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Study on hydrogen bonds of carboxymethyl cellulose sodium film with two-dimensional correlation infrared spectroscopy

Wei Li, Bingjie Sun, Peiyi Wu *

Key Laboratory of Molecular Engineering of Polymers of Ministry of Education, Laboratory of Advanced Materials and Department of Macromolecular Science, Fudan University, Shanghai 200433, PR China

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ABSTRACT

Carboxymethyl cellulose is widely used in many industrial aspects and also in laboratory due to its good biocompatibility. However, special researches on infrared especially aiming at the hydrogen bonds structure of carboxymethyl cellulose were relatively poor. We demonstrate here a full view of infrared spectroscopy in the temperature range of 40–220 °C, mainly aiming at the hydrogen bonds in the NaCMC film. The two important transition points was defined with DSC and together with Infrared analysis, that is, 100 °C corresponding to the complete loss of water molecules and 170 °C to the starting temperature point the O6H6 being oxidized. The series of IR spectra during heating from 40 to 220 °C was analyzed by the two-dimensional correlation method. We found that the water molecules bound with C=O groups and OH groups. With the evaporating of water molecules, the hydrated C=O groups gradually transited into non-hydrated C=O groups. As the temperature continued to increase, the intrachain hydrogen bonds were weakened and transited into weak hydrogen bonds. When the temperature was higher than 170 °C, the O6H6 groups were gradually oxidized and thus the interchain hydrogen bonds formed between CH_2COONa groups and O6H6 were weakened. In summary, we defined the main sorts of hydrogen bonds in carboxymethyl cellulose and pictured the changes of the hydrogen bonds structure during heating process, which may provide for the further application in both industry aspects and laboratory use.

1. Introduction

Carboxymethyl cellulose, an important ionic ether derivative of cellulose and usually used as its sodium salt (NaCMC), is widely applied in a lot of industrial sectors including food, paper making, paints, pharmaceutics, cosmetics and mineral processing (Barbucci, Magnani, & Consumi, 2000). Recently, due to the good biocompatibility, NaCMC attracts more attentions as a representative water-soluble polysaccharide in many research fields such as drug delivery (Benmouhoub, Simmonet, Agoudjil, & Coradin, 2008; Kulkarni & Sa, 2008; Yi & Zhang, 2007), tissue engineering (Jiang et al., 2008; Pasqui, Rossi, Di Cintio, & Barbucci, 2007) and polymer blends (Barbucci et al., 2000; Marci, Mele, Palmisano, Pulito, & Sannino, 2006), etc. Although it is getting more and more important in both industry and in the laboratory, and the hydrogen bonds in NaCMC were mentioned in many works (Barbucci et al., 2000; Said, Abd Alla, & El-Naggar, 2004; Yi & Zhang, 2007), special research works on infrared especially aiming at the hydrogen bonds structure were relatively poor, which is probably because of its strong water absorption and the resulting high complexity in hydrogen bonds on infrared spectroscopy.

As we know, the hydrogen bonding structure in cellulose was studied intensively. Chanzy (Marechal & Chanzy, 2000; Nishiyama, Langan, & Chanzy, 2002; Wada, Chanzy, Nishiyama, & Langan, 2004) et al. studied the crystal structure and hydrogen bonding network of cellulose with the application of synchrotron X-ray and infrared spectroscopy and obtained relatively complete infrared assignments of the hydrogen bonding region. Kondo (Hishikawa, Inoue, Magoshi, & Kondo, 2005) monitored a deuteration process of the noncrystalline regions in cellulose with two-dimensional correlation infrared spectroscopy, which was proved a powerful tool to study hydrogen bonding networks in cellulose. More recently, Ozaki (Kokot, Czarnik-Matusewicz, & Ozaki, 2002; Watanabe, Morita, & Ozaki, 2006a; Watanabe, Morita, & Ozaki, 2007) et al. utilized a newly developed method, perturbation-correlation moving-window two-dimensional correlation spectroscopy, to investigate the temperature-dependent changes of hydrogen bonds in I_α and I_β cellulose, elucidating the phase transition at 220 °C was mainly induced by the dissociation of intrachain hydrogen bonds. In contrast to the structure of cellulose, the structure of the NaCMC was just substituted part of the O6H6 groups with CH_2COONa, as Scheme 1 shows, but the physical and chemical properties (like water solubility and hydrogen bonding structure) change a lot. There are two main differences between cellulose and NaCMC. First, the introduce of the hydrophilic CH_2COONa

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* Corresponding author. Tel.: +86 2165643255; fax: +86 2165640293.
E-mail address: peiyiwu@fudan.edu.cn (P. Wu).

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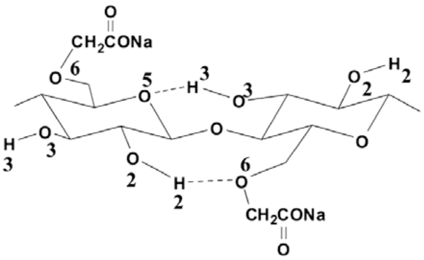


Scheme 1. The scheme of sodium salt of carboxymethyl cellulose.

groups increase the water absorption more or less so that the influence of the water molecules on hydrogen bonds at room temperature cannot be ignored; second, the substitution of CH_2COONa groups is inhomogeneous in both substitutedposition and degree, which increases the complexity of hydrogen bonds. Herein, we casted NaCMC film with aqueous solution and perform the infrared analysis. From the structure of NaCMC shown in Scheme 1, we judge that the O3–H3...O5 and O2–H2...O6 intrachain hydrogen bonds mentioned in many works (Marechal & Chanzy, 2000; Watanabe et al., 2006a, 2007) are influenced little. But due to the substitution of CH_2COONa groups, the O6–H6...O3′ interchain hydrogen bonds (Marechal & Chanzy, 2000; Watanabe et al., 2006a, 2007) in cellulose were influenced a lot in NaCMC film.

Infrared spectroscopy is sensitive to the conformation and local molecular environment of molecules including biopolymers (Watanabe et al., 2006a) and is frequently used in the analysis of hydrogen bonds (Guo & Wu, 2008; Marechal & Chanzy, 2000; Watanabe et al., 2006a, 2007). The basic concept of two-dimensional correlation spectroscopy was originally proposed and later modified by Noda and Ozaki (Noda, 1989, 1990, 1993; Noda, 2004). By spreading spectral peaks over the second dimension, the visualization of complex spectra consisting of many overlapped bands is identified and spectral resolution is enhanced. As a result, it is possible to identify the bands not readily accessible from one-dimensional spectra like highly overlapping hydrogen bonding OH region. Moreover, to investigate the effect of temperature on the structure of chains, we can obtain a set of temperature-dependent spectral signals. After calculation, 2D correlation spectroscopy can provide information about the sequential order of the spectral changes of molecular segments taking place based on the external perturbation. Recently, we have successfully used this powerful tool to study many polymer systems including temperature dependent transition of hydrogen bonds in cellulose diacetate (Guo & Wu, 2008), phase separation of poly(N-isopropylacrylamide) (Sun, Lin, Wu, & Siesler, 2008; Sun, Lin, & Wu, 2007) aqueous solution and poly(vinyl methyl ether) (Guo, Sun, & Wu, 2008) aqueous solution, interactions between water and ionic liquids (Sun, Jin, Tan, Wu & Yan, 2008), water diffusion in several polymer systems (Liu, Wu, Ding, Chen, & Li, 2002; Tang, Wu, & Siesler, 2008), etc. More recently, Ozaki and Morita (Morita, Shinzawa, Noda, & Ozaki, 2006; Watanabe, Morita, & Ozaki, 2006b) developed a new method called perturbation-correlation moving-window two-dimensional correlation spectroscopy (PCMW), which has the advantages to monitor the complicated spectral variation along the perturbation direction and thus define the phase transition point.

2. Experimental

2.1. Materials and sample preparation

The sodium salt of carboxymethyl cellulose (NaCMC) was purchased from Acros (spectrograde, purity > 99.9%) with molecular weight of 90,000 and degree of carboxyl substitution (DS) of 0.7. NaCMC aqueous solution was prepared and then casted onto a CaF_2 plate, which was put into a vacuum oven and dried at 50 °C for 24 h to form NaCMC film with thickness of ca.10 μm. All the water used in the experiment was deionized water.

2.2. Characterization

Thermal Gravimetric Analysis (TGA) of the NaCMC powder and the film was carried out on a Perkin-Elmer Pyris-1 at a rate of 10 °C /min with nitrogen protected. Differential Scanning Calorimetry (DSC) was performed at Mettler Toledo DSC822 and calibration for the temperature scale was performed using indium. As the DSC procedure, the film was cut into small pieces and heated from 50 to 250 °C at a heating rate of 1 °C /min with nitrogen protected. The infrared of the NaCMC film was carried out in the temperature range of 40–220 °C at a heating rate of 1 °C/min with KBr plates. The IR spectra were recorded at a resolution of 2 cm^{-1} using a Nicolet Nexus 470 FTIR spectrometer equipped with a DTGS detector and 64 scans were performed for each spectrum.

2.3. Two-dimensional correlation analysis

The generalized 2D correlation analysis was performed by Shige software provided by Ozaki group, Kwansei Gakuin University, Japan. In the 2D correlation maps, the red regions are defined as the positive correlation intensities while the blue regions are defined as the negative ones. The slice spectra of 2D maps were also plotted by the 2D Shige software. In perturbation-correlation moving-window two-dimensional correlation studies, the window size of $2m + 1$ is refined to 11.

3. Results and discussion

3.1. The water contents in NaCMC powder and film

Due to the strong hydrophilicity, although the NaCMC powder was dried for 24 h at 50 °C in the vacuum oven, it still contained amounts of water molecules, which can be calculated from the TGA curve (see Fig. 1), that is, approximately 8% water content in the dry powder. Also we examined the water content in the NaCMC film we prepared and it is about 7.5%, almost the same as that in the powder. Due to the high water content, the hydrogen bonds formed between water molecules and polymer chains cannot be ignored, which probably formed between water molecules and hydrophilic OH and COONa groups.

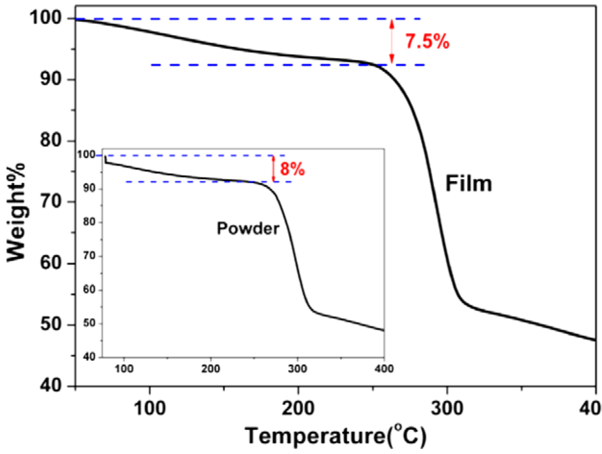


Fig. 1. TGA curve of the NaCMC powder and film. The inset is the curve of NaCMC powder.

3.2. The two important transition temperature points

The DSC curve of the NaCMC film was shown in Fig. 2 and we could recognize two obvious transition temperature points, around 100 and 170 °C, respectively. Obviously, the first point 100 °C is related to the complete loss of water molecules. As to the second point 170 °C, we assume that the transition is due to the structural transitions of the polymer chains. According to Proniewicz (Lojewska, Miskowiec, Lojewski, & Proniewicz, 2005) et al. the transition is probably related to the partial oxidation of the OH groups on the polymer chains. Since the OH groups directly connected to the sugar rings (O2H2, O3H3) are hard to be oxidized under 220 °C (Watanabe et al., 2006a), besides, the degree of substitution of the NaCMC we used is 0.7, we speculate that the oxidation is due to the residual O6H6 groups that are not substituted by the CH_2COONa groups.

Fig. 3 depicts raw infrared spectra with the increasing temperature in the range of 3690–2600 cm^{-1} and 1800–1500 cm^{-1}, respectively. From the spectra, we find that a peak around 1750 cm^{-1} start to arise around 170 °C, it is consistent with the above DSC results. Compared to Proniewicz's (Lojewska et al., 2005) conclusions, the products of the cellulose partial oxidation is carboxyl groups. But it still worth keeping in attention that the carboxyl groups is not oxidized from O2H2 or O3H3 because they are stable at this temperature but from the O6H6 groups that are not substituted by CH_2COONa just as mentioned above. On the other side, the intensity of OH stretching region (3690–3000 cm^{-1}) decrease acutely with the temperature increasing while the intensity of C=O stretching region (1800–1550 cm^{-1}) undergoes little changes.

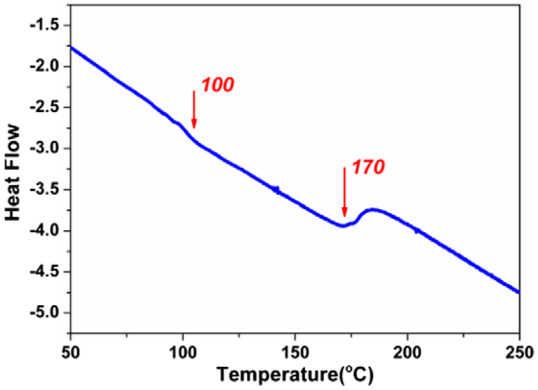


Fig. 2. DSC curve of the NaCMC film from 50 to 250 °C. The two transition points were shown by the red arrows. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

The peak area of the OH stretching range in 3690–3000 cm^{-1} was calculated and plotted in Fig. 4a and obviously the tendency of peak area decreasing slows down at around 100 °C. With the similar method used in our previous work (Guo & Wu, 2008), we draw two tangent lines of two regions, respectively, that intersect at ca.100 °C, which is estimated to be the first transition point, consistent with the DSC results. It is easy to learn that the water molecules escaped completely at 100 °C and make this temperature an important demarcation point. Before 100 °C, with the gradual loss of water molecules, hydrogen bonds formed between water molecules and polymer chains are broken, which contributes a lot to the decrease of the peak area of OH stretching region; after 100 °C, all of the water molecules escape so the rate of the decrease slows down.

In addition, perturbation-correlation moving-window (PCMW) two-dimensional correlation analysis was performed in the range of 1800–1550 cm^{-1}. In the synchronous map (shown in Fig. 4b), we can find that five main peaks appear in this region: 1750, 1660, 1616, 1600, 1580, 1750 cm^{-1} appears after 170 °C and its intensity increases with temperature. The intensity of 1616 cm^{-1} increases before 100 °C and that of the rest peaks decreases with temperature. However, the transition temperature point cannot be directly defined from the PCMW map, probably because the PCMW technique is not effective for this system.

For the peaks distinguished by PCMW, we plotted the peak height versus temperature of 1750, 1660, 1616, 1580 cm^{-1}, respectively, as shown in Fig. 4c. We find that the intensity of 1616 cm^{-1} increases and the intensity of 1660 and 1580 cm^{-1} decreases with temperature before 100 °C. When the temperature is higher than 100 °C, the intensity of above three peaks changes little. From this result we deduce that the three peaks are related to water molecules. 1660 cm^{-1} is related to the bending mode of H_2O molecules (Shen & Wu, 2003), 1616 cm^{-1} is assigned to the hydrated C=O groups and 1580 cm^{-1} is representative of the non-hydrated C=O groups. As to 1750 cm^{-1}, the intensity before 165 °C is nearly zero, and after 170 °C its intensity undergoes a steady increase. Combined with the above analysis and the DSC results, we define that 1750 cm^{-1} is indeed originated from the appearance of COOH groups oxidized from O6H6 groups.

According to above analysis, we find two important transition temperature points: one is 100 °C, corresponding to the complete loss of water molecules and the other is 170 °C, corresponding to the oxidation of residual O6H6 groups. Based on the results, we divided the temperature into three ranges, that is, 40–100 °C, 110–160 °C, 180–220 °C. In the first range, the water molecules evaporate from the system gradually and the hydrogen bonds formed between water molecules and polymer chains were gradually broken, which contributes a lot to the decrease of intensity of the OH

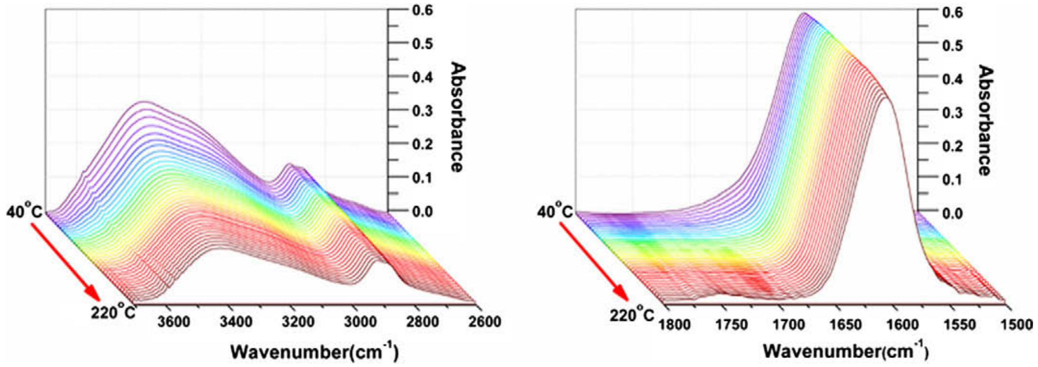


Fig. 3. The temperature-dependent infrared spectrum of NaCMC film in the range of 3690–2600 cm^{-1} (left) and 1800–1500 cm^{-1} (right) from 40 to 220 °C.

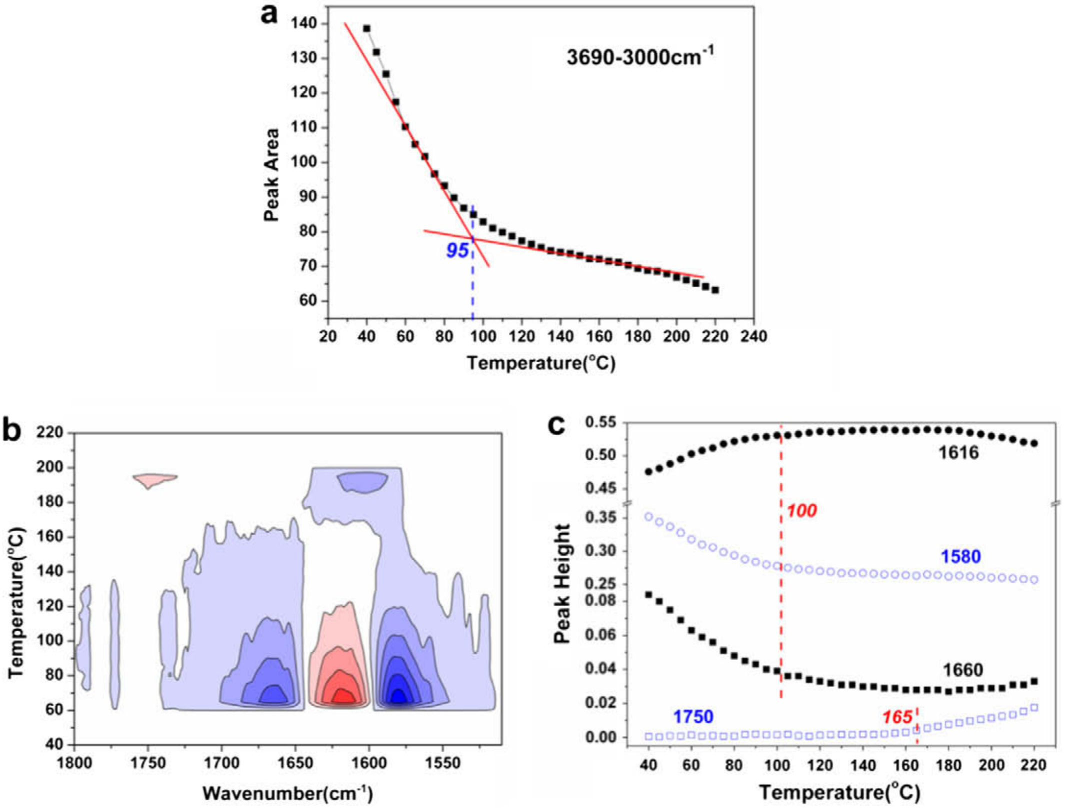


Fig. 4. (a) The peak area of 3690–3000 cm^{-1} region. Two tangent lines of two regions were drawn and intersect at 95 °C. (b) Synchronous PCMW map of 1800–1500 cm^{-1}. (c) The variation of peak height of 1616, 1580, 1660 and 1750 cm^{-1} in C=O stretching regions.

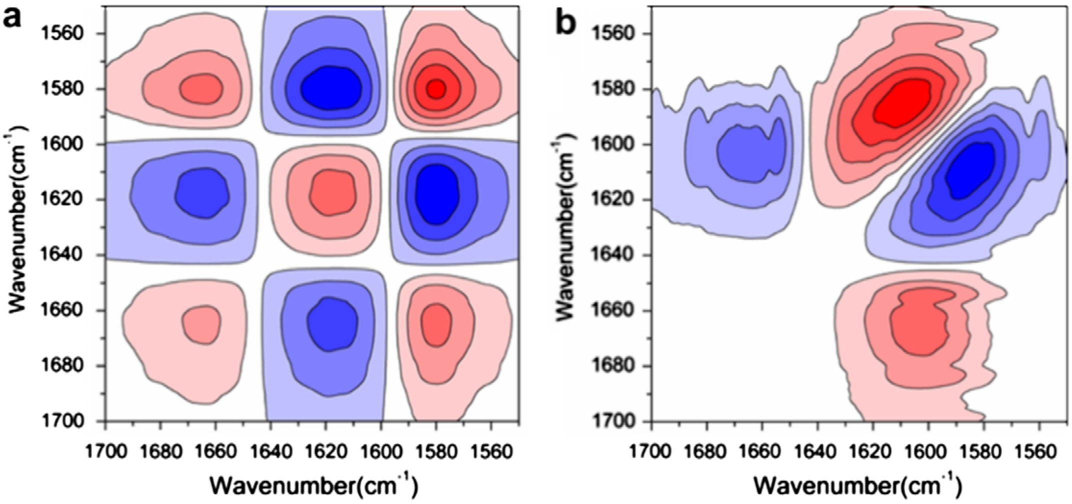


Fig. 5. The synchronous (a) and asynchronous (b) 2D correlation maps of NaCMC film in 1700–1550 cm^{-1} region in the temperature range of 40–100 °C.

stretching region; in the second range, the decrease of inter- and intrachain hydrogen bonds between polymer chains continue to be weakened, which dominate the decrease of OH stretching range; in the third range, besides the changes in the second range, the OH groups were oxidized to COOH groups. Since the peaks in OH stretching region strongly overlap, we use two-dimensional correlation analysis to further study the variation of the hydrogen bonds. The subsection here provides for the further two-dimensional analysis.

3.3. Two-dimensional infrared correlation analysis

3.3.1. The C=O stretching region

Two-dimensional (2D) analysis on 1700–1550 cm^{-1} region in the temperature range of 40–100 °C was performed and the results were shown in Fig. 5. In the synchronous map (Fig. 5a), three autopeaks including 1660, 1616 and 1580 cm^{-1} was obtained as the same as those in PCMW analysis. As we have analyzed above, the intensity of 1660 and 1580 cm^{-1} decreases while the

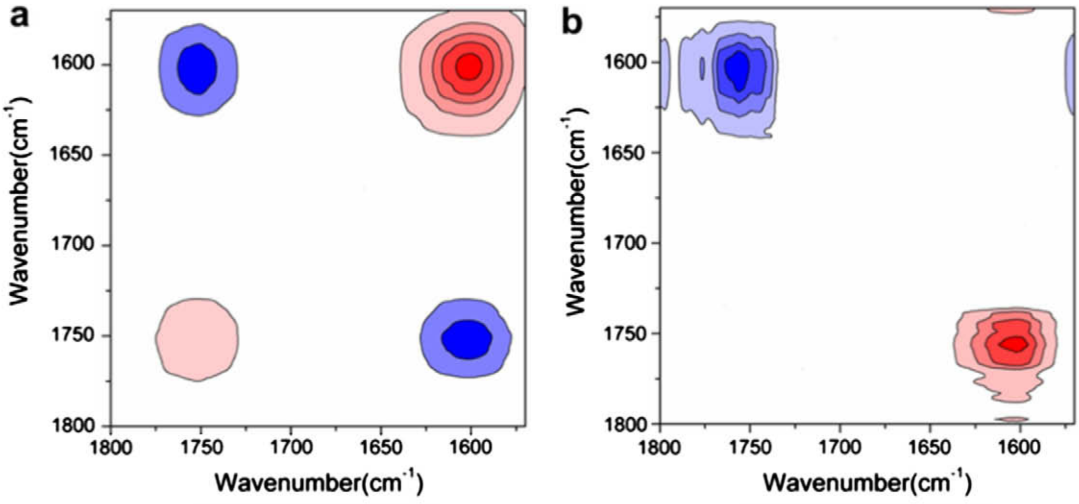


Fig. 6. The synchronous (a) and asynchronous (b) 2D correlation maps of NaCMC film in 1700–1550 cm^{-1} region in the temperature range of 180–220 °C.

1616 cm^{-1} increases. 1660 cm^{-1} is characteristic of the bending mode of OH groups of water molecules, and 1580 cm^{-1} is characteristic of hydrated C═O groups while 1616 cm^{-1} is of non-hydrated ones. In the asynchronous map, there appears a positive correlation peak in (1660, 1616 cm^{-1}) and a negative correlation peak in (1616, 1580 cm^{-1}). According to Noda's rule (Noda, 2004), we can judge that 1660 cm^{-1} varies prior to 1616 and 1580 cm^{-1} also varies prior to 1616 cm^{-1}.Based on the results, it is inferred that the water molecules evaporate first, as a result, the hydrated C═O groups transits into free C═O groups, then the peak at 1616 cm^{-1}, corresponding to the free C═O groups, increases with the hydrated ones broken (see Fig. 6.

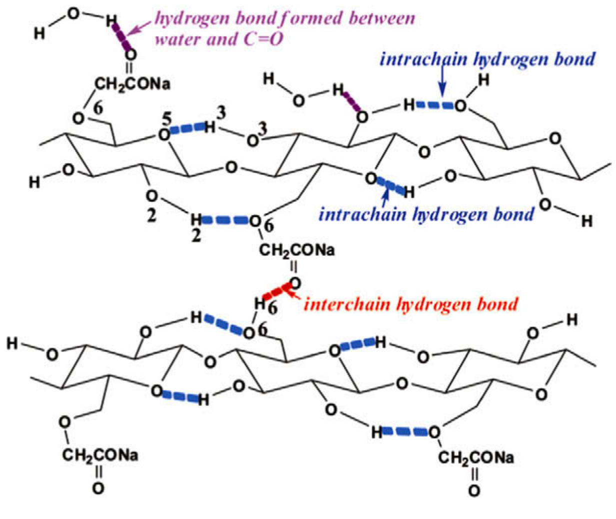
The variation of this region in 110–160 °C range is so small that two-dimensional maps depict only noise peaks (data not shown). In the temperature range of 180–220 °C, on synchronous map there appears two correlation peaks, combined with the raw spectra, we could find that the intensity of 1750 cm^{-1} increases and that of 1601 cm^{-1} decreases. Combined with the asynchronous map, which depicts only one correlation peak at (1750, 1601 cm^{-1}), we can judge that 1750 cm^{-1} varies prior to 1601 cm^{-1}.

In cellulose, according to Chanzy (Marechal & Chanzy, 2000) and Ozaki (Watanabe et al., 2006a), the interchain hydrogen bonds mainly form between O6H6 groups and O3 atoms from another chain, that is, the O6–H6…O3′ interchain hydrogen bonds. As we have clarified above, in the NaCMC film we adopted, just part of O6H6 groups are substituted by CH$_2$COONa groups, so we deduce that the interchain hydrogen bonds mainly form between O6H6 groups and CH$_2$COONa groups, and another type of interchain hydrogen bonds is still O6–H6…O3′. When the temperature arose up to 170 °C, the O6H6 groups started to be oxidized to COOH groups, which were corresponded to the peak of 1750 cm^{-1}. Consequently, the interchain hydrogen bonds formed between O6H6 groups and CH$_2$COONa groups were gradually broken. As a result, the intensity of the interchain hydrogen bonds decreases after the oxidation, consistent with the above two-dimensional analysis that the 1750 cm^{-1} varies prior to 1601 cm^{-1} (shown in Scheme 2).

In summary of this region, we conclude that during the range of 40–100 °C, the hydrated C═O bonds transit into non-hydrated C═O bonds; in the range of 110–160 °C, the C═O region undergoes little changes; and in the range of 180–220 °C, the O6H6 groups are gradually oxidized, which weakens the interchain hydrogen bonds formed between O6H6 groups and CH$_2$COONa groups.

3.3.2. The OH stretching region

The main assignments of OH stretching region is consulted with Marechal's (Marechal & Chanzy, 2000) and Ozaki's (Watanabe et al., 2006a) works, as shown in Table 1. The correlation peaks of 40–100 °C range is too disorderly (data not shown), which is probably due to the existence of water molecules and thus the complicated sorts of hydrogen bonds, including hydrogen bonds formed between OH groups between water molecules and CH$_2$COONa groups, hydrogen bonds formed between OH groups, ones formed between water molecules and OH groups along cellulose chains, intrachain hydrogen bonds including O3–H3…O5 and O2–H2…O6, interchain hydrogen bonds formed between O6H6 and COONa, etc. Those hydrogen bonds overlapped strongly and varied with temperature violently so that the 2D maps in this temperature range come to a mess. The power spectra in synchronous map in this region was plotted and shown in Fig. 8a, in which we can find that there is a shoulder peak at 3270 cm^{-1} besides the main peak at 3390 cm^{-1}. 3270 cm^{-1} is the O2–H2…O6 intrachain hydrogen bonds, and 3390 cm^{-1} varies a lot versus temperature,



Scheme 2. Hydrogen bonds in NaCMC film at room temperature. The intrachain hydrogen bonds are in blue, interchain hydrogen bonds are in red and hydrogen bonds formed between water molecules and C═O groups in purple. (For interpretation of the references to colour in this scheme legend, the reader is referred to the web version of this article.)

Table 1
Wavenumbers and assignments of the OH groups of cellulose and sodium salt of carboxymethyl cellulose.

Cellulose Marechal and Chanzy, 2000; Watanabe, Morita and Ozaki (2006a)		Sodium salt of carboxymethyl cellulose	
Wavenumber (cm^{-1})	Assignment	Wavenumber (cm^{-1})	Assignment
3470	Weak hydrogen bonded OH	3530	Weak hydrogen bonded OH
		3390	Hydrogen bonds with H_2O
3339	O3–H3...O5 intrachain	3330	O3–H3...O5 intrachain
3270	O2–H2...O6 intrachain	3270	O2–H2...O6 intrachain
3301	O6–H6...O3' interchain	In 3360–3200	CH_2COONa...O6' interchain

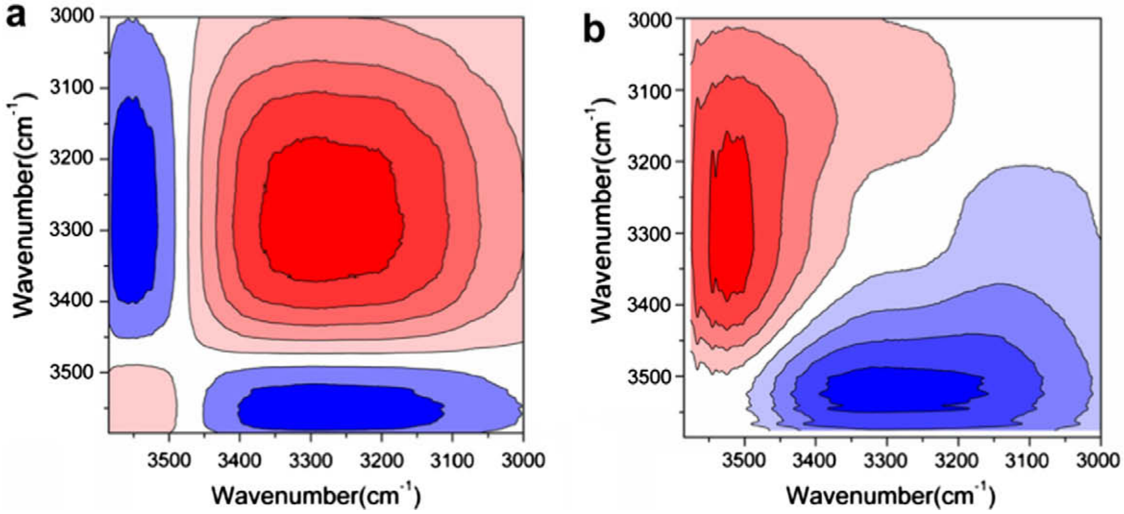


Fig. 7. The synchronous (a) and asynchronous (b) 2D correlation maps of NaCMC film in 3585–3000 cm^{-1} region in the temperature range of 110–220 °C.

probably assigned to the stretching mode of OH groups bonded to the water molecules because of the most violently variation of the peak.

We performed the 2D analysis in the 110–160 °C range and 180–220 °C range and found that although the synchronous maps have a little difference, the general maps in two temperature ranges are very similar. So we performed in the whole range of 110–220 °C and the difference of synchronous maps will be shown as power spectra in Fig. 8a. The 2D correlation maps of 110–220 °C were shown in Fig. 7. Compared to the 40–100 °C range, the water molecules were totally removed and so the complexity of the hydrogen bonds decreases more or less but there still exist many kinds of H-bonds. According to Marechal (Marechal & Chanzy, 2000) and Ozaki (Watanabe et al., 2006a), the peak around 3270 cm^{-1} is representative of intrachain O2–H2...O6 hydrogen bonds, and 3330 cm^{-1} is representative of O3–H3...O5 intrachain hydrogen bonds. The synchronous map depicts a big broad peak around 3380–3200 cm^{-1}. We drew the power spectra of synchronous map in 110–160 °C and 180–220 °C range, respectively (curve2 and curve3 in Fig. 8a), finding that in the range of 110–160 °C, the curve from 3330 to 3270 cm^{-1} is almost flat and in the range of 180–220 °C, 3330 cm^{-1} is the main peak with 3270 cm^{-1} the shoulder peak. Compared to the power spectra in the range of 40–100 °C (curve1 in Fig. 8a), the main peak shifts from 3390 to 3270 or 3330 cm^{-1} with the temperature, which also proves that 3390 cm^{-1} is representative of OH groups related to water molecules. Power spectra of the 110–160 °C range and 180–220 °C range also infer that all peaks vary strongly with the increasing temperature. Further speaking, to some extent, we can infer that the O3–H3...O5 intrachain hydrogen bonds are more stable than O2–H2...O6.

In the asynchronous map, a narrow and long correlation peak appears around 3530 cm^{-1}. We sliced at 3530 cm^{-1} and plotted the slice spectra, as shown in Fig. 8b. From the slice spectra, we can see in the range of 3360–3200 cm^{-1} the spectra is almost flat and so we conclude the hydrogen bonds in this range are still so complicated that even asynchronous spectra cannot differentiate the various hydrogen bonds. From the results of Marechal's (Marechal & Chanzy, 2000) and Ozaki's (Watanabe et al., 2006a), we assign 3530 cm^{-1} to the weak bonded hydrogen bonds.

According to Noda's rule, we can define the interchain and intrachain hydrogen bonds (3360–3200 cm^{-1}) vary prior to the weak hydrogen bonded OH (3530 cm^{-1}). It is obvious that the interchain and intrachain hydrogen bonds was weakened at first and then transited into weak hydrogen bonded OH groups.

3.3.3. Overall scheme

According to the above analysis with various tools, we can now draw a big picture of the transition process of NaCMC film during the heating process. As the 2 shows, at room temperature, the main hydrogen bonds in the film include hydrogen bonds formed between water molecules and C=O groups, the intrachain O3–H3...O5 and O2–H2...O6 hydrogen bonds, and the interchain hydrogen bonds (for the sake of simplicity, we just drew the hydrogen bonds that vary a lot in the heating process). Below 100 °C, as the temperature rises, the water molecules evaporate gradually and the hydrogen bonds formed between water molecules and C=O groups are weakened, making the hydrated C=O groups transit into non-hydrated ones. Meanwhile, the intrachain hydrogen bonds are also weakened. When the temperature continues to rise, in the temperature range of 110–160 °C, the intrachain hydrogen bonds continues to be weakened and the weak hydrogen bonds which at 3530 cm^{-1} start to arise. When the temperature rises up to 170 °C, the O6H6 groups that have not been substituted start to be oxidized and make the interchain hydrogen bonds formed between O6H6 and CH_2COONa groups

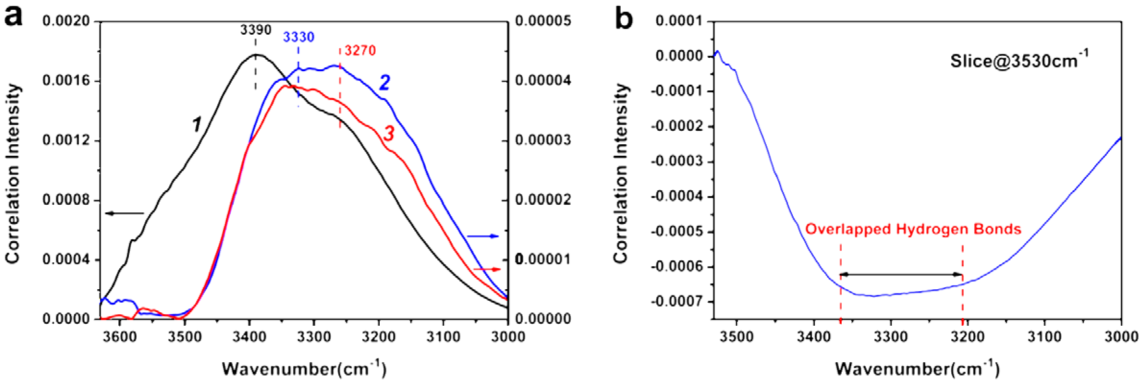


Fig. 8. (a) Power spectra in the temperature range of 40–100 °C (1, black), 110–160 °C (2, blue) and 180–220 °C (3, red) in 3690–3000 cm^{-1} region. (b) Slice spectra at 3530 cm^{-1} of the asynchronous map in the temperature range of 110–220 °C in 3690–3000 cm^{-1} region. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

weakened, at the same time, the amount of the weak hydrogen bonds still increases.

4. Conclusion

In conclusion, we defined the hydrogen bonds in the film and investigated the transition process of hydrogen bonds in NaCMC film during the heating process. First we utilize the DSC together with the PCMW analysis and 1D IR analysis methods to confirm the two important temperature points during heating: 100 °C and 170 °C, which are corresponding to the complete loss of water molecules in film and the starting temperature of O6H6 oxidization, respectively. Then we divided the whole temperature range into three parts and perform the 2D analysis on each range, respectively. We found that the water molecules bound with $C=O$ groups and OH groups. With the evaporating of water molecules, the hydrated $C=O$ groups gradually transited into non-hydrated $C=O$ groups. As the temperature continues to increase, the intrachain hydrogen bonds were weakened and transited into weak hydrogen bonds. But because of the complexity of the hydrogen bonds, we cannot differentiate the various sorts of hydrogen bonds and can just define that they are between 3360 and 3200 cm^{-1}. When the temperature rose up than 170 °C, the O6H6 were gradually oxidized and thus the interchain hydrogen bonds formed between CH_2COONa groups and O6H6 were weakened. In summary, we drew a big picture of the main hydrogen bonds existing in NaCMC film and monitored their transition process during heating, which may provides a lot for the further application of NaCMC in both industry aspects and in laboratory.

Acknowledgements

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