



# Hydroxypropyl methylcellulose substituent analysis and rheological properties



Hannah Akinosho<sup>d</sup>, Samantha Hawkins<sup>b</sup>, Louise Wicker<sup>a,c,\*</sup>

<sup>a</sup> Department of Food Science and Technology, The University of Georgia, 100 Cedar Street, Athens 30602, United States

<sup>b</sup> Richard B. Russell Agricultural Research Center, Agricultural Research Service, United States Department of Agriculture, 950 College Station Road, Athens, GA 30605, United States

<sup>c</sup> Department of Home Economics Education, College of Education, Korea University, Anam-Dong, Seongbuk-Gu, Seoul 136-701, Korea

<sup>d</sup> Department of Chemistry and Biochemistry, Georgia Institute of Technology, 901, Atlantic Dr., Atlanta, GA 30332, United States

## ARTICLE INFO

### Article history:

Received 20 July 2012

Received in revised form 24 May 2013

Accepted 28 May 2013

Available online 6 June 2013

### Keywords:

Hydroxypropyl methylcellulose

FT-IR

Raman

Rheology

Crystallinity

Methylation

## ABSTRACT

The methyl and hydroxypropyl substituents in hydroxypropyl methylcellulose (HPMC) affect the resulting gel properties. These substituents in five HPMC gels were characterized using Fourier transform infrared spectroscopy (FT-IR), Raman spectroscopy, small-amplitude oscillatory shear measurements, and differential scanning calorimetry (DSC). In FT-IR spectra, the most intense peak appeared at  $1053\text{ cm}^{-1}$ , denoting the presence of the glucose ring. The ratio of peak intensities at  $1452\text{ cm}^{-1}$ , which represents  $\text{—C—H}$  absorptions, and at  $1053\text{ cm}^{-1}$  ( $I_{1452}/I_{1053}$ ) and percent methylation from gas chromatography exhibited a linear association ( $r^2 = 0.6296$ ). The broadening of the Raman spectra indicated that the relative crystallinity of HPMC decreases with increasing hydroxypropyl contents. DSC showed no linear relationship between the percent hydroxypropylation in HPMC and the percentage of free water in an HPMC gel. Small-amplitude oscillatory shear measurements revealed that the formation of an entanglements networks and/or weak gel depends on substituent contents.

© 2013 Elsevier Ltd. All rights reserved.

## 1. Introduction

Native cellulose is linked by  $\beta$ -(1→4) glucosidic linkages; hydrogen bonding between neighboring cellulose chains provides mechanical strength in plants and renders cellulose insoluble in water. In caustic solution, the hydrogen bonds between cellulose chains are disrupted, and cellulose swells and absorbs water. In the swollen state, hydroxyl groups are randomly substituted with alkyl substituents such as ethyl, methyl or hydroxypropyl groups to produce a modified cellulose. The relative hydrophobicity or hydrophilicity of the substituent groups affects the solution properties of modified cellulose (Heiko Thielking & Schmidt, 2000). In hydroxypropyl methylcellulose, cellulose contains methyl and hydroxypropyl substituents that are etherified onto the cellulose backbone (Heiko Thielking & Schmidt, 2000). The position, nature, and proportion of substituents affect the resulting properties of HPMC. The substituents have been widely analyzed to assess the changes in the functionality of HPMC. The degree of substitution on HPMC and temperature influences the intermolecular interactions

such as the onset of turbidity during heating, termed cloud point (Greiderer, Steeneken, Aalbers, Vivó-Truyols, & Schoenmakers, 2011; Mitchell et al., 1993), the onset of gelation (Haque, Richardson, Morris, Gidley, & Caswell, 1993; Sarkar, 1995), drug release rates (Viridén, Wittgren, Andersson, & Larsson, 2009), and the viscoelastic properties of the gel (Bodvik et al., 2010).

Cloud point describes the phase separation of HPMC dispersions at sufficiently high temperatures, which is manifested as a cloudy solution. The relationship between substituent content and cloud point has been studied through the enzymatic degradation of HPMC. Highly substituted regions of HPMC experienced less enzymatic degradation than less substituted regions. These fragments, which differed by substitution, were used in cloud point studies; fragments with higher proportions of substituted regions produced the largest shifts in cloud points at the transmission at 50%,  $T_{50}$ , when using UV-vis (Schagerlöf et al., 2006). The heterogeneity of distribution of the substituents in HPMC, possessing the same substituent contents and viscosities, has also been analyzed with respect to release rates of pharmaceuticals. The findings demonstrated that slower drug release rates were associated with more heterogeneous substitution patterns (Viridén et al., 2009).

The extent and nature of substitution influence the viscoelastic properties and affect the application of HPMC in the pharmaceutical, chemical, and food industries. The hydroxypropyl and methyl contents affect the gelling abilities of HPMC. Larger quantities of

\* Corresponding author at: Department of Food Science and Technology, The University of Georgia, 100 Cedar Street, Athens 30602, United States.

Tel.: +1 706 542 1055; fax: +1 706 542 1050.

E-mail address: [lwicker@uga.edu](mailto:lwicker@uga.edu) (L. Wicker).

hydroxypropyl substituents result in weaker gels and lower temperatures for the onset of gelation (Haque et al., 1993). The gels formed can provide an extended release matrix for pharmaceuticals (Viridén, Larsson, & Wittgren, 2010) or be used to enhance the rheological properties of foods such as surimi (Chen, 2007). Establishing structure function relationships based on the substituent content, position, and distribution provide insight into the final characteristics of the gel (Viridén, Larsson, Schagerlöf, & Wittgren, 2010). Limited research characterizes HPMC and its gels based on the methyl to hydroxypropyl ratio and substituent content. Understanding the role of substituents in gel formation is useful in the optimization and selection of HPMC for industrial uses. This study uses attenuated total reflectance Fourier transform infrared spectroscopy (ATR/FT-IR), Raman spectroscopy, differential scanning calorimetry (DSC), and small-amplitude oscillatory shear measurements to characterize the gelling and structural behavior of HPMC as related to its methyl and hydroxypropyl substituents.

## 2. Materials and methods

The five grades of HPMC were supplied by Samsung Fine Chemicals (Seoul, Korea) and differed by the percent methylation, percent hydroxypropylation, and viscosity (Pa S). The data regarding percent hydroxypropylation and percent methylation were supplied by the manufacturer and acquired using gas chromatography (Table 1).

### 2.1. Dispersion preparation

HPMC dispersions were prepared by adding 2 g of powdered HPMC into 100 mL of Type II water at 80 °C. The dispersions were stirred during addition and cooling, until the final temperature reached 25 °C. The dispersions were hydrated for 10 d at 4 °C prior to testing (Šklubalová & Zatloukal, 2008).

### 2.2. Attenuated total reflectance/Fourier transform infrared spectroscopy

The ATR–FT-IR spectra of the five grades of HPMC were obtained using a purged Nicolet 6700 FT-IR Spectrometer (Thermo Electron, Madison, WI) with a diamond crystal ATR (attenuated total reflectance) accessory (Durascope, Smiths Detection, Danbury, CT) and a DTGS detector. A background reading was taken prior to each series of measurements. Spectra of the powdered samples were collected at 25 °C using 64 scans and at a resolution of 4 cm<sup>−1</sup> and were background subtracted. The spectral region ranged from 4000 cm<sup>−1</sup> to 500 cm<sup>−1</sup>.

### 2.3. Raman spectroscopy

Powdered HPMC were analyzed by Sentinel Sure-Cal Spectroscopy (Bruker Optics, Ettlingen, Germany). Samples weighing 4 g were placed in 5 mL glass scintillation vials and capped. The calibration of the instrument was performed automatically prior to each reading. The readings, which consisted of one scan, were taken at a power of 300 mW with a spectral region of 2250 cm<sup>−1</sup> to 250 cm<sup>−1</sup>. Contributions made from the glass vials were subtracted from each spectrum prior to analysis.

### 2.4. Differential scanning calorimetry

Aliquots of 10–15 mg of 2% (w/w) HPMC were weighed into aluminum pans with pins (Cat. No.: ME-00027331, Mettler Toledo, Columbus, OH). The aluminum DSC pans were hermetically sealed and handled with forceps during testing. The samples were heated from −50 °C to 30 °C at a rate of 10 °C/min. The peaks were

analyzed and integrated using the STARe 9.10 software (Mettler Toledo, Columbus, OH). The baselines were calculated using an integrated horizontal baseline, and the peaks were normalized to the weights of the samples. The enthalpy change associated with the energy associated with the melting of loosely bound water in the HPMC solutions ( $\Delta H_{\text{fusion}}$ ) was recorded. The differential scanning calorimeter DSC 1 (Mettler Toledo, Columbus, OH) was calibrated using 6–8 mg of indium standard in an aluminum pan with a pin. An empty aluminum pan with a pin served as the reference pan during calibration and testing. The standard was heated at a rate of 10 °C/min through a range of 100–200 °C. The DSC data were collected to associate the amount of free water in the solution of HPMC with the respective HPMC grade. The percentage of free water in each solution was calculated using Eq. (1) (Anghel & Saitō, 2003).

Percentage of free water =

$$\frac{\Delta H_{\text{fusion}}(\text{free water in HPMC solution})}{\Delta H_{\text{fusion}}(\text{pure water})} \times 100 \quad (1)$$

### 2.5. Dynamic oscillatory measurements

Dynamic oscillatory measurements were conducted on the stress-controlled SR-5000 rheometer (Rheometric Scientific, TA Instruments, New Castle, DE). The gap was set to 0.50 mm, and the cone angle was 4°. A strain sweep was conducted at a frequency of 1 Hz on each of the hydrated samples to determine linear viscoelastic region (LVR). The lowest strain in the viscoelastic region for each HPMC was determined and used in the frequency sweeps of the five samples. A 0.3% strain was used for AN6 and AN50 between frequencies of 0.05 Hz and 5 Hz while 1% strain was used for BN40M, CN40H, and CN10T. A strain of 1.0% could not be used in the analysis of AN6 and AN50 because the linear viscoelastic regions differed between samples and did not coincide during the dynamic strain sweep. The elastic modulus ( $G'$ ), loss modulus ( $G''$ ), and  $\tan \delta$  were collected using a cone (35 mm) and Peltier plate at 25 °C ( $\pm 0.01$  °C).

### 2.6. Statistical analysis

All measurements were conducted on triplicate dispersions. Statistical analyses were performed using the Minitab® 15 software. Significant differences between means were assessed using one-way ANOVA and the  $t$ -test at  $P < 0.05$ .

## 3. Results and discussion

### 3.1. ATR–FT-IR

The peaks obtained from the FT-IR spectrum were used to (1) analyze the structure of HPMC and (2) correlate peak ratios with the percent methylation provided by the manufacturer as determined by gas chromatography. In the FT-IR spectra of the HPMC (Fig. 1), many of the observed bands appeared in the fingerprint region, which encompasses wavenumbers between 1400 and 900 cm<sup>−1</sup>. The five HPMC produced similar spectra but differed in intensity of certain peaks. The most intense peak in the spectra occurred at 1053 cm<sup>−1</sup>, represents out-of-phase vibrations associated with an alkyl substituted cyclic ring containing ether linkages. The peak at 944 cm<sup>−1</sup> represents the in-phase vibrations from ether linkages and appears as a weaker band attached to the band at 1053 cm<sup>−1</sup> (Coates, 2006). Cellulose material possesses glucose molecules that contain one ether linkage in the ring structure and another ether linkage between neighboring glucose molecules (Teegarden, 2004). The spectra obtained reflecting the ether bonds (1053 and 944 cm<sup>−1</sup>) verify the presence of these ethers in the structure of

Download English Version:

<https://daneshyari.com/en/article/10603284>

Download Persian Version:

<https://daneshyari.com/article/10603284>

[Daneshyari.com](https://daneshyari.com)