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The gelation of oil using ethyl cellulose

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ABSTRACT

The characterization of the thermo-gelation mechanism and properties of ethyl cellulose/canola oil oleogels was performed using rheology and thermal analysis. Thermal analysis detected no evidence for thermal transitions contributed to secondary conformational changes, suggesting a gelation mechanism that does not involve secondary ordered structure formation. Rheological analysis demonstrated a relationship between the polymer molecular weight and the final gel strength, the cross-over behavior as well as the gel point temperature. Increasing polymer molecular weight led to an increase in final gel strength, the modulus at cross-over, and the gel point temperature. Cooling/heating rates affect gel modulus only for the low molecular weight samples. A decrease in gel strength with increasing cooling rate was detected. The cross-over temperature was not affected by the cooling/heating rates. Cooling rate also affected the gelation setting time where slow cooling rates produced a stable gel faster.

1. Introduction

The use of oleogels as a way to structure liquid oil has been examined extensively in the last decade. Several strategies have been developed to produce an oleogel based on the nature of the gelator used. Self-assembly of crystalline particles or fibrils created from low molecular weight gelator molecules is one of the techniques used to trap liquid oil. Liquid crystalline mesophases as well as jammed particle systems are two other strategies found in the literature (Marangoni & Garti, 2011). The use of macromolecules as a gelator of oil has also been reported using synthetic polymers, dendrimers, proteins and modified polymers. However, none of these systems are food grade (Pernetti, Malssen, Flöter, & Bot, 2007). In the early 1990's the use of ethyl-cellulose as a gelator of vegetable oils was suggested for cosmetic application by Aiache, Gauthier, and Aiache (1992).

Ethyl-cellulose (EC) is a linear polysaccharide derived from cellulose. Its production involves the replacement of the cellulose's hydroxyl end groups with ethyl end groups. It is characterized by the degree of substitution (DS) or ethoxy content. Water solubility is achieved with DS in the range of 1.0 to 1.5 while solubility in organic solvents is achieved with DS values in the range of 2.4–2.5 (Koch, 1937). EC structure is not fully understood; however, evidence of its semi-crystalline structure was recently reported (Davidovich-Pinhas, Co, Barbut, & Marangoni, 2014). It seems that, among other things, its hydrophobic nature and semi-crystalline characteristics allows it to act as a gelling agent of liquid oils.

Solid-like gelled oil has the potential to mimic solid fat in food applications. Recently, EC based oleogels have been used as a replacement of fats in foods (Marangoni, 2010b), heat resistance agents in chocolate (Marangoni, 2010a), oil binding agents in bakery products (Cattaruzza, Radford, & Marangoni, 2012), and as the basis for cosmetic pastes (Marangoni, 2012). Of particular interest is the use of EC oleogels as an animal fat replacer in meat products (Zetzl, Marangoni, & Barbut, 2012). The use of liquid oil in the form of an oil gel, or oleogel, instead of pieces of fatty animal tissue has health benefits which results from the consumption of mono- or poly-unsaturated fatty acids present in the vegetable oil used to make the gel. The physical gelation of EC with liquid oil is achieved by increasing the polymer/oil mixture temperature above the polymer glass transition (~140 °C) and cooling it to room temperature. Previous work shown that the gel properties are strongly related to the preparation conditions, such as polymer concentration, polymer molecular weight, cooling rate etc. (Gravelle, Barbut, Quinton, & Marangoni, 2014). Therefore understanding the gelation process and the parameters affecting it is a crucial step to further development of such products (Gravelle, Barbut, & Marangoni, 2012; Gravelle, Barbut, & Marangoni, 2013; Zetzl et al., 2012). Classical chemical gelation of polymers is directly controlled by stoichiometry of the cross-linking reaction. This reaction is usually quick and irreversible. Physical gels demonstrate a different behavior arising from the nature of the junction zones which have a finite lifetime. The number of junction zones, their size and position fluctuate with

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time and are strongly affected by environmental conditions. Most of the junction zones arise from the formation of ordered secondary structure (such as helices and "egg-box" cavities). Such systems create an interesting gelation kinetics which never reaches a final equilibrium state due to secondary chain extension, formation or breaking of junction zones, and re-arrangement or stacking of the already formed junction zones (Lefebvre & Doublier, 1998).

This paper examines the gelation kinetic process of EC oleogels using rheology as well as thermodynamic analysis. We have monitored the gelation process using temperature sweep experiments. The effects of EC molecular weight and cooling rate on final gel strength and cross-over behavior were examined. The gelation process of different EC molecular weights was also monitored by differential scanning calorimetry. The gel point temperature was determined, with respect to polymer molecular weight and concentration, using frequency sweep experiments. Gel setting time was also examined using time sweep experiments.

2. Materials and methods

2.1. Materials

Ethyl celluloses (EC) with different viscosities (10 cP, 20 cP, 45 cP, 100 cP) were obtained from Dow Ltd. (Calgary, AB, Canada) and used as received. Viscosities are determined by the manufacturer for 5% (w/v) polymer solutions in 80% toluene and 20% ethanol, measured at 25 °C. According to previous work (Davidovich-Pinhas et al., 2014), an increase in the viscosity of the samples reflects an increase in the sample's molecular weight. Canola oil (No Name®, Loblaws Inc., Toronto, Ontario, Canada) was obtained from the local supermarket and stored at 4 °C.

2.2. Sample preparation

Samples were prepared using different EC viscosities at various concentrations (w/w) in canola oil (CO) to total weight of 10 g. Samples were placed on a magnetic hot plate and mixed at 300 rpm while heated to ~150 °C. After complete dissolution of the EC powder in the canola oil, the samples were poured onto a preheated (150 °C) rheometer plate. An EC concentration of 11% (w/w) was used unless otherwise indicated.

2.3. Differential scanning calorimetry (DSC)

The oleogels' thermal behavior was studied using a Mettler DSC 1 instrument (Mettler Toledo, Mississauga, ON, Canada). EC powder and Canola oil were weighed into sealed aluminum pan, with a hole on the lid, to final EC concentration of 12–16% (w/w). Experiments were conducted using 5 °C min^{-1} heating/cooling rate with 30–40 ml min^{-1} nitrogen flow rate. The experiment was performed by two runs of heating/cooling from 25 °C to 200 °C.

2.4. Rheology measurements

Rheology experiments were performed using an Anton Paar MCR320 rheometer (Anton Paar, Saint Laurent, Canada) equipped with a temperature control unit using a 50 mm cone and plate (2° angle) configuration.

The oleogel cross-over behavior and gel strength were analyzed using temperature sweep experiments in the range of 60–150 °C. All experiments were conducted using a frequency of 30 rad s^{-1} and a % strain within the linear viscoelastic region (LVR) of each sample (determined prior with strain sweep experiments at the temperature range mentioned above). Each experiment was performed as a cycle of cooling, heating and cooling using different cooling/heating rates. The data presented is the average of three replicates.

Gel point temperatures were determined using frequency sweep experiments at different temperatures. The experiments were conducted in the range of 10–100 rad s^{-1} using % strain at the LVR (according to strain sweep experiments conducted at the same temperature range mentioned above).

Gelation setting times were evaluated using the time sweep experiments. 11% (w/w) EC 45 cP gels were cooled down to room temperature, at different cooling rates (1, 3, 5, 8, 10, 15 °C min^{-1}), and then the storage modulus, G′, and loss modulus, G″, were monitored until an equilibrium was reached. Experiments were performed using 0.05% strain and 30 rad s^{-1} frequency. The data presented is the average of three replicates.

In all experiments, samples were poured on the pre-heated rheometer lower plate (150 °C), followed by lowering the upper cone plate to fixed distance of 0.207 mm. Samples were allowed to equilibrate at 150 °C for 5 min prior to starting the experiment.

3. Results and discussion

3.1. Thermal analysis during gelation

The thermal analysis of the EC/CO mixture was achieved by introducing the oil and powder directly into the DSC pan. This setup allowed us to observe the first dissolution and gelation stages. Fig. 1a reveals a thermal event during the first heating stage at ~130–136 °C for the different EC samples. According to our results, the thermal transition temperature increases with the polymer molecular weight, Fig. 1c. Thermal analysis of liquid CO did not reveal any characteristic thermal behavior (Fig. 1), therefore it can be assumed that the thermal behavior seen here is a result of the polymer characteristics. Previous work, in our lab has demonstrated the EC molecular weight dependence of the glass transition temperature in the same temperature range of 130–150 °C (Davidovich-Pinhas et al., 2014). Therefore we can correlate this transition to the EC glass transition. However, while comparing the pure powder glass transition to the one shown in Fig. 1, clear differences in the thermal transition characteristics are observed. For one, in the presence of oil, the thermal transition seems to include the glass transition of the powder superimposed on an endothermic transition involving latent heat (Fig. 1d). It seems that the polymer glass transition is followed by chain dissolution which includes interactions between the solute and solvent, i.e., an endothermic heat of solution. According to the Flory–Huggins free energy of mixing theory, the dissolution of two components is governed by the negative energy of mixing which promotes interactions between the two components in the mixture (Rubinstein and Colby, 2003). Therefore we observe the transition from "glassy" to "rubbery" state which exposes the polymer chains to the solvent followed by the interactions of the chains with the solvent promoting dissolution. This transition was not observed in the second heating stage, suggesting a different thermal characteristic of the polymer in the gel state.

The lack of thermal transitions during the gelation (cooling) and melting (heating) of the gels implies a gelation mechanism and structure that does not involve highly ordered secondary structure formation. Previous work on other thermo-reversible gel systems, such as gellan gum and agarose, has reported the formation of helix structures which then further associate to create a 3D network (Nishinari, 1997). This phenomenon leads to a specific exothermic thermal transition during the gelation process which is similar to crystallization and endothermic thermal transition during the melting of the structures. This thermal behavior was also observed in the heat set gelation of methyl cellulose (Li, 2002) and curdlan (Zhang, Nishinari, Williams, Foster, & Norton, 2002). The gelation mechanism and gel structure of EC based oleogels is not fully

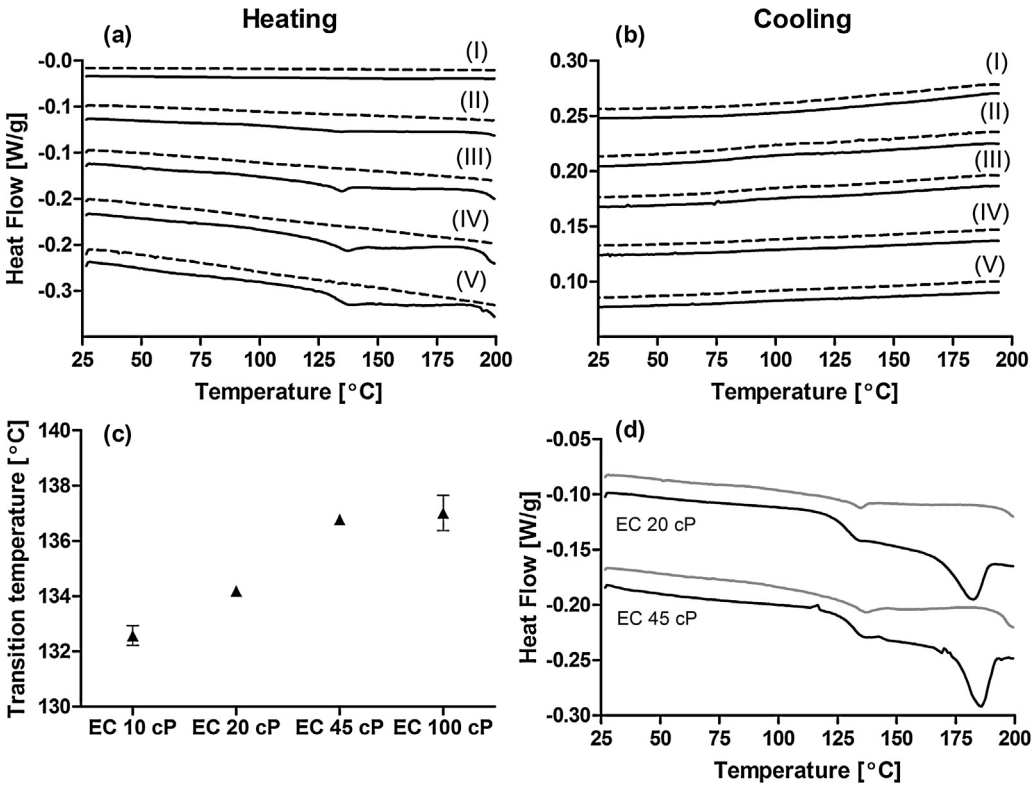

Fig. 1. DSC thermograms during heating (a) and cooling (b) of canola oil (I) with, EC 10 cP (II), EC 20 cP (III), EC 45 cP (IV), and EC 100 cP (V) during two cycles of heating/cooling (5° min^{-1}). First cycle (solid line) second cycle (dashed line). Curves were shifted vertically by factor A. The peak transition temperature values obtained from the first heating (c) and the comparison of the thermogram obtained during heating of EC powder (black) and the mixture with canola oil (gray).

understood and therefore it is not easy to determine the origin of the behavior.

It is important to note that although the samples were not mixed during the dissolution of the powder a very clear homogenous gel was obtained at the end of the experiment (pictures not included).

3.2. Rheological analysis

A gel is a soft, solid or solid-like material, which consists of two or more components, one of which is a liquid, present in a substantial quantity (Kavanagh & Ross-Murphy, 1998). By weight gels are mostly liquid, yet they behave like solids due to a three-dimensional cross-linked network within the liquid. It is the cross-links that give a gel its structure and properties. According to the classical definition of the gel point and the commonly accepted classification of the sol–gel transition, a unique rheological behavior is observed in the gel state (Payro′ & Llacuna, 2006). Gel state is defined as the point where the liquid component (i.e., loss modulus, G″), is considerably smaller than the solid component (i.e., storage modulus, G′). The sol–gel transition describes the process (or series of processes) which leads to the formation of the final gel state (Kavanagh & Ross-Murphy, 1998). It can be analyzed by monitoring changes occurring in the solid (G′) and liquid (G″) like components of a material in a continuous rheology experiments. We have used temperature sweep, time sweep and frequency sweep experiments at different temperatures in order to study the gelation process.

Strain sweep experiments were conducted prior to these experiments, in order to determine the linear viscoelastic region (LVR) for each EC sample. The experiments were conducted at two angular frequencies (10 and 100 rad s^{-1}) in order to determine the LVR in a wide frequency range.

3.2.1. Temperature sweep experiments

Typical temperature sweep experiments are presented in Fig. 2. A clear cross-over between G' and G'' was observed. It is evident from the results that the gels display reversible thermal gelation behavior demonstrated by the similarity of the gelation curves during the two cooling cycles, indicative of physical cross-linking. The heating phase displays different behavior compared to the cooling phase suggesting hysteresis during the gel–sol transition. Such behavior was also reported in other polysaccharide thermoreversible gel systems such as agarose (Aymard et al., 2001), carrageenan, gellan gum and gelatin (Harris, 1990). Mangionea, Giacomazza, Bulone, Martorana, and Biagio (2003) studied the gelation of kappa-carrageenan and detected hysteresis behavior by using both rheology and optical rotatory dispersion (ORD). Hysteresis behavior was also observed in methyl cellulose gelation from an aqueous solution (Li, 2002). Further examination of the hysteresis behavior observed in our experiments with respect to polymer molecular weight and cooling/heating rates will be discussed below.

The temperature sweep curves Fig. 2 reveal a continuous increase or decrease in moduli during the cooling/heating process. Such behavior could suggest a gelation mechanism that does not include the formation of an organized secondary structure such as helices. Previous work done on methyl cellulose gelation demonstrated similar continuous temperature sweep results without step-like transitions (Li et al., 2001). In their research, the authors confirmed that the gelation process was attributed to hydrophobic interactions (Li, 2002; Li et al., 2001). Several studies involving "cold" setting of food gels such as agarose (Braudo, Muratalieva, Piashchina, & Tolstoguzov, 1991), kappa-carregeenan (Mangionea et al., 2003) and gellan gums (Miyoshi, Takaya, & Nishinari, 1996) demonstrated step-like temperature transitions during gelation. They correlated this behavior to conformational transitions such as

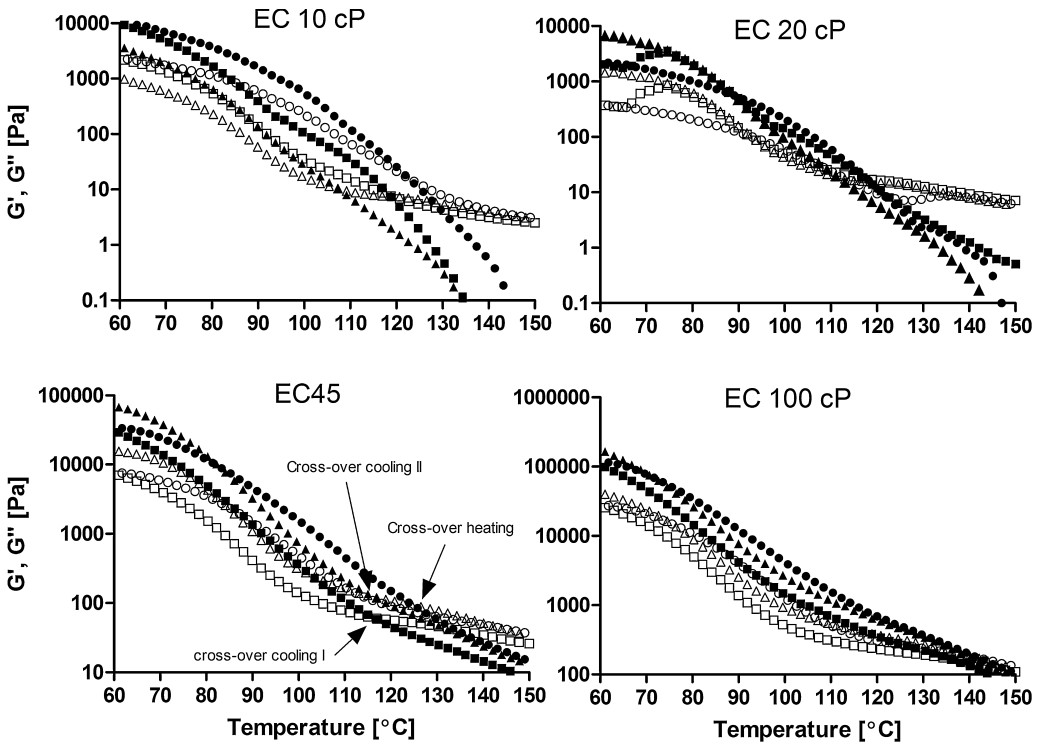

Fig. 2. Typical temperature sweep experiments obtained for all EC samples at 5 °C min^{-1} cooling/heating rate during the first cooling (■), heating (●), and second cooling (▲). G' (closed symbol) and G'' (open symbol).

coil-helix or coil-double helix transitions, followed by their association to a final 3D gel structure. Miyoshi et al. (1996) who worked with gellan gums determined two separate transition temperatures during the cooling process, T_{ch} for the coil to helix transition and T_{sg} for the sol–gel transition which corresponds to helix aggregation. The thermal gelation of organogels formed by sugarcane or candelilla wax in soybean oil also presented a step like transition upon cooling using both rheology and DSC analysis. The two steps were correlated to the formation of the fat crystals followed by their aggregation, resulting in a three dimensional crystalline network (Rocha et al., 2013).

Therefore, it is evident from our thermal analysis, using both rheology and DSC, that EC/CO gelation mechanism does not include an organized secondary structure formation. These observation is in line with previous work done on the interactions involved in the EC oleogels formation by Laredo, Barbut, and Marangoni (2011) which proposed a polymer gel network based on hydrogen bonds. Further study is requiring in order to clarify this hypothesis. According to our results it seems that EC oleogel gelation mechanism does not follow other typical polymer thermo reversible systems and therefore display a unique gelation mechanism.

3.2.1.1. Effect of molecular weight and cooling rate on the final gel strength. Fig. 3 shows the analysis of the final gel strength with respect to cooling rate and EC molecular weight. As expected, we observed an increase in gel strength with increasing polymer molecular weight up to EC 45 cP. The latter has similar strength as EC 100 cP. Similar results were obtained by Sarkar (1979) who worked on the gelation of methylcellulose in aqueous media. In that work, he detected increases in gel strength with increasing molecular weight, which gradually leveled off at an average molecular weight of 140 kDa. Rochas, Rmaudo, and Landry (1990), who worked with different fractions of kappa carrageenan, also found a positive correlation between gel strength and polymer molecular weight which leveled off at 180 kDa. This critical molecular weight was found to be independent of polymer concentration and ionic content.

The effect of cooling rate was only observed in the low molecular weight samples EC 10 cP and EC 20 cP (Fig. 3), where a gradual decrease in gel strength with increases in cooling rate were observed. The cooling process involves molecular re-arrangement of the EC chains into a three dimensional structure, i.e., the gel network. This process evolves from a series of local energy minima, leading to a final global low energy state. Transformations between states require energy and time. Slow cooling remains closer to the equilibrium state, and allows the system to better arrange itself into a more stable final network structure, thus producing stronger gels. This observation was also seen in gelatin, other thermo-reversible gel system (Harris, 1990). They found that snap-chilled gelation produced significantly softer gels than expected, while 'tempered' gels held at a temperature just above gel point produced stronger gels. It seems that the sites involved in junction zone formation via hydrogen bonding, which leads to gel formation, cannot form efficiently if not given sufficient time. Another thermo-reversible polymer, curdlan, exhibited a similar behavior during its sol–gel transition, suggesting that a stronger gel network was developed at a slower cooling rate (Funamia, Funamib, Yadab, & Nakaob, 1999). Similar behavior was detected in waxy crude oil gels cooled from 35 °C to 15 °C at three different rates (0.05, 0.5, 1.0 °C min^{-1}) (Visintin, Lapasin, Vignati, D'Antona, & Lockhart, 2005). They correlated this behavior to the time needed for the gel to build-up from the crystal formation and aggregation, which led to more extended gel micro-domains. Previous work done in our lab (Gravelle et al., 2013) reported the existence fractionation phenomenon in EC gels. A soft core with a firm shell was reported while using different gelation conditions. Sample homogeneity was achieved upon gelation under slow cooling conditions, suggesting that a slow gelation process of EC oleogels leads to the formation of a stronger, more stable and homogeneous network.

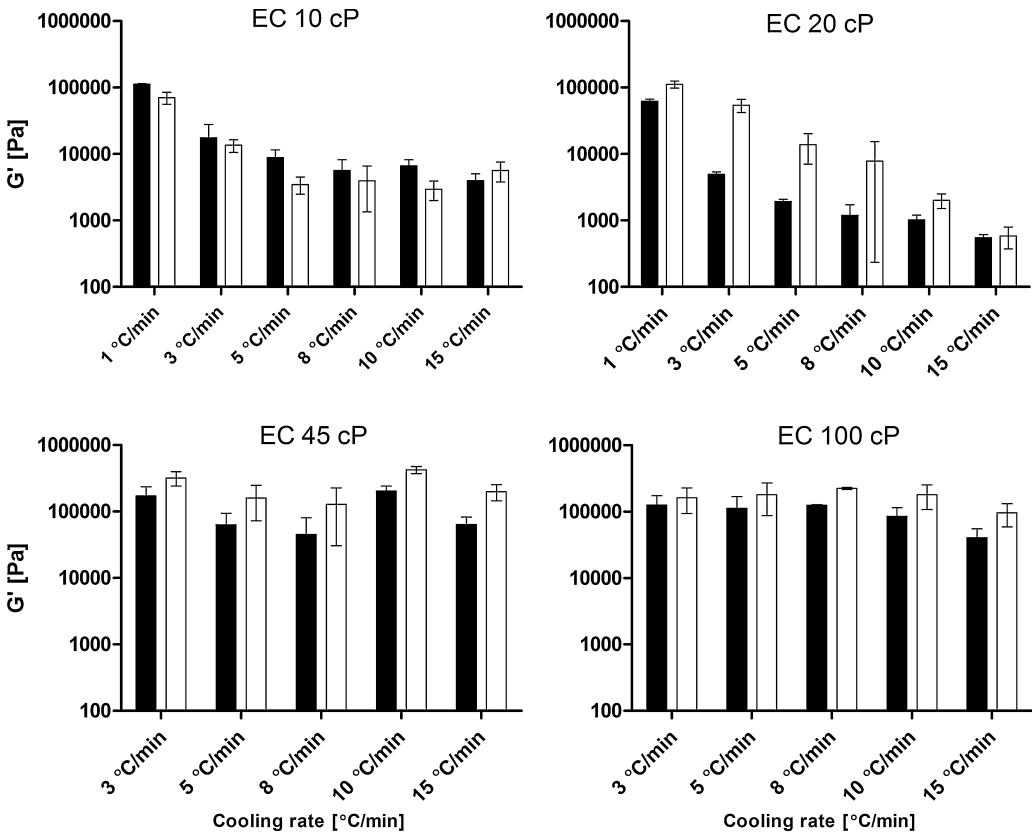

Fig. 3. Storage modulus, at 60 °C, for different EC samples after the first (black) and second (white) cooling phases using different cooling rates. Temperature sweep experiments were conducted at 30 rad s^{-1} angular frequency and % strain at the LVR region.

A slower cooling rate provides more time for crystal growth or polymer re-arrangement, resulting in the formation of more crystals or more junction zones, which leads to stronger gels. Conversely, under high cooling rates, there is insufficient time for crystal growth or polymer interactions, resulting in the formation of less junction zones, which leads to softer gels.

The effect of cooling rate was not detected in the high molecular weight samples. It seems that at higher polymer molecular weights, the chains are too long for the cooling rate effect to alter gel strength. Significant higher modulus values were observed at the second cooling run compare to the first run in some of the samples. This observation did not have a consistent trend and therefore we suspect that incomplete melting of the gel network occurred after the first run led to higher modulus at the second run.

3.2.1.2. Effect of cooling rate and molecular weight on the cross-over behavior. Fig. 4 shows the gel strength at the cross-over ($G' = G''$) point with respect to cooling/heating rate and polymer molecular weight. An increase in gel strength at the cross-over point with increases in polymer molecular weight was observed. Overall, EC 10 cP and EC 20 cP demonstrated a unique cross-over behavior while EC 45 cP and EC 100 cP exhibited similar tendencies. These observations are in line with the results obtained from the final gel strength analysis.

No significant differences between the first and second cooling cross-over modulus was observed in the samples. However, different modulus values were observed when comparing cross-over points during heating and cooling phases, demonstrating the hysteresis behavior discussed above. EC based gels demonstrated an increase or decrease in the modulus during heating for EC 10 cP and EC 20 cP, respectively, whereas EC 45 cP and EC 100 cP did not demonstrate any hysteresis behavior. According to these results, the hysteresis effect depends on the polymer molecular weight. Similar behavior was reported for gelatin/cosolute mixtures for gelatin of different molecular weights. The presence of hysteresis during cooling/heating treatments was detected only for lower molecular weight gelatin samples (Kasapis, Al-Marhoobi, & Mitchell, 2003). It seems that the plasticizing properties of low molecular weight polymer chains participate in the hysteresis effect.

Fig. 5 shows the effects of polymer molecular weight and cooling/heating rate on the temperature at cross-over. The cross-over temperature, i.e., the temperature where $G' = G''$, can provide an estimate of the gel point temperature (Kavanagh & Ross-Murphy, 1998). A clear increase in cross-over temperature with increase in polymer molecular weight was observed. The hysteresis effect could also be observed in the temperature at cross-over for the low molecular weight samples, EC 10 cP and EC 20 cP (note: not at all cooling/heating rates). It is clear that the EC 10 cP sol–gel transition at the second cooling phase appears at lower temperatures compared to the first cooling phase, whereas, the gel–sol transition occurs at a higher temperature compared to both cooling transition temperatures. It seems that the plasticizing effect of low molecular weight polymer chains also contributes to the change in temperature at cross-over as well. This behavior appears in part in the EC 20 cP and EC 45 cP samples depending on the cooling rate, but not for the higher molecular weight sample, EC 100 cP.

We did not detect a clear tendency in the cross-over temperature behavior with respect to cooling/heating rate in all EC samples. It appears that the cooling rate does not affect the temperature at the cross-over in the same fashion as the modulus at cross-over. Curdlan "hot" gels demonstrated a similar tendency where the heating rate did not affect the setting transition temperature (Funami, Funami, Yada, & Nakao, 2000). Different behavior with

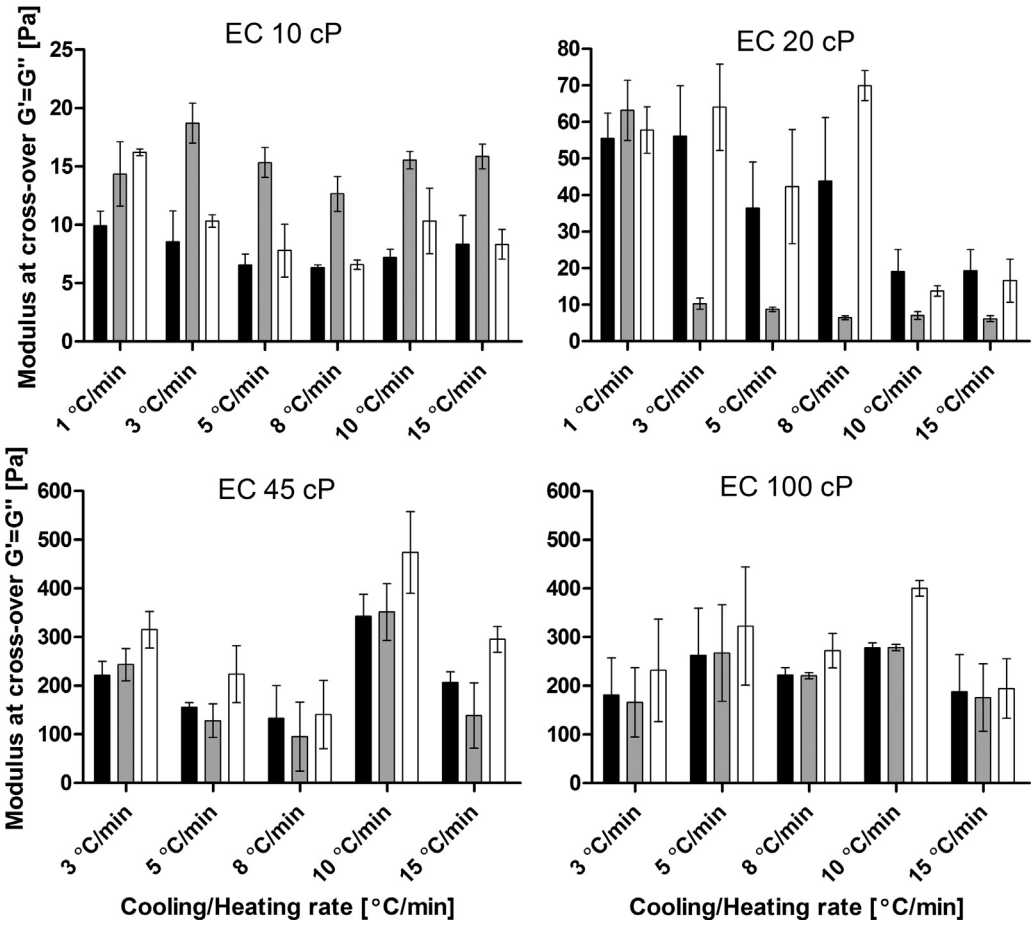

Fig. 4. Modulus at cross over, $G' = G''$, during the first cooling (black), heating (gray) and the second cooling (white) steps for different EC samples at different cooling/heating rates. Data obtained using temperature sweep experiments at 30 rad s^{-1} angular frequency and % strain at the LVR region.

a decrease in gel point temperature with decreasing cooling rate was demonstrated by Doesburg and Grevers (1959) for pectin gels at different degrees of esterification and pH. Similar results were obtained for agarose gels cooled at 3.0, 1.0, 0.29, and 0.08 °C min^{-1} (Aymard et al., 2001).

3.2.2. Gel point temperature determination

The gel point can be estimated by the temperature where a transition between the loss and storage modulus occur, i.e., the temperature where $G' = G''$. However, previous work has shown that such analysis can only provide a rough estimate of the gel point due to the frequency dependence of the modulus (Tung & Dynes, 1982). In order to quantify the gel point temperature accurately the method developed by Winter and Chambon (1986) was utilized. This method involves analysis of frequency sweep experiments at different temperatures. The gel point temperature can be evaluated from a multi-frequency plot of $\tan\delta$ (G''/G') with temperature. The gel point is determined as the frequency-independent value of $\tan\delta$, i.e., the point where all frequencies give the same $\tan\delta$ value. This analysis has been successfully used for cold-set gels such as gelatin (Michon, Cuvelier, & Launay, 1993), chitosan/pectin mixtures (Nordby, Kjøniksen, Nystrom, & Roots, 2003) as well as for heat-set gels such as ethyl(hydroxyethyl) cellulose (Nystrom, Walderhaug, Hansen, & Lindman, 1995). Fig. 6 shows typical frequency sweep experiments at three different temperatures for different EC samples. At higher temperatures, G'' is larger the G', indicating a liquid-like state, while at lower temperatures the opposite tendency is observed, indicating a gel state. The gel point temperature appears in-between those temperatures.

Fig. 7 illustrates the gel point temperature analysis for the different EC samples. As expected, an increase in gel point temperature is observed with increasing EC molecular weight. These results are in line with the temperature at cross-over analysis presented before. Other thermo-reversible gel systems such as agarose (Normand, Lootens, Amici, Plucknett, & Aymard, 2000) and kappa-carrageenan (Rochas et al., 1990) also exhibited a decrease in gel point temperature with a decrease in polymer molecular weight.

The effect of polymer concentration on the gel point temperature was determined using the same analysis (Fig. 8). Polymer concentration seems to have a relatively small effect on gel point temperature compared to polymer molecular weight. A slight decrease in the gel point temperature, with increases in polymer concentration was observed. Gelation temperature dependence on polymer concentration for other thermo-reversible polysaccharide gels have shown different tendencies. Agar (Normand et al., 2000) and pectin (Hinton, 1950) gels display an increase in gelation temperature with increasing polymer concentration. Gellan gum gel did not show such behavior in one study (Harris, 1990), while in another study, it did show similar behavior as agar and pectin (Miyoshi et al., 1996). Other heat-set thermo-reversible systems showed a decrease in the setting temperature with increases in polymer concentration (Miyazaki et al., 1998; Sekiguchi, Sawatari, & Kondo, 2003). Heat-set gels of *O*-methylcellulose displayed a negative relation between polymer concentration and setting temperature (Sekiguchi et al., 2003). Several studies reported on the heat-set gels of ethyl(hydroxyethyl)cellulose/surfactant mixtures

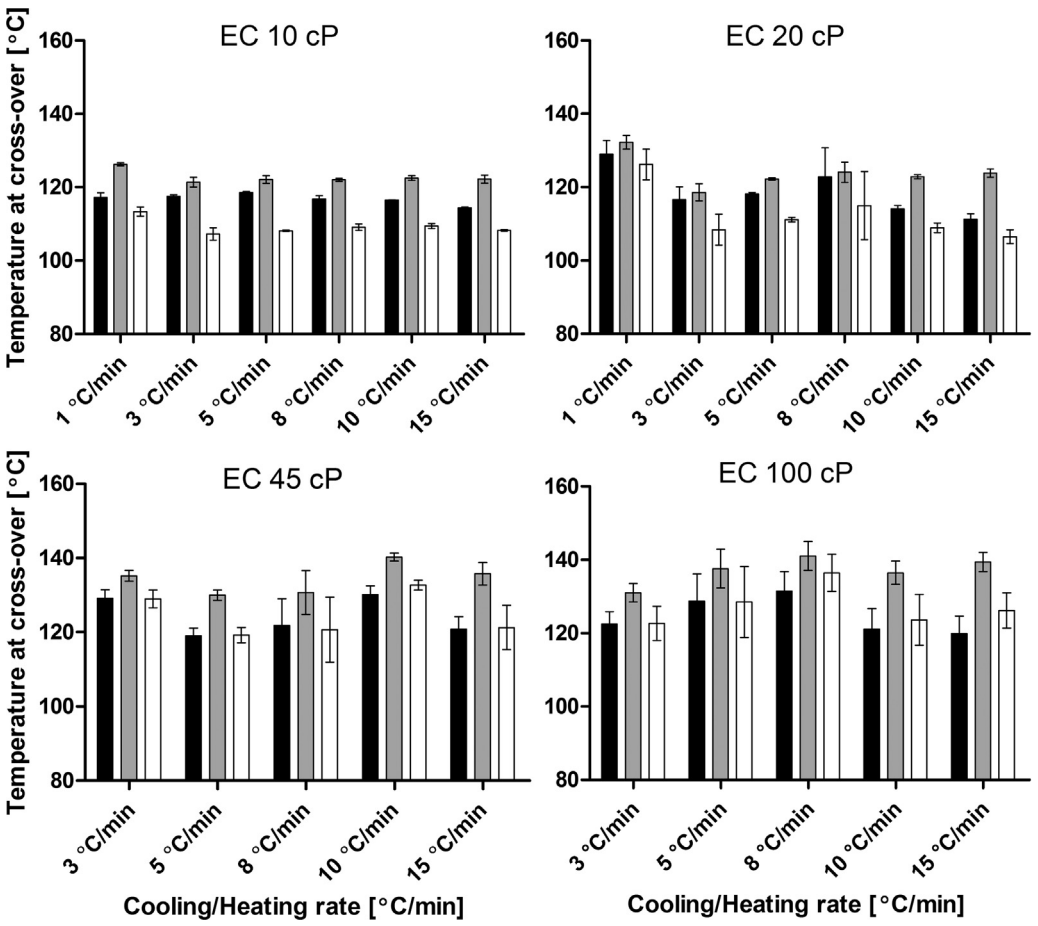

Fig. 5. Temperature at cross over, $G' = G''$, during the first cooling (black), heating (gray) and the second cooling (white) steps for different EC samples at different cooling/heating rates. Data obtained using temperature sweep experiment at 30 rad s^{-1} angular frequency and % strain at the LVR region.

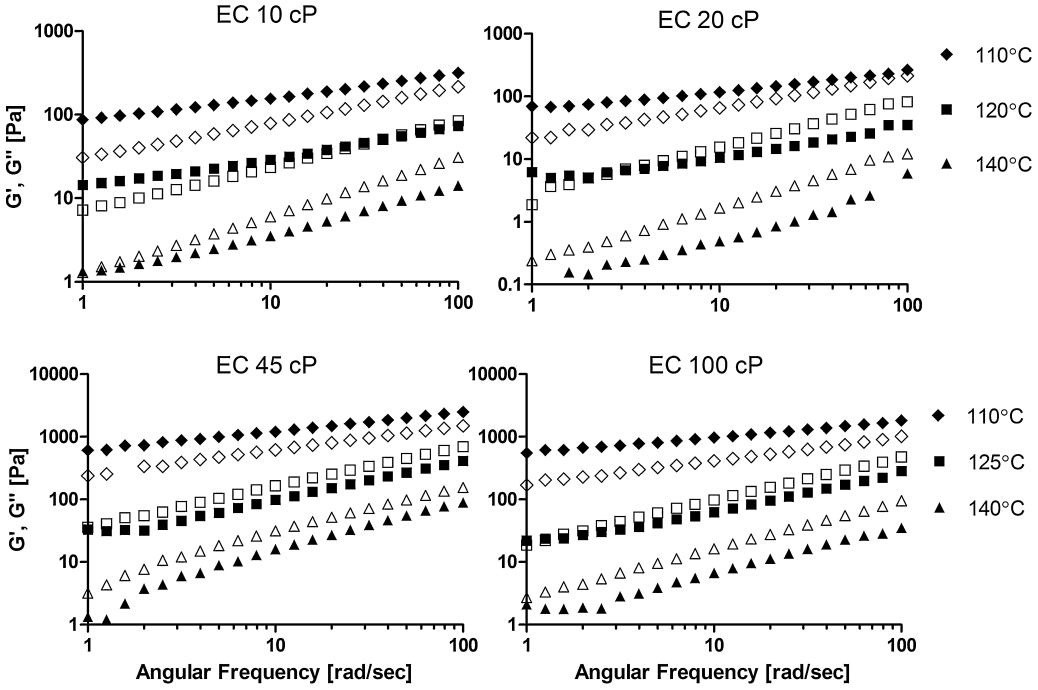

Fig. 6. Frequency sweep experiments obtained for different EC samples at three different temperatures. Experiments were conducted at the LVR region. G' (closed symbol) and G'' (open symbol). Curves were shifted vertically by factor A.

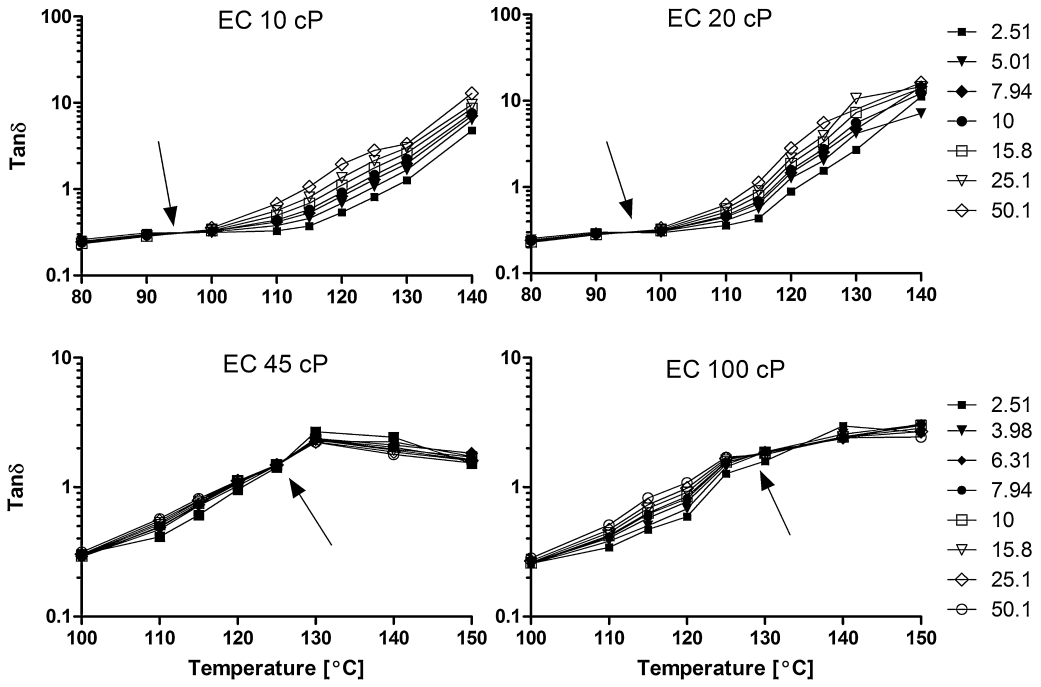

Fig. 7. Viscoelastic loss tangent as a function of temperature for different EC samples at different angular frequencies. Data obtained from the frequency sweep experiments. The gel point temperature is indicated by arrow.

and revealed a shift to lower gel point temperatures with increasing polymer concentration (Kjøniksen, Nystrom, & Lindman, 1998; Nystrom et al., 1995).

3.2.3. Gelation setting time

The time needed for EC oleogels to set was determined in order to evaluate the time required before conducting further analysis on the gels. Setting time was found to be cooling rate dependent (Fig. 9). As expected, a slow cooling rate keeps the system close to equilibrium and therefore minimizes setting time effects. No significant differences were observed between the two higher cooling rates (10 and 20° min^{-1}). Similar behavior was observed for thermally induced waxy crude oil gels which were cooled from 35 °C to 15 °C at different cooling rates (0.05, 0.5, 1.0 °C min^{-1})

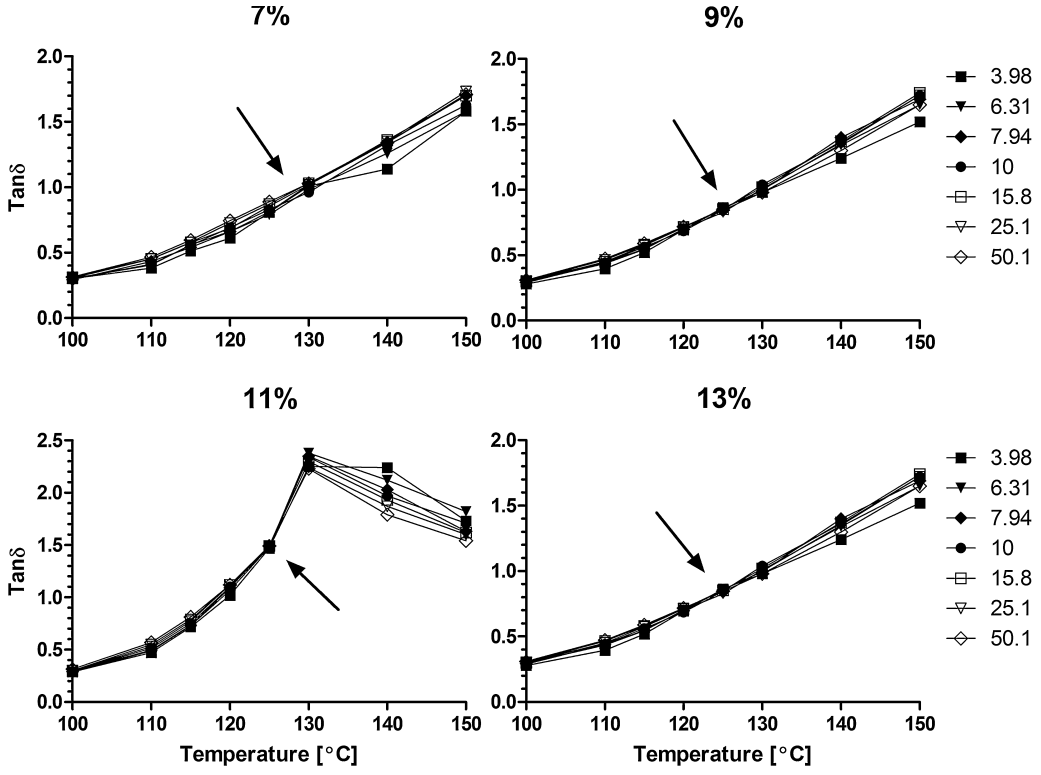

Fig. 8. Viscoelastic loss tangent as a function of temperature for EC 45 cP at different EC concentrations at different angular frequencies. Data obtained from the frequency sweep experiments. The gel point temperature is indicated by arrow.

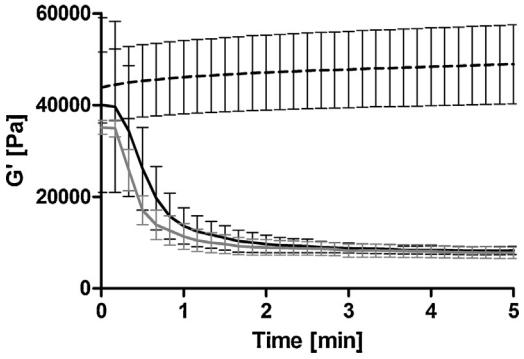

Fig. 9. The time depended storage modulus obtained for 11% EC 45 cP with canola oil gels cooled at 5 °C min^{-1} (dashed line), 10 °C min^{-1} (black solid line), and 20 °C min^{-1} (gray solid line).

(Visintin et al., 2005). The authors also noted that the final G′ value obtained, at the different cooling rates, was stable over time; i.e., suggesting particular gel microstructure determined by the cooling rate. Eleya and Turgeon (2000) worked on the thermo-reversible gelation kappa-carrageenan in an aqueous environment reported a step like increase in G′ after cooling to the target temperature, 20 °C, with approximately constant G′ value afterwards, when cooling from 45 to 20 °C at 1° min^{-1}.

4. Conclusion

The characterization of the thermo-gelation of EC/CO oleogels was performed using rheology and thermal analysis. Thermal analysis using both DSC and rheology suggested that the gelation mechanism of EC oleogels does not involve the formation of an ordered secondary structure, as is the case for many typical thermo reversible polymer gels. DSC results detected a characteristic thermal transition which involves the polymer glass transition followed by interaction between polymer chains and solvent, i.e., canola oil, leading to polymer dissolution.

Rheological analysis suggested a clear relationship between polymer molecular weight and final gel strength, cross-over behavior as well as gel point temperature. Increasing polymer molecular weight led to an increase in final gel strength, modulus at cross-over, and gelation temperature. Cooling/heating rates affected gel properties (i.e., moduli) only for the low molecular weight samples. A decrease in gel strength with increases in cooling rate upon setting was observed. However, this behavior was not observed for the gel point temperature: none of the EC samples were affected by the cooling/heating rate upon setting. A clear relation was also found between the gelation setting time and the cooling rate. Slow cooling rates yielded a more stable gel of higher elastic modulus.

References

Aiache, J. M., Gauthier, P., & Aiache, S. (1992). New gelification method for vegetable oils I: Cosmetic application. *International Journal of Cosmetic Science*, *14*, 228–234.

Aymard, P., Martin, D. R., Plucknett, K., Foster, T. J., Clark, A. H., & Norton, I. T. (2001). Influence of thermal history on the structural and mechanical properties of agarose gels. *Biopolymers*, *59*, 131–144.

Braudo, E. E., Muratalieva, I. R., Piashchina, I. G., & Tolstoguzov, V. B. (1991). Correlation between the temperatures of formation/breakdown of the gel network and conformational transitions of agarose macromolecules. *Carbohydrate Polymers*, *15*, 317–321.

Cattaruzza, A., Radford, S., & Marangoni, A. G. (2012). *Dough products comprising ethylcellulose and exhibiting reduced oil migration*. WO/2012/066277.

Davidovich-Pinhas, M., Co, E., Barbut, S., & Marangoni, A. G. (2014). Physical structure and thermal behavior of ethylcellulose. *Cellulose*, *21*, 3243–3255.

Doesburg, J. J., & Grevers, G. (1959). Setting time and setting temperature of pectin jellies. *Journal of Food Science*, *25*, 634–645.

Eleya, M. M. O., & Turgeon, S. L. (2000). Rheology of *k*-carrageenan and *b*-lactoglobulin mixed gels. *Food Hydrocolloids*, *14*, 29–40.

Funami, T., Funami, M., Yada, H., & Nakao, Y. (2000). A rheological study on the effects of heating rate and dispersing method on the gelling characteristics of curdlan aqueous dispersions. *Food Hydrocolloids*, *14*, 509–518.

Funamia, T., Funamib, M., Yadab, H., & Nakaob, Y. (1999). Rheological and thermal studies on gelling characteristics of curdlan. *Food Hydrocolloids*, *13*, 317–324.

Gravelle, A. J., Barbut, S., & Marangoni, A. G. (2012). Ethylcellulose oleogels: Manufacturing considerations and effects of oil oxidation. *Food Research International*, *48*, 578–583.

Gravelle, A. J., Barbut, S., & Marangoni, A. G. (2013). Fractionation of ethylcellulose oleogels during setting. *Food Function*, *4*, 153–161.

Gravelle, A. J., Barbut, S., Quinton, M., & Marangoni, A. G. (2014). Towards the development of a predictive model of the formulation-dependent mechanical behaviour of ethylcellulose oleogels. *Journal of Food Engineering*, *143*, 114–122.

Harris, P. (1990). *Food gels*. Essex: Elsevier Applied Science.

Hinton, C. L. (1950). The setting temperature of pectin jellies. *Journal of the Science of Food and Agriculture*, *1*, 300–307.

Kasapis, S., Al-Marhoobi, I. M., & Mitchell, J. R. (2003). Molecular weight effects on the glass transition of gelatin/cosolute mixtures. *Biopolym*, *70*, 169–185.

Kavanagh, G. M., & Ross-Murphy, S. B. (1998). Rheological characterization of polymer gels. *Progress in Polymer Science*, *23*(3), 533–562.

Kjøniksen, A.-L., Nystrom, B., & Lindman, B. (1998). Dynamic viscoelasticity of gelling and nongelling aqueous mixtures of ethyl(hydroxyethyl)cellulose and an ionic surfactant. *Macromolecules*, *31*, 1852–1858.

Koch, W. (1937). Properties and uses of ethylcellulose. *Industrial & Engineering Chemistry*, *29*, 687–690.

Laredo, T., Barbut, S., & Marangoni, A. G. (2011). Molecular interactions of polymer oleogelation. *Soft Matter*, *7*, 2734–2743.

Lefebvre, J., & Doublier, J.-L. (1998). Rheological behavior of polysaccharides aqueous systems. In S. Dumitriu (Ed.), *Polysaccharides: Structural diversity and functional versatility* (pp. 357–409). New York, NY: Marcel Dekker.

Li, L. (2002). Thermal gelation of methylcellulose in water: Scaling and thermoreversibility. *Macromolecules*, *35*, 5990–5998.

Li, L., Thangamathesvaran, P. M., Yue, C. Y., Tam, K. C., Hu, X., & Lam, Y. C. (2001). Gel network structure of methylcellulose in water. *Langmuir*, *17*, 8062–8068.

Mangionea, M. R., Giacomazza, D., Bulone, D., Martorana, V., & Biagio, P. L. S. (2003). Thermoreversible gelation of *k*-carrageenan: Relation between conformational transition and aggregation. *Biophysical Chemistry*, *104*, 95–105.

Marangoni, A. G. (2010a). *Chocolate compositions containing ethylcellulose*. WO/2012/066277.

Marangoni, A. G. (2010b). *Polymer gelation of oils*. WO/2010/143066.

Marangoni, A. G. (2012). *Thixotropic compositions*. WO/2012/071651.

Marangoni, A. G., & Garti, N. (2011). An overview of the past, present, and future of organogels. In A. G. Marangoni, & N. Garti (Eds.), *Edible oleogels: Structure and health implications* (pp. 1–18). Urbana, IL: AOCS Press.

Michon, C., Cuvelier, G., & Launay, B. (1993). Concentration dependence of the critical viscoelastic properties of gelatin at the gel point. *Rheologica Acta*, *32*, 94–103.

Miyazaki, S., Suisha, F., Kawasaki, N., Shirakawa, M., Yamatoya, K., & Attwood, D. (1998). Thermally reversible xyloglucan gels as vehicles for rectal drug delivery. *Journal of Controlled Release*, *56*, 75–83.

Miyoshi, E., Takaya, T., & Nishinari, K. (1996). Rheological and thermal studies of gelsol transition in gellan gum aqueous solutions. *Carbohydrate Polymers*, *30*, 109–119.

Nishinari, K. (1997). Rheological and DSC study of sol–gel transition in aqueous dispersions of industrially important polymers and colloids. *Colloid and Polymer Science*, *275*, 1093–1107.

Nordby, M. H., Kjøniksen, A.-L., Nystrom, B., & Roots, J. (2003). Thermoreversible gelation of aqueous mixtures of pectin and chitosan. Rheology. *Biomacromolecules*, *4*, 337–343.

Normand, V. R., Lootens, D. L., Amici, E., Plucknett, K. P., & Aymard, P. (2000). New insight into agarose gel mechanical properties. *Biomacromolecules*, *1*, 730–738.

Nystrom, B., Walderhaug, H., Hansen, F. K., & Lindman, B. (1995). Rheological behavior during thermoreversible gelation of aqueous mixtures of ethyl(hydroxyethy1)cellulose and surfactants. *Langmuir*, *11*, 750–757.

Payro; E. R., & Llacuna, J. L. (2006). Rheological characterization of the gel point in sol–gel transition. *Journal of Non-Crystalline Solids*, *352*, 2220–2225.

Pernetti, M., Malssen, K. F. V., Flöter, E., & Bot, A. (2007). Structuring of edible oils by alternatives to crystalline fat. *Current Opinion in Colloid & Interface Science*, *12*, 221–231.

Rocha, J. C. B., Lopes, J. D., Mascarenhas, M. C. N., Arellano, D. B., Guerreiro, L. M. R., & Cunha, R. L. D. (2013). Thermal and rheological properties of organogels formed by sugarcane or candelilla wax in soybean oil. *Food Research International*, *50*, 318–323.

Rochas, C., Rmaudo, M., & Landry, S. (1990). Role of the molecular weight on the mechanical properties of kappa carrageenan gels. *Carbohydrate Polymers*, *12*, 255–266.

Rubinstein, M., & Colby, R. H. (2003). *Polymer physics*. New York: Oxford University Press Inc.

Sarkar, N. (1979). Thermal gelation properties of methyl and hydroxypropyl methylcellulose. *Journal of Applied Polymer Science*, *24*, 1073–1087.

Sekiguchi, Y., Sawatari, C., & Kondo, T. (2003). A gelation mechanism depending on hydrogen bond formation in regioselectively substituted *O*-methylcelluloses. *Carbohydrate Polymers*, *53*, 145–153.

Tung, C.-Y. M., & Dynes, P. J. (1982). Relationship between viscoelastic properties and gelation in thermosetting systems. *Journal of Applied Polymer Science*, *27*, 569–574.

Visintin, R. F. G., Lapasin, R., Vignati, E., D'Antona, P., & Lockhart, T. P. (2005). Rheological behavior and structural interpretation of waxy crude oil gels. *Langmuir*, *21*, 6240–6249.

Winter, H. H., & Chambon, F. (1986). Analysis of linear viscoelasticity of a crosslinking polymer at the gel point. *Journal of Rheology*, *30*, 367–382.

Zetzl, A. K., Marangoni, A. G., & Barbut, S. (2012). Mechanical properties of ethylcellulose oleogels and their potential for saturated fat reduction in frankfurters. *Food Function*, *3*, 327–337.

Zhang, H., Nishinari, K., Williams, M. A. K., Foster, T. J., & Norton, I. T. (2002). A molecular description of the gelation mechanism of curdlan. *International Journal of Biological Macromolecules*, *30*, 7–16.