



Contents lists available at ScienceDirect

## LWT - Food Science and Technology

journal homepage: [www.elsevier.com/locate/lwt](http://www.elsevier.com/locate/lwt)

# Effects of different carrageenan types on the rheological and water-holding properties of tofu



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## ARTICLE INFO

## Article history:

Received 25 August 2016

Received in revised form

18 December 2016

Accepted 19 December 2016

Available online 21 December 2016

## Keywords:

Tofu

Carrageenan

 $\kappa/\iota$ -hybrid

Rheological property

Water-holding property

## ABSTRACT

Effects of three carrageenan types including  $\kappa/\iota$ -hybrid carrageenan,  $\kappa/\iota$ -mixture carrageenan, and  $K^+$ - $\kappa$ -carrageenan in the concentrations of 0.5 g/kg, 1.5 g/kg, 2.5 g/kg on the texture, rheological property, microstructure, and water holding property of tofu were compared for texture control. Types of carrageenan repeating units affected the coagulation process by changing the protein aggregation behavior in heated soymilk, resulting in the formation of tofu with distinct rheological and water-holding properties. The hardness and elasticity of tofu with  $\kappa/\iota$ -hybrid carrageenan were higher. The addition of carrageenan increased the expressible water of tofu without varying its syneresis. The stress relaxation data suggested two relaxation mechanisms in tofu. One appears at a shorter time between 0.4 and 15 s for both  $\lambda_1$  and  $\lambda_2$  that represents the aqueous phase with buffering ability in the tofu matrix. The other shows at a longer time around 60–95 s ( $\lambda_3$ ), that represents the network frame structure in the matrix. The addition of carrageenan increased the  $\lambda_3$  of tofu, indicating the decrease of network chain mobility. Tofu became softer and less elastic when the concentration of carrageenan was increased. The above phenomenon might be due to the changes in the network structure of tofu by carrageenan.

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## 1. Introduction

Carrageenans from red seaweed are a family of anionic sulfated polysaccharides. They are divided into three major types, namely kappa ( $\kappa$ -), iota ( $\iota$ -), and lambda ( $\lambda$ -) depending on the number of sulfate groups per repeating disaccharide units consisting of 3-linked  $\beta$ -D-galactopyranose and 4-linked 3,6-anhydro- $\alpha$ -L-galactopyranose (Necas & Bartosikova, 2013). Carrageenans are widely used as stabilizers, thickeners, and gelling agents in food products. Both  $\kappa$ - and  $\iota$ -carrageenan have the ability to form a gel in the presence of specific cations, but the textural properties of the gels are distinct. The  $\kappa$ -carrageenan gel is relatively hard and brittle, while the  $\iota$ -carrageenan forms a soft and flexible gel. These texture behaviors can be modified by varying the polysaccharide concentration, counter ion type or concentration, and by blending with different carrageenan types, as well as by mixing with other hydrocolloids in various ratios (Piculell, 2006). Alternatively, the application of  $\kappa/\iota$  hybrid carrageenan, consists of both  $\kappa$ - and  $\iota$ -repeating units, is also popular in the food industry (Van de Velde,

2008; Villanueva, Mendoza, Rodriguez, Romero, & Montano, 2004). The gel textures of  $\kappa/\iota$ -hybrid carrageenan are some places in between the pure  $\iota$ -carrageenan and the pure  $\kappa$ -carrageenan gels (Chanvrier et al., 2004). Increasing consumer demand for foods with a wide range of textures has resulted in research being carried out on approaches to improve the texture of food products. Carrageenan has several types with diverse rheological properties and is suitable for food texture modification.

Tofu that involved the gelation of soy proteins is a widely and popularly accepted soy product in East Asia. For typical tofu making, soybeans are soaked and ground with water, and then are filtered to produce the raw soymilk. The raw soymilk is heated to 90 °C for 3–10 min, and is cooled down to the room temperature. The soybean curd is generated by the addition of glucono- $\delta$ -lactone (GDL) or calcium sulfate that are commonly used as coagulants. The GDL in the soymilk releases protons slowly resulting in proper gelation of soy proteins but requiring an adequate time. In practice, GDL is typically applied to silken tofu making. On the other hand, calcium sulfate dissociates rapidly at low temperature. The shorter gelation time causes the formation of a discontinuous and weaker curd (Liu & Kuo, 2011). Generally, the calcium sulfate curd is further broken and is pressed to make the tofu. Nevertheless, rearrangement of tofu network is still in progress during storage (Lee & Kuo,

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2014), leading to the syneresis of tofu (Shen & Kuo, 2014). Several hydrocolloids have been applied as gelling agents or stabilizers in tofu preparation, to improve its textural and water-holding properties, or to extend its shelf-life (Chang, Lin, & Chen, 2003; Karim, Sulebele, Azhar, & Ping, 1999; Kim & Han, 2003; Lee & Kuo, 2011). The hydrocolloids would entangle with soy protein molecules during gelation and stabilize the tofu structure that could improve the shelf-life of tofu (Lee & Kuo, 2011; 2014). However, modifying the textural property of tofu by addition of  $\kappa$ /I-hybrid carrageenan or carrageenan blends has not previously been reported.

Understanding the mechanism involving in the interactions between soy proteins and hydrocolloids is important to discover their potential in developing a novel gel texture. Here, the rheological analysis along with stress-relaxation test was used to give a general indication of the structure changes in several food systems under non-destructive condition (Ahmad, Tashiro, Matsukawa, & Ogawa, 2004; Baik & Mittal, 2006; Herrero, Heia, & Careche, 2004; Singh, Rockall, Martin, Chung, & Lookhart, 2006; Sozer, Kaya, & Dalgic, 2008). The scanning electron microscope (SEM) was applied to provide a stereoscopic image of the fine structure of tofu network (Lee & Kuo, 2011; Liu & Kuo, 2011; Shen & Kuo, 2014). The objective of this study was to investigate the effects of different types and concentrations of carrageenan on the rheological and water-holding properties and the microstructure of tofu.

## 2. Materials and methods

### 2.1. Materials

Non-GMO soybeans were purchased from a local supplier. Calcium sulphate 2-hydrate ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) was obtained from J. T. Baker (Avantor Performance Materials, Center Valley, PA, USA). Three types of carrageenan,  $\text{K}^+$ - $\kappa$ -carrageenan,  $\kappa$ /I-hybrid carrageenan, and  $\kappa$ /I-mixture carrageenan, were provided by Chen-Ding Enterprises Co., Ltd. (Taipei city, Taiwan).

### 2.2. Tofu making

Tofu was prepared according to the method of Kao, Sue, and Lee (2003) with modifications on the coagulant type and concentration. Soybeans (275 g) were washed and soaked in a tank of 1375 mL distilled water at room temperature. After 7 h of soaking, another 1375 mL of distilled water was added, and the soybeans were ground with water in a food grinder (CL-010, Great Yen Electric Food Grinder Co. Ltd., Taoyuan city, Taiwan). The grinder was equipped with an automatic centrifugal filter to separate raw soymilk from the okara. Subsequently, the raw soymilk was heated to 95 °C for 5 min with regular stirring, and strained through a 120 mesh sieve. After the heated soymilk was cooled down to about 30 °C in an ice bath, different quantity of carrageenan (0.5 g/kg, 1.5 g/kg, and 2.5 g/kg) was added. The soymilk-carrageenan suspension was reheated to 80 °C and was mixed with freshly prepared 0.4% calcium sulfate solution at a speed of 320 rpm for 10 s. The mixture was then incubated for 20 min to form the curd. The curd was broken and transferred into a wood container (25 cm × 15 cm × 7 cm), and then pressed under 6541 kN/m<sup>2</sup> for 30 min to produce tofu. The tofu was stored for 1 day at 4 °C in a refrigerator for further analysis. Tofu preparing without carrageenan was used as the control.

### 2.3. Yield and composition analysis

The yield of tofu was expressed as the weight of fresh tofu produced per 100 g of soybeans. The moisture content and the

protein content of tofu were determined by the oven drying method and the micro-Kjeldahl method with the nitrogen factor of 5.71, respectively (AOAC, 2000).

### 2.4. Measurement of tofu texture

The texture of tofu was analyzed according to the texture profile analysis (TPA) (Bourne, 1978) using a TA-XT2 Texture Analyzer (Stable Micro Systems Ltd., Haslemere, Surrey, UK). The samples (20 mm diameter × 20 mm height) were compressed twice to 30% of their original height, by a cylinder probe at a constant cross-head speed of 2.0 mm/s. Texture parameters of the samples including hardness, cohesiveness, gumminess, and chewiness were measured and calculated.

### 2.5. Small-deformation stress relaxation test

The stress relaxation test was carried out following the method of Singh et al. (2006) using the Texture Analyzer with the 5 kg load cell. The tofu sample (26 mm diameter × 3 mm height) was compressed to 15% (within linear limit of viscoelastic range) of its original height, by a plate probe with 3 cm diameter at a constant cross-head speed of 0.5 mm/s for 300 s. The force decaying-time curves were recorded and fitted, using the three-element Maxwell model (Peleg & Normand, 1983):

$$E_{\text{total}} = E_{\infty} + E_1 \exp\left(\frac{-t}{\lambda_1}\right) + E_2 \exp\left(\frac{-t}{\lambda_2}\right) + E_3 \exp\left(\frac{-t}{\lambda_3}\right) \quad (1)$$

where  $E_{\text{total}}$  is the modulus of elasticity (Pa) at time  $t$  (s);  $E_{\infty}$ ,  $E_1$ ,  $E_2$ , and  $E_3$  are the elastic moduli (Pa) of the springs;  $\lambda_1$ ,  $\lambda_2$ , and  $\lambda_3$  are the relaxation times (s) of Maxwell elements.

### 2.6. Microstructure of tofu

The microstructure of tofu was closely examined by the scanning electron microscope (SEM, S-3000N, Hitachi Science Systems, Tokyo, Japan). The sample preparation for SEM followed the method of Shen and Kuo (2014). Tofu was cut into small pieces and was pre-treated including processes of fixing, dehydration, defatting, and drying. Dried samples were then coated with gold using the gold sputter (Desk-2, Denton Vacuum, Moorestown, NJ, USA). The observations were made at 15 kV.

### 2.7. Measurements of syneresis, expressible water and entrapped water of tofu

The syneresis of tofu was measured according to the method of Lee and Kuo (2011). Tofu was sliced into a cylinder with 15 mm in diameter and 3 mm in thickness. Six cylinders were weighed and laid on the stainless steel mesh inside a plastic box. The mesh was lifted up with small sticks allowing the exuded liquid to drip away from the sliced tofu samples. The box was then sealed with parafilm to prevent the evaporation of free water and stored at 4 °C for 24 h. The total liquid exuded during the storage period was weighed. Syneresis was expressed as the percentage of exuded liquid weight to the sliced tofu sample weight.

The expressible water and the entrapped water of tofu were determined according to the method of Liu, Chien, and Kuo (2013) with modification on centrifugation condition. The state of water in tofu was classified into expressible water and entrapped water using centrifugation method. Tofu was cut into a cylinder with 15 mm in diameter and 20 mm in height. The sample was centrifuged at 8600×g for 90 min at 4 °C. The expressed fluid was decanted into a weighing pan and weighed. The expressible water of

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