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Use of ultrasound for characterising the gelation process in heat induced $CaSO_4 \cdot 2H_2O$ tofu curd

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ABSTRACT

Mechanical evolution of tofu curd in gelation was investigated using low-power ultrasound and textural analysis. Two independent ultrasonic parameters, velocity and attenuation, were measured at the frequency 1 MHz as a function of time after addition of the calcium sulphate ($CaSO_4 \cdot 2H_2O$) coagulant to heated soya milk. The responsive ultrasonic velocity has a plateau in the beginning of gelation and tends to a lower steady state after the formation of tofu gels. Ultrasonic attenuation exhibits first-order kinetics that matches the development of firmness revealed by textural analysis. Low-power ultrasound explores the formation of tofu gels in the aspects of pre-gelation processes, protein aggregation in gelation, and mechanical evolution in the gel at the post-gelation stage.

1. Introduction

Tofu is usually considered as a salt- or acid-coagulated water-based gel, with soya lipids and proteins and other constituents trapped in its gel networks (Kohyama et al., 1995). It is made by coagulating soya milk – followed by either pressure or heat treatment after the addition of a coagulant. The taste of tofu is significantly affected by its final texture (Kohyama and Nishinari, 1993; Jackson et al., 2002), i.e. the firmness of the tofu gel structure. The textural property is governed by soya milk concentration, coagulant type and concentration, gelation pressure and temperature, and gelation time (Hou et al., 1997; Cai and Chang, 1998).

Addition of the calcium sulphate ($CaSO_4 \cdot 2H_2O$) coagulant into heated soya milk triggers the formation of tofu gels. The formation is a two-step mechanism (Kohyama et al., 1995): soya proteins are denatured and then aggregated by the coagulant. The properties of gel can be properly unveiled with microscopy for the microstructure and with textural analysis or rheological study for the mechanical properties (Kohyama et al., 1995; Toubal et al., 2003; Wang et al., 2005; Berry et al., 2006; Arltoft et al., 2007; Saowapark et al., 2008). These instrumental methods explore the properties of tofu gel in various aspects. However, they are destructive, require laboratory practice, and are unsuitable for real-time applications for tofu production.

Microscopy of tofu gel demonstrates that the spread of proteins, fats, water, and air throughout the network structures correlates with the gelation process (Saowapark et al., 2008), i.e. the structure of tofu gel varies in gelation. Ultrasonics could be a good means in identifying the structural variation, as the behaviour of an ultrasound wave travelling in a medium correlates with the structure of the medium (McClements, 1995; Gür and Ogel, 2001; Llull et al., 2002; Kuo et al., 2008). An ultrasound wave travelling in a medium will have its propagation velocity altered by the density and viscoelasticity of the medium and its power attenuated by the heterogeneous structures in the medium. The viscoelasticity of a medium varies in response to the change of its rheological and textural attributes (Toubal et al., 2003; Foegeding et al., 2003; Wang et al., 2005; Arltoft et al., 2007). Hence, ultrasound possesses the ability to differentiate various media by its propagation velocity and to identify the difference among structures within a given volume by the acoustic impedance of the medium (Knorr et al., 2004; Gan et al., 2006).

The ability of ultrasound in characterising the microstructure of a material elicits its application, for example, in the dairy industry (Dukhin et al., 2005; Gan et al., 2006) and in characterising carrageenans gels (Toubal et al., 2003; Wang et al., 2005). In cheese making, ultrasound has been demonstrated to be a powerful tool, for example, in measuring the mechanical properties of cheese products (Benedito et al., 2000; Cho and Irudayaraj, 2003), determining the suitability of enzymes for milk coagulation (Ay and Gunasekaran, 2003), and exploring the gelation process (Dwyer et al., 2005). Changes in cheese structures were successfully monitored and, as a

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consequence, ultrasonic measurements were used in assessing the changes during cheese ripening. The microstructure and texture of a carrageenans gel is determined by the type and concentration of the used carrageeans and the gelation is sensitive to temperature, a dominant factor in the industry (Arltoft et al., 2007). The gelling temperature can be easily determined from the variation of the storage and loss moduli versus temperature measured using rheology (Toubal et al., 2003; Wang et al., 2005). The rheological technique is expensive and requires laboratory practice and hence ultrasound was adopted as an alternative to rheology in identification of the gelling temperature.

Cheese gel is obtained from milk with the addition of a coagulant under a certain gelation process; the formation of tofu gel is quite similar to that of cheese. The gelation and subsequent changes in the viscoelasticity of both the soya protein (Kohyama et al., 1995; Cheng et al., 2005) and the milk protein (Dwyer et al., 2005) after addition of coagulants follow first-order reaction kinetics, and their rheological properties are sensitive to the conditions of gelation (Foegeding et al., 2003; Cheng et al., 2005; Saowapark et al., 2008). The success of ultrasound in characterising cheeses and carrageeans gels encourages its application in characterising tofu gelation, as the behaviour of ultrasound in a medium depends on the microstructure and hence the rheological properties of the medium. Therefore, it would be of great interest to find a relationship between ultrasonic parameters, such as velocity or power attenuation, and tofu firmness.

2. Fundamentals of ultrasonic characterisation

2.1. Tofu gel networks and viscoelasticity

The gelation mechanism of tofu production assumes that soya proteins in the presence of a coagulant form clusters of gel networks (Kohyama and Nishinari, 1993; Kohyama et al., 1995). Tofu gel networks have irregular structures and constitute clusters of proteins, fats, water, and air bubbles (Saowapark et al., 2008). Fig. 1 shows a conceptual tofu gel network (Kohyama et al., 1995) and a corresponding acoustic model with 2 anticipated boundaries that separate heterogeneous media in the network. The heterogeneity model mimics the fact that the gel network has a heterogeneous structure and an incident acoustic wave is reflected by boundary #1 and transmits through medium #2 towards boundary #2. The same acoustic phenomenon at boundary #1 occurs again at the #2 and subsequent boundaries.

A viscoelastic material incorporates aspects of elastic (solid) and viscous (fluid) behaviours. Using rheology, the viscoelastic property is described by a complex shear modulus G^* which is the sum of a storage modulus G' and a loss modulus G'', as (Foegeding et al., 2003):

$$G^* = G' + jG'' \tag{1}$$

The storage modulus reflects the degree in which a material stores energy (elastic component), while the loss modulus describes the degree of dissipation (viscous component). The two moduli almost coincide when the medium is in a melted state and increase in response to a stronger gel (Toubal et al., 2003; Wang et al., 2005). This rheological phenomenon states that in a viscoelastic medium an intrusive mechanical energy is dissipated to a greater degree if its elasticity increases.

The firmness or maturity of tofu gel can be described with its modulus of elasticity, the storage modulus. The storage modulus of a coagulating tofu gel follows first-order reaction kinetics as a result of subsequent changes in the viscoelasticity of the soya proteins (Kohyama et al., 1995). The storage modulus $G'(t)$ begins to increase at a certain time (t_0) after the addition of coagulant and reaches saturation (G'_{sat}) with a time constant (τ), as:

$$G'(t) = G'_{\text{sat}}(1 - e^{-(t-t_0)/\tau}) \tag{2}$$

In analogy to Fig. 1, Eq. (2) states that the protein network strengthens as a function of time and the ultimate modulus $G'(\infty)$ depends on the parameters and conditions of the gelation process (Cheng et al., 2005; Saowapark et al., 2008).

2.2. Ultrasonic attenuation

The heterogeneity scatters incident ultrasound waves and hence attenuates the intensity of the ultrasound in propagation (McClements, 1995; Llull et al., 2002; Fox et al., 2004). The incident ultrasound wave is partly reflected by and partly transmits through the boundary between two different media, as shown in Fig. 1(b). The ratio of the amplitude of the reflected wave to that of the incident wave is called the reflection coefficient (β_r). The reflection coefficient of boundary #1 is calculated by (Blitz, 1968):

$$\beta_{r1} = \frac{\text{power of reflection}}{\text{power of incidence}} = \left(\frac{Z_2\cos\theta_{1i} - Z_1\cos\theta_{2t}}{Z_2\cos\theta_{1i} + Z_1\cos\theta_{2t}}\right)^2 \tag{3}$$

where $Z_k = \rho c$ is the acoustic impedance of medium #k, with ρ the density of the medium and c the velocity of the ultrasound travelling in the medium. The fraction of ultrasound that transmits into the subsequent medium is described with a transmission coefficient (β_t), as:

$$\beta_{t1} = 1 - \beta_{r1} = \frac{4Z_1Z_2\cos\theta_{1i}\cos\theta_{2t}}{(Z_2\cos\theta_{1i} + Z_1\cos\theta_{2t})^2} \tag{4}$$

Similarly, the fraction transmitting into medium #3 across boundary #2 is:

$$\beta_{t2} = \frac{4Z_2Z_3\cos\theta_{2i}\cos\theta_{3t}}{(Z_3\cos\theta_{2i} + Z_2\cos\theta_{3t})^2}\cdot\beta_{t1} \tag{5}$$

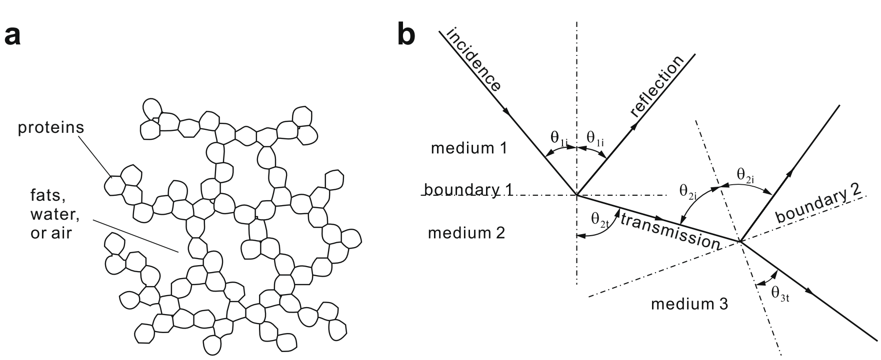

Fig. 1. (a) A conceptual gel network of $CaSO_4 \cdot 2H_2O$ tofu (Kohyama et al., 1995) and (b) acoustic model of two boundaries in a heterogeneous medium.