Investigation of the hydrogen-bond structure of cellulose diacetate by two-dimensional infrared correlation spectroscopy

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ABSTRACT

Temperature-dependent structural changes in hydrogen bonds in cellulose diacetate (CDA) were investigated by Fourier transform infrared spectroscopy (FT-IR). The O—H stretching vibration band was selected to explore the structure changes. Two-dimensional correlation spectroscopy (2DCOS) in combination with moving-window technique was applied to analyze the overlapping O—H band due to various kinds of hydrogen bonds. By virtue of this powerful method, the inter-chain and intra-chain hydrogen bonds in cellulose diacetate can be identified. Moreover, typical temperature with great spectral variation was visualized by the moving-window analysis. In the temperature region of 35–100 °C, the absorbed water in the hydrogen-bond matrix broke away, and the structure of hydrogen bonds in CDA changed accordingly. When temperature increased into a higher region, both the inter-chain hydrogen bonds (comparatively strong but relatively unstable) and the intra-chain hydrogen bonds (comparatively weak but stable) began to decrease, and the inter-chain hydrogen bonds were weakened prior to the intra-chain hydrogen bonds.

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1. Introduction

Cellulose and its derivatives are an important class of natural macromolecules. Typically, cellulose is a liner polymer of 1-4 linked β-ᴅ-glucose (Fig. 1A), it is the most common component found in the cell walls of higher plants. This polysaccharide constitutes the most abundant, renewable polymer resource available today worldwide, and owning to its biodegradability and renewability, cellulose becomes the most welcome green material, which has aroused great interests in the studying and modification of its structure and properties. Cellulose acetate (CA) is such one of the important derivative, widely usable due to its desirable physical properties involving good optical clarity in film form and a comparatively high modulus and adequate flexural and tensile strengths in fiber form (Aoki, Teramoto, & Nishio, 2007). CA is widely applied in membrane materials, cigarette filters, textile, plastic, food and pharmaceutical industries, and etc. Up to now, it has been known that the excellent properties of this nature polymer come from mainly two reasons: on one hand, its high degree of polymerization and the linear orientation of the molecules and, on the other hand, its ability to form inter-chain and intra-chain hydrogen bonds which stabilize the molecule itself and connect it to neighboring ones and to form micro fibrils. (Hinterstoisser, Akerholm, & Salmean, 2003) Since the hydrogen-bond matrix

in the CA polymer plays a key role in its properties, it has been of great importance to investigate the structure of the hydrogen-bond matrix, to distinguish and specify different kinds of hydrogen bonds in CA polymer, which will provides a deeper understanding into this environmental protective functional material, and consequently expands the industrial applications.

In recent years, much work has been published on the characterization of the hydrogen-bond matrix in both cellulose and cellulose acetate using various techniques, among which Fourier transform infrared spectroscopy (FT-IR) has proved to be one of the most powerful methods. (Hinterstoisser & Salmean, 2000; Ilharco & Barros, 2000; Kokot, Czarnik-matusewicz, & Ozaki, 2002; Watanbe, Morita, & Ozaki, 2006) FT-IR spectroscopy can monitor the structure of individual chemical groups. Each chemical group may have one or more specific absorption bands in the infrared spectra, and the spectral features of the peaks (peak shape, peak area, and peak position, etc) will change while the chemical environment is altered or the chemical groups interact with each other. Therefore, investigation of the spectral features and comparison with the available database will help to obtain the new information of the molecular structure in certain experimental conditions. However, the information provided by the original spectra is too limited to study the interactions between the chemical groups. Moreover, in many cases, a broad strong band, especially the O—H stretching vibration band, may cover many sub-peaks, and the spectral features of these sub-peaks cannot be readily identified in the original data set. Therefore, we must seek help from

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additional mathematical methods. The generalized two-dimensional correlation spectroscopy (2DCOS), proposed by Noda (Noda, 1993; Noda, Dowrey, Marcott, Story, & Ozaki, 2000), is such one powerful technique. 2DCOS can be applied to interpret spectroscopic intensity fluctuations due to external physical or chemical perturbations, such as temperature, pressure, electric field strength, concentration and so on (Ataka & Osawa, 1998; Gregoriou, Chao, Toriumi, & Palmer, 1991; Jiang, Wu, & Yang, 2003; Nakano, Shimada, Saitoh, & Noda, 1993; Noda, Story, & Marcott, 1999; Ozaki, Liu, & Noda, 1997; Wang et al., 1998). Thus, by virtue of this powerful technique, the temperature-dependent FT-IR spectra of CA polymer can be investigated much more detailedly: the sub-peaks overlapped in the broad O—H stretching vibration band can be identified, and even more, the motion sequence of different hydrogen bonds under the temperature heating process can be clarified.

The moving-window technique was firstly proposed by Thomas and Richardson (2000), and has recently been developed by Morita, Shinzawa, Noda, and Ozaki (2006). The main advantage of this mathematic method is that, it can reveal the extreme points of a set of nonlinear functional data. Thomas and Richardson applied this so-called windowed autocorrelation analysis to locate the phase transition points of a liquid crystal, 4'-n-octyl-4-cyanobiphenyl (8CB) in the FT-IR spectra (Thomas & Richardson, 2000). Besides, not only the phase transition points, but also other kinds of inflection points in a series of perturbation dependent FT-IR spectra can be visualized by application of this technique, and the continuous variation process in the spectra data set can be readily divided into several relatively sub-sets to be investigated in detail.

In this paper, a film sample prepared from cellulose diacetate (CDA, two of the three hydroxyl on the cellulose glucose are esterified) (Fig. 1B, C and D) was investigated by FT-IR spectroscopy during the heating process. Moving-window technique was used to figure out the temperature ranges where different variations of the hydrogen bonds in the CDA polymer proceed. 2DCOS technique was used to specify the inter-chain and intra-chain hydrogen bonds in the CDA polymer, and provide the variation sequence of these hydrogen bonds.

2. Experimental

2.1. Materials

The cellulose diacetate (Shanghai Chemical Reagent General Plant, 99%) is in white powder state. The powder was kept in vacuum at 60 °C for at least 48 h to remove the absorbed water as much as possible, and then it was mixed with KBr at the ratio of 1:50, and pressed into tablet for the FT-IR experiment.

2.2. FT-IR measurements

FT-IR spectra were recorded by using a Nicolet-470 FT-IR spectrometer with a DTGS detector. Sixty-four scans at a resolution of 4 cm^{-1} were averaged to obtain each spectrum. All spectra measurements were carried out at temperatures from 35–210 °C at an interval of 5 °C. The temperature of the specimen cell was controlled by a thermoelectric device with an accuracy of ±1 °C and the cell was maintained at each temperature for 5 min before the spectroscopic measurement.

2.3. 2DCOS analysis

The evaluation of the 1D FT-IR spectra was performed by Omnic 6.1a and Origin7.5. The spectra in the 35–210 °C range, totally 36 spectra, were used to calculate the 2DCOS result. Before that, the spectra were subjected to smoothing and baseline correction. The 2DCOS calculation was performed using the 2Dshige software (Shigeaki Morita, Kwansei-Gakuin University, 2004–2005) (Morita et al., 2006). The 2DCOS is a function of two independent wavenumbers: v_1/v_2 (Noda, 1993; Noda et al., 2000), where the red regions are defined as the positive correlation intensities, while the blue regions are defined as negative ones.

In the synchronous spectra, auto peaks appearing along the diagonal, which are always positive, representing the degree of autocorrelation of perturbation-induced molecular vibrations. If there appears an auto peak, it demonstrates that the peak at this wavenumber would change greatly under the environmental perturbation. Cross peaks located at off-diagonal positions may be positive or negative, corresponding to the simultaneous or coincidental changes of spectra intensity variations measured at v_1 and v_2. A positive cross peak demonstrates that the intensity variations of the two peaks at v_1 and v_2 are taking place in the same direction (both increase or both decrease) under the environmental perturbation; while a negative cross peak helps to infer that the intensities of the two peaks at v_1 and v_2 change in the opposite direction (one increase, while the other one decrease).

In the synchronous spectra the function between two wavenumbers (v_1/v_2) is defined as $\Phi(v_1,v_2)$, while in the asynchronous spectra it is $\Psi(v_1,v_2)$. If $\Phi(v_1,v_2) > 0$, $\Psi(v_1,v_2)$ is positive (red area) and the band v_1 will vary prior to band v_2; if $\Psi(v_1,v_2)$ is negative (blue area), the band v_1 will vary after the band v_2. However, this rule is reversed if $\Phi(v_1,v_2) < 0$ (Noda, 1993; Noda et al., 2000).
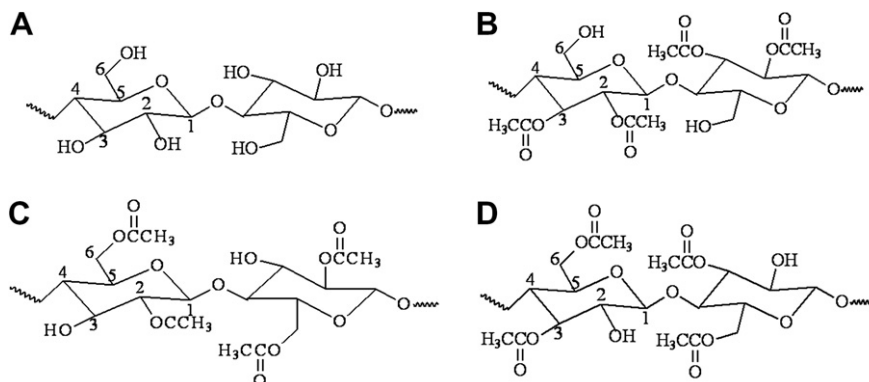

Fig. 1. The molecular conformations of cellulose (A) and cellulose diacetate (B, C and D).

2.4. Moving-window analysis

The moving-window analysis was performed by the 2Dshige software. The parameter $(2m + 1)$ was selected as the maximum value 25, which means 25 spectra selected every time to calculate an average spectrum. The calculation result was plotted by Origin7.5 software, and the recorded temperature of the top spectrum suggested the extreme point of the variation of the hydrogen bonds.

3. Results and discussion

Fig. 2 shows the FT-IR spectra of CDA measured from 35 to 210 °C in the range of 4000–600 cm^{-1}. The changes mainly take place in the ranges of 3800–3200 cm^{-1} and 1800–1700 cm^{-1}, which are assigned to O—H stretching vibration and C=O stretching vibration respectively.

The investigation of the C=O stretching vibration band provides much less information about the variation of the hydrogen-bond matrix during heating. It is known that the C=O groups can only form hydrogen bonds with O—H groups in the CDA sample, however the O—H groups can form hydrogen bond with not only C=O but also other groups, for examples, another O—H group or an -O- group. Therefore, the O—H stretching vibration region contains more useful information to investigate the structural variation of hydrogen-bond matrix in CDA polymer. In Fig. 2, it can be noticed that the whole broad O—H stretching band decreased in intensity upon temperature increasing, and the peak position moved to higher wavenumber during heating. It is suggested that the hydrogen-band matrix in CDA is weakened and partly destroyed during the heating process.

Fig. 3A shows the result of the moving-window analysis in the temperature range of 35–100 °C. It can be observed that the top spectrum was recorded at 100 °C, which indicates that the variation rate of the hydrogen bonds during a heating process has a maximum value, and there might be different transition behaviors among different kinds of hydrogen bonds before and after 100 °C. The peak area variations of the O—H stretching vibration (3700–3100 cm^{-1}) against the temperature are shown in Fig. 3B. It can be noticed that before 100 °C the curve drop much sharper than that after 100 °C, which is consistent with the moving-window result. Therefore, the temperature range (35–210 °C) was divided into two parts: (1) 35–100 °C and, (2) 100–210 °C, to investigate
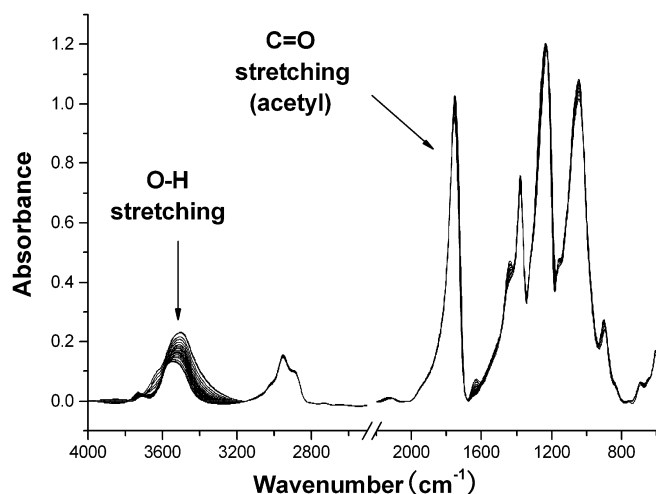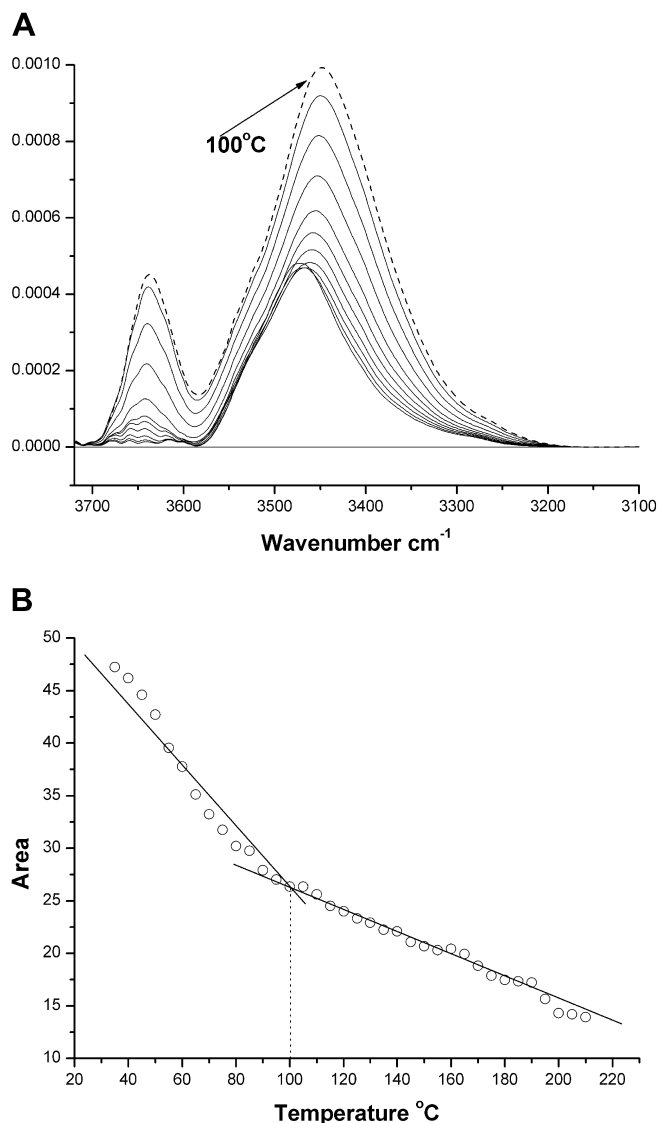
Fig. 3. The moving-window result in the O—H stretching region (A), and the peak area of the O—H stretching band variation curve in the temperature range of 35–210 °C (B).

the particular structure variations of the hydrogen bonds in CDA polymer in a more detailed mode.

3.1. Temperature range of 35–100 °C

Since CDA is a hydrophilic polymer, it can absorb water strongly at ambient temperature. Even if the sample has already been kept in vacuum for a long time, some residual water is still captured tightly by the hydroxyl and acetyl groups through hydrogen bonds. Therefore, it can be concluded that in the lower temperature range of 35–100 °C, besides the slight variations of the hydrogen bonds themselves, the absorbed water molecules breaking from the hydrogen-bond matrix in CDA polymer played a very important role at the meanwhile, and it influenced the structure of the hydrogen-bond matrix in a certain extent.

More information about the variations of the hydrogen-bond matrix of the CDA polymer can be obtained from the 2DCOS spectra in Fig. 4A and B. The assignments of vibration bands in the O—H stretching region of cellulose have been generally acknowledged (Hinterstoisser & Salmean, 2000; Watanbe et al., 2006), and according to the conclusions in these references, the assignments
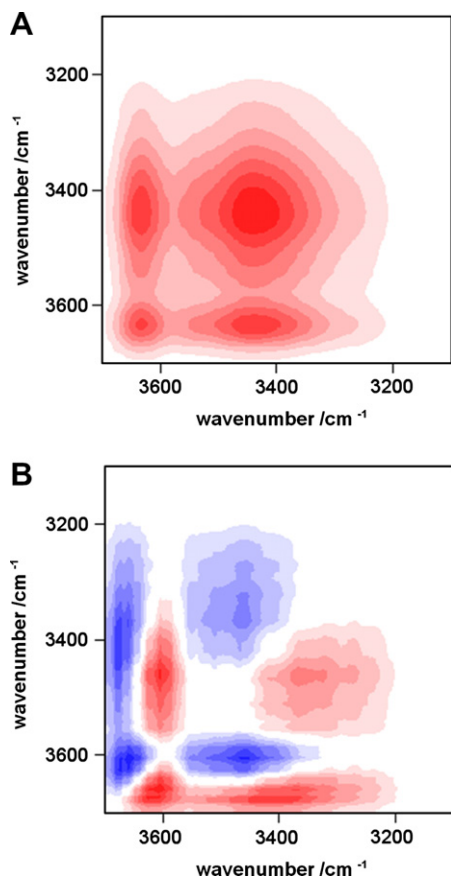
Fig. 2. FT-IR spectra of cellulose diacetate in the temperature range of 35–100 °C.

Fig. 4. The synchronous (A) and asynchronous (B) 2D correlation spectra of the cellulose diacetate in O—H stretching region from 35–100 °C.

of the corresponding bands appearing at the similar wavenumbers in the CDA can be obtained (Table 1). Therefore, the two auto peaks located at 3604 and 3461 cm^{-1} (Fig. 4A) are expected to be assigned to v(OH) of absorbed water and v_1(OH) of intra-chain hydrogen bonded hydroxyl groups, respectively. These two auto peaks are positive correlated, indicating that the two bands are changing in the same direction. Since it has been already known that the amount of absorbed water molecules decrease during this temperature range, it can be concluded that the amount of intra-chain hydrogen bonds also decrease.

Table 1
Wavenumbers and assignments of the hydroxyl groups of cellulose and cellulose diacetate

Cellulose (Hinterstoisser and Salmean, 2000; Watanbe, Morita, & Ozaki, 2006)		Cellulose diacetate	
Wavenumber (cm^{-1})	Assignments	Wavenumber (cm^{-1})	Assignments
3604	Absorbed water	3604	Absorbed water
3542	Free O—H	3544	Free O—H
3463	O2—H2···O6 intra-chain	3478	Intra-chain H-bond $v_1{'}$
		3461	Intra-chain H-bond v_1
3412	O6—H6···O3' inter-chain	3409	Inter-chain H-bond v_3
3344	O3—H3···O5 intra-chain	3369	Intra-chain H-bond v_2
3274	H-bonds in the Iβ phase		
3237	H-bonds in the Iα phase		

In the asynchronous spectrum (Fig. 4B), a positive cross peak located at (3604, 3461 cm^{-1}) (positive in the synchronous spectra) indicates that 3604 cm^{-1} (v(OH) of absorbed water) changes prior to the 3461 cm^{-1} (v_1(OH) of intra-chain hydrogen bonded hydroxyl groups). A negative cross peak at (3461, 3369 cm^{-1}) (positive in the synchronous spectra, which can be conclude from the slice spectrum) indicates that 3369 cm^{-1} (v_2(OH) of intra-chain hydrogen bonded hydroxyl groups) also changes prior to 3461 cm^{-1}. These results show that during the temperature range of 35–100 °C, the water molecules absorbed in the polymer are released and the two kinds of intra-chain hydrogen bonds are changing (most probably partly weakened). The intra-chain hydrogen bond (v_2(OH)) located at 3369 cm^{-1} was concluded to be weakened prior to the intra-chain hydrogen bond (v_1(OH)) at 3461 cm^{-1}.

3.2. Temperature range of 100–210 °C

In order to further obtain the information about the hydrogen-bond matrix in the CDA polymer in higher temperature region, another two 2DCOS spectra were calculated, as shown in Fig. 5A and B. In the synchronous spectrum (Fig. 5A), only one auto peak at 3478 cm^{-1} can be observed, which indicates that when temperature reaches to a high enough region, the change of intra-chain hydrogen bonds dominates the variation of the whole hydrogen-bond matrix in CDA polymer. Additionally, in the asynchronous spectrum (Fig. 5B), two cross peaks can be observed, which are located at (3544, 3478 cm^{-1}) and (3478, 3409 cm^{-1}), respectively. The position of 3478 cm^{-1} band is very close to 3461 cm^{-1} band, which suggests that 3478 and 3461 cm^{-1} may come from the same O—H group, the slight difference in wavenumber may be caused by the absorbed water molecules. When the absorbed water broke away from the hydrogen-bond matrix, the band shifted from 3461 to 3478 cm^{-1} accordingly. (3544, 3478 cm^{-1}) is positive in the asynchronous spectrum, but negative in the corresponding synchronous spectrum, which indicates that 3478 cm^{-1} ($v_1{'}$(OH) of intra-chain hydrogen bonded hydroxyl groups) changes prior to 3544 cm^{-1} (v(OH) of free hydroxyl groups). (3478, 3409 cm^{-1}) is negative in the asynchronous spectrum but positive in the synchronous spectrum, which indicates that 3409 cm^{-1} (v_3(OH) of inter-chain hydrogen bonded hydroxyl groups) varies prior to 3478 cm^{-1} ($v_1{'}$(OH) of intra-chain hydrogen bonded hydroxyl groups). Therefore, the motion sequence is v(OH) (inter-chain) → $v_1{'}$(OH) (intra-chain) → v(OH) (free). These results lead to the conclusion that when temperature is above 100 °C, both the inter-chain hydrogen bonds and the intra-chain hydrogen bonds began to be weakened, the inter-chain hydrogen bonds were destroyed prior to the intra-chain species of hydrogen bonds, and perhaps parts of the inter-chain hydrogen bonded hydroxyl groups translate into the intra-chain hydrogen bonded hydroxyl groups, then change into the free ones.

4. Conclusion

By two-dimensional correlation spectroscopy and moving-window technique, the structural variation of the hydrogen-bond matrix in cellulose diacetate induced by heating was investigated in detail. Four kinds of inter-chain hydrogen bonds and intra-chain hydrogen bonds can be identified, which are 3461 cm^{-1} (intra-chain v_1), 3478 cm^{-1} (intra-chain $v_1{'}$), 3369 cm^{-1} (intra-chain v_2) and 3409 cm^{-1} (inter-chain v_3). 3478, 3461 cm^{-1} may come from the same hydroxyl groups, and 3461 cm^{-1} may assigned to the intra-chain hydrogen bonded hydroxyl groups with the participating of the water molecules. Therefore, this 3461 cm^{-1} may shift to 3478 cm^{-1} according to the breaking away of the absorbed water. The inter-chain hydrogen bonds are comparatively strong but
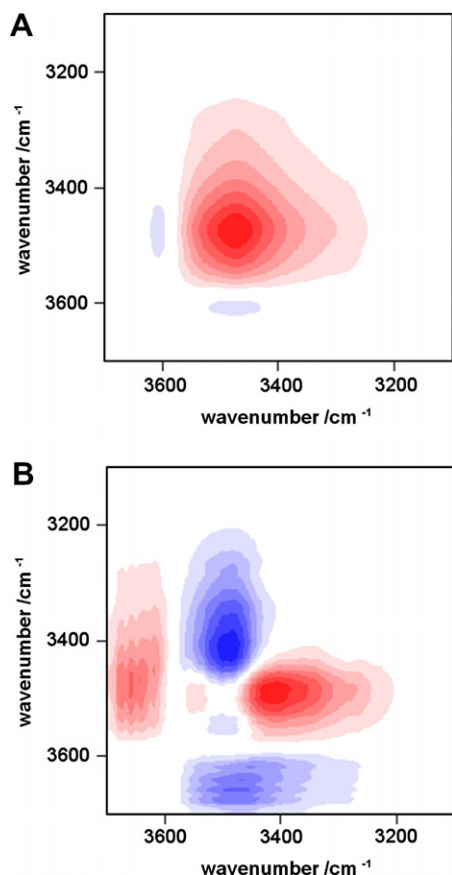
Fig. 5. The synchronous (A) and asynchronous (B) 2D correlation spectra of the cellulose diacetate in O—H stretching region from 100–210 °C.

unstable, while the intra-chain hydrogen bonds are comparatively weak but stable. In the lower temperature range, the water molecules captured in the hydrogen-bond matrix broken away and the structure of hydrogen bonds in CDA changed slightly. When temperature continues to increase, both the inter-chain and intra-chain hydrogen bonds are began to be weakened, and the hydrogen-bond matrix of CDA changes significantly.

References

Aoki, D., Teramoto, Y., & Nishio, Y. (2007). SH-containing cellulose acetate derivatives: Preparation and characterization as a shape memory-recovery material. *Biomacromolecules, 8*, 3749–3757.

Ataka, K., & Osawa, M. (1998). In situ infrared study of water-sulfate coadsorption on gold(111) in sulfuric acid solutions. *Langmuir, 14*, 951–959.

Gregoriou, V. G., Chao, J. L., Toriumi, H., & Palmer, R. A. (1991). Time-resolved vibrational spectroscopy of an electric field-induced transition in a nematic liquid-crystal by use of Step-Scan 2d FT-IR. *Chemical Physics Letters, 179*, 491–496.

Hinterstoisser, B., Akerholm, M., & Salmean, L. (2003). Load distribution in native cellulose. *Biomacromolecules, 4*, 1232–1237.

Hinterstoisser, B., & Salmean, L. (2000). Application of dynamic 2D FTIR to cellulose. *Vibrational Spectroscopy, 22*, 111–118.

Ilharco, L. M., & Barros, R. B. (2000). Aggregation of pseudoisocyanine iodide in cellulose acetate films: Structural characterization by FTIR. *Langmuir, 16*, 9331–9337.

Jiang, H. J., Wu, P. Y., & Yang, Y. L. (2003). Variable temperature FTIR study of poly(ethylene-co-vinylalcohol)-graft-poly(epsilon-caprolactone). *Biomacromolecules, 4*, 1343–1347.

Kokot, S., Czarnik-matusewicz, B., & Ozaki, Y. (2002). Two-dimensional correlation spectroscopy and principal component analysis studies of temperature-dependent IR spectra of cotton–cellulose. *Biopolymers (Biospectroscopy), 67*, 456–469.

Morita, S., Shinzawa, H., Noda, I., & Ozaki, Y. (2006). Perturbation-correlation moving-window two-dimensional correlation spectroscopy. *Applied Spectroscopy, 60*, 398–406.

Nakano, T., Shimada, S., Saitoh, R., & Noda, I. (1993). Transient 2d-Ir correlation spectroscopy of the photopolymerization of acrylic and epoxy monomers. *Applied Spectroscopy, 47*, 1337–1342.

Noda, I. (1993). Generalized two-dimensional correlation method applicable to infrared, Raman, and other types of spectroscopy. *Applied Spectroscopy, 47*, 1329–1336.

Noda, I., Dowrey, A. E., Marcott, C., Story, G. M., & Ozaki, Y. (2000). Generalized two-dimensional correlation spectroscopy. *Applied Spectroscopy, 54*, 236A–248A.

Noda, I., Story, G. M., & Marcott, C. (1999). Pressure-induced transitions of polyethylene studied by two-dimensional infrared correlation spectroscopy. *Vibrational Spectroscopy, 19*, 461–465.

Ozaki, Y., Liu, Y. L., & Noda, I. (1997). Two-dimensional infrared and near-infrared correlation spectroscopy: Applications to studies of temperature-dependent spectral variations of self-associated molecules. *Applied Spectroscopy, 51*, 526–535.

Thomas, M., & Richardson, H. H. (2000). Two-dimensional FT-IR correlation analysis of the phase transitions in a liquid crystal, 4'-n-octyl-4-cyanobiphenyl (8CB). *Vibrational Spectroscopy, 24*, 137–146.

Wang, Y., Murayama, K., Myojo, Y., Tsenkova, R., Hayashi, N., & Ozaki, Y. (1998). Two-dimensional Fourier transform near-infrared spectroscopy study of heat denaturation of ovalbumin in aqueous solutions. *Journal of Physical Chemistry B, 102*, 6655–6662.

Watanbe, A., Morita, S., & Ozaki, Y. (2006). Temperature-dependent structural changes in hydrogen bonds in microcrystalline cellulose studied by infrared and near-infrared spectroscopy with perturbation-correlation moving-window two-dimensional correlation analysis. *Applied Spectroscopy, 60*, 611–618.