Food Hydrocolloids 76 (2018) 150–157

Contents lists available at ScienceDirect

Food Hydrocolloids

journal homepage: www.elsevier.com/locate/foodhyd

Impact of distribution of carboxymethyl substituents in the stabilizer of carboxymethyl cellulose on the stability of acidified milk drinks

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ARTICLE INFO

Article history:
Received 31 August 2016
Received in revised form
23 December 2016
Accepted 27 December 2016
Available online 28 December 2016

Keywords:
Carboxymethyl cellulose (CMC)
Acidified milk drinks (AMDs)
Molecular parameter
Distribution of carboxymethyl substituents
Stability

ABSTRACT

The influences of molecular parameters such as molecular weight (M_w), the degree of substitution (DS) and especially the distribution of carboxymethyl substituents within the anhydroglucose unit (AGU) of carboxymethylcellulose (CMC) on the rheological properties of CMC solutions and the stability of acidified milk drinks (AMDs) induced by this cellulose ether have been comprehensively investigated and evaluated by LUMi-Sizer. The DS and the distribution of carboxymethyl substituents are characterized by means of ^{1}H NMR spectroscopy using a set of acid-hydrolyzing CMC samples. A new CMC molecular parameter of R_i indicating the individual degree of substitution at the position of either C-2 (R_2) or C-6 (R_6) in AGU is proposed to evaluate the influence of distribution of carboxymethyl substituents on the stability of the milk drinks. It is found that the distribution of carboxymethyl substituents also plays a key role in the stability of AMDs. The stability of the drinks increases not only with increasing the M_w and DS but also with decreasing the R_2 or increasing the R_6 of CMC. This fact is explained on the basis of CMC with a higher individual DS at C-2 position resulting in higher electronegativity, thus increasing the electrostatic repulsion between CMC-adsorbed casein particles in the colloidal system, thereby contributing to a better stability to AMDs. These findings provide an insight into fabricating better stability of AMDs induced by CMC.

1. Introduction

Acidified milk drinks (AMDs) exist in many variations including drinking yogurt, fruit milk drinks, and soft drinks containing milk solids as a minor ingredient (Azarikia & Abbasi, 2010; Jensen, Rolin, & Ipsen, 2010). Over the last decades AMDs have achieved increasing popularity leading to large industrial scale production. Such drinks are usually manufactured by direct acidification or fermentation of milk with lactic acid bacteria, followed by homogenization and finally acidification with fruit juices and/or acids (Amice-Quemeneur, Haluk, Hardy, & Kravtchenko, 1995; Liu, Nakamura, & Corredig, 2006). The pH values of these products range from 3.4 to 4.6 (Nakamura, Yoshida, Maeda, & Corredig, 2006). However, casein micelles will aggregate and precipitate in the abovementioned pH range. This phenomenon is mostly due to the decrease in steric repulsive interactions after the collapse of the extended conformation of κ-casein mainly on the casein micelle surface during acidification (Tuinier & de Kruif, 2002). Therefore, AMDs need the addition of stabilizer to prevent the flocculation of milk proteins and subsequent macroscopic whey off.

In the past decade, using polysaccharide hydrocolloids to stabilize AMDs has attracted a great interest (de Kruif & Tuinier, 2001; Doublier, Garnier, Renard, & Sanchez, 2000; Du et al., 2007; Syrbe, Bauer, & Klostermeyer, 1998a). Typical polysaccharides of pectin (Jensen et al., 2010; Laurent & Boulenguer, 2003; Tuinier, Rolin, & de Kruif, 2002) and soybean soluble polysaccharides (SSPS) (Nakamura, Furuta, Kato, Maeda, & Nagamatsu, 2003; Nakamura et al., 2006) have commonly used as stabilizers in AMDs, and especially much attention has been paid to pectin and its effective mechanism of stabilization. The mechanism of pectin stabilization to AMDs is due to the adsorption of pectin to casein particles at and below pH 5.0, and then negatively charged pectin–casein complex being dispersed by electrostatic repulsive interaction (Maroziene & de Kruif, 2000; Tromp, de Kruif, van Eijk, & Rolin, 2004).

However, the properties of pectin and SSPS vary greatly with natural sources and batches. Moreover, the price of pectin is

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http://dx.doi.org/10.1016/j.foodhyd.2016.12.034
0268-005X/

relatively high. Water-soluble carboxymethyl cellulose (CMC) has widespread applications in paper, ceramics, oil well drilling operations, foods, pharmaceuticals, and cosmetics mainly as an emulsifying agent, stabilizer or rheological control agent due to its good binding, thickening, and stabilizing properties (Benchabane & Bekkour, 2008; Biswal & Singh, 2004; Shen, Song, Qian, & Yang, 2010). This cellulose ether is often chosen as a functional agent instead of other gums with comparable properties due to its favorable price-to-performance ratio. Instead of pectin and SSPS, CMC has also been employed as a stabilizer in AMDs to prevent flocculation of milk proteins (Du et al., 2007; Du et al., 2009; Syrbe, Bauer, & Klostermeyer, 1998b; Wu, Du, Li, & Zhang, 2014; Wu, Liu, Dai, & Zhang, 2013). The stabilization mechanism of CMC in AMDs have been demonstrated that during acidification CMC adsorbs onto the casein micelles by electrosorption and the adsorbed CMC layer on the surface of casein could prevent aggregation and sedimentation of casein micelles by electrostatic and steric stabilization. On the other hand, the non-adsorbed CMC can slow down the sedimentation of casein particles by increasing the viscosity of continuous phase (Du et al., 2007; Du et al., 2009; Syrbe et al., 1998b; Wu et al., 2014; Wu et al., 2013).

As one of the most important cellulose derivatives, CMC has a linear structure composed entirely of a backbone of β-(1 → 4)-linked glucopyranose repeating units. In general, cellulose is activated with sodium hydroxide and converted with monochloroacetic acid according to the Williamson ether synthesis yielding CMC (Edali, Esmail, & Vatistas, 2001; Heinze & Koschella, 2005). The reaction conditions have a significant influence on the distribution of substituents of CMC resulting in heterogeneous and homogeneous paths on the distribution of substituents. It was found that CMC samples synthesized under homogeneous reaction conditions using LiCl/N, N-dimethylacetamide (DMAc) as a cellulose solvent contain a significantly higher amount of both 2,3,6-tri-*O*-carboxymethylated and unsubstituted units in the polymer chain than those obtained from a slurry of cellulose in isopropanol and water at comparable DS values (Heinze, Erler, Nehls, & Klemm, 1994).

Physico-chemical properties of CMC can be profoundly influenced by both the degree of substitution (DS) and the substituent pattern in addition to its molecular weight (M_w) (Clasen & Kulicke, 2001; Heinze, Heinze, & Klemm, 1994). As already indicated, the water-solubility of CMC and the rheological properties of CMC solutions do not only depend on the total DS, but also on the distribution of the substituents within the anhydroglucose unit (AGU) and along the polysaccharide chain (Heinze et al., 1994; Kulicke et al., 1996). Furthermore, CMC with the same DS but different distribution of the ionic groups exhibit substantial differences in the time-dependent rheology (Gelman, 1985).

The molecular parameters of CMC (including M_w and its distribution, degree of substitution (DS) and the distribution of carboxymethyl substituents at C-2, C-3, C-6 positions) are some important considerations for the stability of AMDs induced by this polymer. We previously investigated the influence of M_w and DS of carboxymethyl substituents on the interaction between CMC chains and casein micelles (Du et al., 2009). The main conclusion is that the stability of AMDs increases with increasing M_w and DS of CMC. However, the distribution of carboxymethyl substituents should also affects the electrostatic interaction between casein micelles and CMC, and potentially influences the application properties of the final products. We have found that in some cases the stabilities of AMDs induced by CMC with the same M_w and DS are different although the same processing conditions are kept.

To provide a comprehensive understanding regarding the effect of molecular parameters of CMC on the stabilizing functionality in AMDs, the objective of the present work deals with the influence of distribution of carboxymethyl substituents within the AGU on the stability of AMDs in comparison with that of M_w and DS. The influence of carboxymethyl substituents at different positions (C-2, C-3, C-6) in CMC on the electrostatic repulsion and the possible mechanism of interaction between casein and carboxymethyl groups at different positions are also discussed.

2. Materials and methods

2.1. Materials and instruments

Four CMC samples (CMC(I) ~ (IV)) with different certain M_w and claimed DS were purchased from Acros Organics (Morris Plains, New Jersey, USA) and five CMC samples with certain M_w, DS and expected different distributions of carboxymethyl substituents (1# ~ 5#) were kindly supplied by DuPont-Danisco Co., Ltd. (Shanghai, China). Milk powders were obtained from Fonterra Co-operative Group (Wellington, New Zealand). Citric acid monohydrate was purchased from Shanghai Chemical Reagent Co., Ltd. (Shanghai, China). Other reagents were purchased from Aladdin Industrial Inc. (Shanghai, China) and used without further purification. All aqueous solutions were prepared with distilled water.

The ^{1}H NMR spectra were recorded on a Bruker Avance III 400 MHz instrument. The stability of AMDs was evaluated by a LUMi-Sizer (L.U.M. GmbH, Germany). The rheological measurements were performed on a stress-controlled rheometer (AR-G2, TA Instruments, USA) equipped with a 2°1′8″ cone plate geometry (60 mm in diameter, 58 μm gap) at controlled temperature of 25.0 ± 0.1 °C.

2.2. Preparation of AMDs

For preparation of reconstituted milk (8% w/w), low-heat milk power was gradually added in distilled water at 45 °C for 30 min. Meanwhile, CMC and sucrose were dry mixed and dissolved in distilled water, heated at 75 °C by stirring for 20 min and cooled down to ambient temperature. Afterwards, the CMC solution was added to the heat-treated milk solution to obtain 4% (w/w) milk solution containing 0.4% (w/w) CMC and 0.8% (w/w) sucrose. Then the mixture was directly acidified to pH 4.0 by adding 10% (w/w) citric acid with continuous stirring at 1000 rpm. In the next stage, the sample was homogenised at 200 bar with a homogeniser (Rannie TYPE 8.30 H; APV Rannie A/S, Denmark), and pasteurised at 110 °C for 30 s (HZ-SJJ, Shanghai Huizhan technology Co., Ltd., Shanghai, China). The final product was filled into 250 mL bottle, sealed and stored at 4 °C for 24 h.

2.3. Rheological measurements

Steady flow measurements were carried out on a controlled stress rheometer (AR-G2, TA Instruments, USA) to obtain the flow curves of the solutions (1% w/w) of CMC with different M_w and DS. The temperature was controlled by a circulating water bath and peltier system at 25 °C. In brief, the different CMC solutions (1% w/w) were prepared by gently stirring for 2 h. Afterwards, approximately 2–3 mL samples were carefully loaded on the geometry through a syringe needle and then the cone plate was lowered at a very slow speed in order to minimize induced structural changes prior to measurement. The excess samples around the geometry were removed and the exposed surfaces of samples were covered with a thin layer of silicone oil with low viscosity to prevent moisture losses during the testing. The samples were allowed to rest for 10 min prior to measurements to ensure mechanical equilibrium at the time of testing. The shear rate in flow