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Influence of κ -carrageenan on the rheological behaviour of a model cake flour system

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ARTICLE INFO

Keywords:
Modelling
Polysaccharide
Gluten
Starch
Rheology

ABSTRACT

This study examined the effect of κ -carrageenan (κ -C) at various concentrations on the rheological properties of a model cake flour system. Increasing the κ -C concentrations in starch-gluten system led to an increase in both viscosity and G' and G'' moduli, indicating greater firmness of the sample, which caused by the entanglement of κ -C with starch and gluten. Moreover, increasing κ -C also led to decreasing creep compliance, indicating the samples had a higher resistance towards deformation. Gluten was more sensitive for the κ -C concentrations in creep-recovery test and then influenced the changes in starch-gluten system. Lastly, sample with κ -C addition at 10 g/100 g increased the starch gelatinisation onset temperatures from 58.6 to 66.2 °C and from 58.3 to 65.1 °C in the starch and starch-gluten system, respectively. The delay in the starch gelatinisation process could be caused by the lower water activity resulting from the high water holding capability of κ -C. These results enhanced our understanding of the interactions of κ -C with flour components and promote the potential application of carrageenan-containing materials, such as *Eucheuma*, in bakery products.

1. Introduction

Baking products such as cake are made with flour through heating. Starch and gluten are two major components in cake flour. Both starch gelation and gluten denaturation make a contribution to the final texture of cakes during baking. Starch can form a continuous network of particles together with the macromolecular network of hydrated gluten (Song & Zheng, 2007). In cake baking, the role of starch primarily contributes to the formation of cake crumb because it can irreversibly swell, which is followed by the leaching of amylose from the starch granules and the disruption of weak swollen starch granules (Lascombes et al., 2017; Li et al., 2017). Gluten can form a polymeric protein network upon hydration and mixing, and undergo a denaturation process during baking (Lavello, Guerrieri, & Cerletti, 1996; McCann & Day, 2013; Uthayakumaran, Newberry, Phan-Thien, & Tanner, 2002). It determines the crumb structure by affecting the cell expansion during leavening and baking. The independent networks and interaction formed by starch and gluten give rise to the rheological properties of doughs.

Hydrocolloids have been used in baked products for some specific reasons such as improving the shelf life by keeping the moisture content

and retarding the staling (León et al., 2000; Ozge Ozkoc, Sumnu, & Sahin, 2009). Carrageenan is one of the most widely used hydrocolloids (León et al., 2000). Carrageenan is a group of sulphated and water-soluble polysaccharides extracted from red seaweed and exists in many forms (Campo, Kawano, Silva, & Carvalho, 2009). Among these forms, κ -carrageenan (κ -C) has a potential effect on the textural properties of food because of its gel forming capability (Lascombes et al., 2017; Yang, Yang, & Yang, 2018) and is reported as a useful improver for baked products (Bárceñas, Benedito, & Rosell, 2004; Kohajdová & Karovičová, 2009). Furthermore, κ -C shows synergistic effects on the gelation process with locust bean and konjac flour (Saha & Bhattacharya, 2010). From these results, the addition of κ -C can modify the characters of flour and then influence the quality of final baked products.

Rheology can provide the opportunity for evaluating the structural organization and the interactions of the components in dough/flour systems. To date, rheology studies on the interactions of various starch-protein systems have been focused on the effect of starch and various vegetal proteins including gluten in dough systems (Jekle, Mühlberger, & Becker, 2016; Matos, Sanz, & Rosell, 2014). Other studies focused on the rheology of a bread dough/flour system and investigated the

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<https://doi.org/10.1016/j.lwt.2020.110324>

Received 28 April 2020; Received in revised form 28 September 2020; Accepted 29 September 2020

Available online 5 October 2020

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Table 1
Composition of the raw materials.

Sample	Moisture (g/100 g)	Amylose (g/100 g)	Dry gluten (g/100 g)	Starch (g/100 g)
Cake flour	11.6 ± 0.8	23 ± 2	7.7 ± 0.3	82 ± 3
Wheat starch	10.0 ± 0.3	24 ± 2	–	–
Gluten	6.5 ± 0.5	–	–	–
κ-Carrageenan	7.9 ± 0.5	–	–	–

* Values are expressed as means ± standard deviations of triplicates.

Table 2
Composition and labels of the different samples.

Sample group		Sample composition (g/100 g starch, dry basis) ^a		
		Starch	Gluten	κ-carrageenan (κ-C)
Starch system	S	100.00	–	–
	S/κ-C 0.5	99.50	–	0.50
	S/κ-C 1	99.00	–	1.00
	S/κ-C 2	98.00	–	2.00
	S/κ-C 5	95.00	–	5.00
	S/κ-C 10	90.00	–	10.00
Gluten system	G	–	100.00	–
	G/κ-C 0.5	–	95.22	4.78
	G/κ-C 1	–	90.73	9.27
	G/κ-C 2	–	82.89	17.11
	G/κ-C 5	–	65.27	34.73
	G/κ-C 10	–	47.09	52.91
Starch-Gluten system	SG	91.00	9.00	–
	SG/κ-C 0.5	90.55	8.96	0.45
	SG/κ-C 1	90.09	8.91	0.91
	SG/κ-C 2	89.18	8.82	1.82
	SG/κ-C 5	86.45	8.55	4.55
	SG/κ-C 10	81.90	8.10	9.10

^a The κ-C concentrations were based on the mass of dry starch. The starch to gluten ratio of the cake flour was 91/9 based on the chemical analysis.

interactions as a whole (Hesso et al., 2015; Tebben & Li, 2019). However, little is known in the mechanism of κ-C action in cake flour system during the heating process. Thus, a rheological study is needed to better understand the interactions among κ-C, gluten, and starch based on cake flour.

In our previous study, a high dietary fibre content sponge cake was developed through replacing some cake flour by *Eucheuma* powder (Huang & Yang, 2019). *Eucheuma* is a red seaweed and usually used for carrageenan extraction in food industry (Jumaidin, Sapuan, Jawaid, Ishak, & Sahari, 2017; Yang & Yang, 2020). Therefore, starch, gluten and carrageenan coexist in this sponge cake system. To better understand the effects of *Eucheuma* on the final cake system, we aimed to know one major ingredient of *Eucheuma*, κ-C, on the cake system via the interactions among κ-C, starch, and gluten. Thus, the present study aimed to investigate the effect of κ-C on the rheological behaviour of gluten and starch based on the cake flour. The steady shear flow test, frequency sweep test, creep-recovery test, and dynamic mechanical thermal analysis (DMTA) test were conducted. A schematic diagram was proposed and explained based on the results. These results aid our understanding of the interactions of κ-C with cake flour components and promote the potential application of carrageenan-containing materials, such as *Eucheuma*, in bakery products.

2. Materials and methods

2.1. Materials

Wheat starch, gluten, and κ-carrageenan (κ-C, molecular weight of 300–400 kDa and composed ≥ 93% of κ-C as reported by the supplier) were obtained from Sigma Aldrich (Steinheim, Germany), while the cake flour was purchased from PRIMA RND (Prima Group, Singapore,

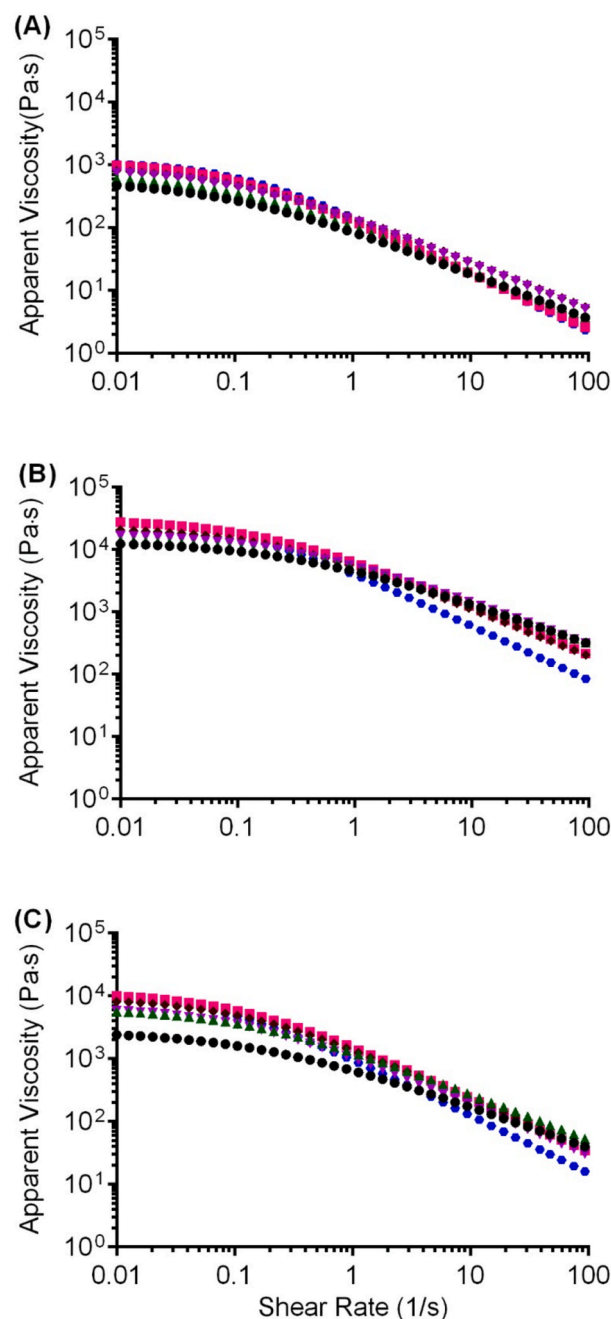


Fig. 1. Steady shear flow curves for the (A) starch system, (B) gluten system, and (C) starch-gluten system. The κ-carrageenan (κ-C) concentrations are: ●, 0 g/100 g; ▲, 0.5 g/100 g; ▼, 1.0 g/100 g; ◆, 2.0 g/100 g; ■, 5.0 g/100 g; ●, 10.0 g/100 g.

Singapore). All the other chemicals and standards in analytical grade (AR) were got from Sigma Aldrich (Steinheim, Germany). The starch content was determined using an enzymatic procedure by producing free glucose, which was then determined by the glucose oxidase/peroxidase method (Carpenter & Ward, 2017). The dry gluten content was determined by a method adapted from Kaushik, Kumar, Sihag, and Ray (2015), which washing the prepared dough until the wash water was clear and then freeze-drying the wet gluten. The moisture content was analysed using the air oven method (AOAC, 2005), which was drying at 105 °C for 12 h. Amylose content was determined by colourimetric method after iodine binding, which was adapted from Haslinda, Cheng, Chong, and Aziah (2009).

The compositions of the raw materials are shown in Table 1. The

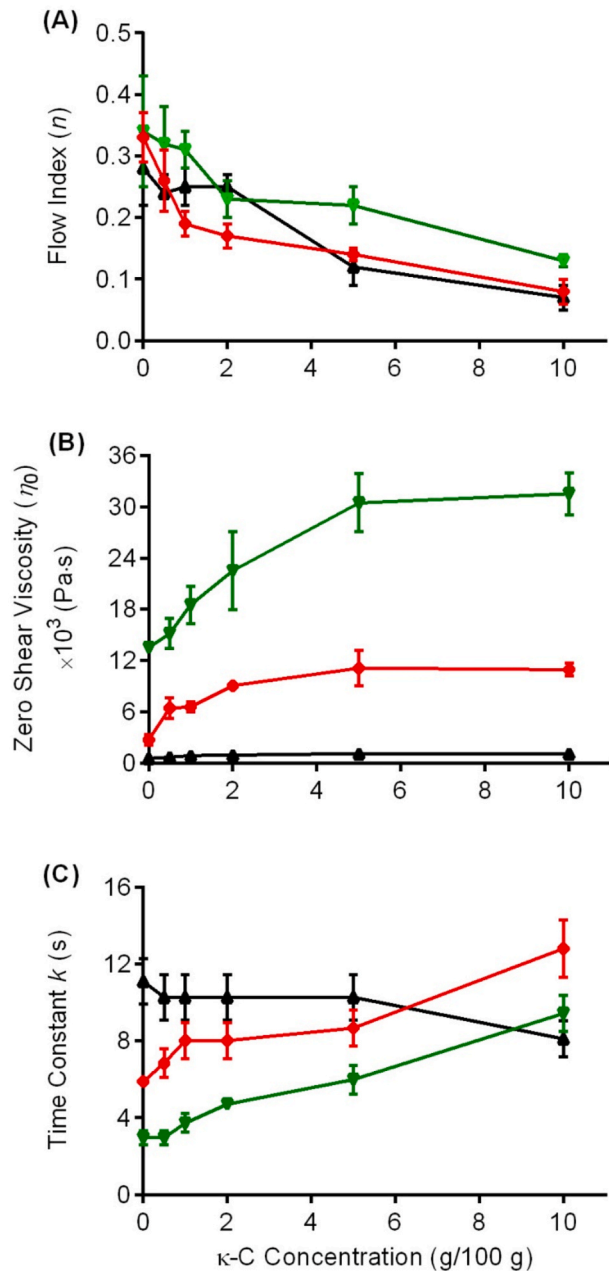


Fig. 2. Cross model parameters fitted for the starch system (▲), gluten system (▼), and starch-gluten system (◆). The parameters are: (A) the flow behaviour index n , (B) the zero shear viscosity η_0 , and (C) the time constant k .

starch to gluten ratio of the cake flour was 91/9 based on the chemical analysis.

2.2. Sample preparation

Starch/ κ -C, gluten/ κ -C, and starch/gluten/ κ -C mixed systems were prepared with variable concentration of κ -C (0.5, 1.0, 2.0, 5.0, and 10.0 g/100 g starch) based on the mass of dry starch (Table 2). The systems were stirred with deionised water based on the moisture content of 68.0 g/100 g dry basis for about 15 min and allowed to stabilise for another 20 min in a sealed container before further tests (Baldino, Laitano, Lupi, Curcio, & Gabriele, 2018; Hernández-Estrada, Rayas-Duarte, Figueroa, & Morales-Sánchez, 2014). The ratio of starch to gluten in the mixed systems was based on the chemical properties of cake flour and was kept constant.

2.3. Rheological tests

Rheological measurements were carried out using a stress-controlled rheometer (MCR 102, Anton Paar, Graz, Austria), equipped with a Peltier temperature controller. A plate-plate geometry (25 mm diameter) was used. Before the measurements, the samples were equilibrated at 30 °C for 5 min and covered with a thin layer of oil to avoid evaporation during measurement (Fu, Che, Li, Wang, & Adhikari, 2016; Yang & Yang, 2020). The measurements were conducted at 30 °C with the exception of dynamic mechanical thermal analysis (DMTA), and with a fixed gap of 1 mm.

2.3.1. Steady shear flow test

The steady shear flow test was conducted over shear rate of 0.01–100 s^{-1} to obtain flow curves. The curves were fitted using Cross model (Ravi & Bhattacharya, 2004) and are shown in Eq (1).

$$\eta = \eta_{\infty} + \frac{\eta_0 - \eta_{\infty}}{1 + (k\dot{\gamma})^{(1-n)}} \quad \text{Eq (1)}$$

where η (Pa·s) is the apparent viscosity, $\dot{\gamma}$ (s^{-1}) is the shear rate, η_0 and η_{∞} (Pa·s) represent the viscosity values at zero and infinite shear rates respectively, k (s) is the time constant and n is the flow index.

Values of η_{∞} were obtained from experimental results corresponding to the equilibrium viscosity obtained at the end of shearing. In scenarios whereby $\eta_0 \gg \eta_{\infty}$, it was assumed that $\eta_0 - \eta_{\infty} \approx \eta_0$. Thus, Eq (1) could be rewritten as Eq (2) (Mori Cortés, Lorenzo, & Califano, 2018; Ravi & Bhattacharya, 2004).

$$\eta = \frac{\eta_0}{1 + (k\dot{\gamma})^{(1-n)}} \quad \text{Eq (2)}$$

2.3.2. Frequency sweep test

The frequency sweep analysis was conducted over frequencies of 0.1–100 Hz at a strain amplitude of 0.1%, which was within the linear viscoelastic region according to the strain sweep tests (data not shown). The storage modulus G' , and loss modulus G'' , were fitted against angular frequency using the expressions shown in Eq (3) and Eq (4) to explain the frequency dependency of G' and G'' .

$$\log G' = \log a' + b' \log \omega \quad \text{Eq (3)}$$

$$\log G'' = \log a'' + b'' \log \omega \quad \text{Eq (4)}$$

where ω (rad/s) is the angular frequency and a' , a'' , b' and b'' are the corresponding fitting parameters (Arp, Correa, & Ferrero, 2018; Moreira, Chenlo, & Torres, 2011). The goodness of model fitting was tested by R -square (R^2) and root mean squared error (RMSE) using MATLAB R2014b (Mathworks Inc., Natick, MA, USA).

2.3.3. Creep-recovery tests

Creep-recovery tests were conducted according to literature (Fu et al., 2016; Moreira et al., 2011) at a constant stress of 50 Pa within linear viscoelastic region. The changes in shear strain as a function of the applied stress was measured for 180 s. The applied stress was then removed and the variation in strain was recorded for another 300 s. The creep data were defined using the creep compliance rheological parameters, $J(t)_C$ (Pa^{-1}) = γ/σ , where γ is the strain and σ is the constant shear stress during the creep test. The creep compliance data of dough samples was fitted to Burgers model, as shown in Eq (5) and Eq (6) for the creep and recovery phases, respectively.

$$J(t)_C = J_0 + J_m(1 - \exp(-t/\lambda)) + t/\eta_0 \quad \text{Eq (5)}$$

$$J(t)_R = J_{max} - J_0 - J_m(1 - \exp(-t/\lambda)) \quad \text{Eq (6)}$$

where J_0 (Pa^{-1}), J_m (Pa^{-1}) and J_{max} (Pa^{-1}) are the instantaneous, viscoelastic and maximum creep compliance values, respectively, t (s) is

Table 3
Parameters of the frequency sweep for different systems.

Group		G' (Pa)				G'' (Pa)			
		$a' \times 10^4$ (Pa)	b' (Pa•s)	R^2	RMSE	$a'' \times 10^4$ (Pa)	b'' (Pa•s)	R^2	RMSE
Starch system	S	3.5	0.10	0.976	0.015	0.9	0.23	0.964	0.037
	S/ κ -C 0.5	4.5	0.12	0.978	0.020	1.4	0.22	0.952	0.041
	S/ κ -C 1	4.6	0.12	0.984	0.026	1.7	0.20	0.936	0.044
	S/ κ -C 2	6.0	0.13	0.991	0.022	1.9	0.20	0.929	0.047
	S/ κ -C 5	7.4	0.14	0.996	0.016	2.6	0.16	0.910	0.051
	S/ κ -C 10	8.9	0.12	0.990	0.025	3.3	0.15	0.902	0.052
	Pooled SD	0.8	0.02			0.4	0.01		
Gluten system	G	0.3	0.31	0.997	0.076	0.1	0.42	0.997	0.029
	G/ κ -C 0.5	0.3	0.29	0.996	0.023	0.1	0.39	0.999	0.032
	G/ κ -C 1	0.5	0.29	0.996	0.030	0.2	0.39	0.997	0.035
	G/ κ -C 2	0.7	0.28	0.995	0.020	0.3	0.39	0.998	0.012
	G/ κ -C 5	3.0	0.28	0.998	0.016	1.2	0.37	0.995	0.011
	G/ κ -C 10	7.5	0.21	0.993	0.012	3.0	0.32	0.999	0.011
	Pooled SD	0.2	0.04			0.1	0.01		
Starch-Gluten system	SG	5.0	0.13	0.992	0.015	1.5	0.22	0.961	0.038
	SG/ κ -C 0.5	6.5	0.12	0.991	0.016	1.5	0.23	0.969	0.034
	SG/ κ -C 1	7.0	0.12	0.991	0.017	1.7	0.22	0.967	0.036
	SG/ κ -C 2	7.9	0.13	0.992	0.018	2.2	0.21	0.954	0.041
	SG/ κ -C 5	9.3	0.13	0.995	0.013	2.7	0.20	0.958	0.037
	SG/ κ -C 10	9.4	0.15	0.998	0.014	3.1	0.18	0.946	0.041
	Pooled SD	1.0	0.01			0.4	0.01		

* Number of replications: triplicate. S: starch; G: gluten; κ -C: κ -carrageenan. Pooled SD: pooled standard deviation.

the measurement time, λ (s) is the mean retardation time value, while η_0 (Pa•s) is the zero-shear viscosity.

2.3.4. Dynamic mechanical thermal analysis (DMTA) with oscillatory measurements

DMTA with oscillatory measurements was measured according to [Jekle et al. \(2016\)](#) at 0.1% strain amplitude and 1 Hz frequency with some modification. An oscillatory time sweep was conducted for 1 min at the initial equilibrium temperature of 30 °C, followed by a temperature sweep from 30 °C to 98 °C with a temperature increase of 4 °C/min. The sample was held for 3 min at 98 °C at the end of the heating phase. The correlation of loss factor ($\tan \delta$) was got and used to determine the onset of the starch gelatinisation temperature (T_0). The maximum of gelatinisation was defined as T_1 , where T_1 corresponds to the peak of G^* values ([Jekle et al., 2016](#)).

2.4. Statistical analyses

Three technological repetitions were done for each sample. All analyses were carried out independently in triplicate and the results were reported as the mean values, and the pooled standard deviations were calculated.

3. Results and discussion

3.1. Effect of κ -C on the apparent shear viscosity

To investigate the effect of κ -C on the apparent viscosity of the different systems, steady shear flow tests were conducted, and the results are shown in [Fig. 1](#). Overall, the samples exhibited shear-thinning behaviour. Throughout all the three systems, the viscosity remained relatively constant at low shear rates and subsequently increasing shear rates led to decreased viscosity.

The Cross model parameters are summarised in [Fig. 2](#). All systems showed a decrease in n values with increasing κ -C concentration ([Fig. 2A](#)). The addition of partially gelatinized corn starch is the reason of increasing shear thinning behaviour in samples since it has high water holding capacity ([Fu et al., 2016](#)). Here same conclusion can be got because of the addition of κ -C in different systems. The hydrocolloid could swell and have a weaker structure during shearing action and then act as a lubricant ([Fu et al., 2016](#)). Thus, the increasing κ -C

concentration was the reason of the increasing shear thinning behaviour in all samples. However, there was no difference in the decreasing trends among the different systems, indicating that the influence of κ -C on the n values was similar in the different systems.

The addition of κ -C led to an increase in η_0 values in all systems ([Fig. 2B](#)). Values of η_0 indicated the viscosity of the sample independent of shear rate, which was represented as a plateau region in the flow curves ([Rouillé, Della Valle, Lefebvre, Sliwinski, & vanVliet, 2005](#)). The η_0 values of starch-gluten system were between the values of the starch and gluten systems at each κ -C concentration. The addition of κ -C had a more marked effect on gluten than on starch. As a linear anionic hydrocolloid, κ -C has the ability to interact with gluten, resulting in more disordered and less cross-linked protein structures ([Li, Li, & Yadav, 2019](#)). Starch is a larger aggregate and the added κ -C could not interact with it as easily as with gluten.

The values of k were similar in starch system but increased in the other systems with increasing κ -C concentration ([Fig. 2C](#)). The long chain of κ -C might break the aggregation of macromolecules in the gluten and starch-gluten systems because the increase in k values indicates a higher rate of breakdown of agglomerates in the samples ([Ravi & Bhattacharya, 2004](#)). There was no significant breakdown in the starch system because starch is a larger aggregate and is hard to connect with long chain hydrocolloids through forming new bonds without heating.

3.2. Effect of κ -C on the viscoelastic characteristics

The frequency sweep test showed that all samples had $G' > G''$ ([Fig. S1](#)), indicating that the samples had a more elastic than viscous behaviour. In addition, increasing κ -C concentration led to increased G' and G'' values. Higher G' values would also indicate greater firmness of the samples with the addition of κ -C. Similar trends are found in cake batters, model dough systems, and flour paste when hydrocolloids are added to the formulation ([Fu et al., 2016](#); [Hesso et al., 2015](#); [Martínez, Macías, Belorio, & Gómez, 2015](#); [Sanz, Fernández, Salvador, Muñoz, & Fiszman, 2005](#)).

The values of parameters a' , a'' , b' , and b'' for all samples are summarised in [Table 3](#). Only the frequency range of 1–100 Hz was used to fit in [Eq \(3\)](#) and [Eq \(4\)](#) because the values tend to plateau at a lower range (<1 Hz) and indicated structured and gelled samples. The observation that $a' > a''$ in all systems verified the presence of a predominantly

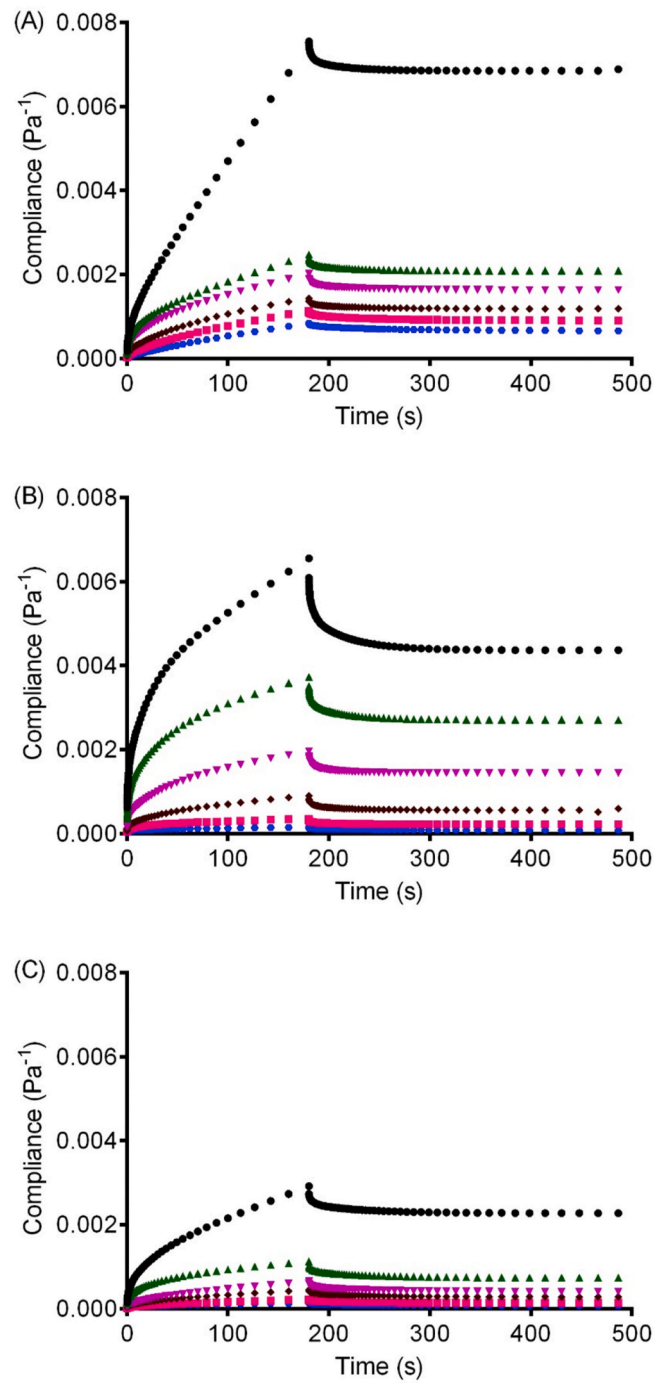


Fig. 3. Creep recovery graphs fitted into Burger's model. (A) Starch system; (B) gluten system; (C) starch-gluten system. The κ -carrageenan (κ -C) concentrations are: ●, 0 g/100 g; ▲, 0.5 g/100 g; ▼, 1.0 g/100 g; ◆, 2.0 g/100 g; ■, 5.0 g/100 g; ●, 10.0 g/100 g.

Table 4
Parameters of Burger's model in the creep phase and recovery phase.

	Sample	Creep phase					Recovery phase			
		$J_0 \times 10^{-4}$ (Pa ⁻¹)	$J_m \times 10^{-3}$ (Pa ⁻¹)	$J_{max} \times 10^{-3}$ (Pa ⁻¹)	λ (s)	$\eta_0 \times 10^8$ (Pa·s)	$J_0 \times 10^{-3}$ (Pa ⁻¹)	$J_m \times 10^{-3}$ (Pa ⁻¹)	$J_{max} \times 10^{-4}$ (Pa ⁻¹)	
Starch system	S	9.3	6.6	7.5	102.0	0.3	7.0	6.4	5.6	
	S/ κ -C 0.5	4.2	2.1	2.5	69.5	1.8	2.1	1.7	3.9	
	S/ κ -C 1	3.8	1.6	2.0	67.4	2.2	1.6	1.2	3.9	
	S/ κ -C 2	2.5	1.2	1.4	74.2	1.9	1.2	0.9	2.5	
	S/ κ -C 5	2.3	0.9	1.1	88.1	2.6	0.9	0.7	2.3	
	S/ κ -C 10	2.3	0.6	0.8	98.6	3.3	0.7	0.5	1.8	
	Pooled SD	1.2	0.4	0.5	6.6	0.7	0.5	0.5	1.3	
Gluten system	G	20.8	4.5	6.5	45.3	0.7	4.4	2.2	20.2	
	G/ κ -C 0.5	10.0	2.7	3.7	41.7	1.5	2.7	1.7	10.2	
	G/ κ -C 1	5.0	1.5	2.0	52.5	2.4	1.4	0.9	5.2	
	G/ κ -C 2	3.4	0.6	0.9	60.1	4.5	0.6	0.3	3.3	
	G/ κ -C 5	1.3	0.2	0.4	34.8	13.8	0.2	0.1	1.4	
	G/ κ -C 10	0.7	0.1	0.2	29.0	33.3	0.1	0.1	0.7	
	Pooled SD	1.3	0.5	0.5	6.3	1.5	0.4	0.3	2.8	
Starch-Gluten system	SG	6.3	2.3	2.9	70.2	1.1	2.28	1.63	0.7	
	SG/ κ -C 0.5	3.3	0.8	1.1	42.3	4.7	0.74	0.35	3.9	
	SG/ κ -C 1	2.5	0.4	0.7	76.7	4.5	0.41	0.16	2.5	
	SG/ κ -C 2	1.7	0.3	0.5	71.4	6.8	0.28	0.11	1.7	
	SG/ κ -C 5	1.3	0.1	0.2	78.1	11.9	0.14	0.08	0.6	
	SG/ κ -C 10	0.1	0.1	0.1	66.5	22.4	0.07	0.01	0.7	
	Pooled SD	0.3	0.2	0.1	5.7	1.4	0.07	0.05	0.2	

* Number of replications: triplicate. S: starch; G: gluten; κ -C: κ -carrageenan. Pooled SD: pooled standard deviation.

elastic rather than viscous structure. Increasing κ -C concentrations led to the increased a' and a'' values in all systems. The gluten showed a differences only at high κ -C concentrations (≥ 5 g/100 g). However, κ -C had an effect on the a' values in the starch system at lower concentrations (≥ 2 g/100 g). The final a' and a'' values in starch-gluten system were closer to those in starch system. The values of b' were similar, while the values of b'' tended to decrease at high κ -C concentrations in the three systems (Table 3). This suggested that the addition of κ -C decreased the frequency dependency and sensitivity of the samples. The decrease in dependency would produce samples with greater stability than the control sample (Fu et al., 2016). The entanglement of κ -C with starch and gluten could result in increased stiffness and firmness of the samples. Similar results are reported by other authors (Martínez et al., 2015).

3.3. Effect of κ -C on creep-recovery tests

The creep deformation and recovery test provides insights into the behaviour of the various samples under mechanical stress and when the mechanical stress is removed. The creep-recovery curves of all systems are shown in Fig. 3. Qualitatively, the creep-recovery curves showed the same shape in each system, whereby the unrecoverable viscous proportion was larger than the recoverable elastic proportion. The curves exhibited a shape similar to that of wheat flour dough, which represented a typical viscoelastic behaviour (Moreira, Chenlo, Torres, & Prieto, 2010; Rouillé et al., 2005; Sivaramakrishnan, Senge, & Chattopadhyay, 2004; Zhang, Mu, & Sun, 2017). The starch-gluten system had lower creep recovery compliance than the other two systems and meant that starch-gluten samples were firmer.

Table 4 summarises the parameters of Burgers model using Eq (5) and Eq (6) in the creep and recovery phase. The values of creep compliances for control samples without κ -C were higher than those for other samples, suggesting these control samples were softer. Thus, the addition of κ -C resulted in firmer samples that were more resistant towards deformation. The values of J_0 , J_m , and J_{max} showed a decreasing trend with increasing κ -C concentration in gluten system and starch-gluten system. The retardation time (λ) is the delayed response to an applied stress, representing the time required for the applied stress

decreasing to 36.8% of the initial stress (Sheng, Wang, Li, Mao, & Adhikari, 2014). The λ values fluctuated with increasing κ -C concentration in all systems, but the starch-gluten system had a similar trend with the starch system. The η_0 in the creep recovery test reflected the flowability of the samples at the end of the applied load. Increasing κ -C concentrations led to an increase in η_0 values, resulting in more viscous samples and greater resistance to flow as compared with the control (Fu et al., 2016). This further validated the results in frequency test whereby the addition of κ -C in all systems led to increases in G'' values.

Similar to the trend in the creep phase, the addition of κ -C led to a decrease in J_0 , J_m , and J_{max} values in the recovery phase. Lower J_m values indicate that the unrecoverable proportion of the sample remains relatively constant during the recovery phase and that recovery is more instantaneous when compared with that under higher J_m values (Moriera et al., 2011). Based on these parameters, gluten was more sensitive for the κ -C concentrations in creep-recovery test and then influenced the changes in starch-gluten system.

3.4. Effect of κ -C on dynamic mechanical thermal analysis (DMTA)

DMTA could be investigated to analyse the effects of temperature on the changes in structure of the sample. This is because the rheological properties of dough and batter systems change during heat treatment due to the changes in starch gelatinisation and protein denaturation (Sasaki, Yasui, & Matsuki, 2000). These changes serve as determinants in the formation of pores, stability, and eventually, the texture of the final baked goods. Fig. 4 shows the changes in G^* values as the temperature increased. Overall, similar to the previous frequency test, increasing κ -C concentrations led to an increase in G^* values, which indicated that the addition of κ -C to the model systems led to an increase in firmness.

With the increase in temperature, the G^* values gradually decreased first, indicating the softening of samples, attributed by the chemical changes due to heat treatment such as weakening of starch and gluten proteins networks (Rosell, Collar, & Haros, 2007). Subsequently, the increase in temperature led to a gradual increase in G^* values in starch and starch-gluten systems, reaching a peak at T_1 . The gluten system showed a different trend compared with that of the other systems

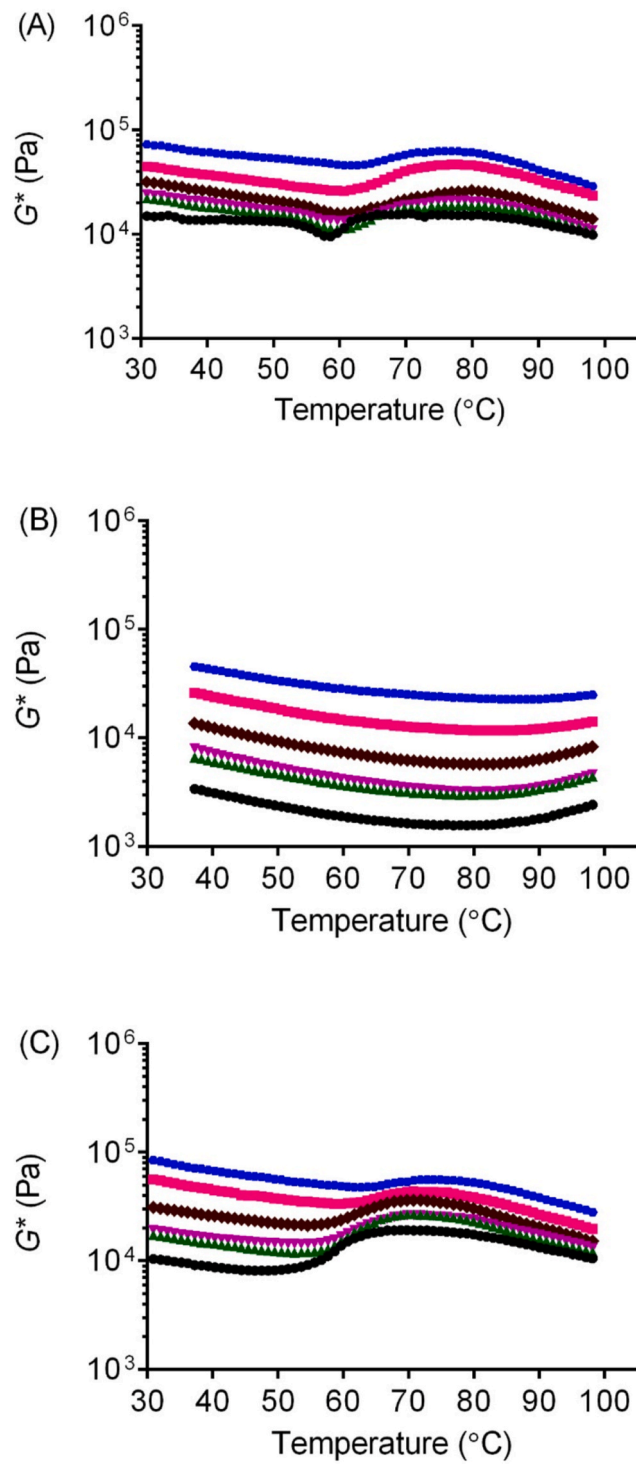


Fig. 4. Complex shear modulus (G^*) over the range of temperature in different systems. (A) Starch system; (B) gluten system; (C) starch-gluten system. The κ -C concentrations are: ●, 0 g/100 g; ▲, 0.5 g/100 g; ▼, 1.0 g/100 g; ◆, 2.0 g/100 g; ■, 5.0 g/100 g; ●, 10.0 g/100 g.

Table 5

Parameters of dynamic mechanical thermal analysis (DMTA) measurements for the different systems.

Group		Parameter	
		T_0 (°C)	T_1 (°C)
Starch system	S	58.6	70.4
	S/ κ -C 0.5	60.3	79.2
	S/ κ -C 1	61.2	79.6
	S/ κ -C 2	63.0	79.6
	S/ κ -C 5	64.4	77.9
	S/ κ -C 10	66.2	77.2
	Pooled SD	0.7	0.8
Starch gluten system	SG	58.3	69.8
	SG/ κ -C 0.5	59.7	71.8
	SG/ κ -C 1	60.7	72.8
	SG/ κ -C 2	61.0	71.5
	SG/ κ -C 5	64.4	72.4
	SG/ κ -C 10	65.1	73.8
	Pooled SD	0.5	0.9

* Number of replications: triplicate. S: starch; G: gluten; κ -C: κ -carrageenan. Pooled SD: pooled standard deviation.

because of the absence of starch (starch gelatinisation process). Subsequently, the increase in temperature after the peak at T_1 in starch and starch-gluten systems would then lead to the decrease in G^* values. The decrease in G^* values after T_1 could be attributed to the disruption of starch granules and the melting of crystalline structure (Champenois, Rao, & Walker, 1998; Jekle et al., 2016). The maximum of gelatinisation temperatures (T_1) are summarised in Table 5. The addition of κ -C increased the T_1 values in both starch and starch-gluten systems. This means that the gelatinisation maximum occurred at a higher temperature.

Fig. 5 shows the changes in $\tan \delta$ values as the temperature increased. The starch and starch-gluten systems had similar trends while the gluten system was different since the absence of starch in it. The onset of the starch gelatinisation temperature (T_0) was determined and summarised in Table 5. The addition of κ -C led to an increase in T_0 , indicating a delay in the onset of the starch gelatinisation process. Delay of the starch gelatinisation process was significant at low κ -C concentrations in both the starch and starch-gluten system.

Carrageenan, as a hydrocolloid, has high water binding capacity (Tan, Tan, & Easa, 2018). Thus, added κ -C would compete with starch for the available water molecules. Wilderjans, Luyts, Goesaert, Brijs, and Delcour (2010) also reported that a lower moisture content in model cake batters results in a delay in the starch gelatinisation process. The delay in the starch gelatinisation process can have positive effects on cake quality because it could delay the onset of structure formation during the baking process, leading to greater spring values and less firmness (Schirmer, Jekle, Arendt, & Becker, 2012; Wilderjans et al., 2010).

3.5. Proposed interactions on the effect of κ -C on the model system

A schematic model was proposed to explain the effects of κ -C on starch and gluten (Fig. 6). As a linear anionic hydrocolloid, κ -C has the ability to interact with gluten, resulting in more disordered and less cross-linked protein structures (León et al., 2000; Li et al., 2019). The interaction between κ -C and starch granules exhibited a partial exclusion effect (Lascombes et al., 2017). The addition of κ -C would interact with limited free water molecules and form κ -C-water complexes, and some κ -C interacted with gluten as well. As a result, the κ -C addition increased the overall formation of the network, which led to higher α' and α'' values in the frequency tests as well as increased firmness of the samples, which translated to a decrease in creep compliance values (Table 3 & Table 4). Moreover, the viscosity of the system increased because of the addition of κ -C led to crowding of molecules (Huc et al., 2014). It is well-known that carrageenan as a hydrocolloid has high

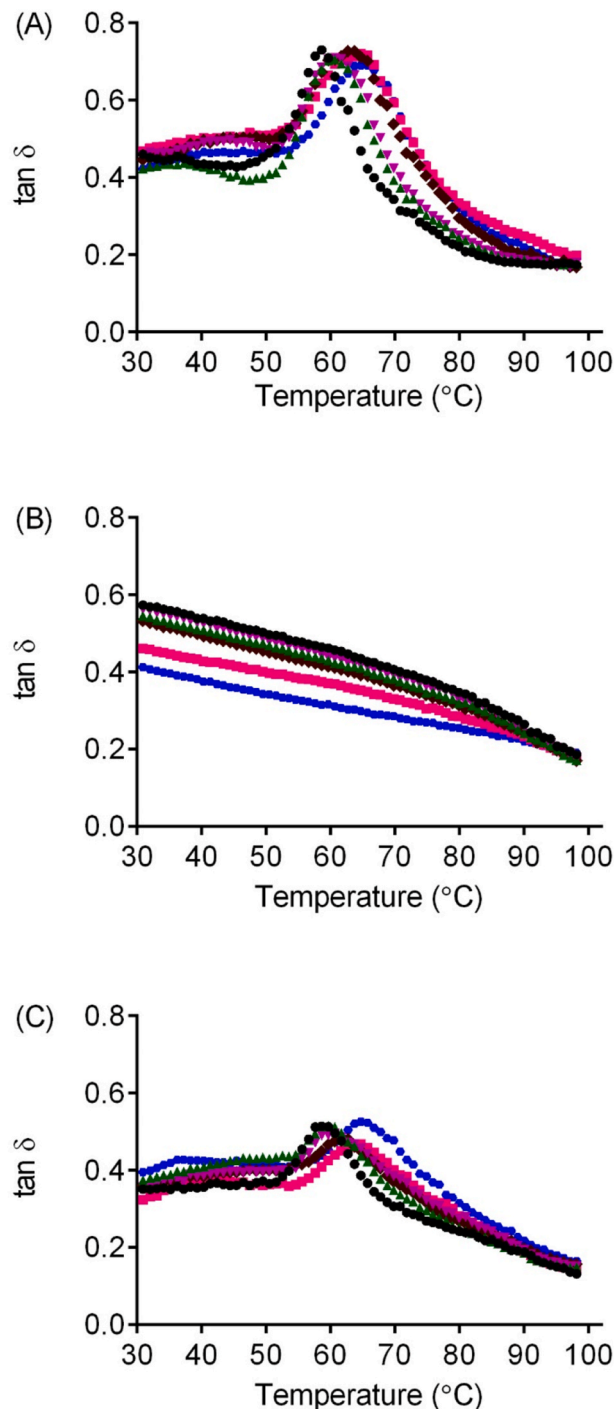


Fig. 5. Values of $\tan \delta$ over the range of temperature in different systems. (A) Starch system; (B) gluten system; (C) starch-gluten system. The κ -C concentrations are: ●, 0 g/100 g; ▲, 0.5 g/100 g; ▼, 1.0 g/100 g; ◆, 2.0 g/100 g; ■, 5.0 g/100 g; ●, 10.0 g/100 g.

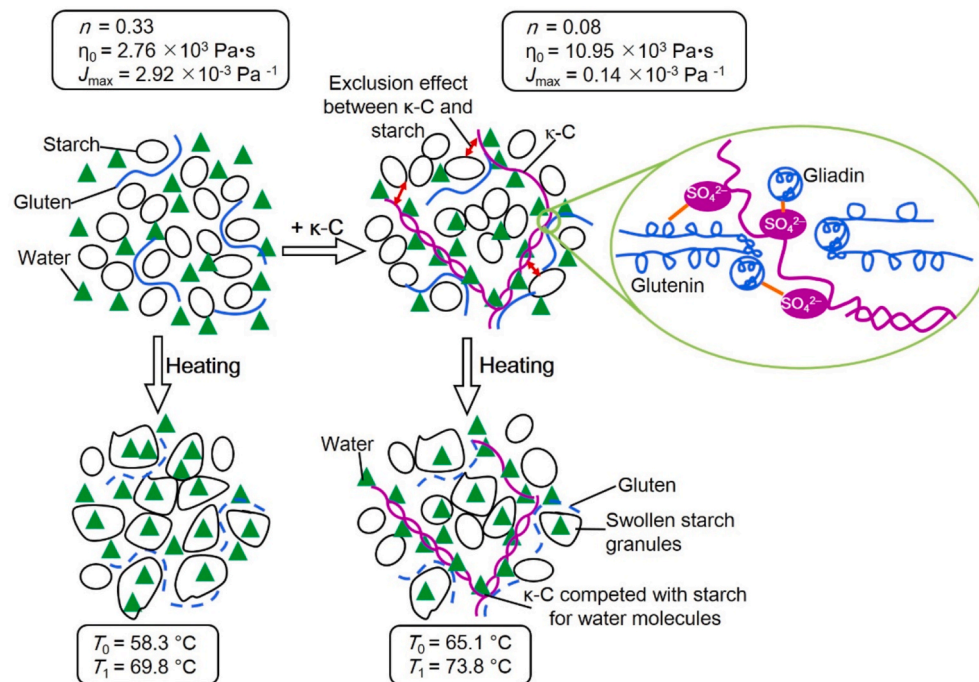


Fig. 6. Schematic diagram of the κ -C effect on starch-gluten system.

water binding capacity (Tan et al., 2018), thus we speculated that the interaction of κ -C and free water molecules may lower the water activity of the system compared with that in the control sample (Fig. 6). The system would require higher energy to overcome the energy barrier required for the starch gelatinisation process (Kim, Patel, & BeMiller, 2013), eventually leading to an increased starch gelatinisation temperature (Table 5).

4. Conclusions

In summary, the addition of κ -C in different systems exhibited different rheological properties. Increasing the κ -C concentrations in all systems led to an increase in both viscosity and G' and G'' moduli, indicating greater firmness of the sample, which caused by the entanglement of κ -C with starch and gluten. Moreover, increasing κ -C also led to decreasing creep compliance, indicating the samples had a higher resistance towards deformation. Gluten was more sensitive for the κ -C concentrations in creep-recovery test and then influenced the changes in starch-gluten system. Lastly, the addition of κ -C caused a delay in the onset of the starch gelatinisation process. The delay in the starch gelatinisation process could be caused by the lower water activity in the system after the addition of κ -C resulting from the high water holding capability of κ -C. These results could provide a better understand of the interactions of carrageenan with cake flour components and could promote the potential application of carrageenan-containing materials like *Eucheuma* in bakery products.

CRedit authorship contribution statement

Min Huang: Data curation, Formal analysis, Investigation, Methodology, Resources, Software, Validation, Visualization, Writing - original draft. **Alicia Hui Ping Theng:** Data curation, Formal analysis, Writing - original draft. **Dongying Yang:** Data curation, Formal analysis, Methodology. **Hongshun Yang:** Conceptualization, Funding acquisition, Project administration, Supervision, Writing - review & editing.

Declaration of competing interest

None.

Acknowledgements

This work was financially supported by the Singapore NRF Industry IHL Partnership Grant (R-143-000-653-281), student support (R-160-002-653-281) and an industry project from Guangzhou Welbon Biological Technology Co., Ltd (R-2017-H-002).

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.lwt.2020.110324>.

References

- AOAC. (2005). Official method 925.10 solids (total) and moisture in flour. In *Official methods of analysis* (18th ed.). Gaithersburg: AOAC International.
- Arp, C. G., Correa, M. J., & Ferrero, C. (2018). Rheological and microstructural characterization of wheat dough formulated with high levels of resistant starch. *Food and Bioprocess Technology*, 11(6), 1149–1163.
- Baldino, N., Laitano, F., Lupi, F. R., Curcio, S., & Gabriele, D. (2018). Effect of HPMC and CMC on rheological behavior at different temperatures of gluten-free bread formulations based on rice and buckwheat flours. *European Food Research and Technology*, 244(10), 1829–1842.
- Bárceñas, M. A. E., Benedito, C., & Rosell, C. M. (2004). Use of hydrocolloids as bread improvers in interrupted baking process with frozen storage. *Food Hydrocolloids*, 18(5), 769–774.
- Campo, V. L., Kawano, D. F., Silva, D. B., & Carvalho, I. (2009). Carrageenans: Biological properties, chemical modifications and structural analysis – a review. *Carbohydrate Polymers*, 77(2), 167–180.
- Carpenter, C. E., & Ward, R. E. (2017). Glucose determination by enzyme analysis. In S. S. Nielsen (Ed.), *Food analysis laboratory manual* (pp. 203–206). Cham: Springer International Publishing.
- Champanois, Y., Rao, M. A., & Walker, L. P. (1998). Influence of gluten on the viscoelastic properties of starch pastes and gels. *Journal of the Science of Food and Agriculture*, 78(1), 119–126.
- Fu, Z., Che, L., Li, D., Wang, L., & Adhikari, B. (2016). Effect of partially gelatinized corn starch on the rheological properties of wheat dough. *Lebensmittel-Wissenschaft und -Technologie- Food Science and Technology*, 66, 324–331.
- Haslinda, W. H., Cheng, L. H., Chong, L. C., & Aziah, A. A. N. (2009). Chemical composition and physicochemical properties of green banana (*Musa acuminata* ×

- balbisiana Colla cv. Awak) flour. *International Journal of Food Sciences & Nutrition*, *60*, 232–239.
- Hernández-Estrada, Z. J., Rayas-Duarte, P., Figueroa, J. D. C., & Morales-Sánchez, E. (2014). Creep recovery tests to measure the effects of wheat glutenins on doughs and the relationships to rheological and breadmaking properties. *Journal of Food Engineering*, *143*, 62–68.
- Hesso, N., Loisel, C., Chevallier, S., Marti, A., Le-Bail, P., Le-Bail, A., et al. (2015). The role of ingredients on thermal and rheological properties of cake batters and the impact on microcake texture. *Lebensmittel-Wissenschaft und -Technologie- Food Science and Technology*, *63*(2), 1171–1178.
- Huang, M., & Yang, H. (2019). *Eucheuma* powder as a partial flour replacement and its effect on the properties of sponge cake. *Lebensmittel-Wissenschaft und -Technologie- Food Science and Technology*, *110*, 262–268.
- Huc, D., Matignon, A., Barey, P., Desprairies, M., Mauduit, S., Sieffermann, J. M., et al. (2014). Interactions between modified starch and carrageenan during pasting. *Food Hydrocolloids*, *36*, 355–361.
- Jekle, M., Mühlberger, K., & Becker, T. (2016). Starch–gluten interactions during gelatinization and its functionality in dough like model systems. *Food Hydrocolloids*, *54*, 196–201.
- Jumaidin, R., Sapuan, S. M., Jawaid, M., Ishak, M. R., & Sahari, J. (2017). Characteristics of *Eucheuma cottonii* waste from East Malaysia: Physical, thermal and chemical composition. *European Journal of Phycology*, *52*(2), 200–207.
- Kaushik, R., Kumar, N., Sihag, M. K., & Ray, A. (2015). Isolation, characterization of wheat gluten and its regeneration properties. *Journal of Food Science & Technology*, *52*(9), 5930–5937.
- Kim, H. S., Patel, B., & BeMiller, J. N. (2013). Effects of the amylose–amylopectin ratio on starch–hydrocolloid interactions. *Carbohydrate Polymers*, *98*(2), 1438–1448.
- Kohajdová, Z., & Karovičová, J. (2009). Application of hydrocolloids as baking improvers. *Chemical Papers*, *63*(1), 26–38.
- Lascombes, C., Agoda-Tandjawa, G., Boulenguer, P., Le Garnec, C., Gilles, M., Mauduit, S., et al. (2017). Starch–carrageenan interactions in aqueous media: Role of each polysaccharide chemical and macromolecular characteristics. *Food Hydrocolloids*, *66*, 176–189.
- Lavelli, V., Guerrieri, N., & Cerletti, P. (1996). Controlled reduction study of modifications induced by gradual heating in gluten proteins. *Journal of Agricultural and Food Chemistry*, *44*(9), 2549–2555.
- León, A. E., Ribotta, P. D., Ausar, S. F., Fernández, C., Lanada, C. A., & Beltramo, D. M. (2000). Interactions of different carrageenan isoforms and flour components in breadmaking. *Journal of Agricultural and Food Chemistry*, *48*(7), 2634–2638.
- Li, Y., Li, C., Gu, Z., Hong, Y., Cheng, L., & Li, Z. (2017). Effect of modification with 1,4- α -glucan branching enzyme on the rheological properties of cassava starch. *International Journal of Biological Macromolecules*, *103*, 630–639.
- Li, J., Li, J., & Yadav, M. P. (2019). Effect of different hydrocolloids on gluten proteins, starch and dough microstructure. *Journal of Cereal Science*, *87*, 85–90.
- Martínez, M. M., Macías, A. K., Belorio, M. L., & Gómez, M. (2015). Influence of marine hydrocolloids on extruded and native wheat flour pastes and gels. *Food Hydrocolloids*, *43*, 172–179.
- Matos, M. E., Sanz, T., & Rosell, C. M. (2014). Establishing the function of proteins on the rheological and quality properties of rice based gluten free muffins. *Food Hydrocolloids*, *35*, 150–158.
- McCann, T. H., & Day, L. (2013). Effect of sodium chloride on gluten network formation, dough microstructure and rheology in relation to breadmaking. *Journal of Cereal Science*, *57*(3), 444–452.
- Moreira, R., Chenlo, F., & Torres, M. D. (2011). Effect of sodium chloride, sucrose and chestnut starch on rheological properties of chestnut flour doughs. *Food Hydrocolloids*, *25*(5), 1041–1050.
- Moreira, R., Chenlo, F., Torres, M. D., & Prieto, D. M. (2010). Influence of the particle size on the rheological behaviour of chestnut flour doughs. *Journal of Food Engineering*, *100*(2), 270–277.
- Mori Cortés, N., Lorenzo, G., & Califano, A. N. (2018). Food grade microemulsion systems: Sunflower oil/castor oil derivative-ethanol/water. Rheological and physicochemical analysis. *Food Research International*, *107*, 41–47.
- Ozge Ozkoc, S., Sumnu, G., & Sahin, S. (2009). The effects of gums on macro and microstructure of breads baked in different ovens. *Food Hydrocolloids*, *23*(8), 2182–2189.
- Ravi, R., & Bhattacharya, S. (2004). Flow behaviour of chickpea (*Cicer arietinum* L.) flour dispersions: Effect of additives. *Journal of Food Engineering*, *65*(4), 619–624.
- Rosell, C. M., Collar, C., & Haros, M. (2007). Assessment of hydrocolloid effects on the thermo-mechanical properties of wheat using the Mixolab. *Food Hydrocolloids*, *21*(3), 452–462.
- Rouillé, J., Della Valle, G., Lefebvre, J., Sliwinski, E., & vanVliet, T. (2005). Shear and extensional properties of bread doughs affected by their minor components. *Journal of Cereal Science*, *42*(1), 45–57.
- Saha, D., & Bhattacharya, S. (2010). Hydrocolloids as thickening and gelling agents in food: A critical review. *Journal of Food Science & Technology*, *47*(6), 587–597.
- Sanz, T., Fernández, M. A., Salvador, A., Muñoz, J., & Fiszman, S. M. (2005). Thermogelation properties of methylcellulose (MC) and their effect on a batter formula. *Food Hydrocolloids*, *19*(1), 141–147.
- Sasaki, T., Yasui, T., & Matsuki, J. (2000). Effect of amylose content on gelatinization, retrogradation, and pasting properties of starches from waxy and nonwaxy wheat and their F1 seeds. *Cereal Chemistry*, *77*(1), 58–63.
- Schirmer, M., Jekle, M., Arendt, E., & Becker, T. (2012). Physicochemical interactions of polydextrose for sucrose replacement in pound cake. *Food Research International*, *48*, 291–298.
- Sheng, S., Wang, L., Li, D., Mao, Z., & Adhikari, B. (2014). Viscoelastic behavior of maize kernel studied by dynamic mechanical analyzer. *Carbohydrate Polymers*, *112*, 350–358.
- Sivaramakrishnan, H. P., Senge, B., & Chattopadhyay, P. K. (2004). Rheological properties of rice dough for making rice bread. *Journal of Food Engineering*, *62*(1), 37–45.
- Song, Y., & Zheng, Q. (2007). Dynamic rheological properties of wheat flour dough and proteins. *Trends in Food Science & Technology*, *18*(3), 132–138.
- Tan, H. L., Tan, T. C., & Easa, A. M. (2018). The use of selected hydrocolloids to enhance cooking quality and hardness of zero-salt noodles. *International Journal of Food Science and Technology*, *53*(7), 1603–1610.
- Tebben, L., & Li, Y. (2019). Effect of xanthan gum on dough properties and bread qualities made from whole wheat flour. *Cereal Chemistry*, *96*(2), 263–272.
- Uthayakumaran, S., Newberry, M., Phan-Thien, N., & Tanner, R. (2002). Small and large strain rheology of wheat gluten. *Rheologica Acta*, *41*(1), 162–172.
- Wilderjans, E., Luyts, A., Goesaert, H., Brijs, K., & Delcour, J. A. (2010). A model approach to starch and protein functionality in a pound cake system. *Food Chemistry*, *120*(1), 44–51.
- Yang, D., & Yang, H. (2020a). Effects of ethanol on gelation of iota-carrageenan. *Lebensmittel-Wissenschaft und -Technologie- Food Science and Technology*, *126*, Article 109281.
- Yang, D., & Yang, H. (2020b). The temperature dependent extraction of polysaccharides from euclidean and the rheological synergistic effect in their mixtures with kappa carrageenan. *LWT- Food Science and Technology*, *129*, Article 109515.
- Yang, Z., Yang, H., & Yang, H. (2018). Characterisation of rheology and microstructures of κ -carrageenan in ethanol-water mixtures. *Food Research International*, *107*, 738–746.
- Zhang, D., Mu, T., & Sun, H. (2017). Comparative study of the effect of starches from five different sources on the rheological properties of gluten-free model doughs. *Carbohydrate Polymers*, *176*, 345–355.