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Shear work induced changes in the viscoelastic properties of model Mozzarella cheese

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ABSTRACT

Three model Mozzarella type cheeses (full-fat, non-fat and full-fat with added tri-sodium citrate) were prepared by working cheese components together at 70 °C in a twin screw Blentech cooker. G′ at 70 °C increased with shear work input suggesting work thickening. At lower shear work inputs (<30 kJ kg^{-1}), cheese behaved like a viscoelastic liquid exhibiting typical entangled polymer melt behaviour with moderate frequency dependence. A definite critical point for structural and viscoelastic transition was identified at higher shear work levels (~58 kJ kg^{-1} at 150 rpm). Excessive shear work levels (>70 kJ kg^{-1}) resulted in a viscoelastic solid material exhibiting low frequency dependence. Similar viscoelastic property changes occurred in non-fat cheese suggesting that major changes were taking place in the protein matrix during working. Good correlation was found between oscillatory rheological properties such as G′ and LT_{max} and the melting properties of test cheeses.

1. Introduction

Pasta-filata type cheeses such as Mozzarella are known for their fibrous macroscopic and microscopic structure (McMahon, Fife, & Oberg, 1999). The fibrous structure means that they are anisotropic in both microstructure and mechanical properties (Bast et al., 2015). The cooking and stretching steps during cheese manufacture promote the formation of fibrous structure through kneading action. This not only creates the desirable texture but also helps in the distribution of fat and serum channels within the cheese matrix (McMahon et al., 1999). The heterogeneous distribution of these channels is required to facilitate melting during baking of a pizza because they allow migration of fat and moisture to the cheese surface, preventing the surface from drying and thus facilitating flow of the molten cheese on the pizza (Rudan & Barbano, 1998). The energy supplied as shear work during the working of molten cheese is used for formation of new bonds and breakage of some bonds. The dynamics of these two reactions governs the melt and stretch characteristics of the cheese. For the cheese to flow on a pizza, the bonds between protein molecules should be flexible and transient so that they break temporarily and are subsequently reformed with different protein molecules in the structure. Pasta-filata cheeses are also required to stretch. The stretching characteristics are governed by the relaxation and reformation of bonds between adjacent protein molecules during deformation (Lucey, Johnson, & Horne, 2003). These melt and stretch properties of pasta-filata type cheeses are related to the proportion of calcium associated with proteins (Joshi, Muthukumarappan, & Dave, 2002; Lucey & Fox, 1993).

Oscillatory rheology has been widely used for characterisation of the melting behaviour of cheese because the methods are relatively straightforward (Ak & Gunasekaran, 1996; Guinee, Feeney, Auty, & Fox, 2002; Hsieh, Yun, & Rao, 1993; Hussain, Grandison, & Bell, 2012; Joshi, Muthukumarappan, & Dave, 2004; Karoui, Laguet, & Dufour, 2003; Ma, Balaban, Zhang, Emanuelsson-Patterson, & James, 2014; Rock et al., 2005; Subramanian & Gunasekaran, 1997; Tunick et al., 1993; Udyarajan, Horne, & Lucey, 2007; Venugopal & Muthukumarappan, 2003). Measurement of storage modulus (G′), loss modulus (G″) and loss tangent (LT or tan δ) with respect to strain amplitude, frequency and temperature are common ways of performing experiments. G′ is an index of stiffness or elasticity of a material and is also a measure of the energy stored and released in one oscillation cycle. G″ indicates the energy lost per oscillation cycle through viscous dissipation (Lucey et al., 2003). LT, a ratio of viscous to elastic properties, is related to

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the relaxation of bonds in the cheese matrix (Lucey, 2002) and can be used as an indicator of cheese meltability or flowablity (Lucey et al., 2003). LT can also be used as a material function to describe viscoelastic behaviour (Steffe, 1996).

Strain amplitude sweeps are usually conducted to determine the linear viscoelastic limit of a material. Frequency sweeps are useful to characterise the state of a material during processing. They have been widely used in characterising the viscoelastic behaviour of polymer melts. Entangled polymeric networks demonstrate significant frequency dependence whereas viscoelastic solids show very little frequency dependence. Temperature sweeps are important to understand the melting behaviour of a material. Decreases in dynamic moduli with increase in temperature reflect softening of the cheese matrix upon heating. A crossover temperature for G'–G'' on a temperature sweep indicates the gel–sol transition point (Schenkel, Samudrala, & Hinrichs, 2013). The maximum value of LT on a temperature sweep (LT_{max}) is considered as an indicator of melt (Mounsey & O'Riordan, 1999) and/or flow (Guinee, Auty, & Mullins, 1999). Oscillatory rheology has been successfully used to distinguish between the following aspects of cheeses – different cheese types, range of fat levels, effect of storage, processing conditions, compositional differences (Mounsey & O'Riordan, 1999). We have used each of the above methods to explore changes in the properties of model Mozzarella cheeses during working.

Before our work only two studies had investigated the effect of working of Mozzarella cheese on rheology and functionality (Mulvaney, Rong, Barbano, & Yun, 1997; Yu & Gunasekaran, 2005). Both studies used thermo-mechanical energy to create pasta-filata structures and both concluded that screw speed and temperature could be used as process control variables to obtain the desired functionality. Both used a narrow shear work range (2–6.5 kJ kg^{-1}) and studied the combined effect of thermal and mechanical energy. Our recent work reported changes in steady shear rheology during the mechanical working of cheese in a Blentech twin-screw cooker (Sharma, Munro, Dessev, Wiles, & Buwalda, 2016). Rheology and melt functionality were strongly dependent on total shear work input. Apparent viscosity at 0.01 s^{-1} increased exponentially with shear work input increasing 198 fold over the shear work range of 2.8–185 kJ kg^{-1}, indicating strong work thickening behaviour. Good negative correlation ($R^2 = 0.90$) was found between apparent viscosity and melt score. Our objective in this study was to explore the effect of shear work input on the oscillatory properties of three model Mozzarella cheeses. Our main focus was to study changes in full-fat cheese. Non-fat cheese and cheese with tri-sodium citrate added were also prepared to study shear-induced changes in the absence of fat and with minerals chelated. A broad range of shear work (2–185 kJ kg^{-1}) was used to exaggerate any work thickening effects and changes in structure.

2. Materials and methods

2.1. Materials

Renneted and acidified protein gel manufactured from skim milk was obtained at −20 °C from Fonterra Research and Development Centre (FRDC) pilot plant, Palmerston North, NZ. The proximate composition of the protein gel was typically about 50% moisture and 46% protein. The frozen blocks were thawed for 1 d at 11 °C and ground in a Rietz grinder (Rietz Manufacturing, Santa Rosa, CA, USA) with 6 mm grind size. Cream was obtained from FRDC as a fresh lot on each trial day. Cheese salt was obtained from Dominion Salt (Mount Maunganui, New Zealand). Tri-sodium citrate (TSC) was obtained from Jungbunzlauer (Basel, Switzerland).

2.2. Manufacture of model mozzarella cheeses

Model Mozzarella cheese was made at FRDC by mixing, cooking and working protein gel, cream, water and salt in a counter rotating twin-screw cooker (Blentech, model CC-0045, Blentech Corporation, Rohnert Park, CA, USA). The batch size and working volume of the cooker were 25 kg and 29.45 L, respectively. Three types of model Mozzarella cheese were made: full-fat, non-fat, and full-fat with 0.5% TSC as a chelating agent. The target composition of full-fat cheese was 23% fat, 21% protein, 53% moisture and 1.4% salt. All results are for full-fat cheese unless otherwise noted. Non-fat cheese used the same protein/moisture and protein/salt ratios as full-fat cheese. Sharma et al. (2016) give further details of the processing methods, sampling times, sample storage conditions and final compositions. Screw speeds of 50, 150 and 250 rpm were used for shear work treatment. Each run was repeated on a different day at least one month after the first run to ensure that similar results were obtained with raw materials obtained from different lots but with similar composition.

Shear work input was calculated by numerical integration of the torque–time curve with respect to time (Sharma et al., 2016). The meltability of Mozzarella cheese was measured by the modified Schreiber test (Muthukumarappan, Wang, & Gunasekaran, 1999) with some variations (Sharma et al., 2016).

2.3. Dynamic rheological measurements

The dynamic rheological properties of the cheeses were studied on an Anton Paar MCR 301 rheometer (Anton Paar, Graz, Austria) with a 20 mm diameter serrated plate geometry (PP20/P2) and a Peltier temperature hood (H-PTD 200) (Sharma et al., 2015, 2016). Disc-shaped cheese samples of 20 mm diameter and ~2 mm thickness were prepared and equilibrated for 2 min at test temperature as previously except that a 1 N normal force was used to define the measurement gap at 20 °C (Sharma et al., 2015). A ring of soybean oil was placed around the sample periphery to avoid moisture loss during rheological measurements.

Strain amplitude sweeps ranging from 0.01 to 100% were conducted at 0.1, 1 and 10 Hz and at 70 °C to determine the linear viscoelastic (LVE) limit of the cheeses. In temperature sweeps, amplitude and frequency were 0.2% and 1 Hz respectively and temperature was increased from 20 °C to 90 °C. To ensure nearly isothermal conditions during temperature sweeps, the rate of temperature rise of the Peltier heating system was maintained at 1.8 °C per min. Preliminary experiments placing a thermocouple in the thermal centre of the specimen and monitoring temperature rise at different heating rates had shown that this slow heating rate was necessary. Frequency sweeps were conducted by applying frequencies in descending order from 100 Hz to 0.01 Hz at 70 °C using 0.2% strain amplitude. The frequency dependence of G' and G'' for the molten cheeses was fitted to the following equations (Steffe, 1996; Tunick, 2011):

$$G' = k_{elastic}\omega^n \quad (1)$$

$$G'' = k_{viscous}\omega^n \quad (2)$$

where n, $k_{elastic}$ and $k_{viscous}$ are constants, and n is the degree of frequency dependence. All rheological measurements were conducted at least in duplicate. All data points are the means of the two or more replicates.