Characterization and Solubility Effects of the Distribution of Carboxymethyl Substituents Along the Carboxymethyl Cellulose Molecular Chain

Pinyu Yu, a,b Yufeng Hou, a Hongjie Zhang, a,c,* Wenhui Zhang, a Shuo Yang, a,* and Yonghao Ni a,b

Sodium carboxymethyl cellulose (CMC) is a major cellulosic derivative that has a wide variety of applications. The solubility of CMC is affected by the degree of substitution (DS) of carboxymethyl groups and their distribution along the CMC molecular chain. In this study, an enzymatic hydrolysis technique was used to determine the distribution of carboxymethyl substituents. Two key parameters, namely the average length of the molecular chain segments not susceptible to enzymatic hydrolysis by cellulases (\( L_{\text{Sn}} \), including chains fully substituted or containing single unsubstituted unit) and the average length for the molecular chain segments susceptible to enzymatic hydrolysis (\( L_{\text{Gn}} \), unsubstituted chains segments), were obtained. This approach was subsequently applied to characterize four CMC samples having similar DS values (~0.80). The distributions of carboxymethyl substituents along the CMC molecular chain were found to be drastically different. The \( L_{\text{Sn}} \) varied from 9.6 to 49.5, while the \( L_{\text{Gn}} \) was almost constant (from 4.5 to 5.4). This information was correlated to the CMC solubility. The swelling ratio and the dynamic contact angle revealed that the CMC samples with higher \( L_{\text{Sn}} \) exhibited stronger swelling and wettability than those with lower \( L_{\text{Sn}} \). The dissolving time of the CMC molecule decreased substantially with the increase in \( L_{\text{Sn}} \).

Keywords: Carboxymethyl cellulose; CMC; Solubility; Enzymatic hydrolysis; Cellulase; Substituent distribution

Contact information: a: Tianjin Key Laboratory of Pulp and Paper, Tianjin University of Science and Technology, Tianjin 300457, P. R. China; b: Limerick Pulp and Paper Centre, Department of Chemical Engineering, University of New Brunswick, Fredericton, NB E3B 5A3, Canada; c: China National Pulp and Paper Research Institute Co. Ltd., Beijing 100102, P. R. China;
*Corresponding authors: hongjiezhang@tust.edu.cn; yangshuo1018@163.com

INTRODUCTION

Sodium carboxymethyl cellulose (CMC), one of the major cellulosic ethers, is widely used as a binding, thickening, and stabilizing agent (Lee et al. 2018; Zhang et al. 2018). The solubility of CMC in water is a key parameter in these applications. It is well known that the degree of substitution (DS) and the molecular size are two important factors affecting the CMC solubility (Klemm et al. 2005; Jahan et al. 2011; Xu et al. 2013). Theoretically, three hydroxyl groups of each anhydroglucose unit (located at C2-, C3-, and C6 positions) in CMC are available for more carboxymethyl group substitutions. Thus, the maximum DS (the number of substituent groups per glucose unit) value that can be achieved is 3.0. Generally, a DS value with higher than 0.6 is required for CMC to have good water solubility.
In essence, there are two key fundamental issues associated with the carboxymethyl groups in CMC: 1) the overall carboxymethyl group content of the CMC molecular chain; and 2) the carboxymethyl group content on each glucose unit. Physical and chemical properties of CMC are mainly determined by DS, distribution of substituents, and degree of polymerization. Among above properties, the DS and homogeneity of substituent distribution have more influence on the solubility and rheological behavior of CMC (Zhao et al. 2003). In the literature, many have focused on the DS of CMC solubility (Reuben and Conner 1983; Käuper et al. 1998; Capitani et al. 2000; Oudhoff et al. 2004). However, the distribution of the carboxymethyl groups on the CMC molecular chain has received much less attention. The homogeneity of substituent distribution is influenced by many factors, such as the types and composition of solvent (Zhao et al. 2003). It is difficult to control the substituent location of CMC, but some researchers have made some interesting discoveries. Cheng et al. (1996) synthesized CMC in a two-phase medium containing benzene/ethanol/water and found that the sequence of distribution of carboxymethyl group of the products in AGU was C$_6$ > C$_2$ > C$_3$; and when the degree of substitution (DS) was low to 1.0, the approximate value of C$_2$: C$_3$: C$_6$ was 1.45: 1: 2.15; when the DS was being increased to values higher than 1.0, the proportional distribution of substitution among C$_2$, C$_3$, and C$_6$ groups was not dependent on the substitution degree. Liu et al. (1997) prepared a series of 2,3-O-carboxymethyl celluloses (CMC's), which were regioselectively substituted at the C$_2$ and C$_3$ position, and examined their water solubility. Moreover, spectroscopic and chromatographic methods were developed to determine the presence of carboxymethyl groups on the C$_2$-, C$_3$-, and C$_6$ positions of the individual glucose unit (Reuben and Conner 1983; Käuper et al. 1998; Oudhoff et al. 2004). Another method consisting of two dimensional $^{13}$C nuclear magnetic resonance (NMR) and capillary electrophoresis was used to determine the carboxymethyl groups on the C$_2$-, C$_3$-, and C$_6$ positions of the glucose unit (Capitani et al. 2000; Oudhoff et al. 2004; Kono et al. 2016). Based on a cellulase degradation technique, Gelman (1982) characterized the distribution of substituent groups along the CMC chain by measuring both the viscosity and the reducing sugar content.

The hypothesis of the present research is that the CMC solubility is influenced not only by the DS and the molecular size (Jahan et al. 2011; Rani et al. 2014), but also by the distribution of the carboxymethyl groups along the CMC molecular chain. Even with the same/similar DS, the CMC solubility could be different, depending on the distribution of carboxymethyl substituents along the CMC molecular chain. In this study, the distribution of the substituent groups in the CMC molecular chain was quantitatively determined based on a modified enzymatic hydrolysis technique, and using two parameters, namely $\bar{L}_{5n}$ (the average length for the CMC molecular chains not susceptible to hydrolysis by cellulases, including chains fully substituted or containing single unsubstituted unit) and $\bar{L}_{6n}$ (the average length for the unsubstituted CMC molecular chains susceptible to enzymatic hydrolysis). Then, this approach was applied to four different CMC samples with similar DS (approximately 0.8), and the results were correlated to the CMC solubility/hydrophilicity, which were evaluated in terms of the swelling and wetting capacity of CMC, based on the swelling ratio ($D_{\text{swelling}}/D_{\text{dried}}$) and the dynamic contact angle measurement, respectively. Furthermore, these results were also correlated to the dissolving time of the same CMC samples, which was directly measured using focused beam reflectance measurement (FBRM) analysis.
EXPERIMENTAL

Materials

Fibrous CMCs used were four commercial samples purchased from mills in the Shandong Province in China. Their DS values were 0.73, 0.75, 0.76, and 0.80. Other properties of these samples are shown in Table 1. The morphology analysis of CMC was completed using a fiber tester (Mode 912; L&W Inc., Kista, Sweden) and the crystallinity was measured with X-ray diffraction (XRD, Mode D8; Bruker, Madison, WI, USA).

Table 1. Characteristics of CMC Samples

<table>
<thead>
<tr>
<th>Number</th>
<th>DS</th>
<th>Mean Length (mm)</th>
<th>Mean Width (μm)</th>
<th>Crystallinity (%)</th>
<th>Purity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.75</td>
<td>2.279</td>
<td>48.1</td>
<td>18.03</td>
<td>95</td>
</tr>
<tr>
<td>2</td>
<td>0.76</td>
<td>2.128</td>
<td>55.7</td>
<td>19.60</td>
<td>95</td>
</tr>
<tr>
<td>3</td>
<td>0.80</td>
<td>1.944</td>
<td>52.8</td>
<td>23.51</td>
<td>95</td>
</tr>
<tr>
<td>4</td>
<td>0.73</td>
<td>1.431</td>
<td>51.7</td>
<td>25.85</td>
<td>95</td>
</tr>
</tbody>
</table>

The chemicals used were of analytical grade, including H\textsubscript{2}SO\textsubscript{4}, NaHCO\textsubscript{3}, ethanol, HCl, and 3,5-dinitrosalicylic acid (DNS), and were purchased from Jiangtian Chemicals Co., Ltd. (Tianjin, China). Cellulase, glucose oxidase, and catalase samples were obtained from Novozymes (China Investment Co., Tianjin, China).

Methods

Enzymatic hydrolysis technique

The enzymatic hydrolysis technique was used to determine the substituted ($\bar{L}_{SN}$) and the unsubstituted ($\bar{L}_{GN}$) molecular chain lengths of CMC samples. First, a 25 mL CMC solution was prepared in a 100-mL conical flask at a consistency of 0.01 g/mL, with its pH adjusted to 5.5 using acetic acid (HAc) buffer solution. Then, a pre-set amount of cellulase solution, with a large excess amount, was added to the flask to ensure a complete enzymatic degradation of CMC molecular chains. During the enzymatic hydrolysis process, the flask was continuously shaken on a thermostated shaker at 40 °C for 30 h. Subsequently, the flask was boiled to deactivate the enzyme for ending the cellulase treatment. Next, 1.0 mL of an enzyme mixture of catalase (1 mg/mL) and glucose oxidase (2 mg/mL) was added into the flask containing the cellulase-treated hydrolysate, and the pH was adjusted to 7.5 using 0.1 M KH\textsubscript{2}PO\textsubscript{4}. Then, the flask with its contents was kept at 35 °C for 1.0 h. Finally, the solution was boiled again. The enzymatic hydrolysate was then used to determine the reducing sugar content by following the colorimetric method using the DNS reagent (Saqib and Whitney 2011). The principle of this method is based on the stoichiometric reactions between the DNS reagent and reducing sugars so that DNS is reduced to 3-amino-5-nitrosalicylic acid, which has a characteristic absorption at 540 nm, while simultaneously, the reducing sugars are oxidized.

Preparation of CMC handsheet

Because CMC that is intended for commercial use is generally preserved in the form of a water-soluble sodium salt, the acidification of CMC should be performed to test
its solubility, which is in favor of forming handsheets. In this process, the sodium carboxymethyl cellulose (Na-CMC) is acidified and transformed into its protonated form (CMC), through which the intermolecular hydrogen bonding throughout the polymer chain could be enhanced (Roshan et al. 2012).

As shown in Fig. 1, the dissolution process involves following steps: First, an acidification method (25% H₂SO₄, 35 °C, and 2 h) was applied to the CMC solution followed by repeated washing of the acidified product with water until the pH value became neutral. Subsequently, 80% ethanol was used for removing the soluble salts. Then, the acidified CMC handsheet sample was prepared with a standard sheet former, vacuum heated, and followed by drying. To bring it back to a soluble condition, the CMC handsheet was sprayed using a 10% NaHCO₃ solution and again dried.

**Measurements of the dynamic contact angle and solubility**

The swelling ratio, which is characterized as $D_{\text{swelling}}/D_{\text{dried}}$, was measured following the reported method (Cuissinat et al. 2008). The dynamic contact angle of the CMC handsheet sample was determined on a dynamic contact angle tester (FIBRO System AB, Stockholm, Sweden) in accordance with the TAPPI T558 (2010) standard. In addition, the CMC solubility was directly assessed based on the FBRM technique (Mettler Toledo, Redmond, WA, USA), which showed real time changes in the microfibrillar size during the dissolving process. First, a CMC handsheet was cut into square pieces (30 mm × 30 mm), then these small pieces were placed in a beaker filled with 100 mL water under the conditions of 25 °C and 400 r/min stirring speed. Subsequently, FBRM (Mettler Toledo, Redmond, WA, USA) was used to monitor the change in the size of CMC samples.

**RESULTS AND DISCUSSION**

**Determination of CMC Substituent Distribution Based on the Enzymatic Hydrolysis Technique**

Cellulase is a multicomponent enzyme system, consisting of a) endoglucanases (EGs) that hydrolyses cellulosic molecular chains randomly, b) cellubiohydrolases (CBHs) that hydrolyses cellobiose from the polymer ends, and c) cellobiases that hydrolyses cellobiose to glucose. These enzyme components act together during the degradation of cellulose, which can convert the complex cellulose structure into simple glucose molecules. For the CMC molecular chains especially, the cellulase can only cleave glycosidic bonds between two adjacent unsubstituted units along the CMC chain.
molecular chain; thus, the molecular chain is converted to glucose (G) units and substituted chains (GS), as shown in Fig. 2(a). The DNS assay was used to measure the total amounts of G and GS \( N_E \), following a procedure in the literature (Saqib and Whitney 2011).

The cleaved glucose units (G) can be oxidized by glucose oxidase to gluconic acid (G-COOH) as shown in Fig. 2(b), while the G-units at both ends of the GS chains cannot be oxidized. The amount of GS \( N_{GS} \) was measured based on the DNS method as mentioned above. Therefore, the amount of G \( N_G \) equals the total amount of G and GS \( N_E \) minus the amount of GS \( N_{GS} \).

![Schematic diagram of enzymatic hydrolysis](image)

**Fig. 2.** Schematic diagram of enzymatic hydrolysis: cellulase can only cleave glycosidic bonds between two adjacent unsubstituted units among the CMC molecular chain

**Evaluation of CMC Substituent Distribution by Calculating \( \bar{L}_{SN} \) and \( \bar{L}_{GN} \)**

There is reducing hemiacetal on the end of G and GS, and the total reduction value (E) of \( (G + GS) \) can be measured by potentiometric titration. G can be oxidized by glucose oxidase to gluconic acid, but AGU at both ends of the GS molecule cannot interact with the enzyme. Based on this principle, the number of G and GS \( (N_{GS}, N_G) \) in the CMC hydrolysate can be measured. Once the \( N_{GS}, N_G, W, \) and \( M_{CMC} \) values are known, the average number of substituted units (the average number of S contained among GS) can be obtained following Eq. 1,

\[
\bar{L}_{SN} = \frac{W}{M_{CMC}} \frac{N_G}{N_{GS}} - 2
\]

where \( \bar{L}_{SN} \) is the mean length of the substituted CMC molecular chain length, \( W \) is the sample weight (g), and \( M_{CMC} \) is the average molecular weight (Da). To remove the effect of the two G-units at both ends of the GS, Eq. 1 includes a term of “subtracting 2”.

If the CMC molecular chain is long enough, the concentrations of GS and G from the enzymatic hydrolysis will essentially be equal, and the average number of unsubstituted units in the CMC molecular chain can be calculated following Eq. 2,

\[
\bar{L}_{SN} = \frac{N_G}{N_{GS}} + 2
\]

where \( \bar{L}_{SN} \) is the mean length of the unsubstituted CMC molecular chain length.
As shown in Table 2, $L_{Sn}$ of the CMCs (with the similar DS) was in the range of 9.5 to 49.5, indicating that although the DS was almost the same (approximately 0.8), the distribution of these carboxymethyl groups into the number of anhydroglucose units could be very different. These results imply that even though the DS of various CMC samples is similar, there will be two different scenarios:

1) A certain amount of carboxymethyl groups are allocated evenly on the CMC molecular chain, which also means an increasing number of substituted anhydroglucose units (AGU) on each chain, and every single substituted AGU tends to maintain fewer carboxymethyl groups. Therefore, the average length of the substituted CMC molecular chain is expected to be higher, as it can be more frequent to see that single G-units are fixed between two S-units along the target substituted chain. In this way, a higher $L_{Sn}$ value and a lower $L_{Gn}$ value would be presented.

2) By contrast, a dense distribution of carboxymethyl groups can result in a shorter fragment of $G_{Sn}G$ compared to 1), since the single S unit, in this case, tends to get fully substituted by carboxymethyl groups followed by its decreased quantity in total and more G units can be cleaved from the CMC chain according to the hydrolysis rules. Consequently, it shows a lower $L_{Sn}$ value and a higher $L_{Gn}$ value, and it’s fair to say that the carboxymethyl groups are less uniformly distributed along the CMC molecular chain.

Table 2. Results on the Carboxymethyl Substituent Distribution Along Different CMC Molecular Chains

<table>
<thead>
<tr>
<th>Number</th>
<th>$M_{CMC}$</th>
<th>$N_{E}$ ($\times 10^{-5}$mol)</th>
<th>$N_{GS}$ ($\times 10^{-5}$mol)</th>
<th>$L_{Sn}$</th>
<th>$L_{Gn}$</th>
<th>Crystallinity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>222.15</td>
<td>11.6</td>
<td>3.4</td>
<td>49.5</td>
<td>5.4</td>
<td>18.03</td>
</tr>
<tr>
<td>2</td>
<td>222.95</td>
<td>13.0</td>
<td>4.8</td>
<td>33.6</td>
<td>4.7</td>
<td>19.60</td>
</tr>
<tr>
<td>3</td>
<td>226.15</td>
<td>16.4</td>
<td>7.3</td>
<td>20.6</td>
<td>4.5</td>
<td>23.51</td>
</tr>
<tr>
<td>4</td>
<td>220.43</td>
<td>34.7</td>
<td>13.1</td>
<td>9.6</td>
<td>4.7</td>
<td>25.85</td>
</tr>
</tbody>
</table>

Note: $M_{CMC} = 162.14 + 80.018$ DS

As it can be seen in Table 2, the $L_{Sn}$ value among four samples remained stable (about 5), which is attributable to the G-units being cleaved one by one so the average length of unsubstituted AGU units is supposed to be regular. With the decrease of $L_{Sn}$ value, an upward trend was evident in both crystallinity and $N_{GS}$, which reveals the fact that the distribution pattern and scale of CMC molecule correlates highly with the uniformity of carboxymethyl groups on CMC chains on the premise of similar DS value.

Swelling Ability and Wettability Analyses

The CMC solubility is usually influenced by its swelling ability and the wettability. The swelling of the fibrous CMC is mainly influenced by the bulk groups in the molecular chains. The polar attraction between water molecules and hydrophilic functional groups, e.g., carboxymethyl groups and hydroxyl groups, results in the penetration of water molecules through the amorphous region of CMC (Fatehi et al. 2013), which causes the swelling of the fibrous CMC. In this experiment, the water penetration into cellulose fiber and fiber swelling ability can be quantified by the...
swelling ratio, which is also known as \( D_s/D_d \). \( D_s \) is the diameter of CMC fiber after swelling, and \( D_d \) is the diameter of CMC fiber before swelling. The above data were obtained by optical microscope and measuring software.

As shown in Table 3, the \( D_s/D_d \) of the fibrous CMC with the highest \( \bar{L}_{Sn} \) was 2.81. As the \( \bar{L}_{Sn} \) increased, the swelling ability of the fibrous CMC increased, indicating that water molecules improved accessibility to the interior of the fibrous CMC, thus resulting in an increased solubility.

**Table 3.** The \( D_s/D_d \) of Various Fibrous CMC Samples

<table>
<thead>
<tr>
<th>Number</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \bar{L}_{Sn} )</td>
<td>49.5</td>
<td>33.6</td>
<td>20.6</td>
<td>9.6</td>
</tr>
<tr>
<td>( D_s/D_d )</td>
<td>2.81 ± 0.2</td>
<td>2.75 ± 0.2</td>
<td>2.55 ± 0.3</td>
<td>2.31 ± 0.3</td>
</tr>
</tbody>
</table>

Contact angle measurement is an effective and simple way to characterize surface wetting, which has been widely used in biological and technological systems. Generally, the contact angle can be determined by recording the video of a water drop on a solid surface, and then the Young equation is introduced to explain the results (Huhtamäki et al. 2018). This type of determination could work on the wettability of CMC handsheets as well, which is well practiced in the literature. For example, Liu et al. (2016) measured the contact angle of paper surface, which was coated with different amounts of CNC/Ag/beeswax composites. They studied its impact on antibacterial and hydrophobic properties of paper products. The wettability of the solid surface is mainly determined by the surface chemical composition and its three-dimensional microstructure (Šikalo et al. 2005). Due to the same papermaking conditions and related process, the three-dimensional microstructure has no significant influence on the wettability of the CMC handsheets. Hence, the chemical composition is the main factor influencing the wettability of the fibrous CMC matrix (or CMC handsheets). The rich hydrophilic groups (carboxymethyl groups and hydroxyl groups) on the CMC molecular chain will favor the water penetration process (Liu et al. 2014).

*Fig. 3.* The spreading rate of dynamic contact angle of fibrous CMC matrix
Figure 3 displays the results from the dynamic contact angle measurements. For all of the four samples studied, the contact angle decreased with increasing contact time. The CMC samples with higher $L_{Sn}$ exhibited consistently lower contact angles than those with lower $L_{Sn}$. Furthermore, Fig. 3 shows that the slope of these dynamic contact angle lines follows the order of $<1 > < 2 > < 3 > < 4$, indicating that the water spreading rate was faster for the CMC sample with a higher $L_{Sn}$. The above results support the conclusion that more uniform distribution of carboxymethyl groups (with higher $L_{Sn}$) on the CMC molecular chain favors the overall wetting process because of the improved dipole interactions between water molecules and these substituted hydrophilic carboxymethyl groups on the CMC molecular chains (Etter 1990). With the increase of the $L_{Sn}$ under a similar DS value, the electrostatic interactions were enhanced, thus leading to a more pronounced effect on the contact angle decrease (overall wetting process).

![Comparison](image)

**Fig. 4.** An illustration of the effect of carboxymethyl group distribution along the CMC molecular chain on water mobility

As shown in Fig. 4, when the water molecules interact with the CMC molecular chain, the dipole forces are in play between the water molecules and the functional groups (carboxyl groups and hydroxyl groups), which is well documented in the literature (Scallan 1983). Consequently, the water molecules penetrate into the CMC molecular chain quickly. Carboxyl groups have a higher affinity for water molecules than hydroxyl groups. Thus, the dipole interactions were improved and the “mobility” of the water molecules along the CMC molecular chain was enhanced, when the content of AGU in carboxymethyl group increased (namely higher $L_{Sn}$).

In the literature, it has been reported that more carboxyl groups in organic compounds and the presence of supramolecular structures have similar beneficial effects on their wettability/water mobility (Etter 1990; Desiraju 1996).
Determination of the Dissolving Time of the Fibrous CMC Handsheets

The CMC solubility was further assessed using the FBRM technique, which was based on the dissolving process of the fibrous CMC handsheets. The CMC dissolving process was achieved at the expense of hydrogen bonding in the fibrous CMC handsheets. Based on the discussion above, an increased water penetration and absorption capacity of the fibrous CMC, led to the formation of “water-bridges” (as shown in the inset of Fig. 5), ultimately resulting in the dissolution of CMC. Essentially, the water penetration/adsorption/swelling process was faster for the CMC samples with a higher $L_{Sn}$ value than those with a lower $L_{Sn}$ value. This was further confirmed by the results shown in Fig. 5, which indicated that the dissolving times were 21 s for the CMC with $L_{Sn} = 49.5$, 18 s for the CMC with $L_{Sn} = 33.6$, 16 s for the CMC with $L_{Sn} = 20.6$, and 12 s for the CMC with $L_{Sn} = 9.6$. These direct dissolution results indicated that an increase in the $L_{Sn}$ was directly correlated to the increased CMC solubility, which was in agreement with the increased swelling ability and wettability results, presented in the previous sections.

![Fig. 5](image_url)

**Fig. 5.** Effect of $L_{Sn}$ on the dissolving time of CMC handsheet, as determined by FBRM

In summary, all of the above results presented thus far support the conclusion that CMCs with similar DS do not necessarily give a similar solubility. Thus, the distribution of substituted carboxymethyl groups along the CMC molecular chain is an important parameter, and a higher $L_{Sn}$ CMC (substitution of carboxymethyl groups onto more AGU units) will have better swelling ability/wettability/solubility than a lower $L_{Sn}$ CMC.

**CONCLUSIONS**

1. The carboxymethyl group distribution profile along the CMC molecular chain was determined by following an enzymatic (cellulase) degradation technique, which
yields the results of the molecular chain length not susceptible to hydrolysis by cellulases ($\bar{L}_{Sn}$) and the fully unsubstituted molecular chain length susceptible to enzymatic hydrolysis ($\bar{L}_{Gn}$). Results showed that although the tested CMC samples indicated similar DS value (approximately 0.8), their $\bar{L}_{Sn}$ varied markedly, ranging from 9.6 to 49.5, while the $\bar{L}_{Gn}$ was almost constant (in the range of 4.5 to 5.4). The $\bar{L}_{Sn}$ was directly correlated to the CMC solubility: both the swelling ability and wettability increased with an increase in $\bar{L}_{Sn}$ as did the $D_s/D_d$ ratio and the dynamic contact angle measurements.

2. The results on dissolving time from the FBRM analyses supported the conclusion that an increase in $\bar{L}_{Sn}$ favoured the dissolving process of the fibrous CMC matrix. The present study provides direct evidence that a uniform distribution of carboxymethyl groups along the CMC molecular chain played an important role in the CMC solubility.

ACKNOWLEDGMENTS

The authors would like to acknowledge the financial support from the National Natural Science Foundation of China (Grant No. 31670588), and the Canada Research Chairs program.

REFERENCES CITED


TAPPI T558 om-10 (2010). “Surface wettability and absorbency of sheeted materials using an automated contact angle tester,” TAPPI Press, Atlanta, GA.

Article submitted: June 23, 2019; Peer review completed: August 26, 2019; Revised version received and accepted: September 19, 2019; Published: September 24, 2019. DOI: 10.15376/biores.14.4.8923-8934