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pH- and Temperature-Dependent Strain Hardening of Sodium Caseinate Gels

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ABSTRACT

Sodium caseinate, a protein ingredient produced from the major protein fraction in bovine milk, can form acid-induced gels that show interesting strain hardening behaviour in large oscillation amplitude shear. For the first time it was investigated whether the strain hardening of sodium caseinate gels depends on the time point at which the strain sweep is conducted. For this purpose, strain sweeps were started at various time points during the acidification, and the G' values were related to those obtained in small amplitude oscillatory shear (SAOS) experiments at the same time. The results showed that the strain hardening behaviour is in fact not constant during the gelation process. Interestingly, the smallest overshoot factor was observed around the maximum G' in SAOS experiments, whereas it increased again with the pH further decreasing.

INTRODUCTION

Sodium caseinate is derived from skimmed milk by acid precipitation of the casein micelles followed by re-suspension in water through neutralisation with sodium hydroxide, and it is applied in varied food formulations due to its technological functionality as thickener, emulsifier, or gelling agent[1].

Sodium caseinate solutions form gels upon slow acidification using chemical acidulants such as glucono-δ-lactone (GDL), and the gelation process can be followed in time-based small amplitude oscillatory shear (SAOS) experiments, where G' shows a rapid increase around the gel point and a maximum around the isoelectric point of the proteins, where electrostatic repulsion is minimal[2] (**Fig. 1**).

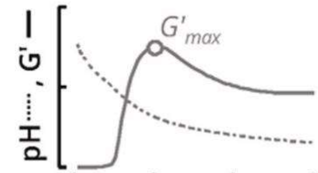

FIGURE 1: Representative illustration of the development of pH (dotted line) and storage modulus G' (full line) of sodium caseinate solutions during acidification with glucono-δ-lactone. G'$_{max}$ indicates the maximum storage modulus around the isoelectric point of the proteins[3]

More interesting, however, are the large deformation properties of such gels, as they have been shown to exhibit a relatively pronounced strain hardening behaviour[3], which is implied by a strong increase in G' and G'' with increasing strain amplitude between the end of the linear viscoelastic region and the fracture point of the gel[4] (**Fig. 2**).

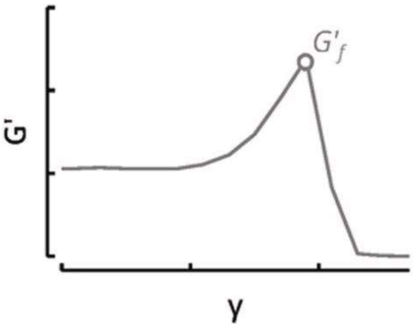

FIGURE 2: Representative illustration of the development the storage modulus G' of sodium caseinate gels with increasing strain amplitude γ. G'_f indicates the storage modulus at fracture[3]

In scientific studies, strain sweep experiments are usually conducted at rather random points of the gelation curve, e.g., towards the end when the pH decay slows down. However, little is known about as to whether the strain hardening behaviour of sodium caseinate is constant during the gelation process. Therefore, strain sweep experiments were conducted at various time points during the acid-induced gelation in this study to characterise the strain hardening as a function of the pH.

MATERIALS AND METHODS

Acid casein powder (Lactoprot GmbH, Kaltenkirchen, Germany) was dispersed in demineralised water and neutralised to pH 6.8 using 1 mol/L NaOH to obtain sodium caseinate solutions. The dispersion was stirred over-night at ambient temperature to ensure complete dissolution of the casein, and the pH and protein concentration were subsequently adjusted to 6.6 and 27 g/kg.

Rheological experiments were conducted using a DHR20 rheometer (TA Instruments, New Castle, DE, USA) equipped with a DIN concentric cylinder geometry (d_i = 28 mm, d_o = 30 mm, h = 42 mm). The sodium caseinate solution was temperature equilibrated in a water bath, mixed with GDL, and subsequently transferred to the rheometer geometry. The GDL concentration was 55, 30, or 20 mg/g at 20, 30, or 40 °C, respectively, to reach similar acidification rates at the three temperatures, as higher temperatures will accelerate the acidification. Gelation was monitored in SAOS experiments at $\omega = 1$ rad/s and $\gamma = 0.003$ for up to 65 min, and the temperature was kept constant using a Peltier element. The measurements were conducted multiple times with strain sweeps from 0.003 to 3.0 started after different time points. G' measured during the strain sweeps were related to the corresponding G' obtained at the same time points in SAOS measurements to characterise the strain overshoot at different points of the gelation process.

RESULTS

Fig. 3 illustrates the results of the strain sweep experiments, which were started at different time points of the acid-induced gelation of sodium caseinate; the G' values are shown relative to the corresponding G' measured in SAOS measurements at the same time points (G'_0). From the results it is obvious that the strain hardening behaviour is not equal throughout the gelation process, and the differences are more pronounced for gels formed at 20 and 30 °C. The overshoot factor showed first a minimum at pH ~4.25 and then a maximum at pH ~3.8. Interestingly, the maximum G' in SAOS was observed at pH ~4.25 (data not shown) and thus correlated with the minimum of the overshoot factor.

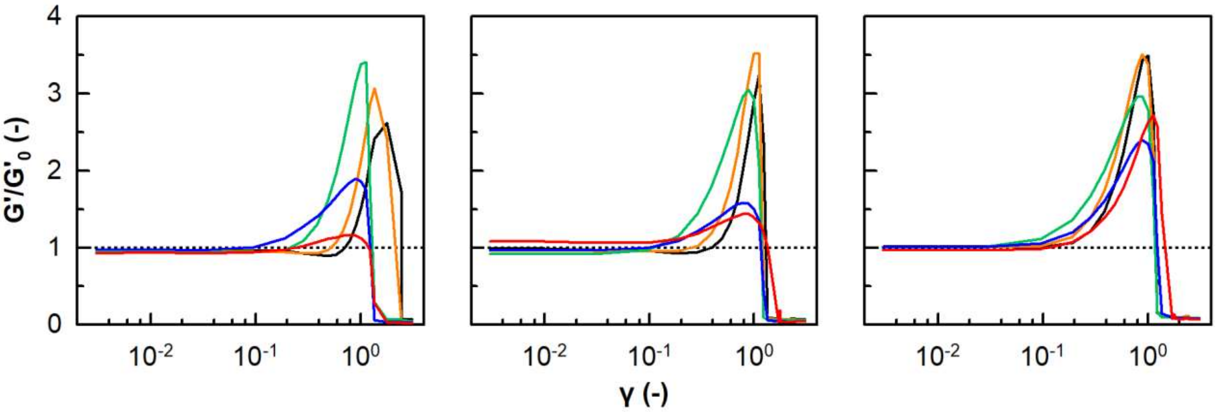

FIGURE 3: Strain sweeps of sodium caseinate gels formed at 20 (left), 30 (middle), or 40 °C (right) started 17.5 (red), 23.5 (blue), 35.5 (green), 50.5 (orange), or 60.5 min (black) after adding glucono-δ-lactone. Storage modulus G' is shown relative to the values measured in SAOS experiments at the same time point (G'_0)

CONCLUSION AND OUTLOOK

The findings of this study demonstrate the importance of considering the pH and temperature when characterizing the strain hardening behaviour of casein gels. Previous work showed that the strain hardening properties are related to water expression in forced syneresis experiments[3], and hence the time point of determination matters. Future analysis will elaborate more on the role of pH and temperature on the strain hardening of sodium caseinate gels.

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