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Influence of molecular weight and degree of substitution of various carboxymethyl celluloses on unheated and heated emulsion-type sausage models

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ABSTRACT

Four carboxymethyl celluloses (CMCs) differing in molecular weight (M_W) and degree of substitution (°DS) were initially characterized in NaCl solution (0.1 M) and on properties of emulsion-type sausage models. The impact of the different CMCs (0–2 wt%) on the rheological behavior and firmness of an emulsion-type sausage models containing 1.8 wt% NaCl was studied. Rheology (unheated/heated) and firmness (heated) showed an increasing effect with increasing CMC concentrations. Addition of >1 wt% CMC led to a decrease in storage modulus of the unheated/heated batter and to a decrease in firmness of heated independent of the CMC-type used. CLSM revealed that high amounts of CMCs prevented formation of a coherent protein matrix. Water-binding capacity indicated that CMC contributed to the water-retention capability of sausage batters. Small differences between the CMCs were observed using various °DS and similar M_W. Results indicate that the addition of low CMC concentrations (≤0.5 wt%) may help to reduce fat content.

1. Introduction

Increasing consumer demand paid today attention to diet and health, in particular fat replacement is a main claim in foods. For this reason, the main approaches to reduce the fat levels in meat products are the usage of more raw lean meats, or the replacement of fat with lower caloric ingredients and/or water (Jiménez-Colmenero, 1996). Having both few calories and fat-like characteristics while not changing flavor, mouthfeel, viscosity, or other sensory properties, this is difficult to accomplish for fat replacers (Keeton, 1996). Additionally, the fat replacers such as cellulose gums have to be compatible with the food matrix also with regard to e.g. salt concentration and hence ionic strength (Arinaitwe & Pawlik, 2014; Chatterjee & Das, 2013).

The addition of water for fat reduction requires the use of water-binding agents, such as carrageenan, konjac, short-chained polyfructoses (Candogan & Kolsarici, 2003; Jiménez-Colmenero et al., 2010; Vandendriessche, 2008), cellulose fibers such as microcrystalline cellulose, carboxymethyl cellulose (CMC) (Barbut & Mittal, 1996; Schuh et al., 2013), or fibers from oat bran, rye bran, and barley (Petersson, Godard, Eliasson, & Tornberg, 2014a; Petersson, Godard, Eliasson, & Tornberg, 2014b).

The physicochemical properties of the different CMCs including water solubility and polymer expansion are dependent on the degree of substitution (°DS), substitution groups, and molecular weight (M_W) (Shand, Schmidt, Mandigo, & Claus, 1990). The higher the number of °DS the higher is the number of anionic carboxyl groups on the glycopyranose monomer. CMCs are often applied as sodium salts due to their improved water solubility. Moreover, CMCs are non-digestible polymers and are therefore not only used as thickener and emulsion stabilizers, but also as fat replacers in meat products (Barbut & Mittal, 1996; Gibis, Schuh, & Weiss, 2015; Mittal & Barbut, 1993; Schuh et al., 2013). These macromolecules were found to improve the cooking yield in low-fat meat products and only low amounts were required for the desired water-holding effect in comparison to microcrystalline cellulose (Gibis et al.,

Abbreviations: CMC, carboxymethyl cellulose; M_W, molecular weight; °DS, degree of substitution; CLSM, confocal laser scanning microscopy; Eq., equation; NaCl, sodium chloride; LMW, low molecular weight; MMW, medium molecular weight; HMW, high molecular weight.

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2015; Jiménez-Colmenero, 1996). However, recent studies have shown that high concentration of CMC (≥1 wt%) can also lead to a decrease of firmness of the finished product (Gibis et al., 2015; Lin, Keeton, Gilchrist, & Cross, 1988; Ruusunen et al., 2003) based on an improvement of water-retention (14–30%) as shown for low-fat breakfast sausages (Mittal & Barbut, 1993).

The objective of the study was on the one side the characterization of the physicochemical properties of the CMC polymer chains in salt solution for the fundamental understanding. On the other side, the investigation of the influence of each type of added CMCs into the formulation of emulsion-type sausage model on water-binding, rheological behavior, morphological microstructure, and textural properties prior and after heating. We hypothesized that, besides the concentration, the molecular weight and degree of substitution of CMCs influence their properties in salt solution and in the salted emulsion-type sausage model, because salt is necessary for the solubilization before heating and is important for the gelatization of the myofibrillar proteins after heating and consequently the preparation of emulsion-type sausages (Tornberg, 2005). Regarding this, we investigated four different CMCs (0–2 wt%) with various M_Ws and °DS in sodium chloride (NaCl) solution and salted emulsion-type sausage model.

2. Materials and methods

2.1. Materials

Sodium CMCs (approximately 6–8% sodium) were provided by Danisco A/S (Aarhus, Denmark). Characteristics of the CMCs are listed in Table 1.

Calcofluor White as fluorescent stain and acetone were purchased from Fluka Chemie AG (Basel, Switzerland). Sodium chloride (Bad Reichenhaller, Heilbronn, Germany) was used for the determination of M_W. Pork meat and back fat were purchased from a local retailer (MEGA, Stuttgart, Germany). The pork (approx. 73 wt% water, 8 wt% fat, 19 wt% protein) and the back-fat (approx. 8 wt% water, 90 wt% fat, 2 wt% protein) was standardized. Further ingredients were curing salt (Südsalz GmbH, Heilbronn, Germany), diphosphate (Chemische Fabrik Budenheim KG, Budenheim, Germany), ascorbic acid, and Lyoner seasoning (Gewürzmüller, Korntal-Münchingen, Germany).

2.2. Determination of molecular weight and characterization of CMCs

The M_Ws of CMCs were determined using a Paar Physica MCR300 rheometer equipped with a double coaxial cylinder and Rheoplus/32 V3.331 operating system (Anton Paar Germany GmbH, Ostfildern, Germany). Shear stress versus rate of diluted CMC solutions (0.1 mol/L NaCl) were recorded. The dynamic viscosity of the solvent η_s and 0 – 0.9 g/L CMC solutions η were characterized to calculate the reduced viscosity η_{red}, inherent viscosity from relative viscosity η_{rel}, and the intrinsic viscosity [η] according to Huggins (1942) or Kraemer (1938) with Eqs. (1) and (2), respectively:

$$[\eta] = \lim_{c\to 0}(\eta_{red}) = \lim_{c\to 0}\left(\frac{\eta-\eta_s}{c\eta_s}\right) \quad (1)$$

$$[\eta] = \lim_{c\to 0}\left(\frac{ln(\eta_{rel})}{c}\right) = \lim_{c\to 0}\left(\frac{ln\left(\frac{\eta}{\eta_s}\right)}{c}\right) \quad (2)$$

The intrinsic viscosity [η] and M_W are correlated by the Mark-Houwink equation:

$$[\eta] = K_\eta \cdot {M_W}^a \quad (3)$$

where [η] is intrinsic viscosity, M_W is molecular weight, K_η and a are constants for a given solvent and temperature, respectively. For the calculation of M_W from the Eqs. (1) and (2), K_η and a were selected from a other study (Kulicke, Clasen, & Lohman, 2005) as $K_\eta = 1.23\cdot10^{-2}$ and $a = 0.91$ in a sodium chloride solution (0.1 mol/L). The exponent ν can be correlated with the exponent a in the $[\eta]$–M_W relationship through the equation $a = 3\nu - 1$. The exponent ν of 0.63 is in the similar range as in a described from 0.57 to 0.62 depending on pH, indicating good solvent conditions for 0.1 mol/L NaCl for semi-flexible polymers such as CMC (Arinaitwe & Pawlik, 2014). The general critical overlap concentration (c^*) requires diluted polymer solutions for the determination of the onset of entanglement of polymers (Eq. (4)).

$$c^* = \frac{1}{[\eta]} \quad (4)$$

Additionally, the radius of gyration Rg was obtained with (Eq. (5)) using the intrinsic viscosity [η] and is given by Chatterjee and Das (2013).

$$R_g = \left(\frac{[\eta]}{[\eta]_\theta}\right)^{1/2.43} \cdot \sqrt{\frac{1}{6}} \cdot \sqrt[3]{\frac{\overline{M}_n[\eta]_\theta}{\phi}} \quad (5)$$

where ϕ is a Flory universal constant (2.86×10^{23} mol^{-1}), [η] is the intrinsic viscosity, $[\eta]_\theta$ is the intrinsic viscosity in theta solvent, and the M_n the average molecular weight of the polymer (Chatterjee & Das, 2013). The value of $[\eta]_\theta$ can be determined by using the intrinsic viscosity as the sodium chloride solution becomes infinitely high $[\eta]_\theta = [\eta]_{I\infty}$.

For high ionic strength, this value can be obtained with the following equation using a linear regression (Arinaitwe & Pawlik, 2014):

$$[\eta] = A + B\sqrt{I} \quad (6)$$

where A is the intercept of the equation, which is the $[\eta]_\theta = [\eta]_{I\infty}$ the intrinsic viscosity at infinite ionic strength.

2.3. Determination of persistence length

The flexibility of CMC chains was assessed by analyzing the persistence lengths L_p from molecular weights and intrinsic viscosities of the used CMCs based on a recent study (Arinaitwe & Pawlik, 2014),

$$\left(\frac{{M_w}^2}{[\eta_0]}\right)^{\frac{1}{3}} = A_0 \cdot M_L \cdot {\phi_{0,\infty}}^{-\frac{1}{3}} + B_0 \cdot {\phi_{0,\infty}}^{-\frac{1}{3}} \cdot \left(\frac{2L_p}{M_L}\right)^{-\frac{1}{2}} \cdot {M_w}^{-\frac{1}{2}} \quad (7)$$

where A_0 and B_0 (1.052) are suggested coefficients, Flory's constant, $\phi_{0,\infty}$ with 2.86×10^{23} mol^{-1} was obtained from an earlier study (Bohdanecky, 1983) as described by Arinaitwe & Pawlik (2014).

2.4. Preparation of CMC hydrocolloid dispersion

According to Schuh et al. (2013), a concentrated, homogenous dispersion of each CMCs was prepared by mixing CMC powder and tap water under high shearing. 10% of the respective CMC solution was then added later to the emulsion-type sausage formulation. In the emulsion-type sausage model, the CMC concentrations of 0.5, 1, and 2%, respectively, in the final product were manufactured.

2.5. Preparation of emulsion-type sausage model

According to Schuh et al. (2013), a emulsion-type sausage model composed of 50 wt% lean meat, 28 wt% fat, 22 wt% ice, curing salt (1.8 wt%), diphosphate (0.2 wt%), ascorbic acid (0.05 wt%), and