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Gelation behaviour of aqueous solutions of different types of carrageenan investigated by low-intensity-ultrasound measurements and comparison to rheological measurements

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Abstract

The gelation of different carrageenans in aqueous solutions was investigated by ultrasound at 7.8 MHz and by oscillating rheological measurements. The gelation of κ-, κ/ι-hybrid-carrageenan as well as a mixture of κ- and ι-carrageenans causes an increase in ultrasonic attenuation and a decrease in ultrasonic velocity. However, the gelation of ι-carrageenan, which could be detected by the oscillating rheological measurement, did not cause detectable changes in the ultrasonic measurement. Different gelation behaviours of a κ/ι-hybrid-carrageenan and a mixture of κ- and ι-carrageenans were observed by both techniques. This illustrates that the analytical techniques studied, which are based on different principles, can differentiate the gelation behaviour of different carrageenan systems. This might have important implications on the elucidation of gel formation mechanisms which, for complex systems, cannot be explained using only one single analytical technique.

Keywords: Ultrasound; Carrageenan; Rheology; Gelation

Industrial relevance: Temperature dependent changes in carrageenan containing foods influence the texture of foods. Therefore, the characterization of the gelation behaviours of carrageenans is a routine in product design. Ultrasonic technique is an interesting relatively new option for material characterizing due to its potential to be applied both off-line and on-line. For such applications, fundamental knowledge about the dependence of the ultrasonic parameters on the structural changes of carrageenans is required. Results of this work show that the ultrasonic method can sensitively differentiate between different types of carrageenan. This allows the application of the ultrasonic technique as a novel method for quality control purpose, probably also for other hydrocolloids and proteins.

1. Introduction

The application of high-intensity-ultrasound is well established, e.g. in ultrasonic baths, used to dissolve substances or to homogenize samples. In this case the mechanical energy of ultrasonic waves is used for particle destruction. In contrast to that, low-intensity-ultrasound can be used as a non-destructive method to analyse material properties. The basic principle is that the ultrasonic wave properties change during travelling through a sample due to interactions with the sample. The main advantages of the application of ultrasound are that it is a rapid, non-destructive, sensitive method and suitable for concentrated and opaque samples. However, low-intensity ultrasound measurements are not yet widely applied in the food branch. This is because in complex systems such as foods the ultrasonic parameters are influenced by many factors.

The most important parameters of ultrasound are ultrasonic velocity and attenuation. If a longitudinal ultrasound wave travels through a viscoelastic medium, the ultrasonic velocity U is a function of the bulk modulus K' and the storage modulus G' of the medium (Audebrand, Doublier, Durand & Emery, 1995)

$$U = \sqrt{\left(K' + \frac{4}{3}G'\right) * \frac{1}{\rho}} \quad (1)$$

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In many food systems, such as gels, G' is much smaller than K' (Povey & McClements, 1988). Eq. (1) can then be simplified to:

$$U = \sqrt{\frac{K'}{\rho}} \tag{2}$$

The bulk modulus K' is derived from the reciprocal of the compressibility κ:

$$U = \sqrt{\frac{1}{\rho \cdot \kappa}} \tag{3}$$

The attenuation of sound is defined as the loss of energy observed while a sound wave propagates through a sample. The major causes of attenuation are absorption and scattering. When an ultrasonic wave travels through a material, a part of the ultrasonic energy converts into heat due to material viscosity, thermal conduction and molecular relaxation. Scattering occurs in heterogeneous systems, when an ultrasonic wave is scattered by a discontinuity, so it cannot be detected and is regarded as lost energy. The attenuation provides information about the physicochemical properties of materials, e.g. concentration, viscosity, molecular relaxation, and microstructure (McClements, 1995).

Most food systems are aqueous systems. The change of structure in a sample is always accompanied by the change of hydration of molecules, which causes a change of the compressibility. Thus, it is possible to detect a structural change (e.g. gelation) by ultrasonic measurement in a product during processing or to compare different products.

Some researchers have investigated the gelation process in different food systems using ultrasound, e.g. egg white (Bae, 1996; Bae & Kim, 1998), polysaccharide (Audebrand et al., 1995; Gormally, Pereira, Wyn-Jones & Morris, 1982; Toubal, Nongaillard, Radziszewski, Boulenguer & Langendorff, 2003) and milk gels (Benguigui, Emery, Durand, & Busnel, 1994; Gunasekaran & Ay, 1994; Nassar, Nongaillard & Noel, 2001). They observed a change of ultrasonic parameters due to the formation and aging of a gel.

In this work the gelation behaviour of carrageenans was monitored. Carrageenans are hydrocolloids extracted from red seaweeds. They are sulphated D-galactans linked alternately via α $(1\rightarrow3)$ and β $(1\rightarrow4)$ bonds. Carrageenans are used widely in the food industry as gelling and stabilizing agents.

The main types of carrageenans are κ-, ι- and λ-carrageenans. κ- and ι-carrageenans form gels at low temperatures. Different models for the gelation mechanism have been proposed by different researchers. The double helix model proposed by Anderson, Campbell, Harding, Rees and Samuel (1969) and later modified to the domain model by Morris, Rees and Robinson (1980) is widely accepted. The domain model assumes that in the sol state at high temperature the carrageenan molecules exist as random coil. A temperature decrease induces the formation of double helices. Intermolecular association through double helices leads to the formation of small independent domains involving a limited number of chains. Aggregation of helices in different domains via cations enables more long-range cross-linking for the gel formation.

λ-carrageenan does not form a gel because its molecules contain more sulphate residues than the other two carrageenans. Hence, the formation and aggregation of the helical chains are inhibited. It only becomes more viscous upon temperature decrease.

In this work, we investigated the sol/gel and gel/sol transition in carrageenan solutions by measuring the ultrasonic velocity and attenuation during cooling and heating. The results are compared with the rheological data obtained by oscillatory measurements. It was the purpose of this study to investigate an important gel and structure forming system, namely carrageenan, and to assess the applicability of low intensity ultrasound as a suitable technique for the characterisation of complex mixtures of various types of carragerenans versus the rheological method as an established technique. Later on, this assessment should enable us also to characterize structures of more complex food systems.

2. Materials and methods

Three different carrageenans were used for the experiments: κ-, ι-, and κ/ι-hybrid-carrageenan. The carrageenans were provided by Danisco Cultor, Braband, Denmark. All the carrageenans were not standardized respecting their gel strength. The natural κ/ι-hybrid-carrageenan has a κ:ι-ratio about 0.6. This ratio was determined by the supplier using FT-IR calibrated by reprecipitated carrageenans from Sigma, St. Louis, USA (Hansen & Wichmann, 1999). It was shown by electrophoresis that the κ- and ι-units are located in the same macromolecule chain and not a mixture of κ- and ι-macromolecules (de Vries, 2002). All carrageenans contained traces of other carrageenans (<5%) and salt ions. Table 1 shows the ion concentrations in 0.3% carrageenan solutions determined with the flame photometer ELEX 6361 from Eppendorf AG, Hamburg, Germany.

In the present work, 0.3%, 0.5%, 1%, and 2% (w/w) aqueous solutions of different carrageenans were investigated. To investigate the influence of potassium ions K^+ on the gelation of κ-carrageenan, 0.5% κ-carrageenan with 0.04%, 0.08%, 0.16%, and 0.32% (w/w) K^+ added was used. K^+ was added as KCl (purity: ≥99.5%, Merck KGaA, Darmstadt, Germany).

Table 1
Ion concentrations in 0.3% (w/w) carrageenan solutions

	Na^+ [mg/l]	K^+ [mg/l]	Ca^{2+} [mg/l]
κ-carrageenan	0.3	14.6	0.3
ι-carrageenan	3.7	12.8	7.2
hybrid-carrageenan	0	24.8	1.5