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Time–temperature studies of κ-carrageenan gelation in the presence of high levels of co-solutes

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Abstract

The effect of oscillatory frequency and temperature on the viscoelastic storage and loss moduli were investigated for κ-carrageenan (0.5% w/w): high co-solute (sucrose/corn syrup) (80 and 85% w/w) systems using time–temperature superposition (TTS) and the modified Cole–Cole (MCC) analysis. Thermal rheological scans (0.15 Hz) and isothermal frequency (ITF) (0.15–15 Hz) scans were performed over a temperature range of 5–85 °C, during cooling and heating. Flow behavior was characteristic of a rubber over the majority of temperatures examined. TTS failed at all temperatures for the 80% (w/w) co-solute samples, and between 25 and 85 °C for the 85% (w/w) co-solute samples. In contrast, the MCC analysis superposed ITF data over a greater temperature range, but only with data corresponding to the rubber–glass transition zone. Successful superposition occurred when the short-range relaxation of chains became overwhelmed by the response of the co-solute medium. κ-Carrageenan was proposed to form a weakly cross-linked network.

Keywords: Carrageenan; Gelation; Co-solutes; Time–temperature superposition; Modified Cole–Cole; Thermal scans; Gel

1. Introduction

κ-Carrageenan is an important gelling polysaccharide extracted from several species of red seaweed (*Rhodophyceae*). Structurally, it consists of repeating disaccharide units of alternating (1→3)-α-D-galactose-4-sulphate and (1→4)-β-3,6-anhydro-D-galactose residues (Harding, Day, Dhami, & Lowe, 1997; Lahaye, 2001; Millane, Chandrasekaran, Arnott, & Dea, 1988; Thành et al., 2002). The mechanical properties of a wide range of polysaccharide: sugar systems have been reported in the literature (Evageliou, Kasapis, & Hember, 1998; Kasapis, Al-Alawi, Guizani, Khan, & Mitchell, 2000; Kasapis, Al-Marhoobi, & Khan, 2000; Kasapis & Sworn, 2000; Lopes da Silva & Goncalves, 1994; Richardson & Norton, 1998; Tsoga, Kasapis, & Richardson, 1999). In general, in the presence of low levels of sugar, gel strength increases with increasing concentrations of sugar until ∼50–60% (w/w) (depending on polysaccharide-type and experimental conditions), attributed to the formation of an increasing number of thermally stable junction zones (Oakenfull & Scott, 1986). Once a gel network is formed, G' becomes independent of frequency.

At intermediate levels of sugar (∼60–75% w/w), polysaccharide gels experience a significant drop in strength and develop a slight frequency dependence of G'. Sucrose preferentially associates with water, reducing the amount of water available to the polysaccharide chains, which then leads to the destabilization of the network structure (Papageorgiou, Kasapis, & Richardson, 1994). This dramatic change in mechanical behavior can occur over a narrow sugar concentration range (Evageliou et al., 1998; Nickerson, Paulson, & Speers, 2004; Whittaker, Al-Ruqaie, Kasapis, & Richardson, 1997).

At higher levels of sugar (> ∼75% w/w), an apparent rise in gel strength occurs, and G' exhibits stronger temperature and frequency dependence. At these levels of sugar, polysaccharides are severely water deficient. The spatial distribution of chains in solution is, however, uncertain. Evageliou et al. (1998), Kasapis, Al-Marhoobi, & Giannouli (1999) and Whittaker et al. (1997) have suggested that polysaccharide chains exist as a very weak, sparsely cross-linked network. In contrast, Nickerson et al.

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(2004), and Richardson and Norton (1998) suggested that little or no network exists; proposing instead that polysaccharide chains are present as small ordered 'macromolecular assemblages', 'gel islands' or 'gel particulates' embedded within a viscous sugar matrix.

Investigation of the temperature and frequency dependence of the viscoelastic properties of polysaccharide: high sugar materials will give information concerning macrostructure transformations within the sample during gelation. However, rheological examination of the viscoelastic behavior is limited experimentally to a finite range of the viscoelastic spectrum even though the rheological properties may vary by several orders of magnitude with changing temperature. A technique commonly used to circumvent this problem is 'time–temperature superposition' (TTS). This principle expands the frequency domain beyond the upper and lower measuring range of the rheometer by implementing a shift factor, which adjusts isothermal frequency (ITF) data based on an arbitrarily selected reference temperature in order to superpose, and form a master curve (Ferry, 1980; Williams, Landel, & Ferry, 1955). Thermorheologically simple (TRS) materials have similar relaxation behavior with changes in temperature, where ITF data superpose easily. By contrast, viscoelastic ITF data of thermorheologically complex (TRC) materials fail to superpose. This type of behavior is typically found in crystalline materials, polymer blends, and multi-component systems, where relaxation behavior changes with temperature (Han & Kim, 1993). Information can be gained pertaining to macroscopic transformations within a material based on the success or failure of TTS. An alternative resolution for this problem is the modified Cole–Cole (MCC) analysis (Baek & Han, 1995; Han & Jhon, 1986; Han & Kim, 1993; Han, Kim, & Kim, 1989; Harrell & Nakajima, 1984). This technique superposes ITF data without data manipulation. Its success and failure for superpossibility is analogous to TTS when studying TRS and TRC materials, except the MCC analysis is applicable to multi-phase and blended polymeric materials (Han & Kim, 1993).

In the present study, thermal rheological scanning, TTS and the MCC analyses were used to investigate the behavior of κ-carrageenan: high co-solute (sucrose plus corn syrup) systems in response to changes in temperature and oscillatory frequency. The findings give insight into mechanisms relating polysaccharide interactions to the mechanical spectra, in order to better control their use in products such as in 'gummy' confectionary products.

2. Materials and methods

2.1. Sample preparation

κ-Carrageenan powder (Genugel carrageenan, lot #93756, 1999) (CP Kelco, San Diego, CA) consisting of 77.47% (w/w) polymer, 14.35% (w/w) potassium, 7.3% (w/w) water, and minute amounts of calcium (0.12% w/w), sodium (0.64% w/w), magnesium (0.12% w/w) (atomic adsorption), and phosphorous (0.002% w/w) (colorimetric analysis) was used without purification. κ-Carrageenan was dispersed in distilled–deionized water (DDW) at room temperature with a magnetic stirrer, heated to 100 °C and allowed to boil for 5 min. Sucrose (up to 50 g) was then added, followed by corn syrup (DE 42, 18% moisture) under continuous stirring. Samples were allowed to boil until specific κ-carrageenan (0.5% w/w) and co-solute (80 and 85% w/w) concentrations were reached (∼20 min). Evaporative losses were corrected for by the addition of appropriate amounts of 100 °C DDW. No attempt was made to control pH in this study.

2.2. Rheological measurements

Oscillatory shear deformation was applied using a Bohlin CS10 rheometer (Bohlin, Inc., Cranberry, NJ) equipped with a 40 mm parallel plate fixture. The hot sample was loaded onto the pre-heated fixture (85 °C) and was allowed to equilibrate for 5 min. Mineral oil was applied along the outer edge of the fixture to prevent evaporative losses. Thermal cooling and heating scans were performed at temperatures ranging between 85 and 5 °C at a rate of 1 °C min^{-1}, at a frequency of 0.15 Hz and a maximum strain amplitude of 2%. Duplicate measurements were made and pooled.

Isothermal oscillatory frequency sweeps (0.15–15 Hz) were performed at temperatures between 85 and 5 °C during cooling and heating scans for TTS and MCC analyses, after a 5 min equilibration period once the rheometer reached the desired temperature (as determined by preliminary experiments using a thermocouple). Duplicate samples were measured, but data were not pooled due to the sample dependence of moduli, which prevented proper superposition. However, duplicate samples did show similar successes or failures of both the TTS and MCC analyses. Temperature was controlled using a circulating water bath. All measurements were made within the linear viscoelastic region at a maximum strain amplitude of 2%. The low strain was chosen arbitrarily to ensure the samples remained within the linear region at all measured temperatures and frequencies. The 2% strain remained constant during all isothermal frequency sweeps.

3. Results and discussion

3.1. Thermal scans

Flow behavior was characteristic of a rubber ($G' > G''$) over the majority of the temperatures examined for the 0.5% (w/w) κ-carrageenan: 80% (w/w) co-solute sample, during

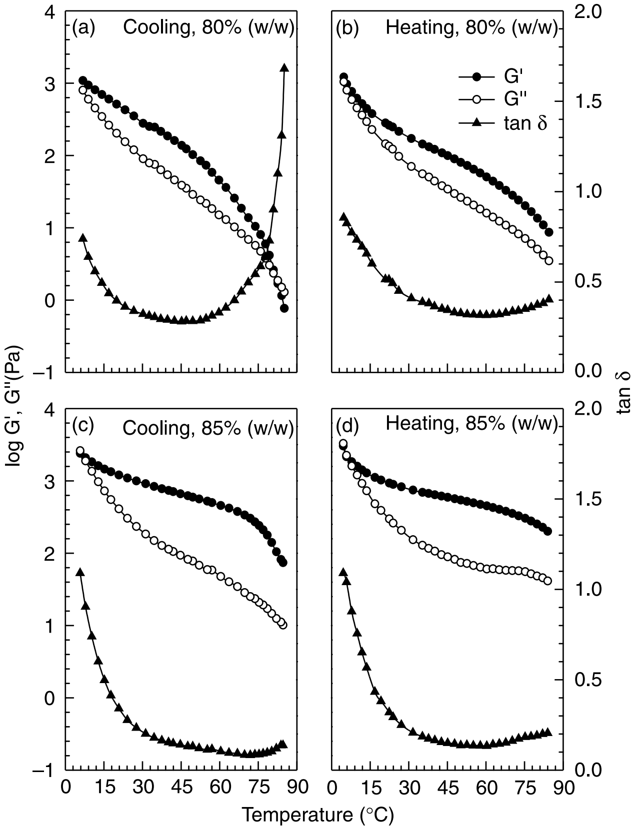

Fig. 1. G', G'' and tan δ as a function of temperature during cooling (left) and heating (right) for 0.5% (w/w) κ-carrageenan plus 80 (a and b) and 85% (c and d) (w/w) co-solute samples ($n=2$).

both cooling and heating (Fig. 1(a) and (b)). At higher temperatures (>80 °C) during cooling, G' crossed G'' signifying the end of the terminal zone of the viscoelastic spectrum, where long-range relaxation mechanisms dominate (i.e. relaxation over the entire chain length) (Fig. 1(a)). The sample remained in the rubbery zone over the remaining temperature range, where relaxation is attributed to both long- and short- (i.e. relaxation through vibrational movements between points of entanglement or junction zones) range mechanisms (Ferry, 1980). On heating, the 80% (w/w) co-solute sample was relatively thermally reversible, except at higher temperatures where the sample remained in the rubbery zone, rather than crossing back into the terminal region (Fig. 1(b)).

Flow behavior of the 0.5% (w/w) κ-carrageenan: 85% (w/w) co-solute sample was also characteristic of a rubber over the majority of the temperature range examined during cooling, until ∼7–8 °C where G'' crossed G' to enter into the rubber-to-glass transition region, where short-range relaxation mechanisms dominate (Ferry, 1980) (Fig. 1(c)). Evageliou et al. (1998) and Kasapis (2001) reported that the cross-over to the rubber–glass transition zone shifted to higher temperatures with increased levels of sugar, analogous to the present findings. Thermal rheological scans were thermally reversible on heating (Fig. 1(d)), except at higher temperatures (>75 °C), where during cooling G' increased more sharply than it decreased on heating.

The lack of complete thermal reversibility at higher temperatures with both co-solute concentrations suggests that there are thermally stable ion-mediated cross-links present. A similar trend was also found by Evageliou et al. (1998) in κ-carrageenan: high glucose syrup samples. It is proposed that in the present study, a weak flexible polysaccharide cross-linked network exists, supporting the hypotheses put forth by Evageliou et al. (1998), Kasapis et al. (1999) and Whittaker et al. (1997). If a strong cross-linked network was present, structures formed during cooling are proposed to show a greater amount of thermal hysteresis when heated.

In contrast, Nickerson et al. (2004) using gellan polysaccharides at similar levels of co-solute as the present study observed a rise in magnitude of G' at higher temperatures during heating. They hypothesized that gellan polymers were present as gel 'particulates' or 'islands' embedded within a co-solute matrix rather than forming a continuous network. The absence of a similar rise in magnitude of G' on heating in the present study may be caused by the large residual K^+ (14.35% w/w) content in the κ-carrageenan powder, which enhances network stability through ion-mediated associations.

The magnitude of G' and G'' was greater at all temperatures for the κ-carrageenan samples with 85% (w/w) co-solute than at the 80% (w/w) level. Whittaker et al. (1997) suggested that this rise in magnitude is caused by the increased contribution of entropy to the viscoelastic parameters. With increased levels of co-solutes, κ-carrageenan chains experience greater water depletion, where rheological behavior becomes more dependent on the flow properties of the co-solute medium.

3.2. Time–temperature superposition

The κ-carrageenan: 80% (w/w) co-solute samples behaved as a TRC material during both cooling and heating, where ITF data failed to superpose to form a master curve (not shown). In the presence of 85% (w/w) co-solutes, TTS was only successful at 15 and 5 °C during both cooling and heating; at all other temperatures, ITF data failed to superimpose (not shown). Lack of superposition is indicative of temperature dependent relaxation mechanisms that are occurring within the material. These relaxation mechanisms are hypothesized to be both long- and short-range, whereby chains in the flexible network relax as the flow properties of the co-solute medium change with temperature. At lower temperatures (i.e. 15 and 5 °C), the 85% (w/w) co-solute samples behaved as a TRS material where no changes in relaxation mechanisms occurred with temperature. It is proposed that the increased viscosity of the co-solute medium at lower temperatures inhibited temperature dependent relaxation mechanisms of the polysaccharide network. On heating, viscosity became reduced enough to allow relaxation mechanisms to occur above 15 °C, leading to the failure of TTS.

3.3. Modified Cole–Cole analysis

Isothermal frequency data for the κ-carrageenan: 80% (w/w) co-solute sample during both cooling and heating superposed only at low temperatures (5 and 15 °C), at frequencies corresponding to the rubber–glass transition of the viscoelastic spectrum (Fig. 2). Han and Kim (1993) found that the MCC analysis is more sensitive to macrostructure transformation than TTS. The lack of superposition at higher temperatures suggests that the material is TRC. It is proposed that the weak κ-carrageenan network is stabilized by semi-crystalline ion-mediated junction zones and polymer–polymer interactions. Zarraga, Pena, Munoz, and Santamaria (2000) attributed the lack of superposition of ITF data in homopolymeric polyvinyl chloride (PVC) systems to the formation of randomly dispersed microcrystallites. These domains are analogous to the semi-crystalline junction zones formed in polysaccharide gels, in relation to the temperature dependent relaxation mechanisms involved during junction zone formation. At lower temperatures, it is proposed that short-range relaxation of chains becomes negligible relative to the relaxation behavior of the viscous co-solute matrix, which overwhelms any temperature dependent effects of the weak κ-carrageenan network. Zarraga et al. (2000) observed a similar phenomenon in PVC-HDPE (high density polyethylene) blends, where the HDPE phase dominated the viscoelastic response and the presence of PVC microcrystalline junction zones was undetected. Successful superposition of ITF data in the MCC master curve suggests the sample behaved as a TRS material under certain experimental conditions (i.e. at temperatures and frequencies corresponding to moduli that are within the rubber–glass transition region of the viscoelastic spectrum) (Fig. 2).

Fig. 3 shows the frequency dependence of G' and G'' at 5, 15 and 25 °C during cooling (a–e) and heating (b–f) to clarify the flow behavior near the beginning of the rubber to glass transition. Samples were thermally reversible over this temperature range (5–25 °C). At 25 °C during both cooling and heating, G' increased gradually, typical for the rubbery plateau zone (Fig. 3(e) and (f)). The dynamic loss modulus on the other hand, went through a plateau then increased dramatically as frequency increased. At 15 °C, a similar profile was evident, except the onset of the significant rise in

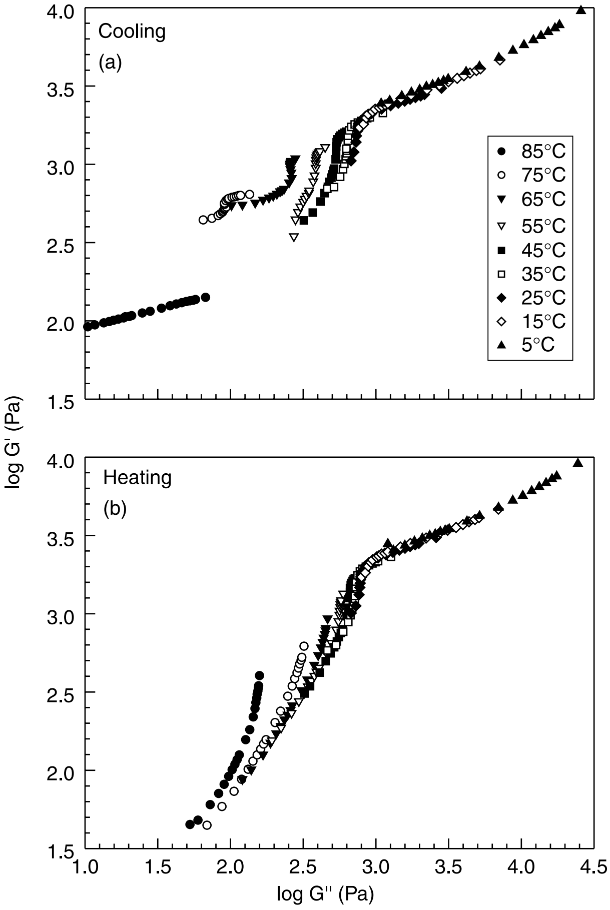

Fig. 2. Modified Cole–Cole analysis during cooling (a) and heating (b) for a 0.5% (w/w) κ-carrageenan: 80% (w/w) co-solute sample.

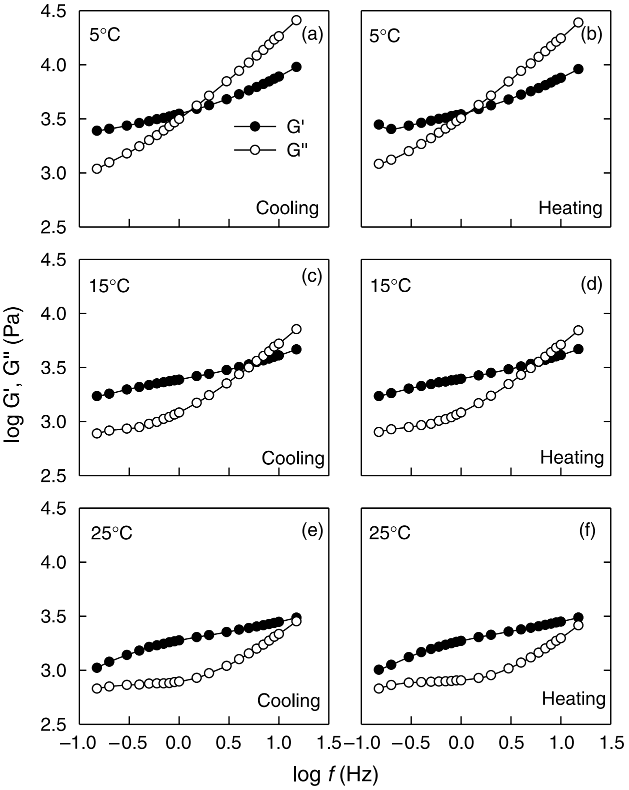

Fig. 3. Frequency (f) dependence of G' and G'' for a 0.5% (w/w) κ-carrageenan: 80% (w/w) co-solute sample during cooling (left) and heating (right) at 5 (a and b), 15 (c and d) and 25 °C (e and f).

G'' shifted to lower frequencies, and a cross-over point appeared, where G'' became greater than G' as the material entered into the rubber–glass transition zone (Fig. 3(c) and (d)). At 5 °C, G'' increased sharply over the complete frequency range, crossing over G' at lower frequencies than at 15 °C (Fig. 3(a) and (b)). In addition, the magnitude of both G' and G'' increased with decreasing temperature over the complete frequency range, which is congruent with thermal cooling and heating scans (Fig. 1(a) and (b)).

A reduced MCC master curve of ITF data from 5 and 15 °C, at frequencies corresponding to the rubber–glass transition zone of the viscoelastic spectrum is given in Fig. 4(a) and (b) during cooling and heating, respectively. The curvature is indicative of micro-phase separation. In completely miscible systems, a log G' vs. log G'' plot would be linear (Han & Kim, 1993). The corn syrup used in the present study consists of a mixture of degraded starch hydrolysis products of different molecular weights, which is then combined with the disaccharide, sucrose. Both the corn syrup and sucrose had a dextrose equivalence of 42. Therefore, the heterogeneous co-solute matrix may have been detected by the MCC analysis as a slight curvature in Fig. 4(a) and (b). The application of the MCC analysis for the co-solute medium alone (not shown) was prevented by the scattering of G' data in the ITF scans caused by limitations in the sensitivity of the rheometer.

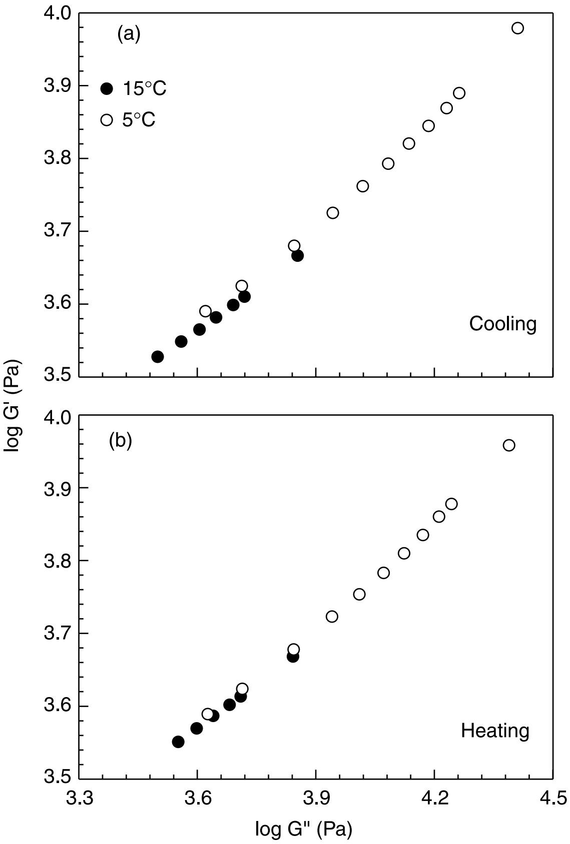

Fig. 4. Reduced modified Cole–Cole analysis during cooling (a) and heating (b) for a 0.5% (w/w) κ-carrageenan: 80% (w/w) co-solute sample.

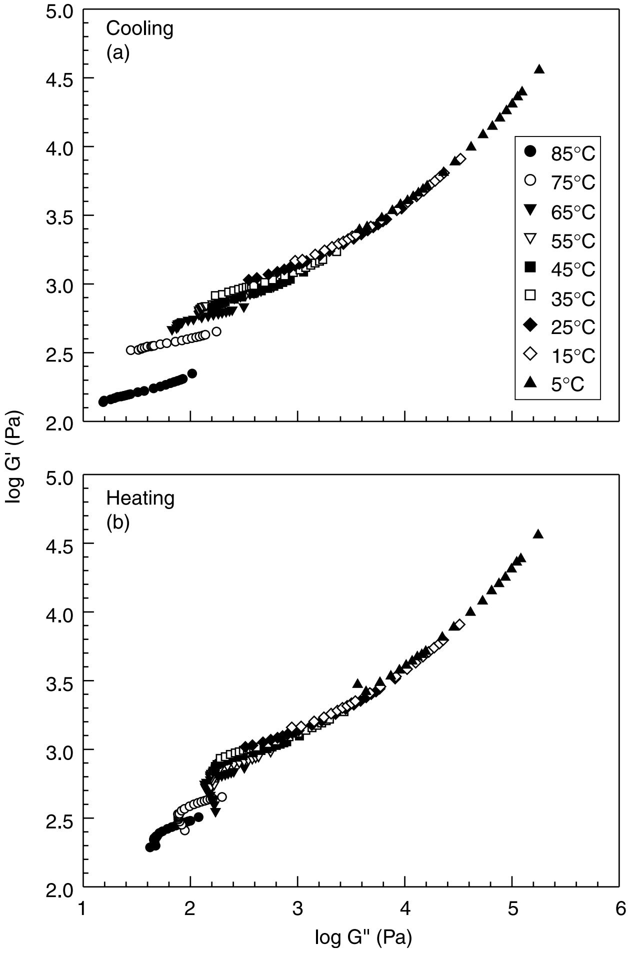

Fig. 5. Modified Cole–Cole analysis during cooling (a) and heating (b) for a 0.5% (w/w) κ-carrageenan: 85% (w/w) co-solute sample.

Analogous to the 80% (w/w) co-solute samples, ITF data for the κ-carrageenan: 85% (w/w) co-solute samples during both cooling and heating superposed only at lower temperatures (5–35 °C) by MCC analysis, and at frequencies corresponding to the rubber–glass transition region (Fig. 5(a) and (b)). In contrast, superposition of ITF data using the TTS principle was successful only at 5 and 15 °C (not shown). Fig. 6 shows the frequency dependence of G' and G'' at 5, 15, 25, 35 and 45 °C during both cooling and heating. The data were thermally reversible, which is congruent with thermal rheological scans over this temperature range (Fig. 1(c) and (d)). The dynamic storage modulus remained relatively constant at higher temperatures (25–45 °C) (Fig. 6(e)–(j)), until reaching well into the rubber–glass transition zone (5–15 °C), where it had a more pronounced rise in magnitude with increasing frequency (Fig. 6(a)–(d)). The cross-over of G'' with G' was also found to shift to lower frequencies with decreasing temperatures. A reduced MCC master curve during cooling and heating is shown in Fig. 7, to include only ITF data corresponding to

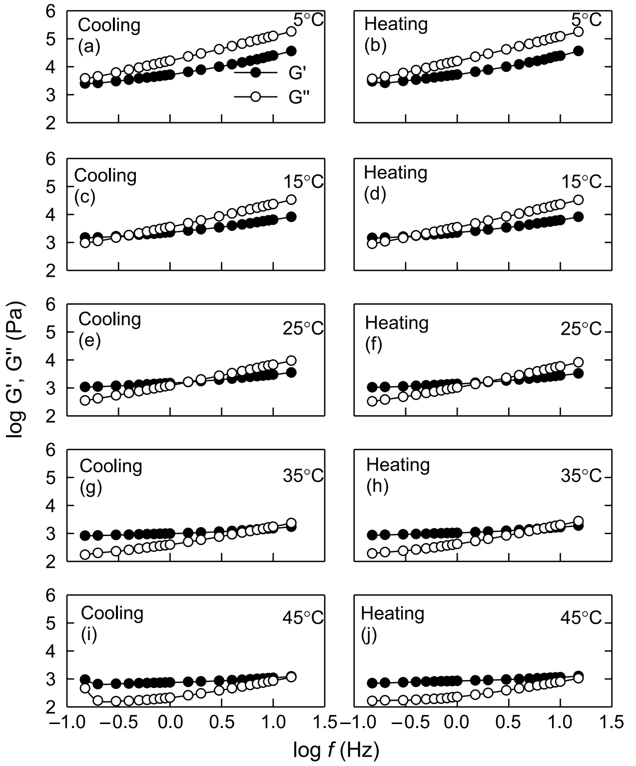

Fig. 6. Frequency (f) dependence of G' and G'' for a 0.5% (w/w) κ-carrageenan: 85% (w/w) co-solute sample during cooling (left) and heating (right) at 5 (a and b), 15 (c and d), 25 (e and f), 35 (g and h) and 45 °C (i and j).

the rubber–glass transition zone. Curvature in both the cooling and heating reduced MCC master curves suggests the presence of micro-domains proposed to consist of starch hydrolysis products from the corn syrup.

4. Conclusions

κ-Carrageenan polymers in the presence of high levels of co-solute are proposed to exist as a weakly cross-linked flexible network, whose behavior is dominated by the viscoelastic response of the co-solute medium. TTS failed at all temperatures, and between 25 and 85 °C for the 80 and 85% (w/w) co-solute samples, respectively. In contrast, the MCC analysis superposed ITF data over a greater temperature range, but only with data corresponding to the rubber–glass transition zone, where short-range relaxation became overwhelmed by the response of the co-solute medium. Failure of TTS and MCC is probably the result of the formation of semi-crystalline junction zones. In contrast, a system where polymers were proposed to be present as gel particulates, such as gellan: high co-solutes, showed a rise in G' with increasing temperature during heating (Nickerson et al., 2004). There, TTS and MCC analyses were successful over the majority of the temperatures examined, due to the absence of semi-crystalline junction zones; and a strong inflection point was proposed to be associated with the presence of gel particulates embedded within the co-solute medium.

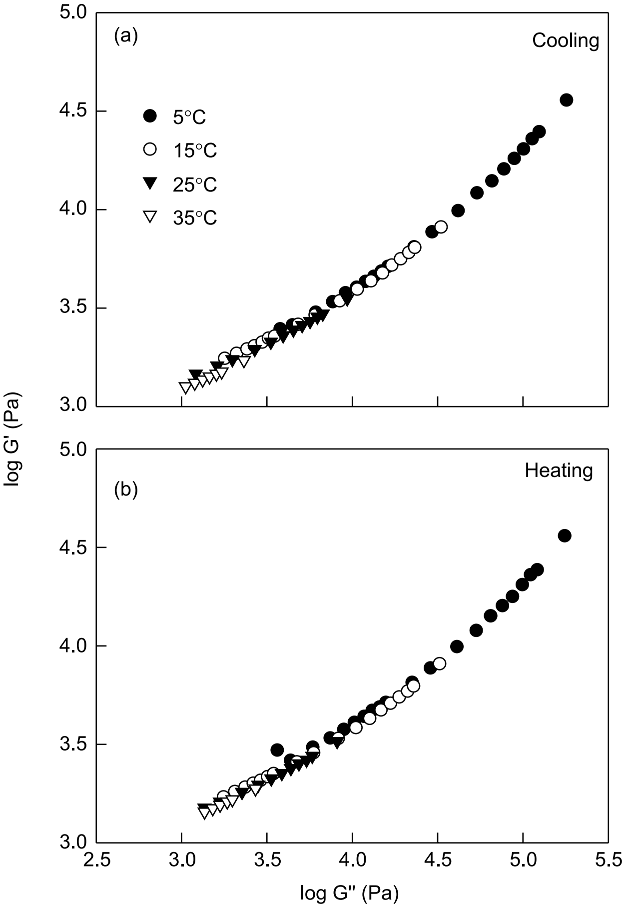

Fig. 7. Reduced modified Cole–Cole analysis during cooling (a) and heating (b) for a 0.5% (w/w) κ-carrageenan: 85% (w/w) co-solute sample.

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