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Properties of acid gels made from sodium caseinate-maltodextrin conjugates prepared by a wet heating method

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ABSTRACT

Covalent attachment of polysaccharides to proteins (conjugation) via the Maillard reaction has been extensively studied. Conjugation can lead to a significant improvement in protein functionality (e.g., solubility, emulsification, and heat stability). Caseins have previously been successfully conjugated with maltodextrin (Md), but the effect on the detailed acid gelation properties has not been examined. We studied the effect of conjugating sodium caseinate (NaCN) with 3 different sized Md samples via the Maillard reaction in aqueous solutions. The Md samples had dextrose equivalents of 4 to 7, 9 to 12, and 20 to 23 for Md40, Md100, and Md200, respectively. The conjugation reaction was performed in mixtures with 5% NaCN and 5% Md, which were heated at 90°C for 10 h. The degree of conjugation was estimated from the reduction in free amino groups as well as color changes. Sodium dodecyl sulfate-PAGE analysis was performed to confirm conjugation by employing staining of both protein and carbohydrate bands. The molar mass of samples was determined by size-exclusion chromatography coupled with multi-angle laser light scattering. After the conjugation reaction, samples were then gelled by the addition of 0.63% (wt/vol) glucono-δ-lactone at 30°C, such that samples reached pH 4.6 after about 13 h. The rheological properties of samples during acidification was monitored by small-strain dynamic oscillatory rheology. The microstructure of acid gels at pH 4.6 was examined by fluorescence microscopy. Conjugation resulted in a loss of 10.8, 8.8, and 11.9% of the available amino groups in the protein for the NaCN-Md40 conjugates (C40), NaCN-Md100 conjugates (C100), and NaCN-Md100 conjugates (C200), respectively. With a decrease in the size of the type of Md, an increase occurred in the molar mass of the resultant conjugate. The weight average molar masses of NaCN-Md samples were 340, 368, and 425 kDa for the conjugates C40, C100, and C200, respectively. Addition of Md to NaCN dispersion resulted in slightly shorter acid gelation times even without the conjugation reaction. The storage modulus (G′) of acid gels was significantly lower in conjugated samples compared with the corresponding (unreacted) mixtures of Md and NaCN. The sample with the lowest G′ value at pH 4.6 was the C40 conjugate. Fluorescence microscopy showed that gels made by conjugates had slightly larger pores. These results indicate that conjugation of casein modified its acid gelation properties, presumably by the Md polysaccharide moiety hindering aggregation and rearrangements of the casein network.
Key words: sodium caseinate-maltodextrin conjugate, rheological property, acid milk gel

INTRODUCTION

Sodium caseinate (**NaCN**) is extensively used in food industry as a functional ingredient in a wide variety of products due to its versatile functional properties, including solubility, heat stability, foaming, and emulsifying capacities (Dalgleish, 1997; Dickinson, 2003). Maltodextrin (**Md**) powders are widely used in the food industry as stabilizers (texture and bulking modifiers), for example, in food emulsions (Loret et al., 2004), or as an aid in spray drying. Maltodextrin is a hydrolysis product of starch consisting of α-(1, 4) and α-(1, 6) linked D-glucose polymers, oligomers, or both, with dextrose equivalent (**DE**) values less than 20. Maltodextrin is a complex mixtures of high and low molecular weight materials, Md samples with low DE values retain longer oligosaccharide chains (Kasapis et al., 1993).

In recent years there has been significant research interest in altering protein functionality through conjugation with reducing sugars or polysaccharides (Oliver et al., 2006; Liu et al., 2012; O'Mahony et al., 2016). This conjugation process is usually performed by heating and exploiting the Maillard reaction. The covalent

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attachment of sugars to proteins can modify the surface charge, molar mass, and other physical or functional properties of this new protein-carbohydrate conjugate. The conjugation of whey proteins has been extensively studied (Fenaille et al., 2003; Jiménez-Castaño et al., 2005; Zhu et al., 2010; Sun et al., 2011; Wang and Ismail, 2012; Spotti et al., 2014).

Conjugation of Md to NaCN via the Maillard reaction leads to significant improvement in the functional properties of the caseins (Shepherd et al., 2000). Shepherd et al. (2000) reported that casein-maltodextrin conjugates had excellent emulsifying properties. O'Regan and Mulvihill (2009) showed that NaCN-Md conjugates had improved solubility compared with NaCN, particularly in environments around the isoelectric point of the protein. Conjugation also resulted in increase in casein solubility and foaming ability (Grigorovich et al., 2012). Hiller and Lorenzen (2011) reported that yogurt made by fortification of milk with NaCN, which had previously undergone conjugation, had little effect on gel strength or whey drainage. Hiller and Lorenzen (2011) did not report on the dynamic rheological properties or microstructure of these gels. Corzo-Martínez et al. (2010) studied the effect of the Maillard reaction on the rheological properties of NaCN. After NaCN was conjugated with galactose and lactose, the viscosity of the conjugates was higher than the non-conjugated NaCN. It was suggested that conjugation affected the rheological properties of conjugates due to casein aggregation and covalent crosslinking (Corzo-Martínez et al., 2010). The DE value of Md likely affects its functional properties because the DE value is inversely related to the degree of polymerization of the molecule (Dokic-Baucal et al., 2004).

The majority of these conjugation studies were conducted under dry-heating conditions to promote the reaction between protein and carbohydrate (Shepherd et al., 2000; O'Regan and Mulvihill, 2009; Morris et al., 2004; Grigorovich et al., 2012). However, the dry-heating method takes a long time to complete the reaction and is not favorable for industrial application. Zhu et al. (2008) developed an alternative wet-heating method for this conjugation reaction. In this wet-heating method, the reaction is done in a liquid environment but with very high concentrations of polysaccharides, which act as a macromolecular crowding agent hindering protein unfolding during the heat treatment (Zhu et al., 2008).

Rheological behavior is associated with functional properties of food proteins, such as foaming properties, gelling capacity, and also affects the textural qualities of food, for example, mouth feel, taste, and shelf-life stability (Herh et al., 2000). Acidification of NaCN with glucono-δ-lactone (**GDL**) has been used to prepare model casein gels (Lucey et al., 1997a,b). Acidification of milk reduces the charge on caseins, dissolving some of the insoluble calcium phosphate crosslinks and modifying internal bonding between caseins (Lucey, 2016). Gelation occurs at some critical point when electrostatic repulsion is reduced and is not sufficient to overcome attractive forces like hydrophobic interactions (Lucey, 2016). Acid gels made with NaCN are a simpler model milk protein system due to the absence of insoluble calcium phosphate as well as the lack of a micellar structure.

In this study, we studied the conjugation reaction between NaCN and Md with different molecular weight in aqueous solutions via the wet-heating method. The rheological properties and microstructure of acid-induced gels made from NaCN-Md conjugates were investigated.

MATERIALS AND METHODS

Materials

Sodium caseinate (protein content ~90%) was obtained from Kerry Ingredients (Beloit, WI). The maltodextrins, Maltrin40 (**Md40**), Maltrin100 (**Md100**), and Maltrin200 (**Md200**) with DE values of 4–7, 9–12, and 20–23, respectively, were obtained from Grain Processing Corporation (Muscatine, IA). The GDL (Sigma-Aldrich, St. Louis, MO) was used as an acidogen. All other chemicals were of analytical grade (Sigma-Aldrich).

Preparation of the NaCN-Md Conjugates

The NaCN and Md (i.e., the Md40, Md100, and Md200) were individually dissolved in Milli-Q water at 10% (wt/vol), equal volumes of the aqueous solutions were mixed together, and final concentrations of maltodextrin and sodium caseinate in the mixture were 5%. The sample solutions were stirred on a magnetic stirrer at room temperature (~22°C) for 2 h to completely dissolve the mixture. Sodium azide (NaN_3, 0.02% wt/wt) was added to prevent bacterial growth in these samples. Aliquots of the solutions were placed in a water bath heated at 90°C for 10 h. Samples were then taken out of the water bath and immediately cooled in an ice bath. Triplicates were performed for each experiment.

Determination of Extent of Conjugation

Determination of Available Amino Groups. The degree of conjugation was estimated using a colorimetric assay to determine the change in free amino groups. The concentration of available amino groups in NaCN, NaCN-Md mixtures, and conjugates were