

Mechanical vs calorimetric glass transition temperature in the oxidation of linoleic acid from condensed κ -carrageenan/glucose syrup systems

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ABSTRACT

Lipid oxidation remains a concern leading to deterioration of the organoleptic quality in processed goods, but it should be minimized by considering changes in the structural properties of foods. The present work investigates the effect of glass transition temperature on the oxidation of linoleic acid at different concentrations of κ -carrageenan/glucose syrup. A combination of 0.5, 1, 2 and 3% (w/w) κ -carrageenan and 82.5, 82, 81, 80% (w/w) glucose syrup were mixed with 1.5% (w/w) linoleic acid and 0.5% (w/w) lecithin to prepare samples with a total solid content of 85% (w/w). Physicochemical properties of these mixtures were recorded using Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). This was followed by estimation of the mechanical (T_{gm}) and calorimetric (T_{gc}) glass transition temperatures using small deformation dynamic oscillation in-shear and modulated differential scanning calorimetry (MDSC). The linoleic acid oxidation in the condensed polysaccharide/co-solute system was evaluated by monitoring the accumulation of hydroperoxide (ROOH) with UV-vis spectroscopy over a wide temperature range (-25 to 0 °C). The oxidation phase was modelled following a sigmoidal kinetic model indicating initiation and propagation stages of lipid oxidation. ROOH production increased as a function of time and temperature. The structural relaxation of the polymeric matrix influenced the oxidation rate at the initiation stage. At the propagation phase, T_{gm} appears to control the rate of ROOH formation (k_f) and decomposition (k_d) in all preparations, as compared to T_{gc} , an outcome that makes the former an important concept of quality control.

1. Introduction

The utilisation of polyunsaturated fatty acids (PUFA) in the human diet has been continuously expanding due to dietary guideline recommendations to supplant saturated lipids (Nogueira, Scolaro, Milne, & Castro, 2019). An issue related to utilising unsaturated lipids in foods is their high susceptibility to free radical-induced lipid peroxidation, which increases with the degree of unsaturation (Domínguez et al., 2019). Among the polyunsaturated fatty acids, linoleic acid, i.e. an omega-6 fatty acid, is essential for human metabolism. It possesses a 18:2n-6 chemical structure consisting of more than one cis double bonds that make it highly vulnerable to lipid oxidation (Saini & Keum, 2018). This vulnerability during storage of processed foods, often leads to the formation of fatty acid peroxides that may cause damage to the structure of adjacent proteins and enzymes (Marangoni et al., 2020).

In general, the oxidation process in polyunsaturated fatty acids occurs rapidly following three successive stages of initiation, propagation

and termination (Toorani & Golmakani, 2021). Identification and subsequent quantification of compounds derived from oxidation reactions at each stage is the focus of current research since it can affect distinctly the quality of vegetable oils. Oxidisable substrates may yield high levels of hydroperoxides (ROOHs), which are the first compounds of lipid peroxidation and possess specific significance as the precursor of secondary lipid oxidation products, e.g. aldehydes (hexanal), ketones, alcohols or pentyl furans (Domínguez et al., 2019).

Accumulation of ROOHs at different stages and transfer phases of lipid oxidation can be interpreted by a sigmoidal kinetic model that involves several indices of convenient quality control. These include the rate constant of the initiation phase (k_i), the rate constant of the pseudo first-order formation of ROOHs (k_f) at the propagation phase and the rate constant of the pseudo second-order decomposition of ROOHs (k_d) at the propagation phase (Farhoosh, 2018). Combining observations of the aforementioned indices from the sigmoidal model with the structural characteristics of lipids and the ensuing physicochemical events can

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provide valuable information that potentially retards the oxidation phase transfer in processed formulations, e.g. commercially baked goods and fast foods.

High-solid food systems often consist of amorphous components that transform from the rubbery to the glassy state upon rapid cooling at the so-called glass transition temperature (T_g) (Fan & Roos, 2017). Above T_g , reaction rates increase dramatically due to the accelerated molecular mobility of the polymeric matrix and the bioactive reactant (Fan & Roos, 2017). Using the concept of the mechanical glass transition temperature (T_{gm}), it was proposed that the structural characteristics of a starch network are critical considerations of the enzymatic activity of the entrapped α -amylase in the polysaccharide matrix (Chaudhary, Pan-yoyai, Small, Shanks, & Kasapis, 2017). It has been reported in the literature that the variation in T_{gm} is related to the ability of the biopolymer to form a network, a process which rheology is extremely well qualified to follow. In contrast, calorimetry provides information primarily on the mobility of the small-molecule “sugar” co-solute as a function of the total level of solids (Kasapis, 2006; Kasapis, Al-Marhoobi, & Mitchell, 2003). Vitrified materials may also retard the formation of hydroperoxides in encapsulated rapeseed oil by entrapping the hydrophilic and lipophilic radicals (Orlien, Andersen, Sinkko, & Skibsted, 2000). Further studies have reported on the oxidation rate of bulk vegetable oils and encapsulated fish oil particles without a reference to the structural properties of polymeric carriers (Linke, Weiss, & Kohlus, 2020; Nogueira et al., 2019; Toorani & Golmakani, 2021).

Polysaccharides such as carrageenan can form cohesive three-dimensional structures in the presence of cross-linking counterions. Fani, Enayati, Rostamabadi, & Falsafi (2022) have reported on the encapsulation of bioactive compounds by electrosprayed κ -carrageenan nanoparticles. Paramita, Bannikova, & Kasapis (2015) modelled the release mechanism of omega-3 fatty acids in κ -carrageenan/polydextrose matrices undergoing glass transition. The present investigation adds to literature by dealing with the effect of the glass transition temperature on the oxidation state of linoleic acid from condensed κ -carrageenan/glucose syrup systems. These were prepared by varying the concentrations of the polysaccharide and co-solute in the presence of cross-linking potassium counterions. The fatty-acid oxidation rate was examined by employing the kinetic sigmoidal model discussed earlier and outcomes were correlated with the vitrification properties of these systems. Thus, observations on the physicochemical and morphological characteristics of the polymeric matrix were recorded to provide a valid correlation between the dynamics of glass transition mechanism and the oxidation kinetics of the entrapped bioactive lipid that may lead to a better control of organoleptic quality in related food applications.

2. Materials and methods

2.1. Materials

κ -Carrageenan type III, extracted from *Eucheuma cottonii*, was obtained from Sigma-Aldrich (Sydney, Australia), while glucose syrup, with a total solid level of 81% (w/w) and a dextrose equivalent of 42, was supplied by Edlyn Foods (Victoria, Australia). Linoleic acid (99% purity, $M_w \approx 280.45$ kDa) was purchased from Sigma-Aldrich. Lecithin (emulsifier) was purchased from Melbourne Food Ingredient Depot (Melbourne, Australia). Potassium chloride (KCl), Amberlite IR-120 resin, and reagents for the oxidation analysis i.e. chloroform (CHCl_3), methanol (CH_3OH), 1-butanol ($\text{CH}_4\text{CH}_1\text{O}$), ammonium thiocyanate ($\text{CH}_4\text{N}_2\text{S}$), barium chloride (BaCl_2) and iron (II) sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) were all purchased from Sigma-Aldrich. Deionised Milli-Q Type II water was used throughout experimentation. Cumene hydroperoxide (80%) from Sigma-Aldrich was used to produce the standard curve for ROOH determination.

2.2. Sample preparation

A model system composed of κ -carrageenan/glucose syrup with linoleic acid and lecithin at a total solid of 85% (w/w) was prepared. κ -Carrageenan was first converted into the potassium form following the method applied by Ikasari, Paramita, & Kasapis (2022). This was conducted by soaking 200 g Amberlite IR-120 resin in 0.1 M HCl until pH reached 1, followed by submersion of the resin in 2M KCl solution to convert H^+ to K^+ form. The remaining salt was washed away with water until the filtrate showed a clear solution when titrated with AgNO_3 . The temperature of the resin was then elevated to 90 °C and stirred with 0.5% (w/w) κ -carrageenan for 30 min to perform the ion exchanging process to the potassium form. The κ -carrageenan solution was then dialysed using cellulose-based semi-permeable tubes (height: 20 cm; diameter: 4.3 cm) by submersing in Milli-Q water overnight at ambient temperature. The polysaccharide solution was freeze-dried and used for the following experimentation.

Samples were prepared in a beaker by mixing 0.5, 1, 2, and 3% (w/w) κ -carrageenan in the potassium form with 82.5, 82, 81, and 80% (w/w) glucose syrup, followed by addition of 1.5% (w/w) linoleic acid and 0.5% (w/w) lecithin. In doing so, κ -carrageenan was dissolved in Milli-Q water with constant stirring at 90 °C for 10 min, followed by the incorporation of glucose syrup as the co-solute at 60 °C. The temperature was further reduced to 50 °C, and 1.5% (w/w) linoleic acid as the bioactive compound and 0.5% (w/w) lecithin were added with gentle stirring to reach a total solid of 85% (w/w). Finally, 200 mM of KCl was added to the mixture at this temperature. In the end, beakers were covered with a plastic wrap and further sealed with aluminium foil to prevent exposure to environmental conditions. They were kept in a refrigerator before further analysis.

2.3. Experimental analysis

2.3.1. Fourier transform infrared spectroscopy

Interferograms were recorded using Spectrum Two GladiATR-Fourier transform infrared spectroscopy (PerkinElmer, Pike Technologies, Norwalk, US) following the method used by Panyoyai, Bannikova, Small, & Kasapis (2015). Condensed samples of single glucose syrup, linoleic acid and tertiary systems consisting of κ -carrageenan, glucose syrup and fatty acid were scanned at a wavelength of 700–4000 cm^{-1} with 4 cm^{-1} resolution based on 64 average scans. Experimental results were subtracted from the background solvent signal, and each sample was prepared separately and analysed three times.

2.3.2. Scanning electron microscopy

In the presence of 200 mM KCl, single systems of glucose syrup and κ -carrageenan were compared to the mixture of κ -carrageenan, glucose syrup, linoleic acid and lecithin. The working protocol followed the method by Paramita et al. (2015) with some modifications. Samples were freeze-dried, coated with iridium, and subjected to the intense electron beam and high vacuum conditions of 0.6 Torr using FEI Quanta 200 SEM (Hillsboro, Oregon, USA). High-quality images of the samples were captured at an average of 10–12 mm working distance and magnification of 3000–6000 \times , using an accelerated medium voltage of 30 kV and a spot size of 5.

2.3.3. Modulated differential scanning calorimetry

Measurements of the thermal profile were performed by using Q2000 (TA Instruments, New Castle, DE) with a refrigerated cooling system (RCS90). About 10 mg of samples were placed into T_{zero} aluminium pans, sealed hermetically and subjected to experimentation against an empty pan, which served as the reference. Measurements were run under nitrogen purge at a rate of 50 ml/min. Samples were equilibrated at 20 °C for 20 min, followed by cooling from 20 to –90 °C at a scan rate of 1 °C/min and heating to 80 °C at the same scan rate with a modulation rate of 0.53 °C for every 40s (Rahman, 2009). The glass

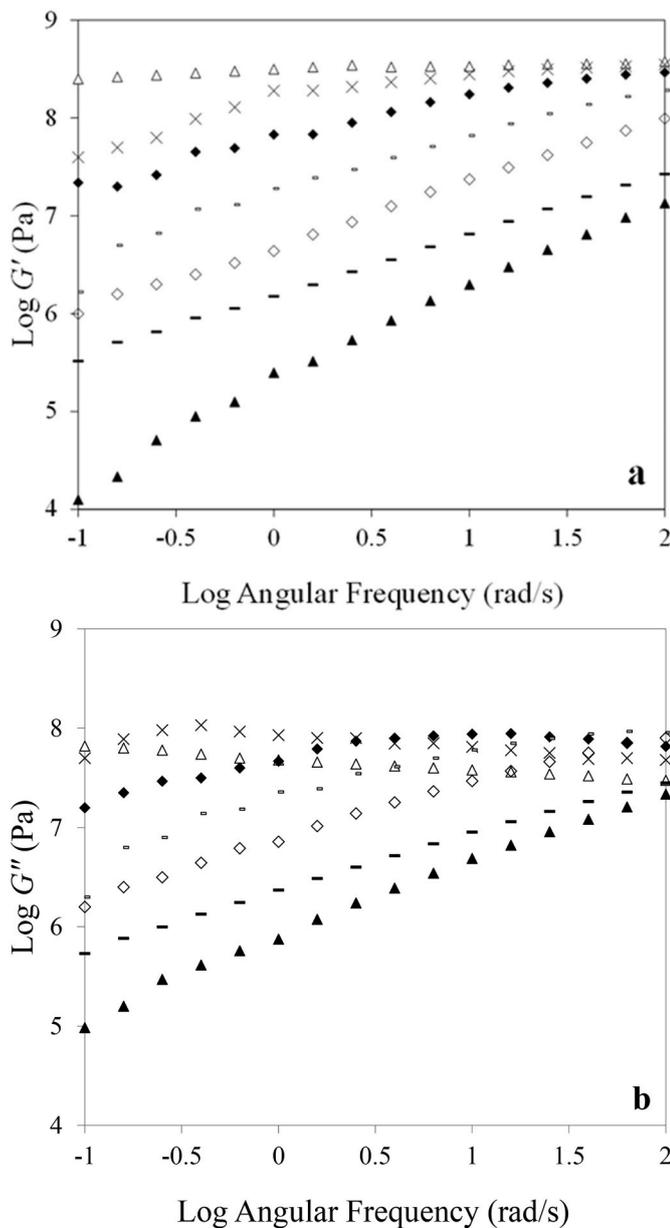


Fig. 5. Mechanical spectra of 0.5% κ -car+82.5% gs+1.5 lin acid+0.5% lec+200 mM KCl as a function of angular frequency (0.1–100 rad/s) for (a) storage modulus (G') and (b) loss modulus (G'') at experimental temperatures of -3°C (▲), -7°C (◊), -11°C (◊), -15°C (◊), -19°C (◆), -23°C (x), -27°C (Δ), arranged successively upwards.

reveals two domains in the temperature dependence of a_T , with the low temperature part being described by the linear relationship of the modified Arrhenius equation (Arridge, 1975):

$$\log a_T = \frac{E_a}{2.303R} \left(\frac{1}{T} - \frac{1}{T_0} \right) \quad (1)$$

where, E_a denotes the activation energy for molecular rearrangements to occur from one conformational state to another and R is the universal

gas constant.

On the other hand, the high part of the shift factor vs temperature dependence is modelled with the Williams, Landel and Ferry equation (Ferry, 1980):

$$\log a_T = -\frac{C_1^0(T - T_0)}{C_2^0 + (T - T_0)} \quad (2)$$

where, C_1^0 and C_2^0 (deg) are the WLF constants that include the concept of free volume in the following form:

$$C_1^0 = \frac{B}{2.303f_0} \quad \text{and} \quad C_2^0 = \frac{f_0}{\alpha_f} \quad (3)$$

where, f_0 is the fractional free volume at T_0 , α_f is the thermal expansion coefficient (deg^{-1}), and B is normally set to one.

Utilisation of equation (2) yields values of C_1^0 (~ 10.6), C_2^0 (~ 53 deg), f_0 (~ 0.042) and α_f ($8.0 \times 10^{-4} \text{ deg}^{-1}$), which are according to experience for natural and synthetic polymers during vitrification (Kontogiorgos & Kasapis, 2017). Results clearly argue that within the glass transition region progress in viscoelasticity follows the principles of the free volume theory whereas structural relaxation in the glassy state is better described by the predictions of the reaction rate theory. The conjunction of these two theoretical approaches can be considered as the mechanical or network glass transition temperature (T_{gm}), which emphasizes the ability of the macromolecule to form a three-dimensional structure (Paramita et al., 2016).

As shown in Fig. 6, increasing levels of κ -carrageenan (0.5, 1, 2 and 3%) yield higher T_{gm} values (-17 , -12 , -7 and -2°C) due to the enhanced ability of the polysaccharide to form cohesive networks. This is supported by the creation of intermolecular associations in the presence of KCl via the induction of electrostatic bonds between potassium ions and sulfate groups of D-galactose residues of the polysaccharide (Thrimawitana, Young, Dunstan, & Alany, 2010). A cursory glance at Figs. 3 and 6 indicates that the T_{gm} estimates for all systems are higher than the calorimetric glass transition temperature, since the latter reflects primarily the level of solids (micromolecular aspect) in the material whereas the mechanical glass transition temperature emphasizes the ability of the polysaccharide/counterion interactions (macromolecular aspect) to form a network (Kasapis, 2008).

3.4. Rate of linoleic acid oxidation in condensed κ -carrageenan/glucose syrup systems

The oxidation process of linoleic acid was followed by monitoring the hydroperoxide (ROOH) accumulation in all samples every 2 h for a total period of observation of 32 h. Readings were obtained as described in the Experimental Analysis Section, yielding a very acceptable relationship between absorbance at $\lambda_{max} = 500$ nm and ROOH concentration (linear regression coefficient, $r^2 = 0.997$) using the Beer-Lambert law. Our analysis was facilitated by considering the three consecutive periods of lipid oxidation. In the initiation phase, ROOH formation follows a zero-order reaction leading to a sharp increase that signifies the onset of the propagation phase. The highest rate of ROOH production is achieved at the turning point of the propagation stage, which signifies decomposition of the hydroperoxide molecules, and this process happens most significantly in the termination phase (Farhoosh, 2018).

Fig. 7(a–d) reproduce the hydroperoxide accumulation during the peroxidation process of 1.5% linoleic acid at different concentrations of κ -carrageenan/glucose syrup over 32 h of observation for the

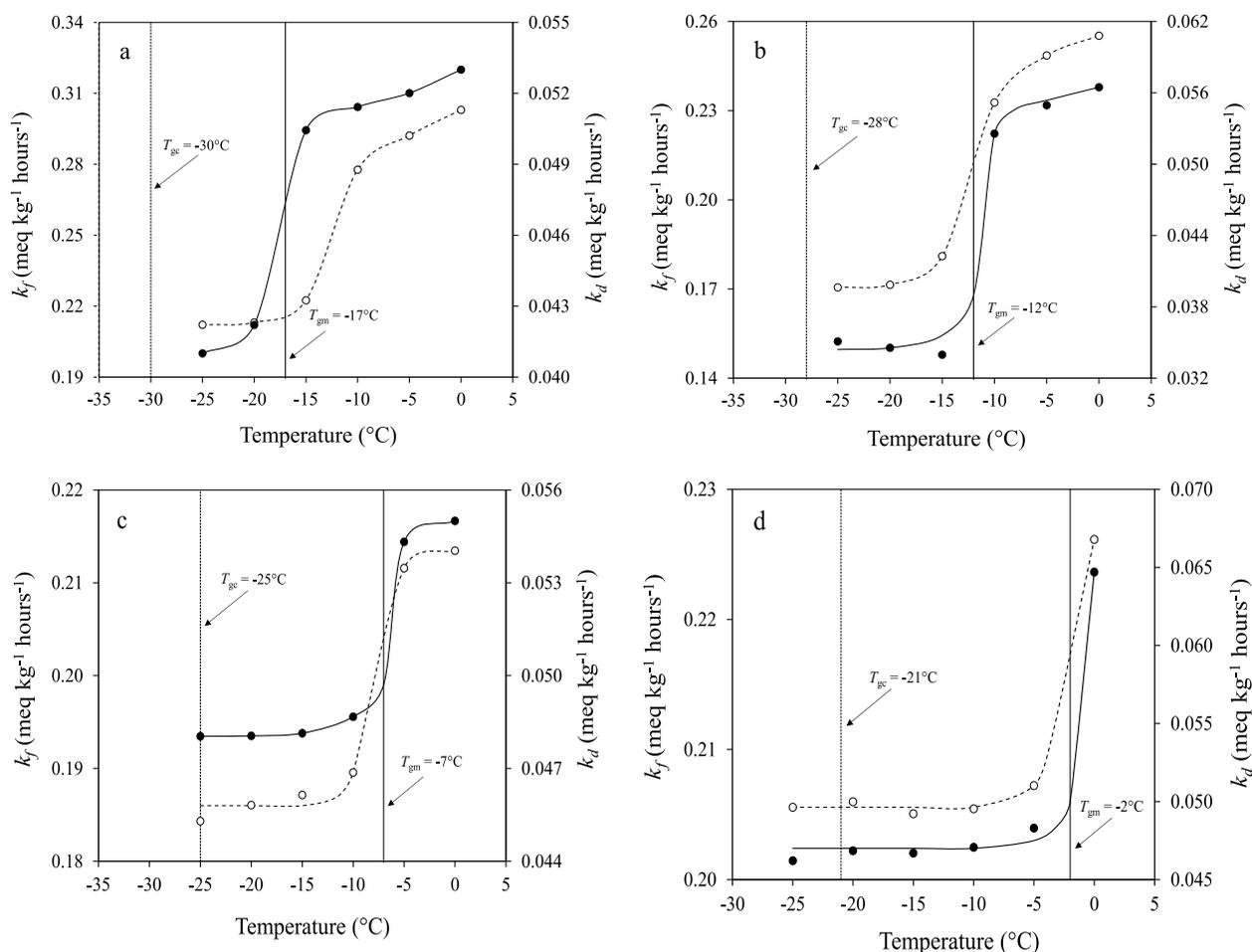


Fig. 9. Rate constant of ROOH formation at the propagation phase (k_f) (○, left y-axis) and rate constant of ROOH decomposition at the propagation phase (k_d) (●, right y-axis) of 1% linoleic acid in (a) 0.5% κ -car+82.5% gs+0.5% lec+200 mM KCl, (b) 1% κ -car+82% gs+0.5% lec+200 mM KCl, (c) 2% κ -car+81% gs+0.5% lec+200 mM KCl, (d) 3% κ -car+80% gs+0.5% lec+200 mM KCl, with indications of the mechanical and calorimetric glass transition temperatures.

4. Conclusions

We designed condensed systems at different concentrations of κ -carrageenan/glucose syrup to carry out studies on the oxidation rate of entrapped linoleic acid. Thus, the rate constants representing the initiation and propagation phases of lipid peroxidation were considered in relation to the structural properties of the polymeric matrix that determine vitrification. It was confirmed that the glass transitions recorded by mechanical measurements occur at much higher temperatures than the calorimetric counterparts thus affording us the opportunity to examine their relevance to lipid peroxidation in these blends. A sigmoidal model was applied successfully to hydroperoxide accumulation data to provide useful indices of lipid susceptibility to oxidation with temperature change and levels of polysaccharide addition in preparations. It was demonstrated that kinetic parameters and rate constants representing the propagation phase in linoleic acid peroxidation are considerably diminished in the vicinity of the mechanical glass transition temperature. As far as we are aware, this is the first time that the utility of T_{gm} , which reflects a barrier effect of the vitrified polymer network on the propagation oxidizability of polyunsaturated fatty acids, is documented for consideration in industrial applications.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Diah Ikasari: Methodology, Data modeling, Writing – original draft. **Vilia Darma Paramita:** Supervision, Data modeling, Writing – review & editing. **Stefan Kasapis:** Funding acquisition, Conceptualization, Supervision, Writing – review & editing.

Data availability

The authors are unable or have chosen not to specify which data has been used.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.foodhyd.2023.108555>.

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