Carbohydrate Polymers 98 (2013) 1389–1396

Contents lists available at ScienceDirect

Carbohydrate Polymers

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

Concentration dependent effects of dextran on the physical properties of acid milk gels

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ARTICLE INFO

Article history:
Received 22 May 2013
Received in revised form 21 July 2013
Accepted 31 July 2013
Available online 8 August 2013

Keywords:
Dextran
Rheology
Acidified milk
Gelation
Syneresis

ABSTRACT

The effect of dextran from *Leuconostoc mesenteroides* (DEX_{500}), added to milk prior to acidification with glucono-δ-lactone (GDL) or *Streptococcus thermophilus* DSM20259, was studied with respect to polysaccharide concentration. The incorporation of 5–30 g/kg DEX_{500} significantly affected gelation behavior. Increasing DEX_{500} concentrations resulted in a linear increase of gel stiffness (GDL gels: $R^2 = 0.96$; microbial acidification: $R^2 = 0.94$; $P < 0.05$) and 30 g/kg DEX_{500} resulted in a 2-fold higher stiffness compared to gels without polysaccharide. The respective stirred gels depicted a significant reduction in syneresis, which decreased from 30.4% (0 g/kg DEX_{500}) to 22.0% (30 g/kg DEX_{500}) for chemically acidified gels after 1 d of storage. Physical characteristics of DEX_{500} in aqueous solution were helpful to explain its behavior in the complex system milk.

1. Introduction

Texture is an important quality attribute of yogurt and yogurt-like products made from milk by fermentation with lactic acid bacteria (LAB), which can be modified by adding stabilizers or by taking advantage of *in situ* produced exopolysaccharides (EPS) (Cerning, 1995; Tamime & Robinson, 1999). Texturizers for fermented dairy products comprise charged (*e.g.*, xanthan, carrageenan, pectin) or uncharged polysaccharides (*e.g.*, guar or locus bean gum, β-glucan) of different origin which are expected to contribute to a smooth texture, to enhance viscosity and to reduce whey separation. In many experimental studies, however, such additives led to softer, more unstable products. For example, Sanchez, Zuniga-Lopez, Schmitt, Despond and Hardy (2000) showed that the addition of 1 g/L locus bean gum altered gel microstructure toward a more porous network, whereas the addition of 5 g/L guar gum or locus bean gum increased apparent viscosity, but lowered gel stiffness (Everett & McLeod, 2005).

EPS produced by dairy LAB are usually uncharged (Vaningelgem et al., 2004), and only low amounts (13–170 mg/L) are necessary to affect product texture. Besides enhanced viscosity and creaminess these polysaccharides also reduce syneresis because of their water binding ability (Folkenberg, Dejmek, Skriver, & Ipsen, 2005; Marshall & Rawson, 1999). Other factors that come into play is ropiness, and whether the EPS are associated with the protein network or located in pores (Folkenberg et al., 2005; Folkenberg, Dejmek, Skriver, & Ipsen, 2006; Hassan, Ipsen, Janzen, & Qvist, 2003). The effects of *in situ* produced EPS have mainly been related to their structure (Folkenberg et al., 2006; Gentes, St-Gelais, & Turgeon, 2011; Ruas-Madiedo, Hugenholtz, & Zoon, 2007). However, we showed in a previous study that the effects of the addition of purified neutral EPS from *S. thermophilus* ST-143 to milk prior to acidification on gel stiffness and viscosity are concentration dependent, and that even amounts of 150 mg/L EPS are sufficient to improve rheological properties (Mende, Peter, Bartels, Rohm, & Jaros, 2013). The addition of charged EPS from marine bacteria influenced gel properties as well, whereas no concentration effect was observed (Girard & Schaffer-Lequart, 2007a).

The stability of the microstructure of acid milk gels depends on the physico-chemical properties of the proteins and polysaccharides (molecular mass, charge, molecular conformation distinguished by chain length, chain stiffness, branching), their ratio, but also on interactions between the macromolecules (Doublier, Garnier, Renarda, & Sanchez, 2000; de Kruif & Tuinier, 2001). Anionic, adsorbing polysaccharides interact with casein at the surface of the micelles through electrostatic interactions; consequently, pH is an important parameter. In the presence of neutral, non-adsorbing polysaccharides direct interactions with proteins play a minor role, whereas depletion effects may induce phase separation (Tuinier, ten Grotenhuis, & de Kruif, 2000). In that case, pH only affects protein self association (Doublier et al., 2000; Syrbe, Bauer, & Klostermeyer, 1998), and the stability of the protein network is based on the competition between phase separation and

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http://dx.doi.org/10.1016/j.carbpol.2013.07.072

protein gelation (Tavares, Monteiro, Moreno, & Lopes de Silva, 2005).

We are particularly interested in the understanding of interactions between uncharged, non-gelling polysaccharides and proteins in milk gels. Commercially available are only EPS from non-dairy LAB (*e.g.* dextran, levan, alternan or reuteran) and among them dextran is the only one approved for use in the food industry (European Commission, 2001). Dextran, mainly utilized in pharmaceutics, medicine, chemical analytics, cosmetics, coatings or paints, is polydisperse with a molecular mass varying from 10^5 to 10^9 Da; defined molecular mass may be obtained by acid or enzymatic hydrolysis (Bovey, 1959; Naessens, Cerdobbel, Soetaert, & Vandammeet, 2005; Rehm, 2010). Commercial dextran is mainly class I from *Leuconostoc mesenteroides* B-512F with a backbone of α-(1,6)-linked glycosyl residues, and approximately 5% α-(1,3)-linked side chains (50–100 residues) (Jeanes et al., 1954; Naessens et al., 2005). It is a flexible, random coil polysaccharide which entangles and aggregates when solution concentration increases (Ioan, Aberle, & Burchard, 2001; McCurdy, Goff, Stanley, & Stone, 1994; Pinder, Swamson, Hebraud, & Hemar, 2006). In aqueous solution, dextran generally exhibits Newtonian behavior up to rather high concentration; ionic strength and pH do not affect viscosity (Kasaai, 2012; McCurdy et al., 1994; Tirtaatmadja, Dunstan, & Boger, 2001).

The application of dextran in milk products is hardly investigated. To the best of our knowledge, only Girard and Schaffer-Lequart (2007a) applied dextran, but in a low concentration (0.5 g/L), where no effects were observed. Encouraged from preliminary experiments the aim of this study was to investigate the effects of different concentrations of dextran on the gelation behavior and on the rheological properties of acidified milk gels and link them to the physical characteristics of the polysaccharide in aqueous solution.

2. Materials and methods

2.1. Materials

Reconstituted skim milk was prepared from low-heat skim milk powder (SMP; Alpavit Käserei Champignon Hofmeister GmbH & Co. KG., Lauben/Allgäu, Germany). Glucono-δ-lactone (GDL) and dextran, molecular mass: 5×10^5 Da (DEX_{500}), was obtained from Sigma–Aldrich GmbH (Taufkirchen, Germany). Microbial acidification was performed with EPS negative *Streptococcus thermophilus* DSM20259 (Mårtensson, Öste, & Holst, 2002) from Deutsche Sammlung für Mikroorganismen und Zellkulturen GmbH (Braunschweig, Germany). Milk serum was obtained by two-step ultrafiltration of reconstituted skim milk (120 g/kg dry matter) using a 0.1 μm polyethersulfone membrane and a 10 kDa Hydrosart membrane (Sartorius AG, Göttingen, Germany).

2.2. Characterization of aqueous dextran solutions

1, 5, 10, 15, 20 or 25 g/L DEX_{500} were dissolved in deionized water, 0.1 or 1.0 mol/L NaCl, or milk serum, and filled into the 1.59 mm capillary of a LOVIS rolling ball microviscometer (Anton Paar GmbH, Ostfildern, Germany). After equilibration to 20 °C, rolling time t was measured at an angle of 70° in two independently prepared solutions using gold-coated steel balls (d = 1.5 mm, ρ = 7.88 g/mL) in six-fold each. Specific viscosity η_{sp} (−) as the solute's contribution to viscosity was calculated by

$$\eta_{sp} = \frac{t_{Sample}}{t_{Solvent}} - 1 \quad (1)$$

Intrinsic viscosity $[\eta]$ (mL/mg) was estimated on the basis of the truncated Huggins (Eq. (2)) or Kramer (Eq. ((3)) equations (Sudduth, 1998) and their respective constants K_H and K_K by plotting η_{sp}/c or $[\ln(\eta_{sp} + 1)]/c$ *versus* DEX_{500} concentration c_{DEX} (g/L), and extrapolating to zero polymer concentration:

$$\frac{\eta_{sp}}{c} = [\eta] + K_H \cdot [\eta]^2 \cdot c \quad (2)$$

$$\ln \frac{\eta_{sp} + 1}{c} = [\eta] + K_K \cdot [\eta]^2 \cdot c \quad (3)$$

Shear viscosity measurements were performed for DEX_{500} in deionized water (5–300 g/L) at 20 °C using an AR-G2 rheometer (TA Instruments, Eschborn, Germany) with a concentric cylinder device (d_i = 28 mm, d_a = 30 mm, h = 42 mm) and Peltier temperature control. Shear rate $\dot{\gamma}$ was increased from 0.1 s^{-1} to 100 s^{-1} in 10 steps per decade. At each data point, pre-shearing was 20 s, and measurement time was 5 s. Critical overlap concentrations of dextran were determined from plots of log specific viscosity in shear ($\eta_{sp,S} = \eta_{DEX}/\eta_{Water} - 1$) *vs.* log ($c\,[\eta]$) (Morris, Cutler, Ross-Murphy, Rees, & Price, 1981).

2.3. Preparation of acid milk gels

800 g reconstituted skim milk (150 g/kg dry matter) was transferred into a stainless steel vessel (d = 120 mm, h = 140 mm), heated to 90 °C for 15 min and cooled in ice water. Before acidification, 200 g deionized water (reference) or DEX_{500} solution was added to achieve a final milk solids content of 120 g/kg and a target c_{DEX} of 0, 5, 12.5 or 30 g/kg.

Acidification was induced either by adding 30 g/L GDL to milk of 30 °C which was made as described above, or by adding 30 g/L *S. thermophilus* DSM20259 starter culture to milk which was adjusted to 37 °C. The starter was prepared anaerobically at 40 °C in MRS broth (de Man, Rogosa & Sharpe, 1960; Merck KGaA, Darmstadt, Germany), followed by a second incubation in enriched skim milk (10 g/L SMP, 10 g/L casein peptone, 5 g/L yeast nitrogen base). At the end of acidification (3 h for GDL, pH 4.6 for *S. thermophilus*), the vessel was transferred into ice water for 10 min. Subsequently, the gel was broken by applying a defined stirring protocol (Mende, Mentner, Thomas, Rohm, & Jaros, 2012), poured into beakers and stored at 6 °C.

2.4. Rheology of set and stirred milk gels

Rheological characterization of microbially acidified gels was carried out with an ARES RFS3 rheometer (TA Instruments, Eschborn, Germany), and of GDL gels with the AR-G2. The RFS3 was equipped with a concentric cylinder device (d_i = 32 mm, d_a = 34 mm, h = 33.5 mm) and a water bath for temperature control (geometry for the AR-G2, see above). Gelation was monitored in dynamic mode by measuring storage modulus G' (Pa) as a function of time. Strain amplitude was set to 0.003, and angular frequency was 1 rad/s. Subsequently, a strain sweep at 1 rad/s was carried out. Stirred gels were characterized by thixotropic loop experiments where the shear rate was linearly increased from 0 to 100 s^{-1} within 100 s, and subsequently reduced to zero within another 100 s. For flow curve measurements, shear rate was increased from 0.03 s^{-1} to 100 s^{-1} with 5 points per decade; after 140 s pre-shearing, viscosity readings were recorded during 5 s.

2.5. Permeability and forced syneresis

The permeability of GDL gels was measured by the tube method (Jaros, Rohm, Haque, Bonaparte, & Kneifel, 2002; van Marle & Zoon, 1995). Gels of a height of approximately 50 mm were formed in glass tubes (d = 4 mm, h = 250 mm) by acidification with GDL (30 °C for 3 h) and stored at 6 °C overnight. The tubes were then transferred into a perspex bath with milk serum (T = 20 °C, pH 4.0) and