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https://doi.org/10.5109/12850

出版情報：九州大学大学院農学研究院紀要. 53 (2), pp.411-416, 2008-10-28. Faculty of Agriculture, Kyushu University
バージョン：
権利関係：

J. Fac. Agr., Kyushu Univ., **53** (2), 411–416 (2008)

Surface Chemical States of Sizing Agents on AKD/Cellulose Blends by X–Ray Photoelectron Spectroscopy

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(*Received Juen 23, 2008 and accepted July 16, 2008*)

To investigate the effect of heat treatment on sizing development and the surface chemical states of sizing agents, alkylketene dimer (AKD)/23MC and ketone/23MC (0.3/99.7, w/w) blend films, as a model of sized papers, were heated and used for the x–ray photoelectron spectroscopy (XPS) and water contact angle measurement. Hydrophobicity of the film and concentration of the alkyl chains at the surface of the films were increased with heating times. On the XPS analysis of AKD/23MC and ketone/23MC blend films, ketone/23MC blend films had much more distribution of alkyl chains on its surface than that of AKD/23MC blend films. The hydrophobicity of the films was closely related to the chemical states of sizing agents at the surface. Increase in concentration of alkyl chains seems to be caused the migration of sizing agent to film surface and its molecular orientation at the blend film surface.

INTRODUCTION

It was indicated that alkylketene dimer (AKD) rarely reacted with cellulose to form β–ketoester, but most of AKD was hydrolyzed to dialkyl ketone in the presence of water (Bottroff and Sullivan, 1993; Roberts, 1996; Seo and Cho, 2005). A prerequisite for reaction of sizing agents with surface groups is the redistribution of sizing agents on fibers and filler surfaces. The mode in which redistribution occurs is also a question of some discussion. Possible ways of distribution of sizing agents on fiber surfaces include:– wetting spreading on paper surfaces by sizing agents (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 (Yu and Garnier, 1997; Seppanen and Tiberg, 2000; Yu and Garnier, 2002), and vapour diffusion and adsorption at paper surfaces layer (Yu and Garnier, 1997).

All these mechanism can occur to some extent after the retention/surface deposition step. Pisa and Murckva (1981) suggested that AKD molecules were oriented by the hydrogen bond (Kondo, 1994) and this orientation caused the hydrophobicity of AKD sized sheet. Hayashi *et al.* (1994) reported that the increasing in the degree of AKD sizing was brought from the rearrangement of its alkyl chains. They sprayed pyrene solution on AKD sized paper and measured its fluorescence spectra to observe the orientation of alkyl chains during aging. If the hydrophobic alkyl chains of sizing materials were able to orient by the hydrogen bonding, the sizing development of AKD sized paper could be explained, in terms of AKD sizing mechanism. Ganier *et al.* (1998), Shen and Parker (2001), Shen *et al.*, (2000; 2002; 2003) extensively studied on wetting and redistribution behavior of AKD and their corresponding ketone. It was observed that AKD spreads on cellulose surfaces via the slow mechanism of surface diffusion of its autophobic precursors, whereas ketone spreads much more rapidly. It suggests that ketone molecules may have a weaker interaction with and/or have energetically unfavorable on the cellulose surface. X–ray photoelectron spectroscopy (XPS), also known as ESCA (electron spectroscopy for chemical analysis), provides a quantitative elemental analysis of the top 1~20 nm of a solid surface (Istone, 1995). Information about chemical bonding and molecular orientation can be also obtained. While XPS is used in the surface analysis of paper, very little has been published in literatures. Salvat (1990) published a general application note based upon analysis of a variety of coated and uncoated paper samples. Brinen *et al.* (1989) used XPS to monitor the concentration of a synthetic sizing agent, HABI [N,N,*O*–tris (octadecyl–carbamoyl) hydroxy–amine], on paper surfaces. HABI was an experimental alkaline sizing agent used in alkaline papermaking. In a study conducted by Pyda *et al.* (1993), XPS was used to study interactions between AKD and calcium carbonate fillers. Shen *et al.* (2001) also tried to examine the migration behavior of AKD by AFM and XPS.

In this study, x–ray photoelectron spectroscopy (XPS) was used to monitor surface chemical states of cellulosic blend films, which contain AKD or hydrolyzed AKD. Water contact angles of the blend films were measured to investigate a relationship between surface chemical characteristics and hydrophobicity of the films. Effect of heat treatment of blend films on their hydrophobicity and surface chemistry were also investigated.

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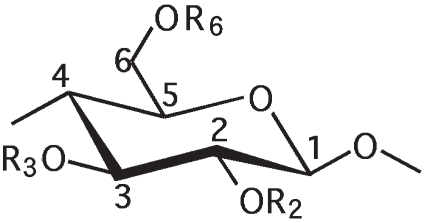
EXPERIMENTAL

Materials

The 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 previous report (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. 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). Since 23MC was found to have a uniform structure, every structural unit of them was regioselectively substituted. The weight–average molecular weights 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.



	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.

Preparation of blend films

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. AKD/cellulose blend gels were prepared in various AKD contents (0.1, 0.3, 0.5, 1, 3, 5, 10, 15, and 20 wt.%) by the same method as described in the previous report (Seo and Cho, 2005). These AKD/cellulose blend gels were pressed to control its water content as 60%, and then heated at 120 °C for various time between two pieces of Teflon sheet. Prepared AKD/23MC and h–AKD/23MC blend films were used for the XPS analysis and the measurement of water contact angle.

Measurements

The XPS was obtained with an ESCA LAB MK2 of VG Scientific Ltd. Mg K–alpha was used as an X–ray source. The anode voltage was set at 15 kV and the anode current at 15 mA. Background pressure in the analytical chamber was adjusted to less than 10^{-8} mmHg. Gold was used as an internal reference. The spectra were referenced by setting 84.0 eV for Au $4f_{7/2}$ peak to eliminate the charge effect. In high–resolution XPS spectra, C1s peaks were deconvoluted into component parts by using curve–fitting techniques and the areas of fitted component curves were calculated mathematically. For peak analysis, the decomposed peak positions were assigned according to Table 1.

Water contact angle was measured by a NRL C. A. Goniometer (Model No. 100–00–115, Rame–Hart, Inc.) at a temperature controlled to 25±0.5 °C. Only advancing contact angles were measured.

Table 1. Chemical shifts of XPS core lines

Functional group	Carbon 1s	Oxygen 1s
C=C	284.73	
C–C	285.00	
C–O–C	286.45	532.64
C–OH	286.55	532.89
*C–O–C=O	286.64	
C=O	287.90	532.23
O–C–O	287.93	533.15
C–O–*C=O	288.99	
–C(=O)OH	289.26	
O–C(–O)–O	289.32	532.99
–C(=O)–O–C(=O)–	289.41	533.91 (532.64)
carbonate(CO_3)	290.44	532.38 (533.93)

* indicates atom for which binding energy is given. For multiple oxygens, =O is given first, followed by –O in parentheses. All values are binding energies in eV relative to C–C at 285.00 eV. (Beamson and Briggs, 1992)

RESULTS AND DISCUSSION

XPS analysis

The XPS survey spectra of AKD/23MC and ketone/23MC blend films were shown in Fig. 2 (A) and Fig. 2 (B), respectively. The peaks due to the photoelectrons emitted from carbon and oxygen appeared at 287 eV and 531 eV, respectively. The intensity of C1s peak was increased with increasing in AKD and ketone contents. However, the increasing tendency of C1s peaks was different between the spectra of AKD/23MC and ketone/23MC blend films. The ratios of C1s peak area to the sum of C1s and O1s peak area were plotted in Fig. 3. As shown in the figure, the ratios of ketone/23MC blend films were higher than those of AKD/23MC blend films at every addition level. This meant that the concentration of ketone on the blend film surface was higher than AKD.

In XPS spectrum, chemical shifts provided the most useful information for determining chemical states of

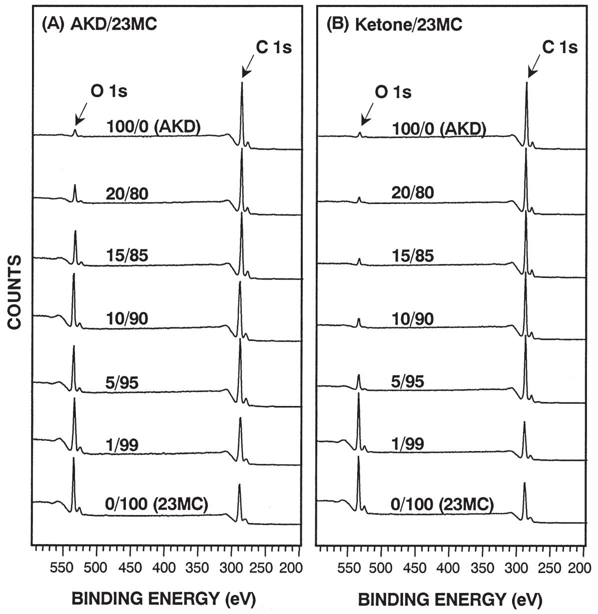


Fig. 2. XPS survey spectra of (A)AKD/23MC blend films and (B) ketone/23MC blend films.

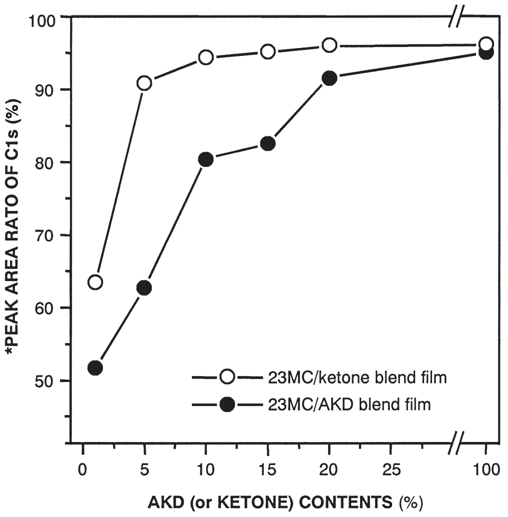


Fig. 3. Effect of AKD and ketone on the peak area ratios of C1s peak.
* Peak area ratio of $C1_s=(C1_s / (C1_s + O1_s)) \times 100$ (%)

samples. Chemical shifts occured when neighboring atoms increase or decrease in the electrostatic shielding around the nucleus of the atom being studied (Istone, 1995). The increase or decrease in shielding resulted in greater or lesser attraction between the nucleus and the core electrons, resulting in a corresponding increase or decrease in binding energy for the photoelectrons being emitted from that atom. Chemical shift data have been compiled from both theoretical models and experimental determinations. Beamson and Briggs (1992) provided an useful source of the chemical shift data for organic materials.

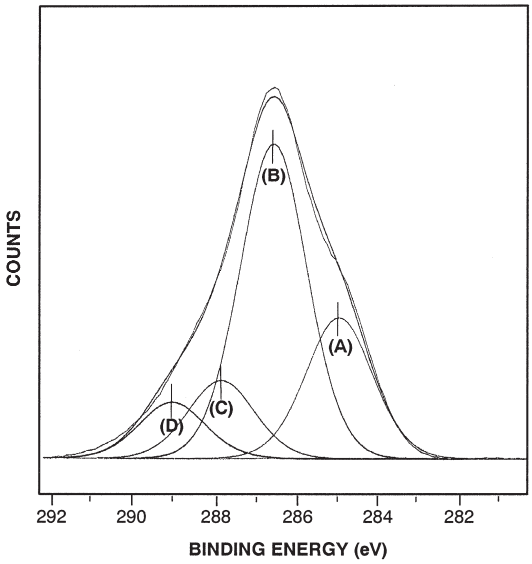


Fig. 4. Deconvoluted $C1_s$ spectrum of AKD/23MC (1/99, w/w) blend film. Each component peak corresponded to (A) C–C, (B) C–OH and C–O–C, (C) O–C–O, and (D) C–O–*C=O.

High–resolution C1s spectra of the blend films were deconvoluted according to the data of Beamson and Briggs (1992) as shown in Table 1. Figure 4 shows typical deconvoluted C1s spectrum of AKD/23MC (1/99, w/w). Deconvoluted spectrum shows the peaks due to following functional groups: (A) C–C, (B) C–O–C or C–OH, (C) O–C–O, and (D) C–O–*C=O.

Observation of changes in the CC peak area might be useful to investigate the arrangement of AKD and ketone molecules on the blend film's surfaces, because AKD and ketone has long hydrocarbon alkyl chains. Ratio of CC peak area to total C1s peak area was plotted in Fig. 5. Since AKD and ketone have similar alkyl chain length, the CC peak ratios in the spectra of AKD/23MC and ketone/23MC blend films shold be similar at the same dosages.

In Fig. 5, however, it was shown that the CC peak area of ketone/23MC blend film increased steeply with increasing ketone contents, while the CC peak area

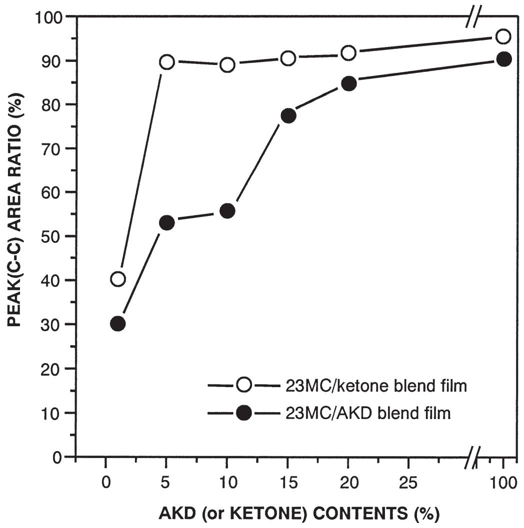


Fig. 5. Effect of AKD and ketone on the ratios of the C–C peak area to total C1s peak area.

increased slowly in the case of AKD/23MC blend film. Differences of CC peak ratios at the same dosage of sizing agents indicated that the concentration of alkyl chains of ketone at the surface of blend films was higher than that of AKD. Differences of the alkyl chains concentration at the film surfaces seemed to be caused by different molecular orientation or arrangement ability of AKD and ketone. It was proposed that ketone had more hydrogen bond formation than AKD in the earlier report. The difference of molecular orientation between AKD and ketone seemed to be related to their ability of hydrogen bonding.

Effect of AKD and ketone on hydrophobicity of the blend films

To investigate the effect of AKD and ketone on hydrophobicity of the blend films, contact angles of water for the blend films were measured. Fig. 6 showed water contact angles of 23MC film and the blend films. Ketone/23MC blend films showed higher contact angles of water than AKD/23MC blend films, especially at low addition levels. Higher hydrophobicity of ketone/23MC blend film than AKD/23MC blend film should be related to higher orientation ability of ketone at film surface than AKD occurred by its greater hydrogen bonding with cellulose. It had been thought that hydrolyzed AKD could not provide sizing effect to papers (Bottroff and Sullivan, 1993; Roberts, 1996; Zhou, 1991; Isogai *et al.*, 1992). From this result, however, it could be proposed that ketone, hydrolyzed AKD, contributes for sizing development of AKD sized paper more than unreacted AKD.

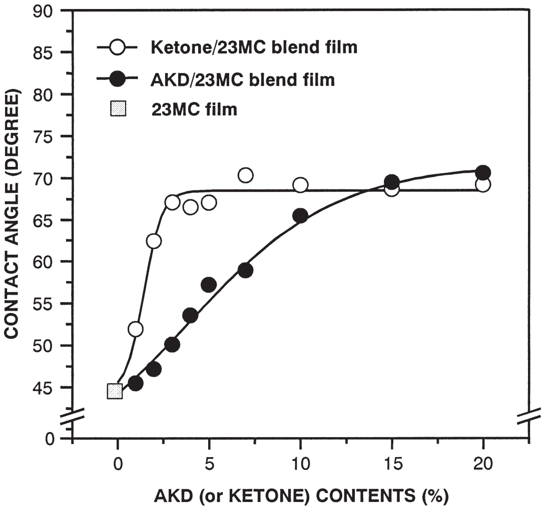


Fig. 6. Effect of AKD and ketone on water contact angle of the blend films.

Effect of heat treatment on hydrophobicity and surface chemical states of the blend films

AKD/cellulose blend gels were used as a model for AKD sized wet web. In order to understand the effect of heat–treatment on hydrophobicity and surface chemical states of AKD sized paper, contact angles of water of heat treated blend films were measured, and then the films were used for XPS analysis. In addition, to find out the minimum addition level of AKD for high contact angle of water, AKD/cellulose blend gels having various AKD contents were treated at 120 °C for 90 minutes.

The results of water contact angles of heat–treated gels were shown in Fig. 7. Water contact angle was increased almost perpendicularly at low dosage of AKD (below 1.0 wt.%). AKD addition level of 0.3 wt.% was selected because the water contact angle of 80 ° was high enough for following experiments. Water contact angles of heat–treated AKD/cellulose blend films were plotted as a function of the heating time in Fig. 8. The water contact angle was increased steeply by heating and leveled off after heating 20 minutes. Figure 9 showed high resolution XPS spectra in the region of $C1_s$

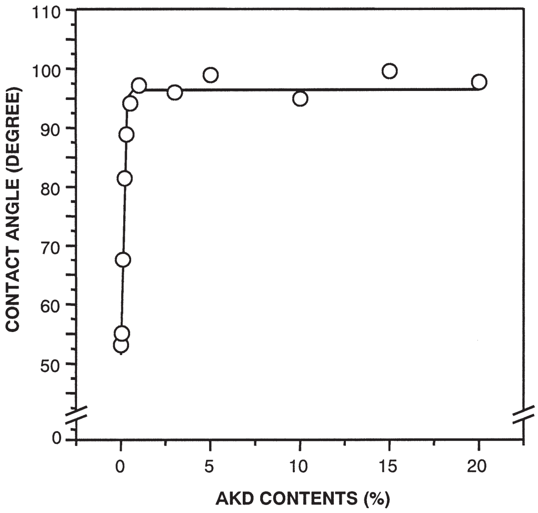


Fig. 7. Effect of AKD contents on water contact angles of AKD/cellulose blend films after heating. The blend gels were heated at 120 °C for 90 minutes. Water content of the blend gels before heating was 60%.

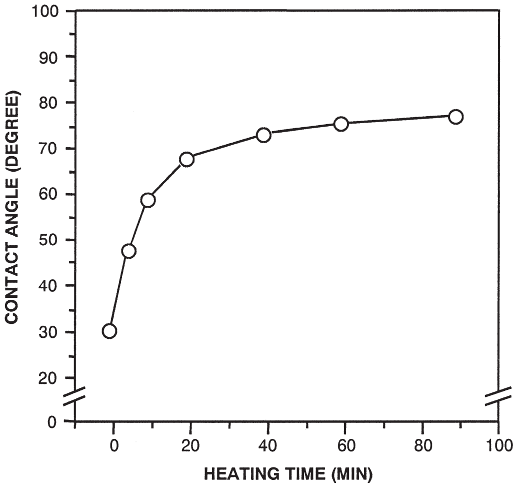


Fig. 8. Effect of heating time on water contact angles of AKD/cellulose blend films. The blend gels were treated at 120 °C. Water content of the blend gels before heating was 60%.

peak. The shoulders at 285.0 eV increased with heating time. These curves were deconvoluted to four component parts, and one of these deconvoluted spectra was shown in Fig. 10. Deconvoluted curves showed that the peak shoulder at 285.0 eV in Fig. 9 is due to the photoelectrons emitted from the carbon single bonded to carbon (C–C). The ratio of C–C peak area to the total area of C1s peak in the deconvoluted spectra was plotted in Fig. 11. The ratio of C–C peak area was increased with heating time. This phenomenon could be explained by next two mechanisms: 1) increased concentrations of the sizing agents at the film surface by their migration, 2) the orientation of alkyl chains of the sizing agents outward at the film surface.

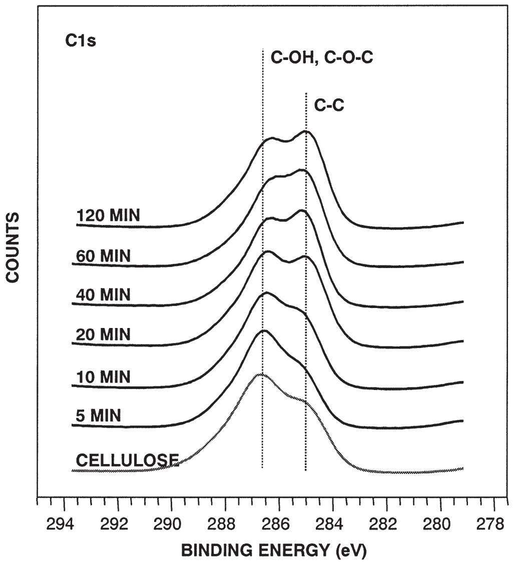


Fig. 9. High resolution XPS spectra of AKD/cellulose (0.3/99.7, w/w) blend films after heating in the region of $C1_s$.

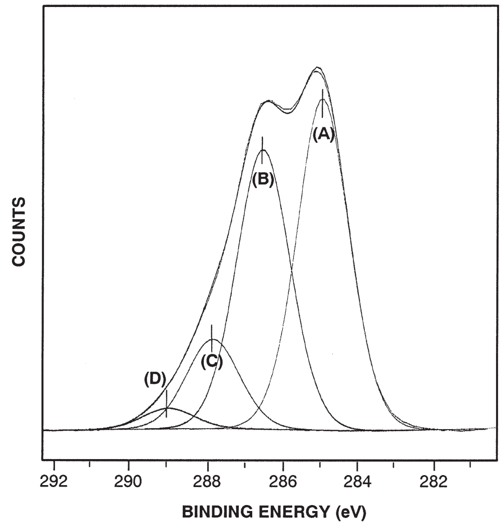


Fig. 10. Deconvoluted $C1_s$ spectrum of AKD/cellulose (0.3/99.7, w/w) blend film heated at 120 °C for 90 minutes. Each component peak corresponds to (A) C–C, (B) C–OH and C–O–C, (C) O–C–O and C=O, (D) C–O–*C=O.

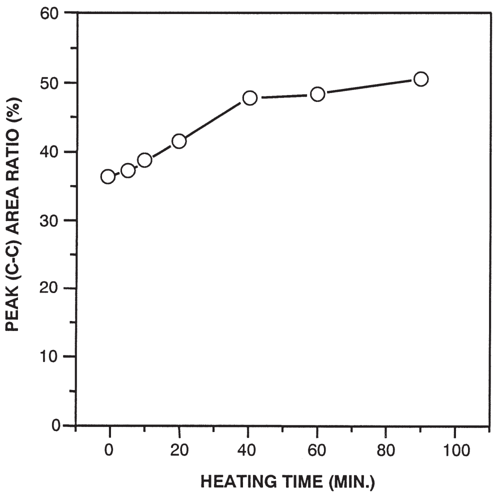


Fig. 11. Effect of heat treatment on the ratios of the C-C peak area to total $C1_s$ peak area of AKD/cellulose (0.3/99.7, w/w) blend film. The blend gels were heated at 120 °C. Water content of the blend gels before heating was 60%.

CONCLUSIONS

In order to understand the effect of heat treatment on sizing development and the surface chemical states of sizing agents, AKD/cellulose blend gels were heated and then the films were used for the XPS analysis and water contact angle measurements.

XPS analysis of AKD/23MC and ketone/23MC blend films showed that ketone/23MC blend films had much more distribution of alkyl chains on its surface than AKD/23MC blend films. Its means that ketone/23MC blend film showed higher hydrophobicity than AKD/23MC blend film. The hydrophobicity of the films were related closely to the chemical states of sizing agents at the surface. Hydrophobicity of the film and concentration of the alkyl chains at the surface of the films was increased with heating times. Increasing of concentration of alkyl chains seemed to be caused by migration of the sizing agent to film surface and the molecular orientation of the sizing agent at the blend film surface.

ACKNOWLEDGEMENTS

The authors wish to thank Dr. Jong–Ho Shin for his technical advice and valuable criticism of the manuscript.

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