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Influence of cyclodextrins on texture behavior and freeze-thaw stability of kappa-carrageenan gel

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ABSTRACT

The influences of cyclodextrins (CDs) on texture characteristics and freeze-thaw stability of κ-carrageenan gel were investigated using texture profile analysis (TPA) and synthesis test. The TPA results demonstrated that the texture behavior of gelatinized κ-carrageenan was obvious influenced by CDs. Hardness was strengthened at low CD concentrations (1–2%, w/w) and then weakened along with the increase of CD concentrations. Springiness was significantly weakened after the CDs were added. Gumminess showed the similar change as hardness and chewiness dropped along with the concentration increasing of CDs, while cohesiveness had little change after the addition of CDs. Moreover, CDs improved the freeze–thaw stability of gelatinized κ-carrageenan. In both texture behavior and freeze-thaw stability aspects, the influences of modified CDs were superior to that of natural CDs. According to the experimental results, a proposed model was given to illuminate the distribution of CDs in the gelatinized κ-carrageenan.

1. Introduction

Natural Polysaccharides and their application has received increasing attention in food and pharmaceutical fields as they are inert, safe, biocompatible, biodegradable, eco-friendly, low cost and abundantly available in nature. Polysaccharides can be obtained from a number of sources including seaweeds, plants, bacteria, fungi, insects, crustacea, animals and even humans (Coviello, Matricardi, Marianecci, & Alhaique, 2007; Prajapati, Maheriya, Jani, & Solanki, 2014). Carrageenans are naturally occurring anionic sulfated linear polysaccharides which extracted from certain red seaweed of the *Rhodophyceae* family (Li, Ni, Shao, & Mao, 2014; Smidsr & Grasdalen, 1982). It is widely utilized in food, daily chemical and pharmaceutical formulation due to its excellent physical functional properties, such as gelling, thickening, emulsifying and stabilizing abilities (Necas et al., 2013). Carrageenans formed by alternate monosaccharide units of D-galactose and 3,6-anhydro-galactose linked by α-1,3 and β-1,4-glycosidic bonds. Depending on the amount and position of the SO^{3-} groups carrageenans can be classified into Lambda (λ), Kappa (κ), Iota (ι), Nu (υ), Mu (μ), Theta (θ) and Ksi (ξ), all containing about 22–35% of sulphate groups (Prajapati et al., 2014) and the sulphate groups influence the solubility and gel property of carrageenans, the higher levels of ester sulphate resulted in lower solubility temperature and lower gel strength (Necas et al., 2013). The three commercial most important carrageenans are κ-, ι- and λ-carrageenan in which have one, two and three sulphate ester groups each dimer units, resulting in theoretical sulphate content of approximately 20%, 33% and 41% (w/w), respectively (De Ruiter & Rudolph, 1997). There into, κ-carrageenan is formed by disaccharide repeating unit of 3-linked-β-D-galactose-4-sulphate and 4-linked-α-3,6-anhydro-D-galactose (Fig. 1a). κ-Carrageenan is predominantly produced by extraction of the tropical seaweed *Kappaphycus alvarezii* which was known in trade as *Eucheuma cottonii* (Campo, Kawano, Silva, & Carvalho, 2009). It is the industrially most important form of carrageenans, rendering it one of the most popular polysaccharides in the food industry for its remarkable thickening or gelling property (Piculell, 2006). Gelation of κ-carrageenan initiates upon cooling below a critical temperature (Tc) that depends on the concentration and the type of cations presented in the sol. A conformational transition of the κ-carrageenan chains from a random coil to a helix occurs during the gelation. The transition accomplishes over a relatively narrow range of temperatures and the fraction of helices increases while decreasing temperature in this range (Nguyen, Nicolai, Benyahia, &

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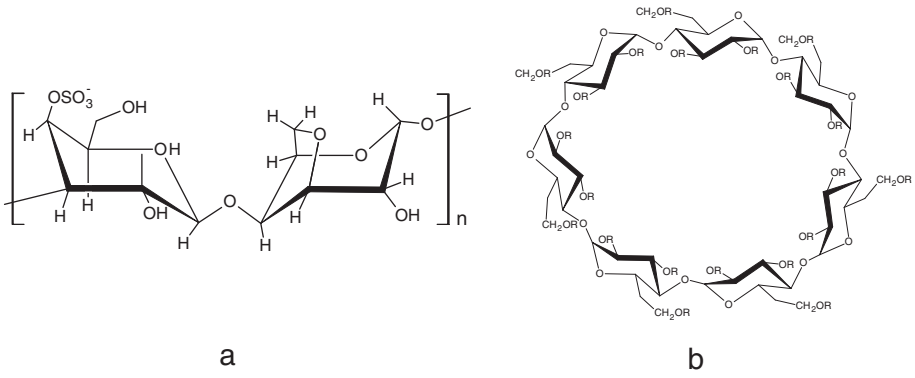

Fig. 1. Chemical structure of κ-carrageenan (a) and CDs (b). For natural CDs, R = H, α-, β- and γ-CD contain 6, 7 and 8 glucose residues, respectively. For modified CDs, R = H or substituent group).

Chassenieux, 2014). There are many detailed studies upon the gelation mechanism, influence of ions and hybrid gels of κ-carrageenan using different techniques such as rheology (Brenner, Tuvikene, Parker, Matsukawa, & Nishinari, 2014; Mangione et al., 2005), texture profile analysis (TPA) (Huang, Kennedy, Li, Xu, & Xie, 2007; Thrimawithana, Young, Dunstan, & Alany, 2010), X-ray scattering (Yuguchi, Thu Thuy, Urakawa, & Kajiwara, 2002), polarimetry (Mangione, Giacomazza, Bulone, Martorana, & San Biagio, 2003), and differential scanning calorimetry (Iijima, Hatakeyama, Takahashi, & Hatakeyama, 2007), etc.

The effect of cations on the physical properties of κ-carrageenan gels has been investigated widely. Nevertheless, the effect of other ingredients on the gelation of κ-carrageenan has been studied relatively little even though there often contain a number of different ingredients in application systems, especially in foods and cosmetics.

Cyclodextrins (CDs) are a series of cyclic oligosaccharides which consisting of (α-1,4)-linked α-D-glucopyranose units with a hydrophobic internal cavity and a hydrophilic exterior (Fig. 1b) (Szejtli, 1998). The most important characteristic of the CDs and its derivatives is the ability to form inclusion complexes with various types of hydrophobic molecules through the non-covalently bonding. Such noncovalent associations can actually improve the water solubility, bioavailability and stability of guest molecules (Loftsson & Duchêne, 2007; Szente & Szejtli, 1999). As the molecular level microcapsule wall material, CDs have widely applications in food, agriculture and the pharmaceutical field (Jin, 2013; Szejtli, 2013). Hence, both inclusion complex of CDs with nutrients and flavors (such as vitamin, carotenoid and essential oil etc.) and κ-carrageenan gel are frequently used in foods, especially in jelly like foods. However, the influence of CDs on the viscoelastic and mechanical properties of κ-carrageenan gel is scarce in the literature. The most extensive study was reported by (Mourtas, Aggelopoulos, Klepetsanis, Tsakiroglou, & Antimisiaris, 2009) who found that carrageenan could serve as a useful jelly vehicle for inclusion complex of CD with acetaminophen although they didn't investigate the influence of CD on physical properties of carrageenan. Lin and Ning (1997) found that antagonism took place between κ-carrageenan and β-CD while more than 25% of β-CD was added. Besides that, effect of CDs on the rheological properties and aging of a complex hydrogel (Carbopol 974 and Natrosol) was investigated by Mourtas et al. (2009). They found the elastic of the hydrogels were strengthened at the presence of 400 mg/mL CD and the gels were almost insensitive to aging.

Here we present a systematic investigation of the influence of adding several CDs and their derivate on κ-carrageenan gel texture by Texture Profile Analysis (TPA) and gel stability in storage by syneresis rate analysis.

2. Materials and methods

2.1. Chemicals

κ-Carrageenan, α-, β-, and γ-CD, hyrdoxypropyl-β-cyclodextrin (HP-β-CD, MW: ~1460) and methyl-β-cyclodextrin (M-β-CD, MW: ~1310) was purchased from Sigma-Aldrich (Shanghai, China). KCl purchased from Sinopharm (Beijing, China). The water used was double distilled and deionized.

2.2. Preparation of the κ-carrageenan gels

A 0.1 g/L stock solution of κ-carrageenan was prepared by directly dissolving the *κ-carrageenan* powder in 0.2% (w/w) KCl solution with stirring under heating in a water bath at 90 °C until the powder dissolved completely. The stock solution should be new prepared before use. Then the gel samples for texture characterization were prepared by pouring 30 g the hot stock solution into six beakers (50 mL) and adding 1%, 2%, 3%, 4%, 5% and 6% (w/w) CD under stirring, respectively, continued stirring for 30 min at 90 °C, and then stopped for 15 min to allow escape of air bubbles. The hot solutions were standing in a 25 °C incubator to form gel and keeping 20 h before test.

2.3. Texture profile analysis

Texture profile analysis (TPA) of the gel systems were evaluated using a TMS-Pro texture analyzer (Food Technology Corporation, Virginia, USA). An analytical probe (12.7 mm diameter black acetate cylinder) was compressed twice into the sample to a depth of 30% sample height at a speed of 20 mm/min. All measurements were done in twice.

2.4. Freeze-thaw stability

Freeze-thaw stability was determined according to the previous methods (Chen, Fu, & Luo, 2015) with a few modifications. The new prepared 0.1 g/L stock solution of κ-carrageenan was kept in a 90 °C water bath with continuous stirring for 30 min. After weighting and transferred to six beakers (50 mL), 2% (w/w) different type of CDs, i.e., α-, β-, and γ-CD, HP-β-CD, M-β-CD were added under stirring, respectively, the remained one was for control. The samples were then cooled in a water bath at 25 °C for 120 min, the gelation samples were carefully divided into five equal parts by weight and then each part was transferred to a centrifuge tube with closed screw cap. The tubes were stored at 4 °C for 16 h to increase nucleation and then frozen at −16 °C for 24 h. To measure