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Regioselectively substituted 2,3–di–*O*–methylcellulose (23MC) was used as cellulose model in blends with alkylketene dimer (AKD). The interaction between sizing materials (AKD and its hydrolyzed product, h–AKD) and cellulose were examined by the analyses of FTIR spectroscopy. This model study showed that the primary hydroxyl groups at C–6 position of 23MC were engaged in hydrogen bonding with lactone oxygen in AKD or its ketone molecule. In addition, these hydrogen bonds formed in the AKD/23MC or h–AKD/23MC blends could be rearranged during drying and heating treatment because long alkyl chain of AKD covalently linked with 23MC disturbs the hydrogen bonding by increasing in their free hydroxyl groups.

INTRODUCTION

The mechanism of alkylketene dimer (AKD) sizing has been extensively studied during last 40 years. The proposed mechanism of AKD sizing was that long and hydrophobic alkyl chains of AKD become firmly oriented at surface of fibers through a formation of covalent ester bonds, and it rendered paper resistant to liquid wetting and penetration (Davis *et al.*, 1956; Roborts and Garner, 1985; Lindström and Söderberg, 1986; Nahm, 1986; Ödberg *et al.*, 1987; Roberts, 1992).

On the other hand, many researchers (Pisa and Murckova, 1981; Roberts and Garner, 1984; Gess and Lund, 1991; Rohringer *et al.*, 1985; Isogai *et al.*, 1992; Taniguchi *et al.*, 1993) questioned the reactivity of AKD, and suggested that AKD would not react with cellulose under the conditions of papermaking. The reaction of AKD in papermaking takes place with water molecules, and is reported to be faster than the reaction with cellulose (Bottroff and Sullivan, 1993; Roberts, 1996; Seo and Cho, 2005).

In the previous paper (Seo and Cho, 2005), the reactivity of AKD toward cellulose and water was examined by FTIR analysis by using AKD/cellulose blend films as a model of AKD sized sheet. Results of the study revealed that AKD reacted rarely with cellulose to form β–ketoester in presence of water and most of AKD was hydrolyzed to ketone and β–ketoacid. Also it was known that water–free condition was required to form β–ketoester linkages. Therefore, it was proposed that AKD did not react with cellulose at least during drying process in papermaking systems with a lot of water. Although it is still unclear whether size development is induced by the reaction of AKD with cellulose, it is gen-

erally accepted to involve three steps (Roberts, 1996; Scott, 1996; Eklund. and Lindstrom, 1991).

The first and second steps are well understood, but hydrophobicity of the sized paper is not fully understood. Possible ways of redistribution of sizing agents on fiber surfaces include wetting spreading (Garnier *et al.*, 1998; Garnier and Godbout, 2000; Shen and Parker, 2001), surface diffusion of size molecules in the form of an autophobic mono–layer and vapour diffusion and adsorption at paper surfaces (Yu and Garnier, 1997; Seppanen and Tiberg, 2000; Yu and Garnier, 2002). Metzler (1983) supposed that the primary bonding mechanism was hydrogen bond formation, but without direct evidence. Pisa and Murckva (1981) detected changes in the intensities of carboxyl, methylene, and aliphatic peaks in the frustrated multiple internal reflectance (FMIR) spectra of the AKD sized sheet as a function of time. They interpreted those changes came from slow orientation by hydrogen bonding between the lactone oxygen and the hydroxyl group of cellulose. It was suggested that this orientation caused the hydrophobicity of the AKD sized sheet. In addition, Kondo *et al.* (1994) reported that the hydrogen bonding formation between celluloses and synthetic polymers could be detected and characterized by FTIR analysis using regioselectively substituted methylcellulose. They detected the hydrogen bonding between hydroxyl groups of methylcelluolse and functional groups of synthetic polymers by the analysis of changes of infrared absorption of O–H or C–O.

In this study, the possibility of the hydrogen bonding between AKD and its ketone and cellulose was examined by FTIR analysis using 2,3–di–*O*–methylcellulose as a model compound of cellulose. If a certain interaction such as a hydrogen bonding between AKD (or its ketone) and cellulose is in existence, it can be detected by the comparison of the infrared spectrum of the blend sample with those of original materials (*i.e.*, AKD (or ketone) and 23MC). The reason of that was hydrogen bonding between AKD and cellulose should affect infrared absorption frequencies of the functional groups involved in the

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EXPERIMENTAL

Materials

Alkylketene dimer (AKD) of a commercial product (Nippon Oils Co. Ltd.) was used. Hydrolyzed AKD (h–AKD) was prepared from the hydrolytic treatment of AKD wax as in the previous paper (Seo and Cho, 2005). AKD and h–AKD used in this work were recrystallized from hexane three times, and their structures were characterized by FTIR, ^{1}H–and ^{13}C–NMR spectroscopy (Seo and Cho, 2005). 2,3–di–*O*–methylcellulose (23MC, Fig. 1 (B)) as a model compound of cellulose was prepared from cotton linter with a degree of polymerization of 1 200 by Kondo's method (Kondo, 1994). 23MC was found to have a uniform structure, and every structural unit of them was regioselectively substituted. The weight–average molecular weight of 23MC was approximately 2×10^4. HPLC–grade N,N–dimethyl–acetamide (DMAc) was purchased from Aldrich Chem. Co. Inc., and stored for more than one week over Linde 3Å molecular sieves. Lithium chloride (LiCl, Aldrich Chem. Co. Inc.) was dried at 125 °C for 3 days and stored in a desiccator until used. HPLC–grade chloroform and methyl alcohol were purchased from Aldrich Chem. Co. Inc., and used without further purification.

Preparation of blend samples

The mixed solvent (chloroform : methanol=4 : 1) and chloroform were used for the preparation of 23MC and AKD (and h–AKD) stock solutions, respectively. Concentrations of the solutions were 0.8 wt.% for 23MC and 1.0 wt.% for AKD and h–AKD. All solutions were filtered and stored in a closed container under nitrogen atmosphere. Separately prepared three stock solutions, AKD, h–AKD and 23MC, were mixed in the desired proportions at room temperature. The relative compositions of the two samples were 1/99, 2/98, 3/97, 4/96, 5/95, 6/94, 7/93, 10/90, 15/85, and 20/80 by weight (AKD/23MC or h–AKD/23MC). After stirring for three days at 40 , blend films of AKD/23MC and h–AKD/23MC were prepared by casting the mixed solution as in the previous paper (Seo and Cho, 2005). One gram of each blended solution was poured into a flat–bottomed glass tray and conditioned to room temperature under reduced pressure for a week. The mixed solvent was evaporated very slowly at room temperature to yield an as–cast film. It was further dried for another one week under high vacuum at 40 °C to completely remove the residual solvent and moisture from the blend films, and then stored in a desiccator. A pure cellulose film was prepared by casting cellulose/LiCl–DMAc solution and washed and dried. Prepared samples were used for Fourier transform infrared (FTIR) analysis. All films were sufficiently thin (~10 micrometer) to obey the Beer–Lambert law.

Measurements

Fourier transform infrared (FTIR) spectra were obtained by a BioRad FTIR spectrophotometer. Samples for FTIR measurements were prepared by the as–cast film or a KBr disk technique. The wavenumber ranging from 4000 cm^{-1} to 400 cm^{-1} were scanned 32 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. Deuterated chloroform was used as a solvent. Chemical shifts were referenced to tetramethylsilane.

To investigate the interaction between AKD and cellulose, the blend samples of both materials are required. However, cellulose is insoluble in common organic solvents since it have three strongly hydrogen bonded hydroxyl groups in a glucose residue as shown in Fig. 2 (A) (Kondo, 1994). Therefore, it is almost impossible to prepare blend films or solutions containing both hydrophobic sizing materials and hydrophilic cellulose. On the other hand, the 23MC is easily dissolved in an organic solvent system, since 23MC have two methoxyl groups at C–2 and C–3 position instead of hydroxyl groups as shown in Fig. 1 (B). Therefore, it is possible to prepare a blend solution using 23MC as a cellulose model compound.
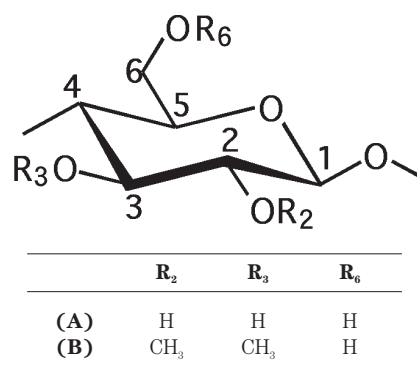

	R_2	R_3	R_6
(A)	H	H	H
(B)	CH$_3$	CH$_3$	H

Fig. 1. Chemical structure of (A) cellulose and (B) 2,3–di–*O*–methylcellulose.
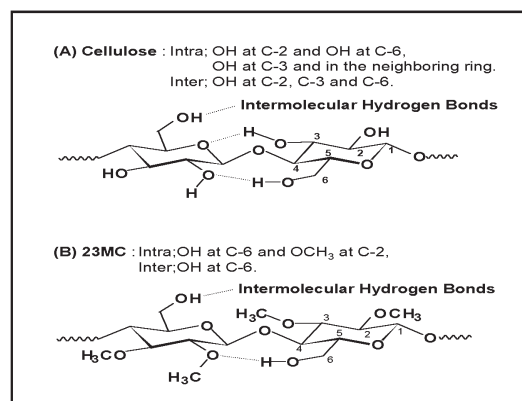

Fig. 2. Schematic representation of possible hydrogen bonds in cellobiose unit of (A) cellulose and (B) 2,3–di–*O*–methylcellulose (Kondo, 1994).

Three different hydroxyl groups in anhydroglucose unit of cellulose can easily be engaged in inter–and intra–molecular hydrogen bondings. Thus, in general, IR spectrum of cellulose displays a broad absorption band in the range of OH stretching vibrations. Since this regioselectively methylated cellulose derivative, 23MC, has less hydroxyl groups to decrease possibilities for hydrogen bonding, it shows narrow OH stretching vibration bands (Kondo, 1994). Therefore, 23MC is very useful to investigate the interaction of cellulose and AKD, because the OH groups at the C–6 position in 23MC may primarily form a range of intermolecular hydrogen bonding with other molecules. Also the peak shifts in the range of OH stretching vibration of 23MC accompanied by a certain interaction can be detected more clearly.

RESULTS AND DISCUSSION

FTIR characterization of AKD/23MC blends

The specific interaction in AKD/23MC blend was examined using FTIR spectroscopy. Figure 3 shows the IR absorption bands bands due to the OH group for 23MC in the blend. In this figure, the dotted lines and the solid lines showed the OH absorption bands of 23MC homopolymer film and the AKD/23MC blend films, respectively. The peak maxima of the blend films are shifted to lower wavenumbers by the maximum shift of 5.0 cm^{-1} from the position of the OH absorption band for 23MC homopolymer. Since the infrared spectra were obtained at the resolution of 0.5 cm^{-1}, the difference of 5.0 cm^{-1} could be considered as a significant change. The extent of the shift was increased with increasing of the AKD content in the blend film.

Figure 4 shows the FTIR spectra of the recrystallized AKD, h–AKD and 23MC. The absorption bands at 1,849 and 1,722 cm^{-1} in the spectrum of AKD correspond to C=O and C=C stretching vibrations, respectively. The high frequencies of C=O and C=C absorption bands were

derived from the angle strain of β–lactone (Ödberg *et al.*, 1987; Searles *et al.*, 1953). AKD has no significant absorption band. While, 23MC had an OH absorption band and no C=O band. Therefore, if there is no interaction between AKD and 23MC, especially between carbonyl and hydroxyl groups, the C=O and OH absorption bands of the blend films should coincide with those of original materials. On the other hand, if they interact, the interaction could be detected by comparing OH or C=O absorption bands of the blend films with those of the originals.

Since 23MC has only a primary hydroxyl group at the C–6 position, the shift of blend samples are indicated due to the interaction of OH groups in 23MC. In addition to the change in peak maxima, the shapes of OH absorption bands for the blends represented by solid lines in Fig. 3 are considerably differed from that for 23MC (dotted line). This suggests a rearrangement of the hydrogen bonding by blending of AKD/23MC. As mentioned above, if there is no interaction between AKD and 23MC, the OH absorption bands of blend films should coincide with the OH absorption band 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 affects a certain interaction between AKD and 23MC. Furthermore, the interaction is supposed to be the hydrogen bonding between the lactone oxygen of AKD and hydroxyl group of 23MC as shown in Fig. 9 (A), because AKD molecule has no other functional group affecting the OH stretching vibration of 23MC.

Possibility of the hydrogen bonding between the sizing agents (AKD or h–AKD) and 23MC molecules were examined by analysis of infrared spectroscopy. The hydroxyl oxygen atom of 23MC, with its great electronegativity, pulled the bonding electrons closer to itself and this made the hydrogen adjacent to the oxygen atom somewhat electron deficient, and gave it a partial posi-
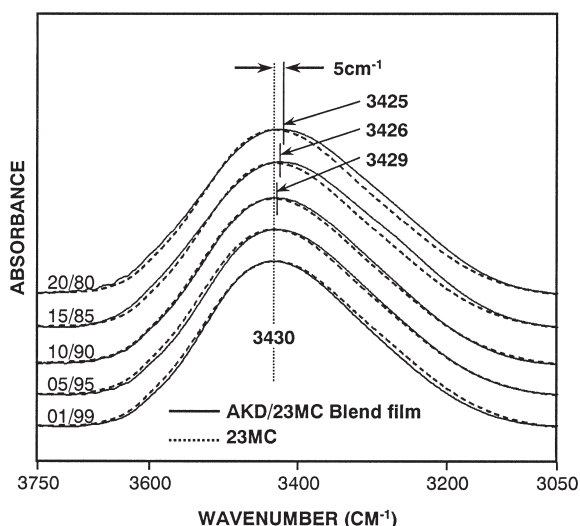
Fig. 3. FTIR spectra of 2,3–di–*O*–methylcellulose film and AKD/2,3–di–*O*–methylcellulose blend films in the region of the OH stretching vibration .
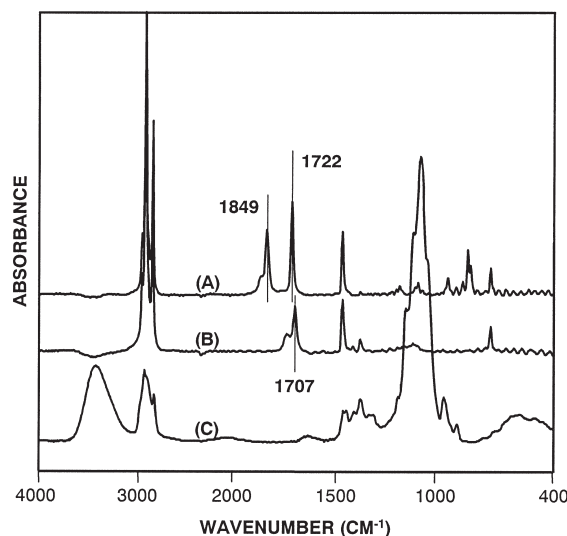

Fig. 4. FTIR spectra of (A) alkylketene dimer (AKD), (B) hydrolyzed AKD (h–AKD), and (C) 2,3–di–*O*–methylcellulose (23MC).

tive charge (δ^+). Thus, the positively polarized hydrogen atom of hydroxyl group formed either intra–or inter–molecular hydrogen bonding with the negatively polarized oxygen atoms.

On the other hand, AKD had a carbonyl group in its four–membered lactone ring. Hydrolyzed AKD, ketone, also had a carbonyl group. The carbon–oxygen double bond is polarized because of the high electronegativity of oxygen relative to carbon. Thus, the carbonyl oxygen of AKD (or h–AKD) became electron rich and bore a partial negative charge (δ^-). Therefore, the most presumable interaction between AKD (or h–AKD) and 23MC was the hydrogen bonding between carbonyl oxygen of AKD and hydroxyl groups of 23MC.

Figure 5 shows deconvoluted three peak components of a typical OH absorption band. Kondo *et al.* (1994) defined those components in the region of OH absorption of cellulose as free OH, intra–and inter–molecular hydrogen bonded OH (Kondo, 1994) for bands (B), (C), and (D) in Fig. 5, respectively. Kondo *et al.* (1994) studied miscibilities of cellulose/PEO (polyethylene oxide) and cellulose/PVA (polyvinyl alcohol) blend systems with regio–selectively substituted methylcellulose using FTIR spectroscopy. They reported that primary hydroxyl groups at C–6 position of cellulose interacted with ether oxygen of PEO in cellulose/PEO blends, and that secondary hydroxyl groups of cellulose and PVA were engaged in hydrogen bonds in cellulose–PVA blends. Therefore, it could be considered that the shifted and broaden band to the lower wavenumbers in Fig. 3 were caused by the inter–molecular hydrogen bonding between AKD and 23MC.

Figure 6 shows the change in IR absorption bands of C=O groups for the blend samples. The C=O stretching vibrations of the AKD/23MC blends are slightly shifted to lower wavenumbers from that for AKD. The shifts of the peak maxima are increased with increasing AKD con-
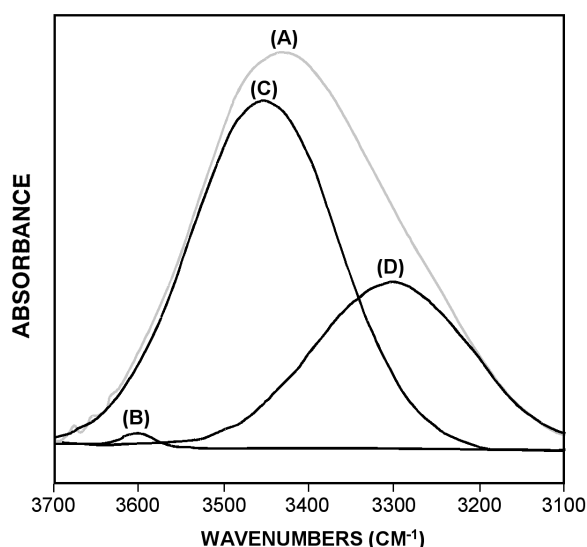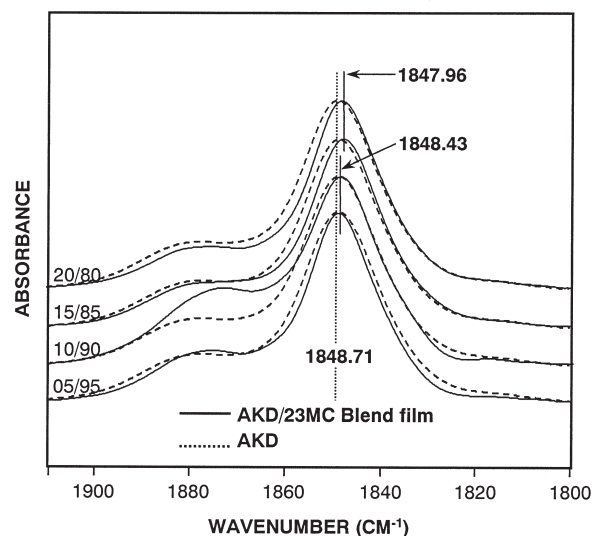
Fig. 6. FTIR spectra of AKD and AKD/2,3–di–*O*–methyl–cellulose blend films in the region of the C=O stretching vibration.

tents, even though the maximum shift (below 1.0 cm^{-1}) is very small. Since the IR spectra were obtained by the resolution of 0.5 cm^{-1}, the difference of 1.0 cm^{-1} could be considered as a significant change, indicating the C=O group of the AKD may be participated in hydrogen bonding with OH group in 23MC. The results from Figs. 3 and 6 have a good agreement with the general theory on IR band shift due to hydrogen bonding (Silverstein *et al.*, 1991). 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.

It is known that the hydrogen bond (written X–H…Y) between hydrogen atom of a donor group X–H, such as OH or NH, and an acceptor atom Y, which is usually O or N, also affects the absorption frequencies of the acceptor group, but the shifts are less than those of the donor group X–H (Lambert *et al.*, 1987). Therefore, even though the shift of C=O absorption band were very small, the shifts of the absorption bands of the blend films due to both OH and C=O support the existence of the hydrogen bonding between AKD and cellulose. Pisa *et al.* (1981) and Metzler (1983) also suggested the possibility of hydrogen bonding between carbonyl oxygen of AKD and hydroxyl group of cellulose.

FTIR characterization of h–AKD and 23MC blends

Possibility of the hydrogen bonding between h–AKD and 23MC is also examined. Figures 7 and 8 show the IR absorption bands of the OH and C=O group, respectively. The peak maxima of OH absorption bands of the blend films shift to lower wavenumbers with the maximum shift of 7.0 cm^{-1} from the position of 23MC. The absorption bands due to the C=O group also slightly shift to lower wavenumbers, which are very similar to the shifts in AKD/23MC blend (Fig. 3).

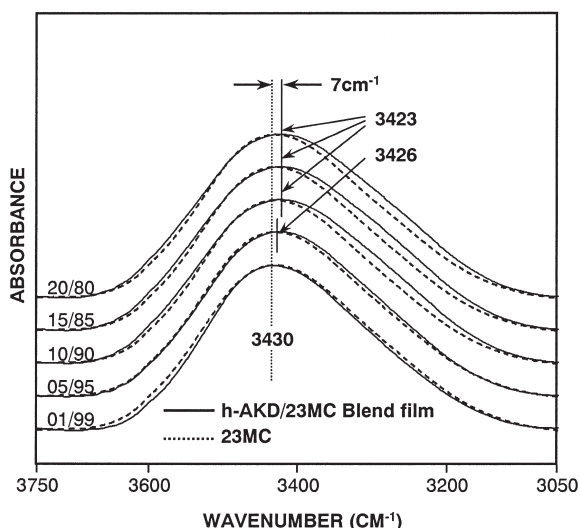The extents of the shifts of both O–H and C=O

Fig. 5. OH infrared absorption band of (A) cellulose and the deconvoluted three peak components, (B) free OH, (C) intra–molecular hydrogen bonded OH, and (D) inter–molecular hydrogen bonded OH (Kondo, 1994).

Fig. 7. FTIR spectra of 2,3–di–*O*–methylcellulose film and h–AKD/2,3–di–*O*–methylcellulose blend films in the region of the OH stretching vibration.
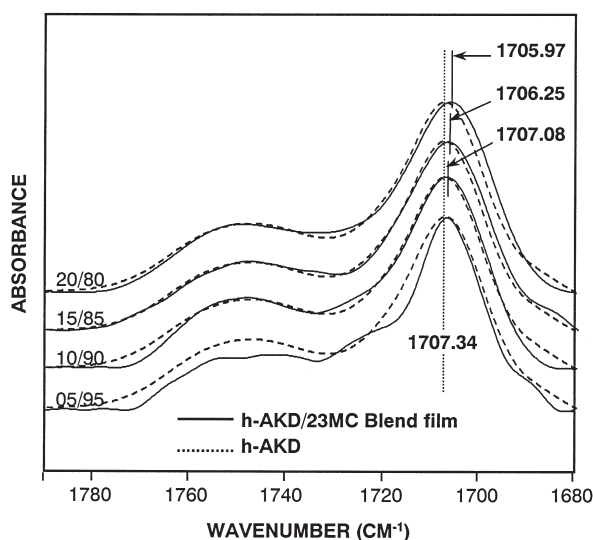

Fig. 8. FTIR spectra of h–AKD and h–AKD/2,3–di–*O*–methylcellulose blend films in the region of the C=O stretching vibration.
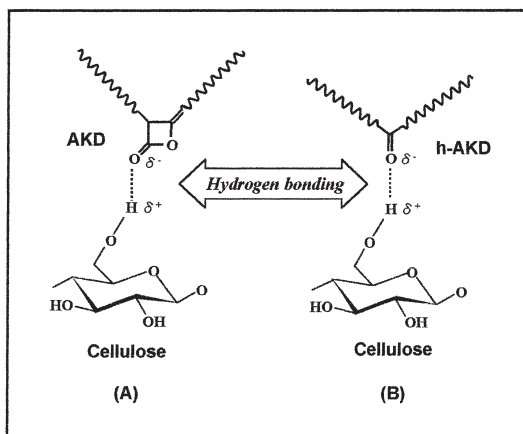

Fig. 9. Schematic representation of the hydrogen bond between (A) AKD and cellulose, and between (B) h–AKD (ketone) and cellulose.

absorption bands of h–AKD/23MC blend are somewhat greater than those of AKD/23MC blend (Figs. 3 and 6). This result seemed to be induced by the higher polarity of the carbonyl group of h–AKD than that of AKD. Since AKD has two oxygens in its lactone ring, the polarization effect of C=O group was lower than that of ketone which had one oxygen molecule. The hydrogen bonding between h–AKD and cellulose was illustrated in Fig. 9 (B). In the papermaking process, the formation of the hydrogen bonding and easter bonding between AKD and cellulose chain could be possible during drying and aging stages. Respectively, after AKD spreading to mono–molecular layer.

CONCLUSIONS

The interaction between sizing materials (alkylketene dimmer, AKD, and its hydrolyzed product, h–AKD) and cellulose were examined by the FTIR spectroscopy. Regioselectively substituted 2,3–di–*O*–methylcellulose (23MC) was used as cellulose model. This study showed that the formation of hydrogen bonding between hydroxy group at C–6 position of 23MC and lactone oxygen in AKD molecule could be presented.

As an initial stage, the hydroxyl groups of 23MC have 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.

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

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