# Carboxymethyl Cellulose Produced at Different Mercerization Conditions and Characterized by NIR FT Raman Spectroscopy in Combination with Multivariate Analytical Methods

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Carboxymethyl cellulose (CMC) is produced commercially in a two-stage process consisting of a mercerization stage followed by an etherification stage. In this work, extended mercerization stages were used when producing CMC from a spruce dissolving pulp. Near infra-red (NIR) Fourier transform (FT) Raman spectroscopy was used to analyse the molecular structures of the CMC and the gel fractions formed in the CMC preparation. Three different CMC groups were obtained, representing backbone structures of cellulose I, cellulose II, and amorphous cellulose. By applying principal component analyses (PCA) to the spectral data, two CMC classes were identified with different degrees of substitution (DS). Thus, a low degree of substitution was obtained in the CMC if the alkaline concentration in the mercerization stage was only 9.0%, and the backbone structure was cellulose I or II. However, if the alkaline concentration was higher (18.25% or 27.5%), then the degree of substitution in the CMC was also higher, and the backbone structure was more amorphous.

*Keywords: Carboxymethyl cellulose; Cellulose backbone structures; Degree of substitution; Extended mercerization; Gel formation; Multivariate analytical methods; NIR FT Raman spectroscopy*

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## INTRODUCTION

Cellulose is a linear macromolecule in which anhydroglucose units (AGU) are linked by β-1,4-glucosidic bonds. The chemical character of the cellulose is determined by the sensitivity of the β-glucosidic linkages to hydrolytic attack and by the presence of three reactive hydroxyl groups: the primary OH on C(6) and the two secondary OHs on C(2) and C(3) in the AGUs (Klemm *et al.* 2001a). In carboxymethyl cellulose (CMC), some of these OH groups are etherified with a carboxymethyl group, and the degree of substitution (DS) corresponds to the average number of carboxymethyl groups per AGU. The DS is an important CMC parameter, determining, for example, its solubility in water. The theoretical maximum of the DS value for cellulose/CMC is 3.0, but the range for commercially available CMC grades is generally in the range 0.4 to 1.5 (Heinze and Koschella 2005). Increasing DS enhances solubility in water; CMC has good water solubility above 0.6. CMC of low DS, *i.e*. less than 0.2 retains the fibrous character of the starting material and is not soluble in water (Borsa and Racz 1995).

The preparation of carboxymethyl cellulose (CMC) involves two reaction stages: mercerization and etherification. These reactions are commercially carried out in water-

alcohol mixtures, usually as a slurry process at 10% pulp consistency. In the first stage the pulp is treated with NaOH at 20 to 30 °C, and the alcohol is usually ethanol or isopropanol. This treatment acts as a swelling and impregnation stage and facilitates penetration of the NaOH into the cellulose structure. The product of this stage is called alkali cellulose (Na-cellulose) and it is highly reactive towards monochloroacetic acid (MCA), or its sodium salt, which is added in the following etherification stage. The reaction between alkali cellulose and the etherification agent is normally carried out at about 50 to 70 °C. Simultaneously, NaOH reacts with MCA to form substantial amounts of the by-products sodium glycolate and sodium chloride (Krässig 1993; Klemm *et al.* 2001b).

The original manufacturing process has been developed considerably since the early start of CMC production in the 1920's. The improvements have made it possible to use CMC in an increasing number of applications *i.e*. in food, pharmaceuticals, toothpaste, detergents, oil drilling mud, paper coating, *etc*. Today, CMC is used to enhance the viscosity, to control rheology of a solution, to avoid separation of water from a suspension, and to improve surface or barrier properties (Stigsson *et al*. 2001). The two major process steps of mercerization and etherification were originally carried out in separate reactors with a dry solids content of about 80 to 90%, and no organic solvent was used (Voss 1939). The original two-step dry process of mercerization and subsequent etherification has now been widely substituted by a one-step slurry process that incorporates the use of an alcohol as a co-solvent. The slurry process achieves a homogeneous blend of the components in the reactor, and the presence of the alcohol promotes an even distribution of monochloroacetate in the reaction mass, resulting in an additional enrichment of NaOH in the cellulose phase, favouring a further decrease in supramolecular order and a more uniform etherification. On the other hand, the alcoholic hydroxyl groups compete with the cellulosic ones for etherification and form low molecular mass ethers. Monochloroacetate consumption by this type of side reaction is however much smaller with isopropanol than with, *e.g.* methanol, due to the lower hydroxyl group reactivity of the former (Klemm *et al.* 2001b). By repeated mercerization-etherification steps, DS values above 1.5 can be obtained, and it has been reported that Kulicke prepared CMC samples with a DS of between 0.7 and nearly 3.0 by a slurry procedure with isopropanol (Kulicke *et al.* 1996).

The accessible part of the cellulose structure is often considered to be identical with the amorphous region of the macromolecule (Jeffries *et al.* 1969). It has been suggested that the mercerization reaction, in which the alkali triggers the conversion of cellulose to Na-cellulose I, always starts in the region of the fibre where a significant amount of amorphous phase is present (Okano and Sarko 1985; Schenzel *et al.* 2009). If the alkali concentration is lowered after the mercerization reaction, the cellulose I structures undergo an irreversible transition into the stable crystalline form, cellulose II. This cellulose type is less reactive and more compact than cellulose I due to a tighter molecular packing with stronger hydrogen bonds (Kolpak and Blackwell 1976; Kolpak *et al.* 1978).

As was reported earlier (Almlöf *et al.* 2012), the fraction of cellulose II in the pulp, prior to CMC preparation, had no impact on the resulting DS value of the CMC when the NaOH concentration in the mercerization stage was 9%. In this case the DS was as low as 0.5, although the NaMCA charge was 2.04 mol NaMCA $mol^{-1}$ AGU. However, when the NaOH concentration in the mercerization stage was higher, *i.e*. 18.25% or 27.5%, the fraction of cellulose II had a negative influence, compared to cellulose I, on

the obtained DS value, which in this case was about 1.0. Furthermore, the filtration resistance of CMC-water solutions increased in the direction towards higher cellulose II content in the original pulp. Lower NaOH concentration and higher temperature in the mercerization stage also increased the filtration resistance, probably due to a more uneven substitution along the cellulose backbone.

Jardeby *et al.* (2004) have shown by use of Fourier Transform, FT, Infrared (IR) spectroscopy that carboxymethylation of mercerized spruce sulfite pulp usually results in a substantial insoluble fraction, *i.e.* a gel that mainly consists of low-substituted cellulose segments. At low DS, most of the chemical modification reactions on the cellulose structures generally occur in amorphous regions or on the surfaces of residual crystalline domains. Aggregates with unevenly distributed substituents may appear in water solutions as highly swollen opaque or transparent macrogel particles. These particles have a distinct influence on the resulting rheological properties and thus on the solution behavior of the total system (Rinaudo *et al.* 2000).

The different forms of cellulose (I, II, and amorphous) can be distinguished by vibrational spectroscopies such as IR or Raman (Nelson and O'Connor 1964; Atalla and VanderHart 1984; Wiley and Atalla 1987). These methods are complementary, since spectral intensities will be obtained for the same vibrational modes. The backbone structural bands in Raman spectra are strong and sharp, and quite large molecules show clear bands. The low frequency region, which is quite sensitive to conformation, is observed with difficulty in the IR spectra, but it is readily observed in the Raman spectra. It is this greater selectivity that leads to the advantage of Raman spectra compared to IR spectra. FT Raman spectroscopy has shown an outstanding ability for characterizing the different backbone structures of cellulose (Wiley and Atalla 1987). In this paper, Near Infrared (NIR) Fourier transform (FT) Raman spectroscopy was therefore used in combination with multivariate spectral data analyses to improve our understanding of the relationship between structural parameters of the cellulose after the mercerization stage and the efficiency of the subsequent reactions in the etherification stage when preparing CMC from a spruce dissolving pulp.

## MATERIALS AND METHODS

A fully bleached and dried sulphite dissolving pulp, produced from *Picea abies* (Norwegian spruce), was provided by Borregaard Chemcell, Sarpsborg, Norway. This is a typical ether pulp that is commercially available. It had an intrinsic viscosity of 1500 $cm^3$ $g^{-1}$ (ISO 5351:2004), a $S_{18}$ value of 7.5% (ISO 692-1982), an ISO brightness of 85% (ISO 2470:1999), and a cellulose II content of < 3% (NIR FT Raman spectroscopy). Ball-milled bacterial cellulose was used as a reference for amorphous cellulose. The CMC was prepared with the following chemicals: Isopropanol (purity 99.7%, VWR International), methanol (purity 99.8%, VWR International), NaOH (purity 97%, MERCK), and sodium monochloroacetate NaMCA (purity 97%, Fluka).

### NaOH Pre-treatment of Pulp

A large sample of dissolving pulp (0.5 kg) was initially ground to fine powder in a knife mill (Fritsch Pulverisette 19, Fritsch GmbH, Idar-Oberstein, Germany). This mechanical treatment decreased the intrinsic viscosity to 1485 $cm^3$ $g^{-1}$ (ISO 5351:2004). Samples (30 g) of the dry powder were mixed with 1 L of 18% NaOH, corresponding to

29.2 mol NaOH $mol^{-1}$ AGU. The samples were then shaken for 30 min at room temperature (r.t.) in an anaerobic atmosphere in plastic bags. The samples were then washed with deionized water to a neutral pH, air dried, and stored at room temperature (r.t.). The obtained samples consisted of approximately 91% cellulose II, which was analytically verified by NIR FT Raman spectroscopy. For reference purposes, a number of samples of the powdered pulp were washed with deionized water, air dried, and stored at r.t. These samples consisted of approximately 78% cellulose I, as again analytically verified by NIR FT Raman spectroscopy.

## Carboxymethylation Procedure

A 17.5 g sample of the dissolving pulp was introduced into a glass reactor together with 224 mL isopropanol and 20.4 mL deionized water. The impeller was held at 350 rpm throughout the reaction, and a reflux condenser was mounted at the glass reactor to avoid evaporation. The reaction batch was purged with $N_2$ continuously to remove oxygen. Fifteen minutes later, either 3.0 g, 6.7 g, or 11 g of NaOH was mixed with 10.2 mL of deionized water and, finally, 39 mL of isopropanol was added to the solution. The NaOH-charges corresponded to 0.65, 1.55, and 2.55 mol NaOH $mol^{-1}$ AGU. The mixture was left at 20 °C, 30 °C, or 40 °C for 1 h, 24.5 h, or 48 h.

In the next step, 49 mL of 87% isopropanol was mixed with 25.65 g of NaMCA, corresponding to 2.04 mol NaMCA $mol^{-1}$ AGU, before being added to the reaction mixture. The temperature was raised during a period of 30 min to 60 °C and then left for 60 min at 60 °C. The reaction was terminated by neutralization with the addition of acetic acid.

After filtration, the product (NaCMC) was washed with 350 mL of 87% isopropanol, 4×350 mL of 70% MeOH, and finally washed with 350 mL pure MeOH. To confirm that all sodium-containing by-products, *i.e.* NaCl and $C_2H_3NaO_3$, had been removed from the washed CMC sample, some $AgNO_3$ solution was added to samples of the final wash filtrate. As no AgCl precipitation ever appeared, it was assumed that all sodium by-products had been removed. Thus, the only remaining sodium ions were those that belonged to the substituted CMC.

## Titrimetric Determination of DS

A 0.5 g sample of CMC, calculated as oven-dry product, was ashed at 700 °C for 15 to 20 min. The ash was then dissolved in 42 mL boiling deionized water before being titrated with 0.1 N $H_2SO_4$, using a 702 SM Titrino from Metrohm® until the solution reached a pH of 4.4. Boiling of the solution was done three times between repeated titrations to evaporate carbon dioxide. The DS value was then calculated from the amount of titrated acid (*b*/mL) and the amount of CMC (*G*/g), using Equation 1 according to Hong *et al.* (1978).

$$DS = \frac{0.162 \left( \frac{0.1\ b}{G} \right)}{1 - 0.080 \left( \frac{0.01\ b}{G} \right)} \quad (1)$$

## Separation of Gel Fraction by Filtration

A 9 g sample of CMC-powder, calculated as oven-dry product, was dissolved in 2 L of deionized water by stirring the solution at 1200 rpm at r.t. for 2 h. The solution was then filtered on a RBU glass filter of VitraPOR® Borosilicate 3.3, with a volume of 4000 mL to isolate the gel fraction and undissolved residuals. The glass filter used was a Por. 3 with a pore size of 15 to 40 μm. The gel fraction values of the CMC water solution were determined after filtration according to Equation 2,

$$\text{Gel fraction (\%)} = \frac{G_f}{G_i} \times 100 \quad (2)$$

where $G_i$ is the initial weight of the dry CMC, and $G_f$ is the weight of the dry insoluble part after extraction with water and a subsequent filtration stage

## NIR FT Raman Spectroscopy

NIR FT Raman spectra of the samples were acquired using a Bruker RFS 100 spectrometer equipped with a liquid nitrogen-cooled Ge diode as the detector. An Nd: YAG-laser, operating with the exciting line $\lambda_0$ = 1064 nm and a maximum power of 1500 mW, served as the light source for the excitation of Raman scattering. All spectra were recorded over the frequency range 3400 to 100 $cm^{-1}$ using an operating spectral resolution of 4 $cm^{-1}$. The cellulosic samples were analyzed in small aluminium cups of the sampling accessory placed across the normal sample holders; 180° backscattering geometry was applied. The spectra were averaged over 400 scans using 350 mW laser power output. These measurements were repeated twice for each sample under the same conditions, and an average spectrum was calculated.

**Table 1.** Characteristic FT Raman Frequencies and their Vibrational Assignments Corresponding to the Allomorphs Cellulose I and II in the Frequency Region Below 1700 $cm^{-1}$, and Vibrations and Group Frequencies of CMC Caused by the Carboxymethylation Reaction (Colthup *et al.* 1990; Schenzel and Fischer 2001)

| Cellulose I ($cm^{-1}$) | Cellulose II | Approximate assignment of the vibrational modes |
|---|---|---|
| 1477 | | ($CH_2$) methylene bending vibrations |
| | 1464 | ($CH_2$) methylene bending vibrations |
| 1455 | | ($CH_2$) methylene bending vibrations |
| 1295 | | ($CH_2$) methylene twisting mode |
| | 1265 | ($CH_2$) methylene twisting mode |
| 1120 | 1116 | (COC) glycosidic stretching; ring breathing |
| 1095 | 1095 | (COC) glycosidic stretching; ring breathing |
| 380 | | (CCC), (CO), (CCO) ring deformation |
| | 355 | (CCC), (CO), (CCO) ring deformation |
| 1611 and 1416 | | ($COO^-$) asymmetric and symmetric carbonyl stretching vibrations |
| 1338 | | wagging vibrations of methylene ($CH_2$) assigned to hydroxymethylene side chain at C(5) |
| 1330-1320 | | wagging vibrations of methylene ($CH_2$) adjacent to an ether group ($-CH_2OR$) |

## Chemometrics

Multivariate chemometric analyses on the averaged NIR FT Raman spectra of all CMC samples were performed by means of the software package OPUS 6.5. (Bruker, Germany). The program OPUS/ *Quant 2* was utilized for subjecting the FT Raman spectra of the CMC samples to principal component analysis (PCA). The multivariate chemometric calculations were carried out on the pretreated spectra. First derivatives and vector-normalized spectra of the frequency range 1800 $cm^{-1}$ to 280 $cm^{-1}$ were used solely. The central idea of the principal component analysis is to reduce the dimensions of a data set while retaining as much as possible of the variation in the data. This reduction is achieved by transforming the data to a new set of variables, the principal components, which are ordered so that the first and the second variables retain most of the variation present in the original variables.

## Experimental

The mercerization experiments were carried out as outlined in Fig. 1. The reference experiments corresponded to: 17.5 g pulp, 1 h, 20 °C, and 27.5% NaOH, where the latter corresponded to 2.55 mol NaOH $mol^{-1}$ AGU. The NaMCA charge in the etherification stage was always kept constant, corresponding to 2.04 mol NaMCA $mol^{-1}$ AGU. The numerical values of the parameters studied in the mercerization stage are given in Table 2.

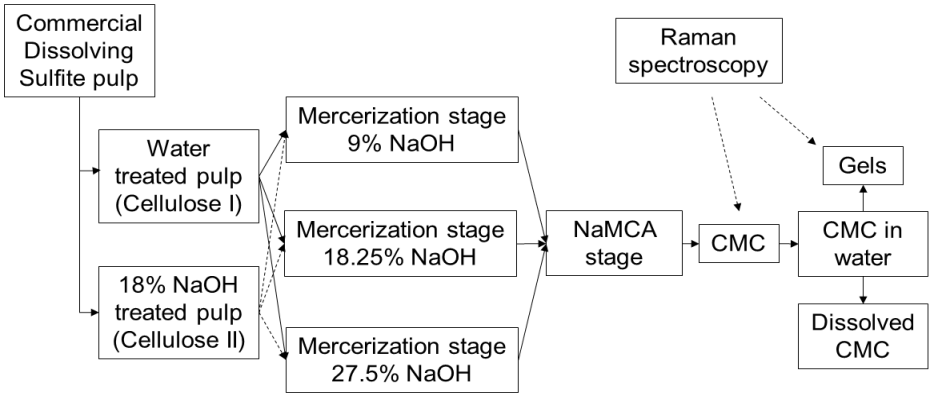


**Fig. 1.** Scheme of the mercerization experiments carried out in this study

## RESULTS AND DISCUSSION

From the experimental parameters shown in Table 2 it can be concluded that the NaOH concentration in the mercerization stage had a distinct influence on the subsequent etherification reaction. When a low NaOH concentration (9%) was used in the mercerization stage, the DS of the CMC was approximately 0.5. However, when a higher NaOH concentration was used (18.25% or 27.5%), the DS was approximately 1.0. CMC prepared with low NaOH concentration (9%) in the mercerization stage exhibited significant gel formation upon dissolution in water. Even at higher NaOH concentrations (18.25% or 27.5%) there was an appreciable extent of gel formation in CMC water solutions if the initial pulp had a high fraction of cellulose II.

**Table 2.** Experimental Parameters Used in the Mercerization Stages as well as Titrimetric DS and Gel Fraction Values

| | | Parameters of mercerization | | | | Data of CMC | |
|---|---|---|---|---|---|---|---|
| Exp. # | Allomorph | Temp. (°C) | Time (h) | NaOH (wt/v-%) | mol NaOH $mol^{-1}$ AGU | DS | Gel fraction (%) |
| 1 | I | 20 | 1 | 9.0 | 0.65 | 0.42 | 63.9 |
| 2 | II | 20 | 1 | 9.0 | 0.65 | 0.49 | 66.8 |
| 3 | I | 40 | 1 | 9.0 | 0.65 | 0.48 | 65.5 |
| 4 | II | 40 | 1 | 9.0 | 0.65 | 0.47 | 70,4 |
| 5 | I | 20 | 48 | 9.0 | 0.65 | 0.50 | 67.0 |
| 6 | II | 20 | 48 | 9.0 | 0.65 | 0.46 | 75.3 |
| 7 | I | 40 | 48 | 9.0 | 0.65 | 0.47 | 68.6 |
| 8 | II | 40 | 48 | 9.0 | 0.65 | 0.46 | 78.1 |
| 9 | I | 20 | 1 | 27.5 | 2.55 | 1.03 | - |
| 10 | I | 20 | 1 | 27.5 | 2.55 | 1.05 | - |
| 11 | I | 20 | 1 | 27.5 | 2.55 | 1.02 | 0.6 |
| 12 | II | 20 | 1 | 27.5 | 2.55 | 0.92 | - |
| 13 | II | 20 | 1 | 27.5 | 2.55 | 0.96 | 2.6 |
| 14 | II | 20 | 1 | 27.5 | 2.55 | 0.95 | - |
| 15 | I | 40 | 1 | 27.5 | 2.55 | 1.05 | 17.5 |
| 16 | II | 40 | 1 | 27.5 | 2.55 | 0.93 | 65.9 |
| 17 | I | 20 | 48 | 27.5 | 2.55 | 1.04 | 0.3 |
| 18 | II | 20 | 48 | 27.5 | 2.55 | 0.95 | 75.3 |
| 19 | I | 40 | 48 | 27.5 | 2.55 | 1.00 | 0.1 |
| 20 | II | 40 | 48 | 27.5 | 2.55 | 0.93 | 22.8 |
| 21 | I/II = 1:1* | 30 | 24.5 | 18.25 | 1.55 | 0.88 | - |
| 22 | I/II = 1:1* | 30 | 24.5 | 18.25 | 1.55 | 0.92 | 10.6 |
| 23 | I/II = 1:1* | 30 | 24.5 | 18.25 | 1.55 | 0.92 | - |

*A mixture of 50% cellulose I and 50% cellulose II; The NaOH concentrations refer to the water fraction of the water-isopropanol system in the mercerization stage.

The cellulose crystallinity after the carboxymethylation reaction was quantified by analysing the FT Raman spectral data of the samples, using the models described earlier (Schenzel and Fischer 2005; Schenzel *et al.* 2009). In this manner, the contents of crystalline and amorphous cellulose in the original dissolving pulp as well as the average content of cellulose I / cellulose II before and after its alkaline pre-treatment and in the CMC samples were determined.

Figure 2 shows the FT Raman spectra of the original dissolving pulp before and after pre-treatment with 18% NaOH. The figure shows that the typical Raman signals for the methylene bending vibrations in the original pulp (1477 $cm^{-1}$ and 1455 $cm^{-1}$) were merged after the NaOH treatment into one single signal at 1464 $cm^{-1}$ in the NaOH-treated pulp. In the same way, the methylene twisting mode (1295 $cm^{-1}$) was shifted to 1265 $cm^{-1}$ after the alkaline treatment, as earlier observed by Schenzel and Fischer (2001).

Changes were also detected for the glucopyranose ring deformations in the low frequency range. The intensity of the signal at 380 $cm^{-1}$ decreased, whereas that of the peak at 355 $cm^{-1}$ increased due to the transition from the glucopyranose ring conformation of cellulose I to the ring conformation of cellulose II. It can thus be concluded that the pulps in Fig. 2 were suitable to serve as model compounds for celluloses I and II, respectively.

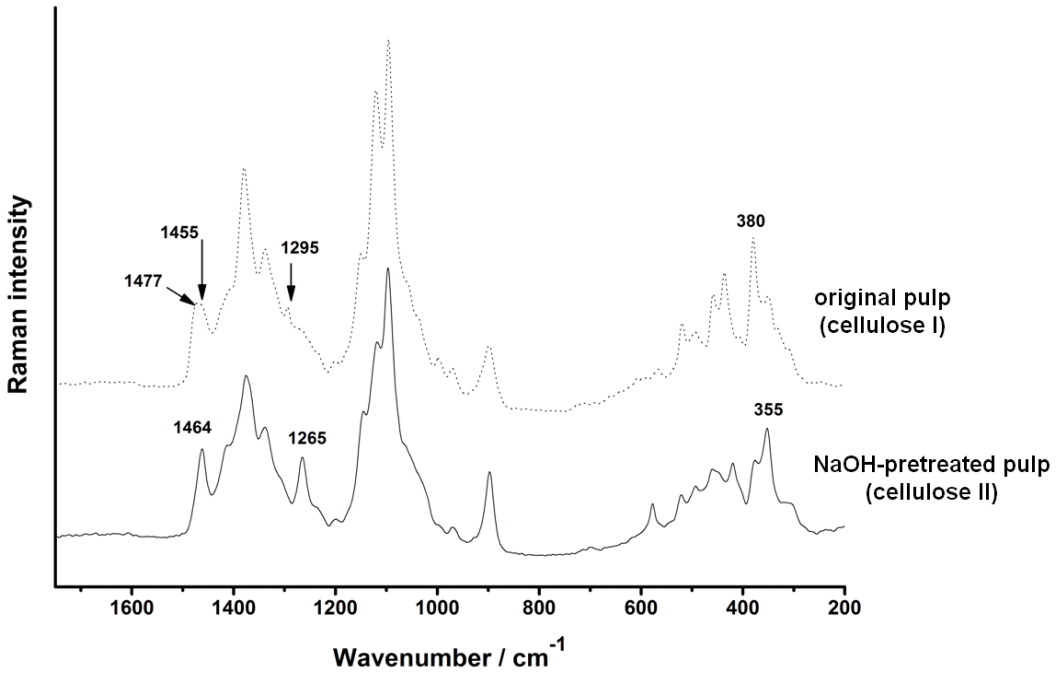


**Fig. 2.** FT Raman spectra of the original dissolving pulp and the NaOH-pretreated pulp, where the NaOH concentration was 18%

By applying PCA to the spectra of the CMC samples, two different scores were identified along the direction of the principal components (PC1) and (PC2). The scatter plot shown in Fig. 3 depicts this.

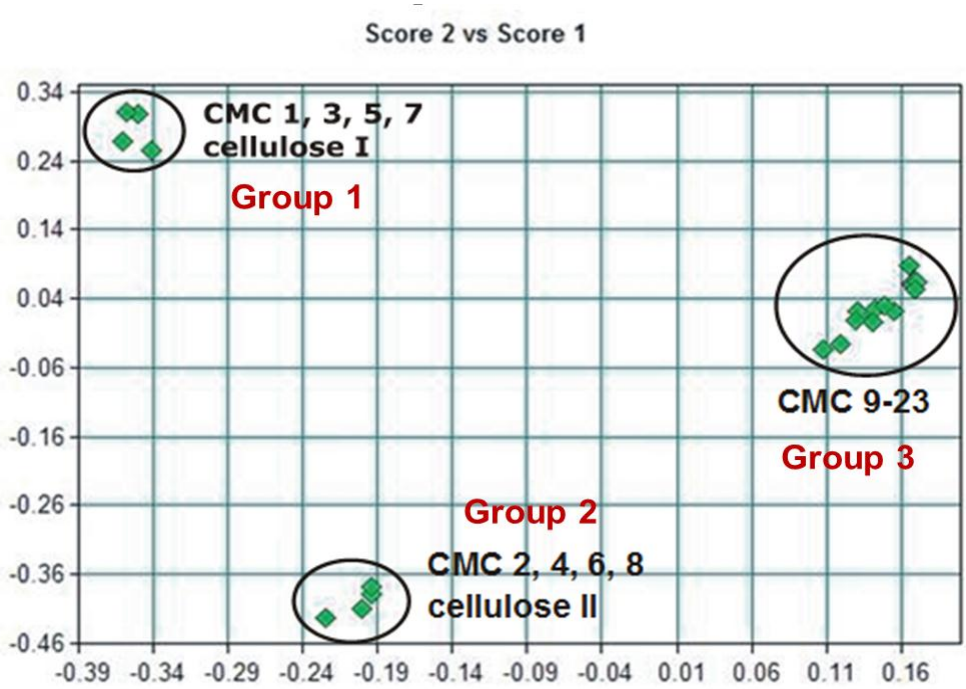


**Fig. 3.** PCA scatter plot of the scores produced from the pre-treated spectra of the CMC samples in the frequency range 1800-280 $cm^{-1}$

As is shown in the figure, the samples were distinguished in relation to their pattern of substitution (PC1) and in relation to the conformational structure of their cellulose skeletons (PC2). A variance of 98.9% was captured by these two first main principal components.

It is clear that the samples can be separated into three groups, which are here denoted as the CMC group (1), the CMC group (2), and the CMC group (3). CMC groups (1) and (2) are mainly different with respect to the second principal component (PC2). This is indicated by positive scores for the samples of the CMC group (1) in contrast to negative scores for CMC group (2). That means they are discriminated by their cellulose backbone structures, which were characterized as cellulose type I for CMC group (1) and cellulose type II for CMC group (2).

The values obtained for (PC1), which mainly reflect the degree of substitution, were similar for both CMC groups. This is consistent with their DS values, which were approximately 0.50 for both groups, as determined by titration. In contrast to groups (1) and (2), the CMC group (3) showed positive values for the first principal component (PC1), indicating a different degree of substitution. This is consistent with the DS values, which were approximately 1.0 for this group, as determined by titration. Since discrimination with respect to the backbone structures of the cellulose skeletons mainly appeared on the second principal component (PC2), samples of CMC group (3) clearly explained such differences in contrast to CMC group (1) and (2), when compared with Fig. 3.

Following the interpretation of the FT Raman spectra as described above, the results of the PCA also suggested different parameter for CMC group (3) with respect to its cellulose backbone structures. The distinctly higher content of amorphous cellulose structures is illustrated here.

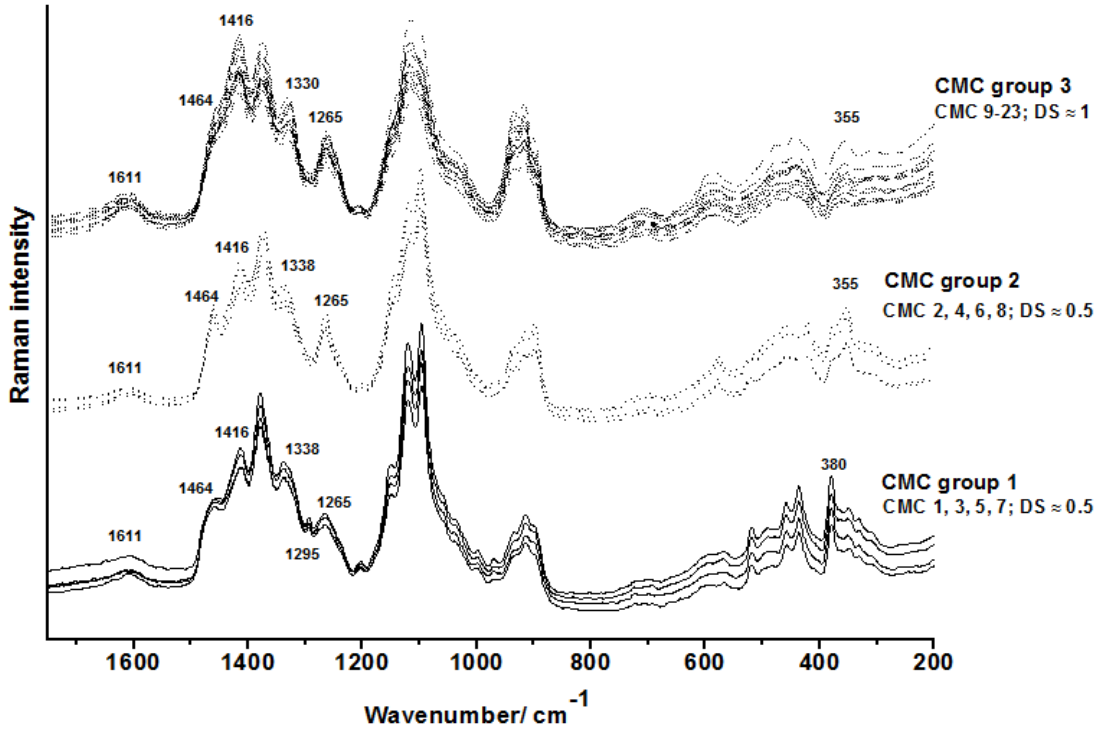


**Fig. 4.** FT Raman spectra of the CMC samples illustrating the different vibrational behaviors of the CMCs (1), (2), and (3) groups

Figure 4 shows the spectra of all the CMC samples grouped according to the outcome of the PCA. Each group is characterized by its typical vibrational behaviour.

Samples in group (1), *i.e.* CMC 1, 3, 5, and 7, were prepared from the dissolving pulp sample, which had a high fraction of cellulose I of approximately 78%. These samples were prepared using a low NaOH concentration (9%) in the mercerization stage (see Table 2). These CMC samples still had cellulose I structure at a fraction of about 69%, apart from approximately 9% of cellulose II and 22% of amorphous cellulose, after the carboxymethylation reaction.

The signal assigned to the twisting mode of the methylene groups at 1295 $cm^{-1}$ and the signal for glucopyranose ring deformation at 380 $cm^{-1}$ confirmed the cellulose I structure. Distinct signals of carbonyl stretching vibrations of an acetate salt, $\nu_{as}(COO^-)$, and $\nu_s(COO^-)$ at 1611 $cm^{-1}$ and 1416 $cm^{-1}$, confirmed the carboxymethylation of the corresponding pulp samples (Colthup *et al.* 1990).

In contrast to group (1), the samples of group (2), *i.e*. CMC 2, 4, 6, and 8, were prepared from the dissolving pulp sample that had a high fraction of cellulose II of 91% approximately. They were then treated with a low NaOH concentration (9%) in the mercerization stage, and they continued to have a cellulose structure of type II at a fraction of about 76%, and 24% of amorphous cellulose, after the carboxymethylation reaction.

The signal assigned to the twisting mode of the methylene groups at 1265 $cm^{-1}$, the methylene bending vibrations at 1464 $cm^{-1}$ and the signal for glucopyranose ring deformation at 355 $cm^{-1}$ confirmed the cellulose II structure. Carbonyl signals at 1611 $cm^{-1}$ and 1416 $cm^{-1}$ confirmed the successful carboxymethylation.

These results suggested that the cellulose structure was unchanged when a low NaOH concentration (9.0%) was used in the mercerization stage. The reason for this was most probably due to the fact that the NaOH concentration was not high enough to complete the transformation from crystalline cellulose to Na-cellulose prior to the carboxymethylation stage. The degree of substitution was low, *i.e.* between 0.42 and 0.50 for the samples in CMC group (1) and (2) (compare Table 2).

The CMC group (3), samples 9 to 23, was prepared from pulp samples with either a high fraction of cellulose I or II and from mixtures of these. The NaOH concentrations were 18.25% or 27.5% in the mercerization stage. In comparison to CMC group (1) and (2), obvious differences were observed in the spectra of CMC group (3), because the content of amorphous cellulose structures was approximately 2.5 times higher than the content of ordered cellulose forms.

Just as shown for the CMC groups (1) and (2), the spectra of group (3) also gave evidence of the successful carboxymethylation of the pulp. This is indicated by the Raman signals of the $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ modes at 1611 $cm^{-1}$ and 1416 $cm^{-1}$. Here, these signals show distinctly higher intensity than in the spectra of the both other groups, suggesting higher DS values for the samples of group (3). This corresponds with DS found by titrimetric determination that gave DS values between 0.88 and 1.05.

The etherification of the CMCs of group (3) also accounts for a marked signal of middle intensity at 1330 $cm^{-1}$ corresponding to wagging vibrations of methylene groups $\omega(CH_2)$ adjacent to an ether group ($-CH_2OR$) (Colthup *et al.* 1990). Contrary to the spectra of CMC group (1) and (2), the signal of the $\omega(CH_2)$ vibrations at 1338 $cm^{-1}$ assigned to the hydroxymethylene side chains at C(5) was disappearing due to the higher degrees of substitution in CMC group (3). Thus only one distinct signal was detected for $\omega(CH_2)$ vibrations adjacent to ether groups ($-CH_2OR$).

As a result, the clustering of CMC samples 1-23 into three distinct groups is more a reflection of differences in the patterns of substitution of the CMC than of differences in their cellulose backbone structures.

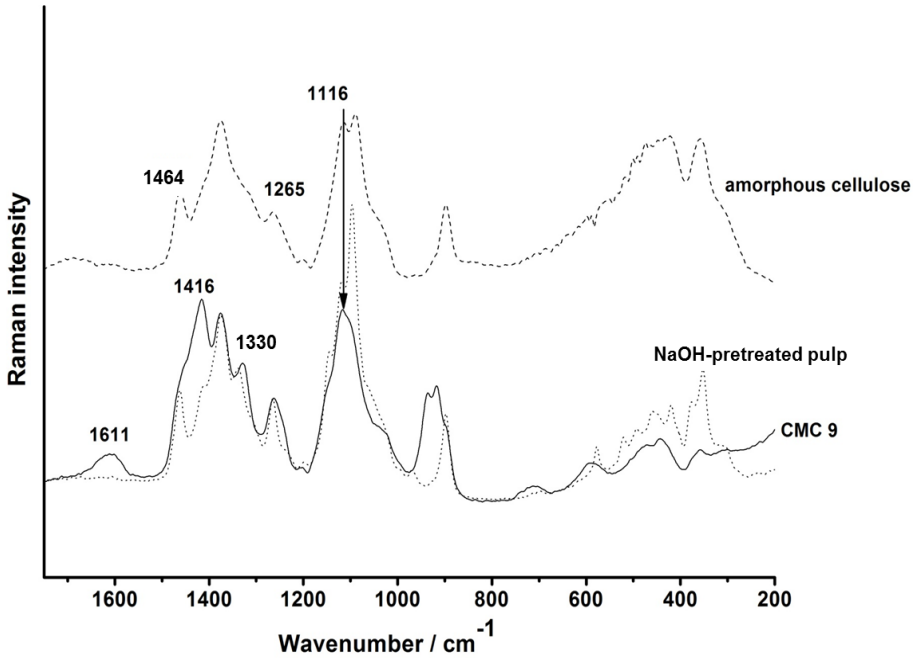


**Fig. 5.** FT Raman spectra of CMC sample 9, a model compound of an amorphous cellulose (ball milled bacterial cellulose) and a NaOH-pretreated pulp, $C_{NaOH}$=18%

The higher degree of substitution in group (3) is accompanied by differences in the cellulose backbone structure in comparison to those of CMC groups (1) and (2), which is indicated in Fig. 5. Here, the spectrum of CMC sample 9 (DS≈1.0), representative for CMC group (3), is shown in comparison to an amorphous cellulose sample (ball milled bacterial cellulose) and a cellulose II sample (NaOH-pretreated pulp).

Here, in addition to the Raman signals confirming the carboxymethylation of CMC 9, a shoulder at 1464 $cm^{-1}$ and the signal at 1265 $cm^{-1}$ reveal vibrations and twisting modes for $CH_2$. These signals appeared also in the spectra of cellulose type II and in amorphous cellulose, characterizing typical conformational arrangements of their backbone structures (Schenzel and Fischer 2001). In the spectrum of CMC 9, the skeletal stretching ν(C-O-C) appeared at 1116 $cm^{-1}$ with a shoulder at 1095 $cm^{-1}$. The shape as well as the frequency of this signal clearly indicates the amorphous form of the cellulose. Broader signals in the spectra of CMC group (3) confirmed the stronger amorphous character of these samples. Thus, the CMC samples in group (3) were carboxymethylated-dissolving pulps of cellulose type II in the presence of significant amounts of amorphous cellulose (approximately 71%). This is probably due to a successful transformation from cellulose to Na-cellulose when the NaOH concentration was either 18.25% or 27.5% during the mercerization stage.

Thus, the results showed that the NaOH concentration in the mercerization stage should be high, *i.e.* > 9.0%, in order to change the skeletal structure of cellulose prior to the carboxymethylation stage. This is in agreement with Sixta (2006), who claims that an initial NaOH concentration of 7% (70 to 80 $g/dm^3$) at room temperature is needed to trigger the formation of Na-cellulose I, and this process is completed at 14 to 16% (160 to

190 g/dm$^3$) NaOH concentration. In the range of NaOH concentrations 14 to 22% (160 to 270 g/dm$^3$), Na-cellulose I prevails, while beyond this concentration level Na-cellulose II is formed (Sixta 2006).

## The Gel Fraction in the CMC Water Solutions

The amount of gel in the CMC water solutions was highly dependent on the NaOH concentration in the mercerization stage and the fraction of cellulose II in the original pulp. CMC that was prepared using a low NaOH concentration (9.0%) in the mercerization stage resulted in CMC water solutions rich in semi-solid, gum-like gels, as determined visually. CMC prepared from pulp rich in cellulose II tended to have a higher content of gel at a given NaOH concentration compared with CMC prepared from pulp rich in cellulose I (see Table 2).

This gel formation was probably due to the low DS. It has been reported earlier that aggregates of non-substituted or poorly substituted regions may appear as highly swollen opaque or transparent macrogel particles (Rinaudo *et al.* 2000) and that insoluble fractions of CMC mainly consist of low substituted cellulose segments (Jardeby *et al.* 2004). At low DS, when large regions of unsubstituted CMC are present, it has been observed that a gel structure may appear in the CMC solution (Stigsson *et al*. 2008).

When comparing the spectra of CMC groups (1), (2), and (3) with the spectra of their gel fractions, intensity differences in the specific Raman signals (1120 cm$^{-1}$ and 1095 cm$^{-1}$) became obvious. This is illustrated for one single sample of each CMC group, as shown in Fig. 6.

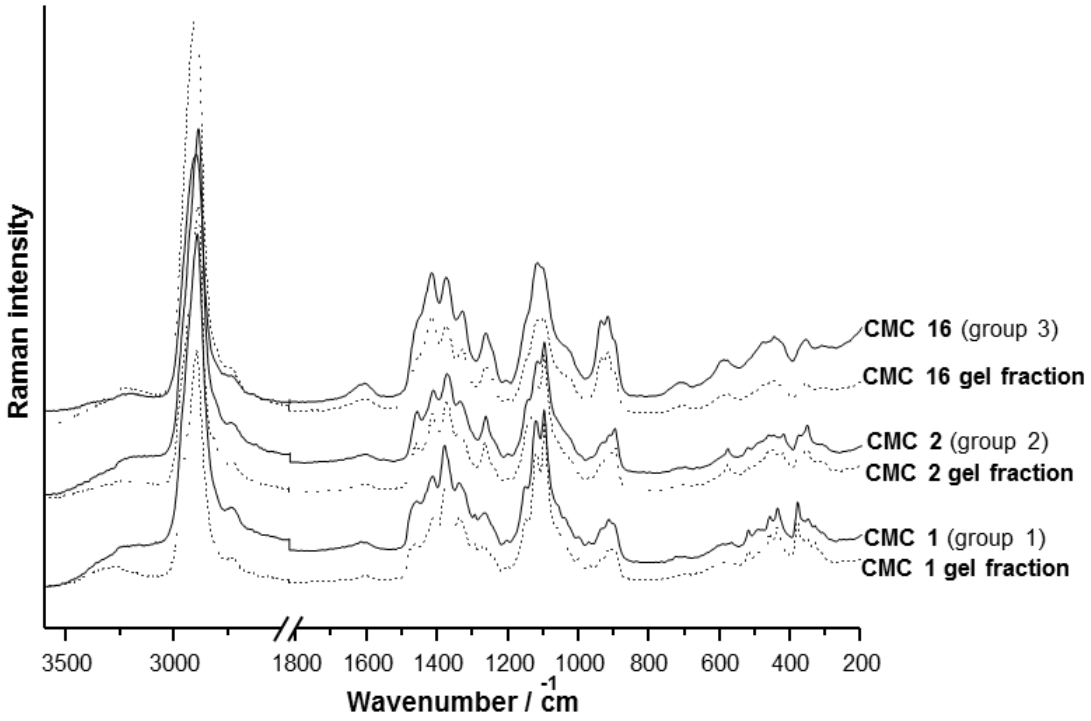


**Fig. 6.** FT Raman spectra of one single delegate of each CMC group (1), (2), and (3) as well as from their gel fraction

A different intensity relation was observed for a characteristic double peak in the spectra of the original samples of CMC groups (1) and (2) compared with the spectra of

their gel fractions. This was not observed for CMC group (3). The signal at 1095 $cm^{-1}$ in the spectra of the gel fraction appeared with higher intensity, whereas the signal intensity at 1120 $cm^{1}$ did not change in comparison to the original CMC. Those changes suggest changes in the skeletal structures of the cellulose, because both signals are assigned to skeletal stretching ν(C-O-C) of the cellulose backbone (Wiley and Atalla 1987; Schenzel and Fischer 2001). These spectral differences could be due to the lower DS and/or more uneven distribution of substituents in the gel fraction than in the original CMC.

No fundamental differences in the structures of the cellulose between the original CMC and their gel fractions were observed for the samples of CMC groups (1) and (2). Thus, CMC group (1) and its gel fractions indicated skeletal structures of cellulose I, while the samples of CMC group (2) and their gel fractions indicated structures of cellulose II (see Fig. 6). Also, no fundamental differences in the skeletal structures between original CMCs and their gel fractions were found for the samples of CMC group (3); in other words no intensity differences of the specific Raman signals were detected. Generally, a high content of amorphous cellulose became obvious for the original samples of CMC group (3) as well as for their gel fractions.

## CONCLUSIONS

1. NIR FT Raman spectroscopy, especially in combination with methods of multivariate analyses, is shown to be an effective method to characterize native cellulose in pulps as well as the reaction product carboxymethyl cellulose (CMC).
2. The CMC samples produced could be ordered with respect to their cellulose backbone structures into the three different groups, *i.e.* cellulose I, cellulose II, and amorphous cellulose. The samples also could be ordered according to the DS of the resulting CMC. When a low NaOH concentration (9%) was used in the mercerization stage, the resulting CMC still had a crystalline cellulose structure, and the DS of the CMC was approximately 0.5. However, when a higher NaOH concentration was used (18.25% or 27.5%), the resulting CMC was more amorphous and the DS was approximately 1.0.
3. The NaOH concentration in the mercerization stage had a distinct influence on the subsequent etherification reaction. CMC samples and their gels, prepared from pulp with a high fraction of either cellulose I or cellulose II, had a skeletal structure of cellulose I or cellulose II, respectively, when the NaOH concentration was low (9%).
4. CMC samples and their gels, prepared with a high NaOH concentration (18.25% or 27.5%) in the mercerization stage had amorphous cellulose structures.
5. Observed spectral differences between the gel fraction and the original CMC, for samples prepared with low NaOH concentration (9%) in the mercerization stage, could be due to lower DS and/or more uneven distribution of substituents for the gel fraction than in the original CMC.
6. CMC prepared with low NaOH concentration (9%) in the mercerization stage had a significant gel formation upon dissolution in water. Even at higher NaOH

concentrations (18.25% or 27.5%) there was a certain gel formation in CMC water solutions if the initial pulp had a high fraction of cellulose II.

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