizing Mechanism (II)

- Hydrogen Bonding -

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1. Introduction

The sizing mechanism of alkylketene dimer (AKD) has been extensively studied during the last four decades. The proposed mechanism of AKD sizing was that the long and hydrophobic alkyl chains in AKD molecules become firmly oriented at the fiber surface through the formation of a covalent ester bond (beta-ketoester bond), which may render a paper resistant to liquid wetting and penetration. The main evidence of the beta-ketoester formation between a lactone ring of AKD and a hydroxyl group of cellulose was mainly based on extraction experiments from AKD sized sheets. It has been believed that a portion of AKD was not solvent extractable and thus a sizing degree of the paper still remained after the solvent extraction (1-4).

On the other hand, many researchers (5-12) still have concerns on the reactivity of AKD, which may not allow AKD to react with cellulose under the conditions for papermaking. Recently, Isogai *et al.* (10) reported that AKD and dialkylketone (hydrolyzed product of AKD) were physically adsorbed on pulp fibers and fillers without forming the beta-ketoester. The report explained that AKD and dialkylketone, trapped in the cellulose matrix by a curing treatment, could not be extracted completely by the Soxhlet extraction with chloroform.

In the previous paper (13), the reactivity of AKD toward cellulose and water was examined by FTIR analysis using the water-swollen cellulose/AKD blend gels as a model of AKD sized paper web. The results revealed that AKD reacted rarely with cellulose to form the beta-ketoester under the presence of water and that most of AKD was hydrolyzed to dialkylketone and beta-ketoacid. Also it was proposed that AKD did not form a significant amount of covalent bonds with cellulose in a papermaking system with excess water. Therefore, the attachment of AKD to cellulose and the development of sizing degree might be explained by a mechanism other than or in addition to the formation of the beta-ketoester.

Although it is unclear whether size development is induced by the reaction of cellulose and AKD, it is generally accepted that all internal sizing agents must meet the following requirements for effective sizing features (14): a) retention on the paper web; b) distribution over the fiber surfaces; c) adhesion to the fibers; and d) orientation on the fiber surfaces to present a hydrophobic surface to the penetrant.

Metzler (15) proposed the hydrogen bonding formation between cellulose and AKD as a primary bonding mechanism, but without direct evidence. Pisa and Murckova (12) detected changes in the intensities of carbonyl, methylene, and aliphatic peaks in the frustrated multiple internal reflectance (FMIR) spectra of the AKD sized sheet as a function of time. They interpreted that the changes were attributed to a slow orientation of AKD by the hydrogen bonding between lactone oxygen and hydroxyl group of cellulose. Recently, Kondo *et al.* (16-19) characterized the hydrogen bonding between cellulose and synthetic polymers using regioselectively substituted methylcelluloses as cellulose model compounds. They examined the interactions of cellulosic blends from the viewpoints of the correlation between hydrogen bonding formation and regiochemistry of OH groups in cellulose using IR spectroscopy; differential scanning calorimetry, and polarized optical microscopy. A regioselectively methylated cellulose derivative, 2,3-di-*O*-methylcellulose (23MC) (20), has the primary OH group at the C-6 position as shown in Figure 1, and can form inter- and intra-molecular hydrogen bonds (21). Therefore, 23MC should be useful in correlating hydrogen bonding formation and physical properties.

In this study, the possibility of the hydrogen bonding between cellulose and AKD was examined by FTIR analysis using 23MC as a model compound of cellulose. If a certain interaction such as the hydrogen bonding between cellulose and AKD exists, it can be detected by the comparison of IR spectra of blend sample with those of individual materials, 23MC and AKD. Hydrogen bonding between two materials should strongly affect their IR absorption frequencies particularly in the functional groups involved in the interaction (22).

2. Experimental

2-1. Materials

A commercial alkylketene dimer (AKD) was purchased as a wax form from Nippon Oils Co., Ltd., Japan. The AKD used in this work was recrystallized from hexane three times, and its structure was characterized by FTIR, ¹H-, and ¹³C-NMR spectroscopy

according to our previous work (13). 2,3-Di-*O*-methylcellulose (23MC) was prepared by Kondos method (20). 23MC was found to have a uniform structure, that is, every structural unit of it was regioselectively substituted. The weight average molecular weight of 23MC was approximately 2×10^4 on the basis of their SEC (size exclusion chromatography) curve calibrated with polystyrene standards. HPLC-grade *N,N*-dimethylacetamide (DMAc) was purchased from Aldrich Chemical Co., Inc., and stored for more than one week over Linde molecular sieves 3Å. Lithium chloride (LiCl, Aldrich Chemical Co., Inc.) was dried at 125°C for one week and stored in a desiccator until used. Other chemicals used in this work were commercial products of the highest available purity and used without further purification.

2-2. Preparation of blend samples

The mixed solvent (chloroform : methanol = 4 : 1) and chloroform were used for the preparation of 23MC and AKD stock solutions, respectively. Concentrations of the solutions were 0.8 wt.% for 23MC and 1.0 wt.% for AKD sample. All solutions were filtered and stored in a closed container under nitrogen atmosphere. The solutions separately prepared were mixed in the desired proportions at room temperature. The relative compositions of the two samples in the mixed solutions were 99/1, 98/2, 97/3, 96/4, 95/5, 94/6, 93/7, 90/10, 85/15, and 80/20 (23MC/AKD) by weights. After stirring for more than two days at 30°C, blend films were prepared by casting from the mixed solution. One gram of each blended solution was poured into a flat-bottomed polypropylene tray (Nalge Co., USA) and conditioned to room temperature under reduced pressure for one week. The mixed solvent was evaporated very slowly at room temperature to yield an casted film. It was further dried for another one week under high vacuum at 40°C to remove any trace of solvent and moisture from the blend films. The casted film was used for measurements of Fourier transform infra-red (FTIR) spectroscopy and differential scanning calorimetry (DSC). All the films prepared in this work were sufficiently thin (~10 micrometer) to obey the Beer-Lambert law (23).

2-3. Measurements

Fourier transform infra-red (FTIR) spectra were obtained by a Perkin-Elmer SPECTRUM 2000 FTIR Spectrophotometer. Samples for FTIR measurements were prepared by the casted film or a KBr disk technique. The wavenumber region ranging from 4000 to 400 cm^{-1} were scanned 64 times at 0.5 cm^{-1} resolution. The intensities with IR absorption range of O-H and C=O stretching vibrations were normalized to

compare peak maxima and shapes of the spectra. The spectra were normalized and deconvoluted by using the software programs named Spectrum for Windows and PE Grams 2000, respectively. Differential scanning calorimetry (DSC) was performed on ~7.0 mg of blend films using TA Instrument Model 2910 in nitrogen atmosphere at a heating rate of 10°C/min. The instrument was calibrated with an indium standard.

3. Results and Discussion

To investigate the interaction between cellulose and AKD, a blend sample of both materials should be required. Unfortunately, cellulose is insoluble in most common organic solvent because it has three strongly hydrogen-bonded hydroxyl groups in a glucose residue (24,25). Therefore, it is almost impossible to prepare blends or solutions containing both hydrophilic cellulose and hydrophobic sizing materials. On the other hand, 2,3-di-*O*-methylcellulose (23MC) having two methoxyl groups at C-2 and C-3 position of the glucose unit as a cellulose model compound is dissolved easily in organic solvent systems, which makes it possible to prepare 23MC/AKD blend solution.

Three different hydroxyl groups in the anhydroglucose unit of cellulose can easily be engaged in inter- and intra-molecular hydrogen bonding. Thus, in general, the IR spectrum of cellulose displays a broad band in the range of OH stretching vibrations. Since two regioselectively methylated cellulose derivatives, 23MC (20) and 6-*O*-methylcellulose (6MC) (26), have less hydroxyl groups to decrease possibilities for hydrogen bonding, they both show narrow OH stretching vibration bands (21). Of these cellulose derivatives, 23MC is especially useful to investigate the interaction of cellulose, because the OH groups at the C-6 position in 23MC may primarily form a range of inter-molecular hydrogen bonds with other molecules. The absorption band due to the hydrogen-bonded OH group in 23MC is much narrower than that for cellulose, because of controlled hydrogen bonding. Thus, the peak shifts in the range of OH stretching vibration of 23MC accompanied by a certain interaction can be detected more clearly than cellulose.

3-1. FTIR Characterization of 23MC/AKD blends

The specific interactions in 23MC/AKD blend system was examined using FTIR spectroscopy. Figure 2 shows the IR absorption bands due to the OH group for 23MC in the blend. In this Figure, both the dotted line and the solid lines show the OH absorption bands in 23MC homopolymer film and 23MC/AKD blend films, respectively.

The peak maxima of the blend samples are shifted to lower wavenumbers by the maximum of 5 cm^{-1} from the position of the OH absorption band for 23MC homopolymer. The extent of the shift is increased with increasing AKD content in the blend film. Since 23MC has only a primary hydroxyl group at the C-6 position of the anhydroglucose unit and AKD has no significant OH absorption band as Figure 3 shows, this shift is due to the interaction with the OH groups in 23MC. In addition to the change of peak maxima, the shapes of the OH absorption bands for the blends represented by solid lines in Figure 2 are differed considerably from that for 23MC (dotted line). This suggests a rearrangement of the hydrogen bonding by blending of 23MC with AKD. If there is no interaction between 23MC and AKD, the OH absorption bands of the blend films should coincide with that of 23MC homopolymer. Therefore, the above changes in peak maxima and the band shape indicate that the OH stretching vibration for 23MC in the blend film is affected by a certain interaction between 23MC and AKD. Furthermore, the interaction is supposed to be hydrogen bonding between the lactone oxygen of AKD and hydroxyl group of 23MC, because AKD molecule has no other functional group affecting the OH stretching vibration of 23MC.

The OH absorption bands of 23MC/AKD blends were deconvoluted into three components by curve fitting method (mixed mode of Gaussian and Lorentzian) to identify the difference between the OH bands for 23MC/AKD blends and that for 23MC homopolymer as shown in Figure 4. The Figure shows a typical OH absorption band with 80/20 (23MC/AKD, w/w) blend composition and the deconvoluted three peak components (solid line). And the OH absorption band is compared with that for 23MC homopolymer film deconvoluted by the same method (dotted line). These components in the region of OH absorption for cellulose are well defined as free OH (27), intra- and inter-molecular hydrogen-bonded OH (17,18,24) for the deconvoluted bands (A), (B), and (C) in Figure 4, respectively. The percent of relative area of each deconvoluted peak attributed to the different OH component were calculated by the following method.

$$\begin{aligned} & \text{Relative area of deconvoluted peak } X (\%) \\ & = [\text{Area of peak } X / \text{Total area of peaks } (A + B + C)] \times 100 \end{aligned}$$

By considering the results of Figures 2 and 4, it can be easily known that the relative ratio of OH component due to the inter-molecular hydrogen bond (trace C) is gradually increased until AKD content reached to 15 wt.% and then saturated. On the other hand, the OH component attributed to the intra-molecular hydrogen bond (trace B)

shows an opposite behavior to that of the inter-molecular hydrogen bonds with increasing AKD content. This indicates that some of the OH groups at C-6 position of 23MC is changed from the intra-molecular hydrogen-bonded OH to the inter-molecular one between 23MC and AKD by the rearrangement of the hydrogen bonding.

Figure 5 shows the change of the spectra of C=O frequencies. The C=O stretching vibrations of the 23MC/AKD blend films are slightly shifted to lower wavenumbers from that for AKD. The shifts of the peak maxima are increased with increasing AKD contents, even though the maximum shift (approximately 1.2 cm^{-1}) is very small. Since the IR spectra were obtained by the resolution of 0.5 cm^{-1} , the difference of 1.2 cm^{-1} can be considered as a significant change, indicating the C=O group of AKD may participated in hydrogen bonding engagement with OH group in 23MC molecular chain. The results from Figures 2 and 5 have a good agreement with the general theory on IR band shift due to hydrogen bonding (22). That is, by the hydrogen bonding, the absorption band of proton donor group (OH) shifts to lower frequencies usually with band widening, whereas that of the acceptor group (C=O) is shifted to a lesser degree than the proton donor group.

3-2. Effect of heating on hydrogen bonding

The casted films of 23MC/AKD blends were heated at 125°C for 30 minutes prior to IR measurement to investigate the effect of heat treatment on the hydrogen bonding. Figure 6 shows OH absorption bands for blend films before and after heating. The solid lines and dotted lines in the Figure are OH bands for the heat-treated 23MC/AKD blend films and the heat-treated 23MC homopolymer film, respectively. The OH band for the casted blend film with 80/20 (23MC/AKD, w/w) blends is also represented by a dash-dot line. Absorption bands due to the hydrogen bonding for the casted 23MC/AKD blend films (dotted lines) are changed to the solid lines by heating the blend films at 125°C . The OH peak maxima of the heat-treated blend films are shifted to higher wavenumbers by the maximum of 7.0 cm^{-1} from that for 23MC homopolymer, and by 12.0 cm^{-1} from that for the as-cast blend film without heating. The peak shape is also changed. That is, in the heat-treated blend films, the OH component due to the presence of free hydroxyl group is increased as described in Figure 4, trace (A). The peak maxima and band shape of the heat-treated blend films represented by the solid line are not the same as the spectrum for 23MC (dotted line) but also for the as-cast film (dash-dot line). This indicates that a new arrangement of hydrogen bonds may occur by heating the blend film. Considering the deconvolution result of Figure 4(A), the shift to higher wavenumbers means the increase of the free hydroxyl groups

without hydrogen bonding. Increasing of free hydroxyl groups implies that the present hydrogen bondings between OH groups of 23MC and C=O groups in AKD molecule are interrupted by the heat treatment.

Figure 7 shows a typical IR region of heat-treated blend films. Two absorption bands at 1848 and 1722 cm^{-1} due to C=O and C=C stretching vibrations present at lactone ring of AKD (dotted line), respectively, are completely disappeared by heating the 23MC/AKD blend films (solid line). Then, two bands appeared at 1737 and 1717 cm^{-1} , which were already defined by the peaks due to the stretching vibrations of carbonyl groups of the beta-ketoester bond and the neighboring ketone, respectively (13). The formation of beta-ketoester in the heat-treated 23MC/AKD blend system is in good agreement with the result that AKD can completely react with cellulose by heat in water-free condition as reported in our previous paper (13). The DSC spectrum of the heat-treated blend film (Figure 8) also shows the reacted AKD with 23MC to form a beta-ketoester bond. The DSC spectrum of the heat-treated 23MC/AKD (80/20, w/w) blend film shows a clear melting point at 118°C (Figure 8, trace A), which is different from that of AKD (trace B). And it is also different from the spectrum of dialkylketone, a fully hydrolyzed product of AKD, represented by trace (C) as a reference. Since the 23MC homopolymer does not melt until it thermally degrades, the clear melting point of the heat-treated blend (trace A) indicates the formation of a chemical bond between 23MC and AKD.

The experimental results indicate that the hydrogen bonding may occur in 23MC/AKD blend between the hydroxyl group of cellulose and the carbonyl group of AKD. However, the hydrogen bonds present in 23MC/AKD blend system are not so simple due to rearrangements of hydrogen bonds by blending followed by heating process. The possible hydrogen bonds, which can be existed in this blend system, are illustrated schematically in Figure 9.

Since 23MC having free OH groups at the C-6 position are comparatively flexible, inter-molecular hydrogen bonds may be formed favorably in 23MC homopolymer film. The OH groups should also form intra-molecular hydrogen bonds with ether oxygen at the adjacent C-2 position (24), as depicted in Figure 9 (A). Some of the inter- and intra-molecular hydrogen bonds present in 23MC homopolymer should be disrupted by blending with AKD (Figure 9 (B)). That is, the C-6 OH groups engaged in the inter-molecular hydrogen bonding with other 23MC molecule and in the intra-molecular one with C-2 OH groups of the same molecule are changed to a new inter-molecular hydrogen bonding with carbonyl groups of AKD. The formation of new hydrogen

bonds is supported by the result that the relative ratio of OH component due to the inter-molecular hydrogen bonding is gradually increased with increasing AKD content, while OH component attributed to the intra-molecular one is decreased by blending (Figures 2 and 4).

As mentioned in Figures 7 and 8, almost all AKD can react completely with 23MC to form the beta-ketoester bond by the heating treatment. Thus, the hydrogen bond present in 23MC/AKD blend is disappeared by the formation of ester bond when the blend is heated under the absence of water (Figure 9 (C)). Since AKD is firmly attached to 23MC through the ester bond, the inter-molecular hydrogen bonds present in 23MC/AKD blend may be disrupted by the long alkyl chain. The disruption of hydrogen bonding is in good agreement with the result of Figure 6, which shows IR peaks of the heat treated 23MC/AKD blend films shift to higher wavenumbers due to the increase of the free hydroxyl component.

4. Conclusions

The interaction between cellulose and AKD was examined by the analysis of FTIR spectra using 23MC as a model compound of cellulose. The model study showed that an interaction, which may be hydrogen bonding between hydroxyl group at C-6 position of 23MC and lactone oxygen in AKD molecule, was present. The formation of hydrogen bonding in 23MC/AKD blend system could be considered as follows:

As an initial stage, the hydroxyl groups at the C-6 position of 23MC had their own inter-molecular hydrogen bonding between 23MC homopolymers as well as intra-molecular one with ether oxygen at the adjacent C-2 position. By blending of 23MC with AKD, some of the inter- and intra-molecular hydrogen bonding was changed to another inter-molecular one with AKD. The changed hydrogen bonding in 23MC/AKD blend system was rearranged once more by the heat treatment because of the formation of beta-ketoester bond. Formation of the ester bond implies a disappearance of active sites for the hydrogen bonding. Furthermore, the long alkyl chains of AKD molecule, which were firmly linked to 23MC through beta-ketoester bond, had to be located between OH groups of 23MC homopolymers and prevent the inter-molecular hydrogen bonding, and then, rendered to free OH groups.

From the model study, it could be suggested that AKD might be attached and oriented on the cellulose surface by the formation of hydrogen bonding and ester bonding at the blending and heating stage, respectively. However, the results of this

work were obtained from 23MC/AKD blend under the water-free system which was not the same as the papermaking condition. Thus, an interaction study on the cellulosic blend with the hydrolyzed product of AKD is also needed because almost all AKD were hydrolyzed to dialkylketone at drying process in the papermaking condition, as reported in our previous paper (13).

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