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Synergistic effect of the locust bean gum on the thermal phase transitions of κ-carrageenan gels

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Abstract

Synergism between κ-carrageenan and locust bean gum (LBG) was studied using the photon transmission technique. Synergistic effects in these polymeric mixtures strongly affected the physical properties of the gel structure. The transmitted light intensities, I_{tr}, versus temperature variations were investigated during the gelation and liquefaction processes. Slight synergistic peaks were detected in gel–sol and sol–gel transition temperatures for high κ-carrageenan/LBG ratios (approx. 80/2). Moreover, apparent synergistic peaks were observed in gel–sol and sol–gel transition activation energies for the mixtures approximately with the ratios of 80/10.

Keywords: Carrageenan; LBG; Photon transmission technique; Synergistic effect

1. Introduction

Carrageenan is a complex mixture of sulfated galactans obtained from many species of red seaweed and marine algae. In general, carrageenan possess a linear galactan backbone with alternating disaccharide repeating sequences of 1,4-linked α-D-galactose and 1,3-linked-β-D-galactose and a variable proportion of sulfate groups on different positions. Individual members of each series carry different amounts of sulfate group, which mainly allow carrageenan to be divided into three major types, namely ι-, κ- and λ-carrageenan (Nijenhuis, 1997). κ-Carrageenan is the less sulfated fraction and the easiest to gel. Carrageenan systems have been widely used in industries such as food, cosmetics, pharmaceuticals, paper and textile (De Ruiter & Rudolph, 1997; Shchipunov, 2003; Tye, 1989). Carrageenan shows a coil-helix conformational transition promoted by a temperature decrease in the presence of cations (Rochas & Rinaudo, 1984).

In general, the κ-carrageenan is known to form thermally reversible gels as a function of temperature. Usually cations such as K^+ and Na^+ are used as gel-inducing agents (Nijenhuis, 1997). Different models have been proposed for the mechanism of gelation of κ–carrageenan. The ordered conformation of κ-carrageenan molecules has been described as a single helix (Smidsrod, 1980), a double helix (Morris, Rees, & Robinson, 1980), a helical dimer (Rochas & Rinaudo, 1984; Rochas & Landry, 1987) and a fibrous model (Ikeda, Morris, & Nishinari, 2001). However, the double helix structure appears to be widely accepted now (Cairns, Atkins, Miles, & Morris, 1991; Fernandes, Gonçalves, & Doublier, 1993). According to this model, double helix formation occurs via nucleation between two isolated carrageenan chains. The double helices then aggregate to form a 3-dimensional network, i.e. the gel structure. During this process, crosslinks are formed by segments of a double helix. These segments are then aggregated by cations such as K^+. The sol–gel phase transition of κ-carrageenan solutions occurs as a result of coil-to-helix conformational transition upon cooling. Further decrease in temperature results in aggregation between ordered helices. On reheating, the gel structure is destroyed and during the gel–sol transition, the shear modulus follows another sigmoidal path back to its initial value, forming a hysteresis loop (Lai, Wong, & Lii, 2000).

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This cooperative process has been generally explained as a "domain model" based on the presence of double helices in the functional zones of the carrageenan gel network (Morris et al., 1980). The addition of cation solutions at an adequate concentration appears to improve the gel strength or the elastic modulus of κ-carrageenan gels via enhancing conformational ordering and subsequent aggregation (Rochas & Landry, 1987). Detailed information on molecular structures of carrageenan determined by the X-ray fiber diffraction analysis may be found in a review by Millane, Nzewi, and Arnott (1989). As an important characteristic of these systems, the decrease in the degree of sulfation from ι-carrageenan to κ-carrageenan makes the gels more rigid, less elastic and brittle, and they require lower concentration of polysaccharides for their formation. In addition, a decrease in the anhydrogalactose content increases both the potassium ion sensitivity and the gelling capacity.

Locust bean gum (LBG) is a water-soluble polysaccharide of the mannan family widely used in the food, pharmaceutical and cosmetic industries as a thickening agent due to its ability to yield high viscosity at low concentrations. LBG is a plant galactomannan extracted from the seed endosperm of carob tree (*Ceratonia siliqua* L.). The primary structure of LBG consists of a backbone of 1,4-linked β-D-mannose units with randomly attached single α-D-galactose side chains at O-6 of the mannose residues. LBG dissolves in hot water and forms a viscous solution whose rheology is typical of that of macromolecular solutions (Doublier & Launay, 1981). The apparent gelation of the LBG solution upon storage and its rheology had been systematically studied (Dunstan et al., 2001; Richardson, Clark, Russell, Aymard, & Norton, 1999). The ability of forming a gel is attributed to the associations between LBG chains (Mao & Chen, 2006). Dea et al. (1977) suggested that the gel network is developed via the interchain association of unsubstituted regions of the mannan backbone of LBG, which is promoted by raising the effective polymer concentration on freezing. It is known that not all the galactomannans yield interchain associations strong enough to form a gel, which is determined by the galactose content of galactomannan.

κ-Carrageenan is synergistic with some gums such as LBG and konjac mannan. The addition of galactomannans, first increases the gel strength and water-binding capabilities as well as modifies the gel texture to be more elastic and resilient, then decreases by a further increase in the galactomannan concentration. Thus, the gel system passes through a "synergistic peak". Such synergistic effects were first found when κ-carrageenan solution was diluted to a concentration too low to gel by itself, but formed a gel upon LBG addition (Dea & Morrison, 1975). The synergistic interaction between κ-carrageenan and LBG in aqueous solution for gelation is well known and has been studied extensively since LBG was found to be effective in improving the apparent gel strength (Dea, McKinnon, & Rees, 1972; Tako, Qi, Yoza, & Toyama, 1998). Dea et al. proposed a mechanism for the interaction between the double-stranded helix of κ-carrageenan and unbranched smooth segments of the D-mannose backbone of the LBG molecule (Dea et al., 1972, Dea & Morrison, 1975). Williams and Langdon (1996) proposed a simple model which is based on rheological, differential scanning calorimetry (DSC) and electron spin resonance experiments for low-content κ-carrageenan–LBG mixtures. According to this model, the three-dimensional carrageenan–LBG gel networks arise when the LBG chains interact with two or more carrageenan helices. As a result of DSC experiments, they found a decrease of enthalpy with an increase in the LBG content in the mixture. This behavior is attributed to interaction of LBG with carrageenan helices and inhibition of carrageenan self-association. Most of these studies have been performed by viscosity, compression and shear measurements (Arnaud, Choplin, & Lacroix, 1989; Chen, Liao, Boger, & Dunstan, 2001; Hernandez, Dolz, Dolz, Delegido, & Pellicer, 2001; Kulicke, Reinhardt, & Arendt, 1998; Tako et al., 1998). κ-carrageenan/LBG ratios are reported as between 4/6 and 9/1 under different total polymer and KCl concentrations. It is well known that increasing the κ-carrageenan or K^+ cation concentration increases the gel strength and gelation temperature (Kara, Tamerler, Bermek, & Pekcan, 2003A; Rochas & Rinaudo, 1984). But, there is no evidence about the corresponding peak in the gel set or destruction temperature in the studies on κ-carrageenan/LBG mixtures which have a strong synergism in viscoelastic properties.

Recently, the cation effect on sol–gel and gel–sol phase transitions of κ-carrageenan (Kara, Tamerler, Bermek, & Pekcan, 2003A), ι-carrageenan (Pekcan & Kara, 2005) and their hybrids (Kara, Arda, & Pekcan, 2005) have been investigated by our group using the photon transmission technique. The same technique was employed to study the hysteresis phenomenon during these phase transitions (Kara, Tamerler, Bermek, & Pekcan, 2003B) and swelling properties (Kara, Tamerler, Arda, & Pekcan, 2003) in similar systems. The aim of the present work was to study the synergistic properties of κ–carrageenan/LBG mixtures by using the photon transmission technique.

2. Experimental

κ-Carrageenan (C1013, commercial grade) and LBG (G0753, from Ceratonia Siliqua seeds) were both obtained from Sigma. Potassium-type κ-carrageenan and LBG powders were used without any further purification. Two sets of experiments were performed to expose the effect of the ratios of polymeric components. For the preparation of all SET1 and SET2 samples 10 cc of distilled water was used. For SET1 sample solutions, κ-carrageenan concentration was held constant (0.8%), while the portion of LBG was increased (see Table 1). The total polymeric content in the sample solutions of SET2 was kept constant as 0.8% w/v. LBG/κ-carrageenan ratios were arranged as between 0 and 1 (Table 2). Here, the carrageenan content was