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Steady and dynamic oscillatory shear rheological properties of ketchup–processed cheese mixtures: Effect of temperature and concentration

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ABSTRACT

The steady and dynamic shear properties of ketchup–processed cheese (K–PC) mixtures were investigated at different temperatures (10–50 °C) and PC concentrations (0–30%). The K–PC mixtures showed a shear-thinning behavior with low magnitudes of yield stress. The consistency coefficient (K) and apparent viscosity (η_{50}) decreased with increase in temperature and concentration. The mixtures followed the Arrhenius temperature relationship, indicating that the magnitudes of activation energies (E_a) were in the range of 8.83–17.16 kJ mol^{-1}. Storage (G'), loss (G'') and complex (G^*) modulus increased with increase in frequency while complex viscosity (η^*) decreased. The K–PC mixtures at concentrations of 0–15% exhibited weak gel-like behavior. Increase in the PC concentration resulted in a decrease in G^*, G', G'' and η^* up to the 15% of PC concentration, showing a plateau value between 0% and 30% concentrations. Cox–Merz rule was not applicable to K–PC mixtures.

1. Introduction

Ketchup, one of the most important tomato products, is produced basically from either cold or hot extracted tomatoes; or directly from concentrates, purees and tomato paste (Sahin and Ozdemir, 2004). Although ketchup is known worldwide; information on this product is limited in the literature (Sharoba et al., 2005). Ketchup is time-independent, semi-solid non-Newtonian fluid having a definite yield stress (Sharoba et al., 2005). Based on dynamic shear data, it was also reported that the Cox–Merz rule was not applicable for commercial tomato ketchup samples (Bistany and Kokini, 1983), exhibiting properties similar to weak gels (Rao and Cooley, 1992).

Processed cheese is a dairy product obtained by mixing natural cheeses with emulsifying salts and water under the influence of heat and agitation. After homogenization of molten blend, the product is packed and cooled. In recent years, reduced- or low-fat processed cheeses have entered the marketplace (Drake and Swanson, 1995).

Milk proteins are commonly used as food ingredients in the formulation of various food products due to their unique functional characteristics like emulsifying, gelling, thickening, foaming and water binding (Kinsella and Whitehead, 1989). In addition to functional properties, milk proteins are also utilized because of their high nutritive value and GRAS status (Bryant and McClements, 1998; Harper, 2000; Hudson et al., 2000). They are used at optimal levels to improve texture, flavor and color of foods as well as to increase the amount of proteins with high biological value (Kilara, 1994). Because of the aforementioned reasons, ketchup could be supplemented or enriched with the sources containing dairy proteins like processed cheese to obtain a nutritionally enriched product.

Starch is commonly used as thickening agent (Sidhu et al., 1997; Srivastava, 1982). It is added to ketchup formulations because it has some functional properties such as formation of typical biopolymer gel network (Mohammed et al., 1998) and alteration of rheological properties such as thixotropic and rheopectic flow properties (Sharoba et al., 2005). Therefore, starch is assumed to play multifunctional role in a condiment system, providing viscosity at key processing points, as well as helping to maintain consistent suspension (Alam et al., 2009). For these reasons, starch is added to tomato ketchup in industry to achieve good quality of the final product (Hoover and Ratnayake, 2002).

Starch and milk proteins are present together in various dairy-based foods including custards (Doublier and Durand, 2008), yoghurts (Keogh and O'Kennedy, 1998) and processed cheeses (Mounsey and Oriordan, 2008a). From a scientific perspective, processed cheese is reported to provide an ideal model system to examine the interactions of the major food components – protein/fat/polysaccharides (starch) and water (Mounsey and Oriordan, 2008b). Studies about the interactions between starch and dairy proteins are limited in the literature compared to those of mixtures of milk proteins and other biopolymers in spite of the industrial

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Nomenclature

T	absolute temperature (K)	η_2	constant for concentration effect (Pa s)
E_a	activation energy (kJ mol^{-1})	$\eta_{c_{\exp,i}}$	experimental apparent viscosity (Pa s)
ω	angular frequency (rad s^{-1})	n	flow behavior index (dimensionless)
η	apparent viscosity (Pa s)	MPE	mean percentage error
η_{50}	apparent viscosity at 50 s^{-1} (Pa s)	MBE	mean bias error
$\eta_{c_{\exp,\mathrm{ave}}}$	average of experimental values (Pa s)	RMSE	root mean square error
χ^2	chi-square	K^*	intercept for complex viscosity (Pa s)
G^*	complex modulus (Pa)	K''	intercept for loss modulus (Pa)
η^*	complex viscosity (Pa s)	K'	intercept for storage modulus (Pa)
C	concentration ((%)$^{-1}$)	G''	loss modulus (Pa)
K	consistency coefficient (Pa s^n)	tan δ	loss tangent (dimensionless)
a_2	constant ((%)$^{-1}$)	EF	modelling efficiency
a_1	constant (dimensionless)	N	number of data points
A_1	constant for a fixed temperature ((%)$^{-1}$)	n_u	number of model parameters
A_2	constant for a fixed temperature (kJ mol^{-1})	$\eta_{c_{\mathrm{pre},i}}$	predicted apparent viscosity (Pa s)
B_1	constant for a fixed temperature (dimensionless)	$\dot{\gamma}$	shear rate (s^{-1})
B_2	constant for a fixed temperature ((%)$^{-1}$)	σ	shear stress (Pa)
η_0	constant for Arrhenius equation (Pa s)	n^*	slope for complex viscosity (dimensionless)
D_1	constant for combined effect ((%)$^{-1}$)	n''	slope for loss modulus (dimensionless)
D_2	constant for combined effect (dimensionless)	n'	slope for storage modulus (dimensionless)
η_3	constant for combined effect (Pa s)	G'	storage modulus (Pa)
η_4	constant for combined effect (Pa s)	R	universal gas constant (kJ mol^{-1} K^{-1})
η_1	constant for concentration effect (Pa s)	σ_0	yield stress (Pa)

importance and extensive investigation of starch and milk proteins separately (Noisuwan et al., 2009). Based on the fact, ketchup–processed cheese (K–PC) mixture could be an example of such interactions as the former includes starch and the later is a source of casein (milk protein) and fat.

Viscosity, usually considered as an important physical characteristic of fluid or semifluid foods is related to the quality of products. Therefore, the flow behavior information may be useful in quality control, energy input calculations, process design and selection of process equipment, such as heat exchangers and pumps. In addition, the rheological properties of fluid foods affect the sensory quality and consequently consumer preference. However, these properties are widely influenced by chemical composition, pH value, processing conditions and also by some added ingredients (Bowland and Foegeding, 2001; Marchesseau and Cuq, 1995; Piska and Šttina, 2004). The viscoelastic properties of macromolecular dispersions can be determined by using dynamic oscillatory shear rheological tests (Rao, 1999). In a dynamic test, sinusoidal strain cycle is utilized for the determination of the storage modulus (G'), loss modulus (G''), complex modulus (G^*) and complex viscosity (η^*). Previous studies indicate the presence of a correlation between steady shear and dynamic shear properties of macromolecular dispersions (Chun and Yoo, 2004). The Cox–Merz superposition rule which relates the complex dynamic shear viscosity (η^*) as a function of angular frequency (ω) to the steady shear flow viscosity (η) as a function of shear rate ($\dot{\gamma}$) has been experimentally confirmed for several macromolecular dispersions (Chun and Yoo, 2004), on the other hand, Da Silva and Rao (1992) reported that Cox–Merz rule was not valid for macromolecular dispersions with either hyperentanglements or aggregates.

No attempt has been made so far to study rheological properties of K–PC mixtures as a function of temperature and concentration. In particular, no information is available on the rheological properties of K–PC mixtures under both steady and dynamic shear. Therefore, this study was undertaken to determine the rheological behaviors of ketchup–processed cheese mixtures in steady and dynamic shear as affected by different temperatures (10–50 °C), concentration ranges (0–30%).

2. Materials and methods

2.1. Production of ketchup–processed cheese mixtures

In order to produce ketchup–processed cheese (K–PC) mixtures, ketchup and processed cheese were separately produced at first. Process flow chart for the production of ketchup (Cemeroğlu, 2004), processed cheese (Üçüncü, 2008) and the K–PC mixtures is presented in Fig. 1. In the production of ketchup, the starch used was stabilised and crosslinked waxy corn starch (Cargill®, Netherlands). In the production of processed cheese, the emulsifying salts (Kasomel®, French) used were mono-, di-, tri-sodium phosphate (Kasomel® 1110 and 1112) and Na-, K-, Ca-polyphosphate (Kasomel® 3392).

2.2. Chemical analysis

pH value, total protein, total fat and total solid contents of the samples were determined as outlined (AOAC, 2000). The pH values were determined at 25 °C using a pH meter (WTW-Inolab Level 3 Terminal, Weilheim, Germany). Protein content of the samples was determined using an automatic nitrogen analyzer (FP 528 LECO, ABD) based on the Dumas method. Gerber method was utilized for the determination of total fat content (Elmer, 1978). To determine total solid content, the samples were dried at 105 °C for about 4 h in a drying oven (Nuve FN 120, Ankara, Turkey) until constant weight. Total sugar analysis was conducted according to the Luff Schoorl method (European Economic Community, 1979). The color values of samples were measured with a colorimeter (Lovibond RT Series Reflectance Tintometer, England) and the color values were recorded as L (brightness), a (±red–green) and b (±yellow–blue). Measurements were made directly upon the samples

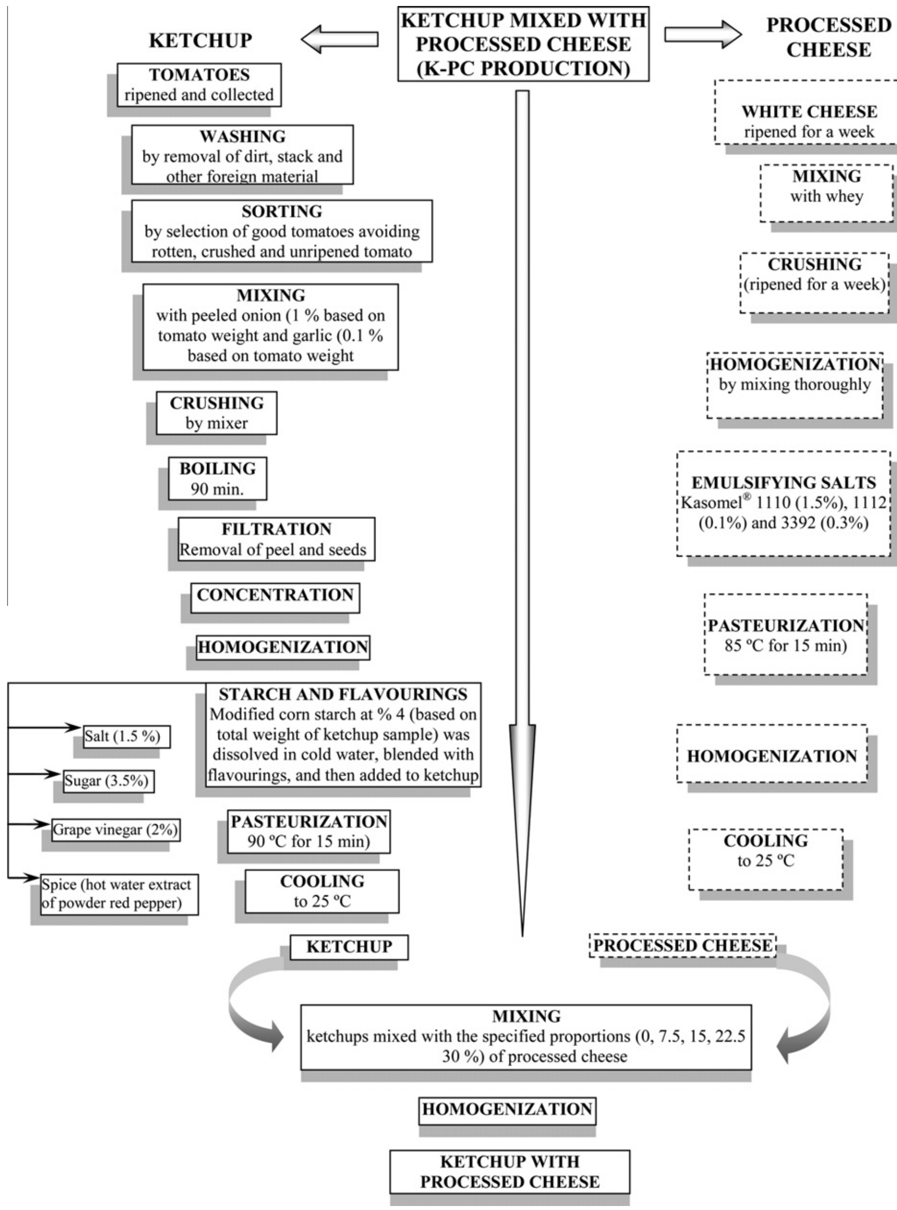

Fig. 1. Process flow chart for production of ketchup with processed cheese.

and carried out four times, one on the middle and three on different parts of the samples.

2.3. Descriptive sensory analysis

For sensory evaluations, samples of 100 mL volume were presented to the assessors in coded glass containers of 100 mL capacity covered with glass dishes. Sensory evaluation was performed in a room with appropriate temperature in open sitting. Panelists had access to deionised water to help cleanse their palates prior to proceeding to the next sample. The sensory analysis was performed by a panel consisting of five females and five males. Prior to the formal analysis sessions, training sessions were performed to define and describe the attributes and testing procedure as well as to make the panel familiarized with samples and methodology. Each sample was subjected to evaluation for its different sensorial (taste, odor, color, consistency, general appearance and overall acceptance) properties. The descriptors used in the evaluation are summarized in Table 1. All samples were evaluated by a panel using descriptive sensory profiling as described in ISO 6564:1985. All sensory attributes were evaluated in a scale from 1 to 9 (low and high, respectively) on five samples, consisting of four K–PC mixtures and one ketchup (control, no added PC) sample. For comparison, all five samples were served simultaneously at room temperature (23 ± 2 °C).

2.4. Rheological measurements

2.4.1. Steady shear properties

Rheological properties of K–PC mixtures were determined using a controlled stress rheometer (Thermo-Haake, RheoStress 1, Germany) equipped with a temperature control unit (Haake, Karlsruhe K15 Germany). The measurements were carried out using a cone-plate configuration (cone diameter 35 mm, angle 4°, gap size 0.140 mm) in the shear rate range of 1–100 s^{-1} at selected temperature range (10, 20, 30 40 and 50 °C). Sample (1.0 ml) was placed between cone and plate and the measurement was started immediately. Total 25 data points were recorded at 10 s intervals

Table 1
Sensorial parameters evaluated and descriptors used.

Attribute	Definition	Explanation and evaluation of procedure	Scale extremes (1–9)
Taste	Liking for uniform view of a product	Stability in view of the product (30 min after preliminary evaluation)	Undesirable–desirable
Odor	Odor intensity	Total intensity of odors	Undesirable–desirable
Color	Color intensity	Total intensity of color	Undesirable–desirable
Consistency	Product viscosity	Force required to turn tongue its around accompanied by the opening and closing of mouth	Low–high
General appearance	Uniformity in external view	Homogen distribution of the cheese particles in the ketchup	Undesirable–desirable
Overall acceptance	Overall liking nature of a product in respect of above attributes	–	Dislike–like

during the shearing. Each measurement was replicated five times on five different samples (each 1 ml) from the same K–PC mixture and PC with two repetitions. The apparent viscosity was determined as a function of shear rate. The flow curves, shear stress versus shear rate were plotted by increasing shear rate. Obtained data were fitted to Herschel–Bulkley model using RheoWin Data Manager (RheoWin Pro V. 2.96, Haake, Karlsruhe, Germany) and yield stress, consistency coefficient and flow behavior index values were calculated according to the following model used to describe shear-induced behavior of the K–PC mixtures.

$$\sigma = \sigma_0 + K(\dot{\gamma})^n \tag{1}$$

The steady shear data was processed in respect of the effect of temperature and PC concentration on apparent viscosity on the K–PC mixtures, as described below.

2.4.1.1. Effect of temperature. In this study, the effects of temperature, PC concentration and their combined effect on the apparent viscosity values were described at a specified shear rate of 50 s^{-1}, which is the shear rate in mouth (Bourne, 2002); therefore, the apparent viscosity measured at this specified shear rate was symbolized as η_{50} for description of these effects. As for temperature dependency of the apparent viscosity, η of K–PC mixtures at a specified shear rate (50 s^{-1}, shear rate in mouth) was described by the Arrhenius model (Saravacos, 1970; Rao et al., 1984).

$$\eta_{50} = \eta_0 e^{(Ea/RT)} \tag{2}$$

2.4.1.2. Effect of PC concentration on viscosity and activation energy. The variation of apparent viscosity with concentration at the specified shear rate of 50 s^{-1} can be described by several models (Rao et al., 1984; Ibarz et al., 1987). These are generally power-law and exponential type models as following:

$$\eta_{50} = \eta_1(C^{a1}) \tag{3}$$

$$\eta_{50} = \eta_2 \exp(a_2 C) \tag{4}$$

For a fixed temperature, activation energy (E_a) for flow depends on the concentration. The variation of activation energy with concentration was modelled by using exponential and power-law functions as following:

$$E_a = A_1(C^{B_1}) \tag{5}$$

$$E_a = A_2 \exp(B_2 C) \tag{6}$$

2.4.1.3. Combined effect of temperature and concentration. For engineering applications, it is very useful to obtain a single equation describing the combined effect of temperature and concentration on the apparent viscosity of K–PC mixtures. For this purpose, the Eqs. (2)–(4) were combined to obtain the following model functions, which describe the combined effect of temperature and concentration at the specified shear rate of 50 s^{-1}:

$$\eta_{50} = \eta_3 \exp(D_1 C + E_a/RT) \tag{7}$$

$$\eta_{50} = \eta_4 C^{D_2} \exp(E_a/RT) \tag{8}$$

2.4.1.4. Performance of the derived models. The performance of derived models (Eqs. (7) and (8)) was evaluated using various statistical parameters such as the mean percentage error (MPE), the mean bias error (MBE), the root mean square error (RMSE), the modelling efficiency (EF) and chi-square (χ^2) in addition to R^2. These statistics allow for the detection of the differences between experimental data and the model estimates. These parameters can be estimated as following (Toğrul and Arslan, 2004):

$$\text{MPE} = \frac{1}{N}\sum_{i=1}^{N}\left[\left(\eta_{c_{\exp,i}} - \eta_{c_{\text{pre},i}}\right)/\eta_{c_{\exp,i}}\right] \times 100 \tag{9}$$

$$\text{MBE} = \frac{1}{N}\sum_{i=1}^{N}\left(\eta_{c_{\text{pre},i}} - \eta_{c_{\exp,i}}\right) \tag{10}$$

$$\text{RMSE} = \left[\frac{1}{N}\sum_{i=1}^{N}\left(\eta_{c_{\exp,i}} - \eta_{c_{\text{pre},i}}\right)^2\right]^{1/2} \tag{11}$$

$$\text{EF} = \frac{\sum_{i=1}^{N}\left(\eta_{c_{\exp,i}} - \eta_{c_{\exp,\text{ave}}}\right)^2 - \sum_{i=1}^{N}\left(\eta_{c_{\text{pre},i}} - \eta_{c_{\exp,i}}\right)^2}{\sum_{i=1}^{N}\left(\eta_{c_{\exp,i}} - \eta_{c_{\exp,\text{ave}}}\right)^2} \tag{12}$$

$$\chi^2 = \frac{\sum_{i=1}^{N}\left(\eta_{c_{\exp,i}} - \eta_{c_{\text{pre},i}}\right)^2}{N - n_u} \tag{13}$$

where $\eta_{c_{\exp,i}}$ is the experimental apparent viscosity, (η_{50}, Pa s) at a specified shear rate of 50 s^{-1}, $\eta_{c_{\text{pre},i}}$ is the predicted apparent viscosity (Pa s), $\eta_{c_{\exp,\text{ave}}}$ is the average of experimental apparent viscosity values (η_{50}, Pa s), N is the number of data points and n_u is the number of model parameters.

2.4.2. Dynamic mechanic analysis

Frequency sweep tests were conducted for all samples using a dynamic oscillatory shear rheometer (RheoStress 1, HAAKE, Germany). Mechanical spectra were plotted over a frequency range of 0.1–10 Hz at 0.5 Pa (within the range of linear viscoelasticity) at selected temperature range (10, 20, 30, 40 and 50 °C). In oscillatory tests, samples are subjected to sinusoidal oscillating stress or strain with a frequency and the elastic or storage modulus G' and the viscous or loss modulus G'' are determined as a function of frequency (Steffe, 1996). Loss tangent, dimensionless number giving a clear indication of whether the material behaves as solid-like or liquid-like behavior, was calculated according to the following equation (Gunasekaran and Ak, 2000).

$$\tan\,\delta = G''/G' \tag{14}$$

The overall response of the sample against to the sinusoidal strain was characterized by the equations of complex modulus G^* (Gunasekaran and Ak, 2000) and complex viscosity η^*:

$$G^* = [(G')^2 + (G'')^2]^{1/2} \tag{15}$$

$$\eta^* = G^*/\omega \tag{16}$$

Plots of ω versus G' and G'' dynamic rheological data were subjected to non-linear regression and the magnitudes of intercepts (K', K'' and K^*), slopes (n', n'' and n^*) and R^2 were computed from raw data according to the following equations (Rao and Cooley, 1982; Yoo and Rao, 1996):

$$G' = K'(\omega)^{n'} \tag{17}$$

$$G'' = K''(\omega)^{n''} \tag{18}$$

$$\eta^* = K^*(\omega)^{n^*-1} \tag{19}$$

Correlations between the values of oscillatory shear parameters (complex viscosity, η^* and angular frequency, ω) and steady shear parameters (apparent viscosity, η and shear stress, $\dot{\gamma}$) were established by using the Cox–Merz rule (Rao and Tattiyakul, 1999; Gunasekaran and Ak, 2000; Juszczak et al., 2004). Cox–Merz rule is used to predict steady shear viscosity from complex shear viscosity and vice versa (Steffe, 1996).

$$\eta^*(\omega) = \eta(\dot{\gamma})|_{\omega=\dot{\gamma}} \tag{20}$$

3. Results and discussion

3.1. pH, proximate composition and color values

The chemical properties of processed cheese, ketchup and the K–PC mixtures are presented in Table 2. Among the samples studied, the pH value of PC was the highest as expected while that of the control sample (0% PC) was the lowest, affecting directly those of the K–PC mixtures. pH values of the K–PC mixtures were observed to increase depending on increase in the PC concentration. Similarly, the highest total protein, fat and solid content were observed in the PC and these values increased linearly as the PC concentration increased in the K–PC mixtures. Conversely, the lowest total sugar content was determined in the PC, decreasing this content of K–PC mixtures. These linear trends could be expected because of the lowest and highest values of ketchup and PC, and vice versa. The brightness value of PC was the highest as expected, giving rise to an increase in the *L* values of K–PC mixtures depending on the PC concentration. On the other hand, no linear increase or decrease was observed on the redness and yellowness values depending on PC concentration.

3.2. Sensory analysis results

Ketchup mixed with processed cheese (K–PC) is a newly developed product; therefore, its sensory properties should also be studied. In this respect, its certain sensory properties were tested by the panellists and the sensory analysis results are presented in Fig. 2. Panellists gave the highest sensory score to the ketchup sample prepared with 15% PC, indicating that inclusion of PC up to this level could be highly acceptable in terms of taste, odor, color, consistency, general appearance and overall acceptance.

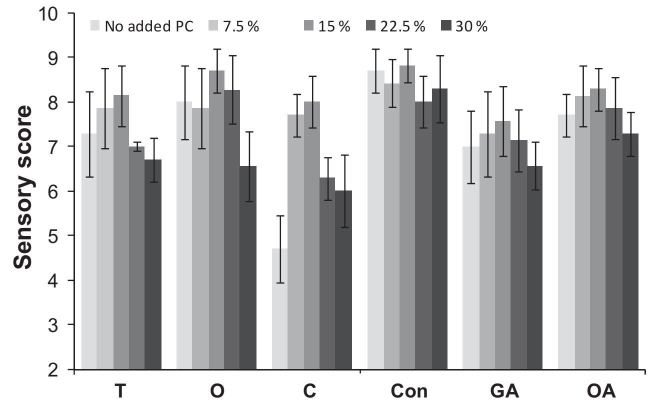

Fig. 2. Sensory analysis results for the K–PC mixtures (PC, processed cheese; T, taste; O, odor; C, color; Con, consistency; GA, general appearance; OA, overall acceptance). Each standard deviation mark represents the related mean ± standard deviation ($P < 0.05$).

3.3. Steady shear properties

The shear stress (σ) versus shear rate ($\dot{\gamma}$) data for the ketchup–processed cheese (K–PC) mixtures prepared with different levels (0% and 15%) of PC and those for PC at temperatures within the range of 10–50 °C are shown in Fig. 3. All K–PC mixtures (including ketchup, 0% PC) had non-Newtonian shear-thinning behavior with values of flow behavior index (n) ranging from 0.61 to 0.82, indicating that a general decrease in the shear-thinning nature as the PC concentration and temperature increased (Table 3). This was also case for PC having non-Newtonian shear-thinning behavior with values of flow behavior index (n) ranging from 0.57 to 0.93, indicating that a general decrease in the shear-thinning nature as the temperature increased. The Herschel–Bulkley model was adequate for describing the flow behavior of the K–PC mixtures since determination coefficients (R^2) were higher than 0.99. But, the Herschel–Bulkley model was not so adequate for describing the flow behavior of PC as it was resulted in some negative yield stress values at 10 and 20 °C (Table 3). Table 3 also reveals that the magnitudes of consistency coefficient (K) values obtained from the Herschel–Bulkley model decreased with the increase in PC concentration and temperature from 10 to 50 °C. Lower values of K indicated a less viscous nature because of increase in fluidity in K–PC

Table 2
Physicochemical properties of processed cheese (PC), ketchup (K) and K–PC mixtures.

Samples	pH	Proximate composition				Color properties		
		Total protein[a] (%)	Total fat[a] (%)	Total solid (%)	Total sugar (%)	*L*	*a*	*b*
Processed cheese (PC)	6.08	5.51	10.6	25.59	7.25	65.78	−0.67	4.14
Ketchup (0% PC)	4.42	–	–	14.58	9.11	18.43	12.15	19.87
Mixtures (%)								
7.5	4.61	0.41	0.78	15.54	8.23	36.56	14.08	25.73
15	4.75	0.83	1.58	16.35	7.60	43.75	14.27	27.25
22.5	4.91	1.24	2.37	17.00	7.40	45.85	12.81	24.31
30	5.04	1.65	3.14	17.91	7.25	48.53	14.10	26.82

[a] (–): Not detected.

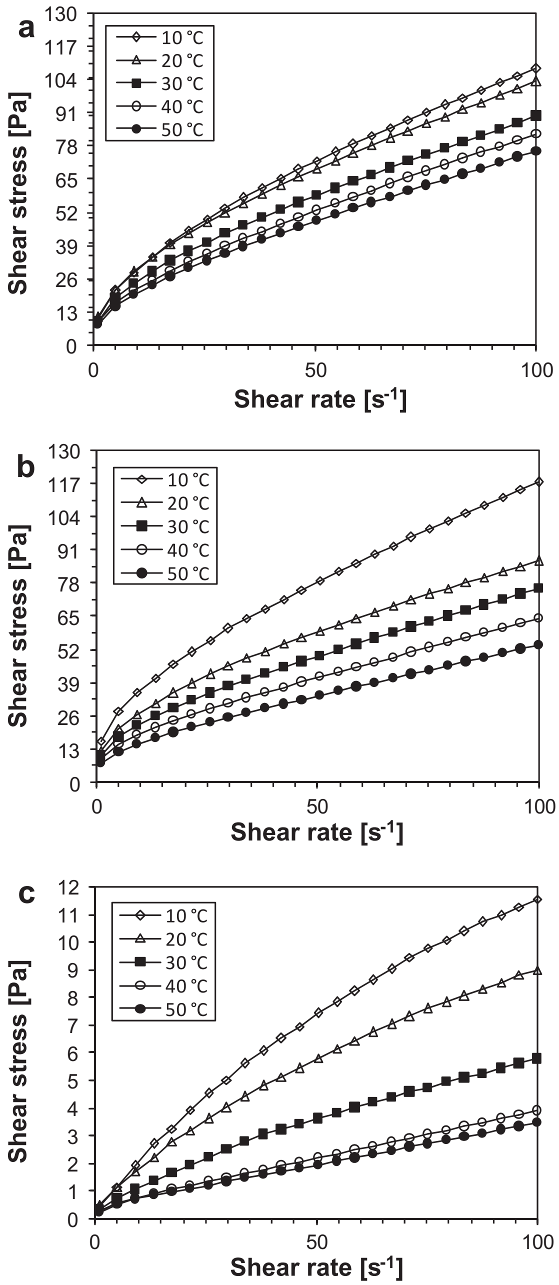

Fig. 3. Shear stress–shear rate plots for the K–PC mixtures prepared with (a) 0% (ketchup) (b) 15% of processed cheese (PC) at different temperatures, and (c) shear stress–shear-rate plots for PC.

mixtures. As for the magnitudes of flow behavior index (n) values, they were observed to increase with the increase in PC concentration. However, n values showed no consistent trend as influenced from temperature, which was in accord with the information by Hassan and Hobani (1998) who reported that generally n is nearly independent of temperature, unlike the consistency coefficient, K. On the other hand, all K–PC mixtures had higher yield stress (σ_0) values than K values for the same mixture in the range of 4.75–11.86 Pa. Therefore, the K–PC mixtures could be defined as shear-thinning fluids with semi-solid character with high magnitudes of yield stress values. The flow properties of PC are also presented in Table 3 showing that the magnitudes of K values decreased and those of n values increased with increasing temperature values from 10 to 50 °C. In addition, PC showed lower magnitudes of yield stress (σ_0) than did K–PC mixtures. Considering these results, the PC could be defined as shear-thinning fluid with semi-solid character with low magnitudes of yield stress.

These results could not be directly comparable with data in literature because no study has appeared to investigate steady shear properties of ketchup formulated with different concentrations of processed cheese. However, the rheological data for K–PC mixtures in this study were separately compared with literature data for ketchup and processed cheese. In this respect, comparable results were reported by Sharoba et al. (2005), Sahin and Ozdemir (2004) and Campanella and Peleg (1987) for ketchup; found by Dimitreli and Thomareis (2004) and Piska and Šttina (2004) for processed cheese. This semi-solid behavior as reported by Rao (1987) could be the result of a complex interaction among the pulp, soluble pectin, organic acids, soluble solids and the high volume concentration of particles.

3.3.1. Effect of temperature on apparent viscosity (η_{50})

The effect of temperature on η_{50} values of fluids at a specified shear rate (50 s^{-1}) could be described by the Arrhenius relationship (Eq. (2), (Rao, 1999), in which the apparent viscosity (η_{50}) decreases as an exponential function with temperature. Linear regression analysis was applied to logarithmic form of Eq. (2) in order to determine the parameters of relation (Table 3). The apparent viscosity (η_{50}) values of K–PC mixtures decreased with increase in temperature from 10 to 50 °C (Table 3). Similar trend was observed in the η_{50} values of PC, decreasing with increase in temperature from 10 to 50 °C (Table 3). A reasonably good agreement was obtained when these results were compared with those reported in previous studies of ketchup (Sharoba et al., 2005) and processed cheese (Dimitreli and Thomareis, 2004). The observed differences between η_{50} values as a result of temperature increase could be attributed to the increase in intermolecular distances due to thermal expansion (Constenla et al., 1989). Thermal energy of the molecules increases with increasing temperature, resulting in the development of molecular distances due to reduction of intermolecular forces; therefore, viscosity of the fluid decreases (Hassan and Hobani, 1998; Arslan et al., 2005).

3.3.2. Effect of PC concentration on apparent viscosity (η_{50})

It is well known that increasing solid content normally increases the consistency. However, an inverse trend is seen in the Table 3, which indicates a linear decrease in the η_{50} values as the PC concentration increased. In other words, PC had a higher total solid content than did ketchup (Table 2), which should have caused that PC would have higher consistency coefficient (K) values than would K–PC mixtures and that K–PC mixtures would have higher consistency coefficient (K) values than would ketchup. This trend could be explained by the lower apparent viscosity (η_{50}) values of PC compared to those of ketchup (Table 3), giving rise to the lower K values of K–PC mixtures. Therefore, addition of a fluid with lower viscosity (PC) to a fluid possessing a higher viscosity (ketchup) should result in a mixture with a lower viscosity and consistency index value as compared to that of pure ketchup.

The observed change in the η_{50} values with PC concentration could also be attributed to the pH values of K–PC mixtures, which increased with increasing PC concentration (Table 2). pH change with PC level was thought to cause charge interaction effects. This assumption could be explained by the fact that increasing pH resulted in increasing charge repulsion between proteins in the system. Marchesseau et al. (1997) suggested that the increase in the net negative charge of proteins (with increasing pH above the isoelectric point of caseins) due to the reduced electrostatic interactions resulted in the increased hydration of casein. Marchesseau et al. (1997) also pointed out that the compactness of the protein microstructure decreased with increasing pH, indicating decreasing

Table 3
Herschel–Bulkley parameters and temperature dependency of K–PC mixtures at different temperatures.

Samples	T (°C)	Herschel–Bulkley parameters				Temperature dependency parameters[a]			
		σ_0 (Pa)	K (Pa s^n)	n	R^{2b}	η_{50} (Pa s)	η_0 (Pa s)	E_a[c] (kJ mol^{-1})	R^{2c}
Mixtures (%)									
0 (Ketchup)	10	4.75	5.95	0.62	1.000	1.51	0.036	8.83	0.989
	20	5.77	5.71	0.61	1.000	1.36			
	30	6.15	3.85	0.66	1.000	1.16			
	40	7.06	2.79	0.71	1.000	1.04			
	50	5.93	2.50	0.70	1.000	0.97			
7.5	10	9.58	5.68	0.63	1.000	1.43	0.018	10.37	0.996
	20	7.99	4.89	0.62	1.000	1.27			
	30	8.96	3.11	0.69	1.000	1.09			
	40	9.31	2.26	0.73	1.000	0.95			
	50	7.52	1.87	0.75	1.000	0.83			
15	10	11.86	5.46	0.64	1.000	1.36	0.005	13.35	0.992
	20	8.46	4.58	0.62	1.000	1.18			
	30	9.41	2.62	0.70	1.000	0.98			
	40	8.85	1.74	0.75	1.000	0.82			
	50	7.31	1.29	0.78	1.000	0.68			
22.5	10	11.33	3.62	0.72	1.000	1.34	0.004	13.63	0.936
	20	8.43	3.54	0.67	1.000	1.07			
	30	8.34	2.08	0.73	0.999	0.77			
	40	8.14	1.39	0.79	0.999	0.75			
	50	7.23	1.09	0.81	0.999	0.66			
30	10	9.56	3.07	0.74	1.000	1.30	0.001	17.16	0.971
	20	6.32	2.66	0.71	1.000	0.99			
	30	6.09	1.77	0.74	0.999	0.70			
	40	6.14	1.15	0.81	1.000	0.66			
	50	5.41	0.88	0.82	0.999	0.52			
Processed cheese (PC)									
	10	−0.92	0.96	0.57	0.999	0.143	1.2×10^{-6}	27.79	0.966
	20	−0.03	0.55	0.61	0.999	0.117			
	30	0.02	0.22	0.70	1.000	0.071			
	40	0.23	0.06	0.89	1.000	0.043			
	50	0.32	0.04	0.93	0.999	0.038			

[a] Temperature dependency on apparent viscosity values at 50 s^{-1}.
[b] R^2 is determination coefficient for the Herschel–Bulkley model.
[c] E_a is the activation energy pooled by the determination coefficient for the Arrhenius equation (Eq. (2)).

Table 4
Effect of processed cheese concentration on apparent viscosity of K–PC mixtures at different temperatures.

Temperature (°C)	Power-law function $\eta_{50} = \eta_1\ (C^{a_1})$			Exponential function $\eta_{50} = \eta_2 \exp(a_2C)$		
	η_1 (Pa s)	a_1	R^2	η_2 (Pa s)	a_2 ((%)$^{-1}$)	R^2
10	1.632	−0.066	0.978	1.462	−0.004	0.949
20	1.840	−0.176	0.948	1.384	−0.011	0.998
30	2.214	−0.332	0.923	1.296	−0.021	0.968
40	1.611	−0.255	0.978	1.061	−0.016	0.990
50	1.565	−0.306	0.889	0.953	−0.019	0.927

Table 5
Effect of processed cheese concentration on activation energy of flow.

Model	A_i	B_j	R^2
Power-law function	A_1 ((%)$^{-1}$)	B_1	
$E_a = A_1\ (C^{B_1})$	5.37	0.33	0.916
Exponential function	A_2 (kJ mol^{-1})	B_2 ((%)$^{-1}$)	
$E_a = A_2 \exp(B_2C)$	9.12	0.02	0.922

protein–protein interactions that caused the decrease in viscosity. Accordingly, Khwaldia et al. (2004) explained a decrease in the apparent viscosity of sodium caseinate (NaCAS) film-forming dispersions by decreasing protein–protein interactions through the hydrogen bonding formation between polypeptide chain of NaCAS and water molecules.

The variation of η_{50} values with concentration could be described by several power-law type and exponential type models. Linearized forms of Eqs. (3) and (4) were plotted and corresponding model parameters are represented in Table 4, which represents the values of the parameters of power law and exponential relationships. From the values of determination coefficients obtained from two models, the exponential model (R^2 = 0.927–0.998) seems to describe better than the power-law model (0.889–0.978) in relating the effect of PC content on the η_{50} values of K–PC mixtures.

3.3.3. Effect of PC concentration on activation energy (E_a)

Table 3 indicates that increasing PC concentration caused an increase in the E_a values. The calculated values of E_a and constant η_0 of PC mixtures increased linearly from 8.83 to 17.16 kJ mol^{-1} and de-

Table 6
Combined effect of temperature and processed cheese concentration on the apparent viscosity.

Eqs. (7) and (8)	Equations for combined effect						Statistical test parameters				
	I	η_i	j	D_j	E_a (kJ mol^{-1})	R^2	MPE	MBE	RMSE	EF	χ^2
$\eta_{50} = \eta_3 \exp(D_1C + E_a/RT)$	3	η_3 (Pa s) 0.0054	1	D_1 (%)$^{-1}$ −0.014	13.63	0.951	−0.428	0.0009	0.0643	0.9431	0.005
$\eta_{50} = \eta_4\ C^{D_2} \exp(E_a/RT)$	4	η_4 (Pa s) 0.0078	2	D_2 −0.227	13.63	0.946	0.010	−0.0027	0.0678	0.9360	0.005

MPE, mean percentage error; MBE, mean bias error; RMSE, root mean square error; EF, modelling efficiency and χ^2, chi-square.

creased from 0.036 to 0.001 Pa s, respectively, with the high determination coefficients (R^2 = 0.936–0.996). The observed E_a values considerably changed with the increase of concentration, indicating that there was an appreciable effect of concentration on E_a. As for the calculated values of E_a and constant η_0 of PC, they were determined to be 27.79 kJ mol^{-1} and 1.2×10^{-6} Pa s, respectively, with the high determination coefficient (R^2 = 0.966) (Table 3). The high E_a values of K–PC mixtures in the concentration range studied and that of PC indicated that their rheological properties were highly temperature-dependent. Similar results were reported by Barreto et al. (2003) who studied sodium caseinate film-forming solutions in terms of caseinate concentration and temperature and determined that the activation energy values increased from 7.5 to 12.1 kJ mol^{-1} as the concentration increased from 10.5% to 13.0% (w/w). On the other hand, values of E_a and their respective concentrations were fitted to Eqs. (5) and (6) by least-squares methods to obtain estimates of the parameters of model. The calculated parameters for these models are presented in Table 5. The dependency of E_a on the PC concentration was better described by the exponential function (R^2 = 0.922) than by power-law function (R^2 = 0.916).

3.3.4. Combined effect of temperature and concentration on apparent viscosity (η_{50})

Multiple linear regression analyses were conducted on the linearized forms of the Eqs. (7) and (8) to obtain their parameters. The values of these constants are presented in Table 6 which indicates the performance of Eqs. (7) and (8) to describe the combined effect of both temperature and PC concentration. It can be seen that both models, Eqs. (7) and (8), adequately described the rela-

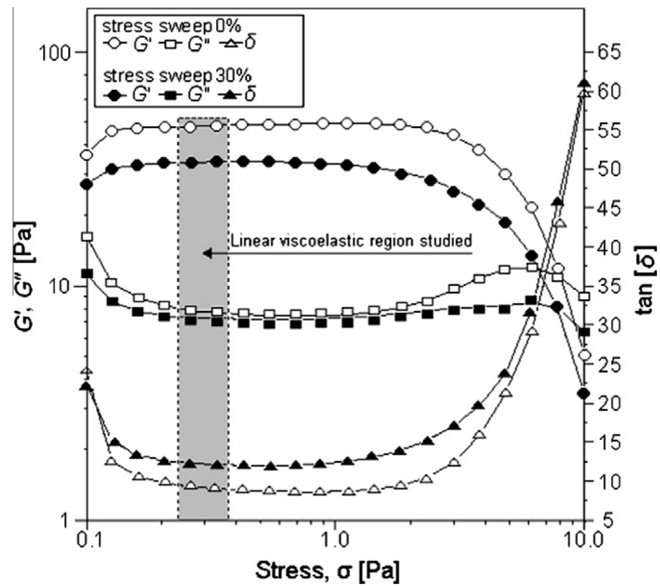

Fig. 5. Region of linear viscoelasticity (variation of storage modulus, G', loss modulus, G'' and loss tangent, tan δ with shear stress) for K–PC mixtures prepared with 0% and 30% PC at 20 °C (ω = 0.1 Hz).

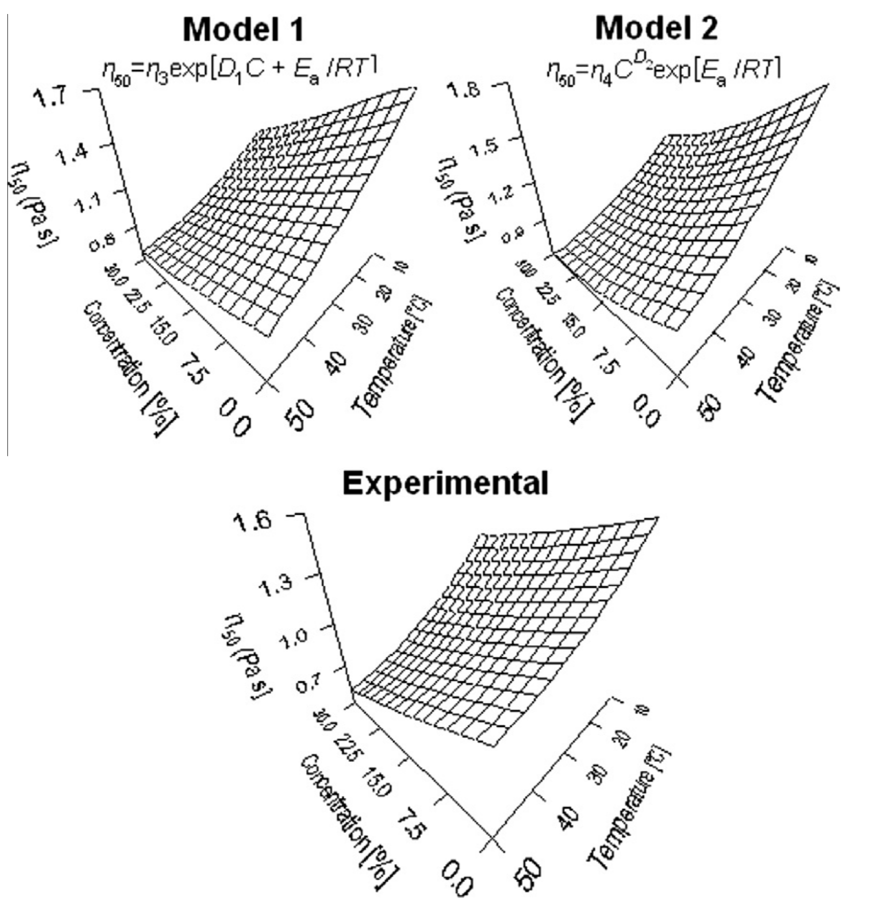

Fig. 4. The plots showing the effect of processed cheese concentration and temperature on η_{50} values. Models 1 and 2 plots were generated according to theoretical values calculated by using Eqs. (7) and (8), respectively. The experimental plot was generated using the experimental results obtained in this study. η_{50} was the apparent viscosity measured at the specified shear rate of 50 s^{-1}, which is the shear rate in mouth.

tionship (R^2 = 0.951 and 0.946, respectively); however, statistical analysis indicated that Eq. (7) better describes the combined effect of temperature and PC concentration on the apparent viscosity (η_{50}) of K–PC mixtures in comparison with Eq. (8). The higher the values of R^2 and EF and the lower the values of MPE, MBE, RMSE and χ^2 are, the better the goodness of fit will be (Toğrul and Arslan, 2004).

Table 6 shows also that the higher values of R^2 and EF and the lower absolute values of MBE, RMSE excluding MPE and χ^2 could be obtained with the statistically fitted model of Eq. (7). A multiple regression analysis on the apparent viscosity (η_{50})–temperature–concentration data showed that the statistically fitted model of Eq. (7) could be proposed to analyze the apparent viscosity of K–PC mixtures and be used as a single model:

$$\eta_{50} = 5.35 \times 10^{-3} \times \exp\left[-0.014C + 1640\left(\frac{1}{T}\right)\right] \tag{21}$$

Fig. 4 shows the three-dimensional plots demonstrating the effect of PC concentration and temperature on the apparent viscosity. These plots were generated according to Models 1 and 2 [Eqs. (7) and (8), respectively] and according to the experimental results obtained. When the plots derived from Models 1 and 2 were examined and compared to the one derived from the experimental results obtained, it could be seen that there was a good agreement between the model plots and the experimental plot. In other

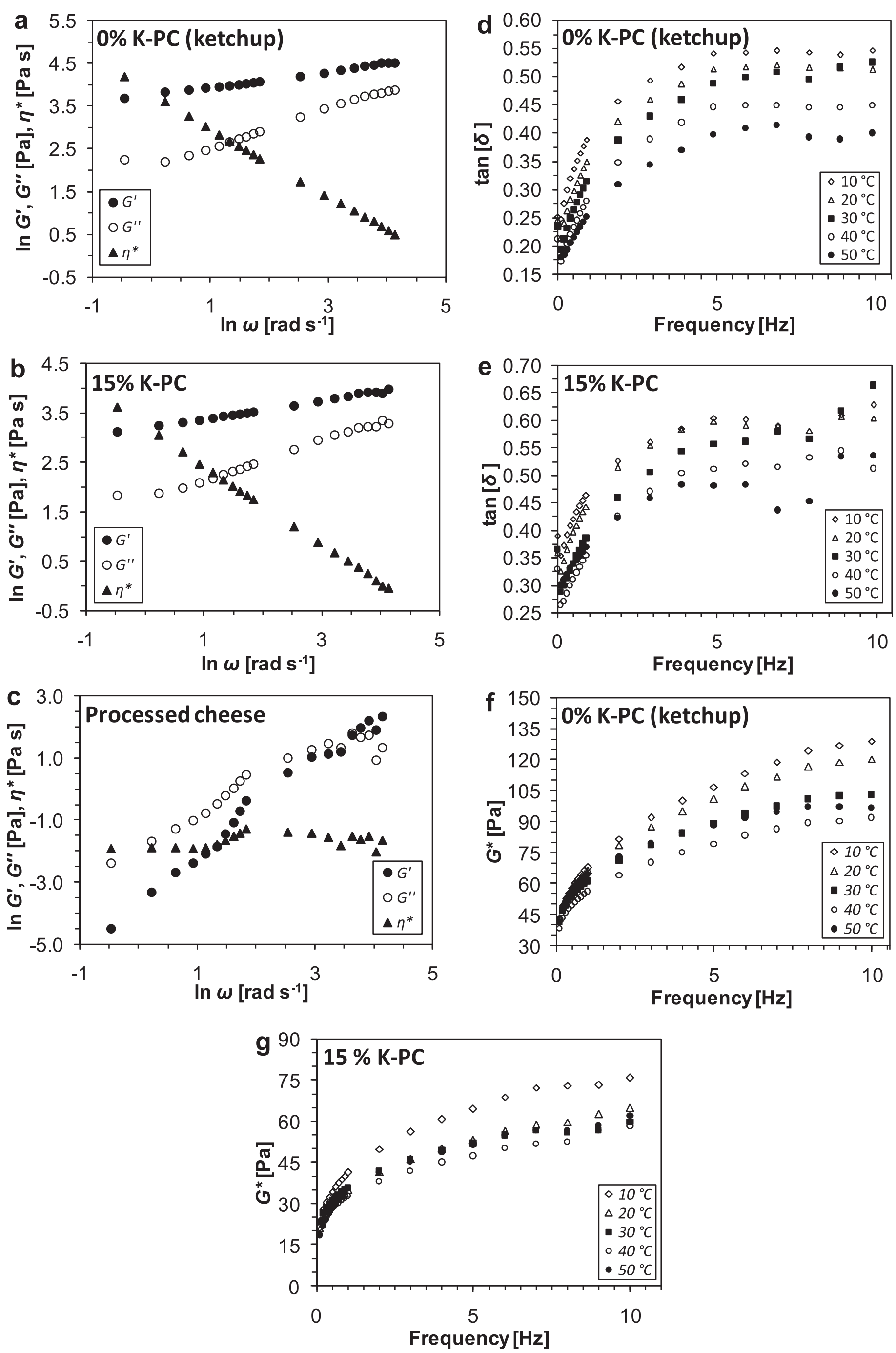

Fig. 6. Frequency sweep test for mechanical spectra. (a), (b) and (c) indicate storage modulus, G', loss modulus, G'' and complex viscosity, η^* values of K–PC mixtures and PC sample at 30 °C (ln G',G'', η^* versus ln ω). (d), (e), (f) and (g) indicate loss tangent, tan δ and complex modulus, G^* of K–PC mixtures at whole temperature range.

words, the model plots and the experimental plots demonstrate the similar results with respect to the effects of PC concentration and temperature on η_{50} values.

3.4. Dynamic shear properties

3.4.1. Stress sweep test

The linear viscoelastic region determined for storage modulus (G'), loss modulus (G'') and loss tangent (tan δ) of K–PC mixtures prepared with 0% and 30% of PC is presented in Fig. 5. The region was observed between 0 and 1.0 Pa values; therefore, 0.5 Pa was the stress value which was used to conduct frequency sweep tests. Fig. 5 also indicates that there were no remarkable variations in trend of different concentrations (0%, ketchup and 30%) of K–PC mixtures for G', G'' and tan δ parameters, revealing that PC addition into ketchup formulation did not change these parameters of ketchup. This can be explained by the fact that both ketchup and K–PC mixtures had elastic nature (Fig. 6) as will be discussed in detail later, giving rise to similar variations in the trend of different concentrations.

3.4.2. Frequency sweep test (dynamic viscoelastic properties)

The oscillatory test, also called the dynamic rheological experiment, can be used for determination of viscoelastic properties of foods. The storage (or elastic) modulus, G' means the magnitude of the energy stored in the material or recoverable per cycle of deformation. On the other hand, the loss (or viscous) modulus, G'' expresses the energy that is lost at viscous dissipation per cycle of deformation. Therefore, for a perfectly elastic solid, all the energy is stored resulting in zero loss modulus and the stress and strain will be in phase. In contrast, for a liquid with no elastic properties, all the energy is dissipated as heat; G' is zero and the stress and strain will be out of phase by $-90°$ (Sharoba et al., 2005).

Fig. 6 shows changes in storage modulus (G'), loss modulus (G''), and complex viscosity (η^*) as a function of frequency for K–PC mixtures prepared with 0% and 15% of PC at 30 °C. The magnitudes of G' and G'' increased with increase in frequency indicating viscoelastic structure of the samples. η^* versus frequency plots also show shear-thinning behavior following power-law model (Fig. 6., Table 7). Plots of frequency versus G' and G'' dynamic rheological data were subjected to non-linear regression and the magnitudes of intercepts, slopes and R^2 are summarized in Table 7. When the storage and loss moduli as well as the complex viscosity were plotted versus frequency, the viscoelastic behavior of the K–PC samples could be described very well by Eqs. (17)–(19) with high determination coefficients (0.962–0.999). Such behavior was in good agreement with those found in some commercial German and Egyptian tomato ketchups (Sharoba et al., 2005) and that determined in reduced fat processed cheese (Subramanian et al., 2006).

From a structure point of view, for true gels ln(G', G'') versus ln ω plots have zero slope, while there are positive slopes and G' is greater than G'' over a whole frequency ranges of ω studied for weak gels and highly concentrated dispersions (Ross-Murphy, 1984). From dynamic oscillatory test data, it was found that the K–PC mixtures at concentrations of 0–30% exhibited weak gel-like behavior because the slopes were positive (n' = 0.173–0.279; n'' = 0.365–0.423) (Table 7) and almost parallel to each other (Fig. 6) and the magnitudes of G' (K' = 30.72–65.83) were higher than those of G'' (K'' = 10.50–24.56) without exhibiting no cross-point of G' and G'' along the whole frequency range studied (Fig. 6). These results suggest that the K–PC mixtures were more

Table 7
Parameters of power-law functions describing storage and loss moduli and complex viscosity.

Samples	T (°C)	$G' = K'(\omega)^{n'}$ K' (Pa)	n'	R^2	$G'' = K''(\omega)^{n''}$ K'' (Pa)	n''	R^2	$\eta^* = K^*(\omega)^{n^*-1}$ K^* (Pa s)	n^*	R^2
Mixtures (%)										
0 (Ketchup)	10	65.83	0.225	0.989	24.56	0.423	0.994	11.27	0.26	0.998
	20	64.91	0.207	0.991	22.08	0.422	0.987	11.01	0.24	0.999
	30	59.78	0.183	0.994	18.69	0.422	0.980	10.06	0.21	0.999
	40	55.06	0.175	0.994	15.31	0.413	0.976	9.17	0.20	0.999
	50	62.08	0.173	0.997	16.18	0.376	0.962	10.26	0.19	0.999
7.5	10	44.77	0.241	0.996	18.67	0.390	0.994	7.765	0.27	0.999
	20	41.62	0.225	0.996	16.30	0.383	0.992	7.155	0.25	0.999
	30	41.66	0.191	0.996	14.64	0.394	0.990	7.086	0.22	0.999
	40	38.95	0.198	0.997	13.03	0.386	0.981	6.578	0.23	0.999
	50	41.93	0.218	0.996	13.54	0.381	0.981	7.048	0.24	0.999
15	10	38.21	0.241	0.996	16.48	0.371	0.993	6.653	0.27	0.999
	20	32.86	0.226	0.997	13.07	0.377	0.993	5.660	0.25	0.999
	30	34.17	0.186	0.995	12.03	0.372	0.985	5.805	0.21	0.999
	40	31.50	0.200	0.994	10.55	0.379	0.982	5.321	0.23	0.999
	50	32.14	0.242	0.996	10.50	0.395	0.991	5.405	0.26	0.999
22.5	10	40.78	0.260	0.998	18.83	0.393	0.993	7.185	0.29	0.999
	20	36.53	0.247	0.998	16.12	0.400	0.990	6.396	0.28	0.999
	30	34.62	0.207	0.995	13.87	0.390	0.974	5.985	0.24	0.999
	40	32.63	0.219	0.997	11.89	0.394	0.976	5.564	0.25	0.999
	50	30.72	0.279	0.993	11.72	0.397	0.985	5.252	0.30	0.999
30	10	53.66	0.224	0.997	20.91	0.381	0.992	9.217	0.25	0.999
	20	48.15	0.212	0.998	17.54	0.374	0.986	8.201	0.24	0.999
	30	48.08	0.187	0.998	15.91	0.378	0.978	8.114	0.21	0.999
	40	40.62	0.191	0.997	15.27	0.375	0.976	6.807	0.21	0.999
	50	46.35	0.233	0.998	12.63	0.365	0.970	7.798	0.25	0.999
Processed cheese (PC)										
	10	0.456	1.203	0.942	1.054	0.692	0.934	0.207	0.880	0.586
	20	0.302	1.239	0.959	0.731	0.732	0.923	0.156	0.900	0.707
	30	0.407	1.467	0.985	0.954	0.859	0.914	0.184	1.055	0.126
	40	5.913	2.666	0.879	9.957	2.089	0.932	2.247	2.252	0.789
	50	2227	1.458	0.358	3161	1.226	0.371	761.3	1.279	0.028

predominantly elastic than viscous. The frequency sweep measurements were consistent with results obtained for some German and Egyptian tomato ketchups (Sharoba et al., 2005) and reduced-fat model processed cheese (Lee and Klostermeyer, 2001) previously. Sharoba et al. (2005) determined that the storage modulus was much larger than the loss modulus for all the tomato ketchups within the applied frequency range (10^{-3}–100 Hz), indicating dominant elastic properties. They also found that tomato ketchup does not show gel structure formation in every case.

The magnitudes of intercepts, slopes and R^2 for PC are also summarized in Table 7. When the storage and loss moduli were plotted versus frequency, the viscoelastic behavior of the PC sample could be described well by Eqs. (17) and (18) with high determination coefficients (0.914–0.985) at the temperatures between 10 and 30 °C. However, after this temperature level, the viscoelastic behavior of PC could not be described well by these equations because of the low determination coefficients. Furthermore, η^* values could not be described well within all the temperature range studied. The possible reason could be explained by the fact that slippage and strong viscoelastic effects played a dominant role, making it impossible to obtain meaningful rheological data (Smith et al., 1980). Furthermore, these results were in accord with the information given by literature where dynamic testing of cheese was reported to be difficult to preform at high temperatures because sample slippage may distort the results (Kuo et al., 2000). From dynamic oscillatory test data, it was found that the PC sample also exhibited weak gel-like behavior because the slopes were positive (n' = 1.203–2.666; n'' = 0.692–2.089) (Table 7). Accordingly, Lee and Klostermeyer (2001) observed the mechanic spectra of model processed cheese spreads at different pH values. Their model samples at pH 5 and 5.2 were solid-like gels with mechanical spectra resembling that of a weak gel (Richardson et al., 1989).

Another popular material function for the description of viscoelastic behavior is the loss tangent (G''/G'), which indicates whether elastic or viscous properties of the material (Fig. 6). In the case of processed cheese, the larger the tan δ value, the more easily the cheese flows. The loss tangent values showed a predominantly elastic behavior (tan $\delta < 1$ or $G' > G''$) for K–PC mixtures over the increased frequency due to the existence of a phase lag between the input sinusoidal signal and the response one (Muñoz et al., 2007). For all temperatures, there was a similar pattern. At lower frequencies, lower tan δ values were the evidence of elastic character. As the frequency increased, the elastic, in the other words, solid-like character decreased.

Total resistance to deformation of a material considered to be elastic solid refers to complex modulus which is expressed in Pa. In contrast, the total resistance to flow of a material considered to be a viscous liquid refers to complex viscosity which is measured in Pa s (Dimitreli and Thomareis, 2008). Fig. 6 shows that mixtures with lower moisture content due to PC addition (Table 2) displayed increased complex modulus values and decreased complex viscosity values over the entire frequency range (due to higher resistance), compared to those with higher moisture content (lower resistance). The complex modulus increases while the complex viscosity decreases across the frequency range. Furthermore, mixtures exhibited more increase in complex modulus with increasing

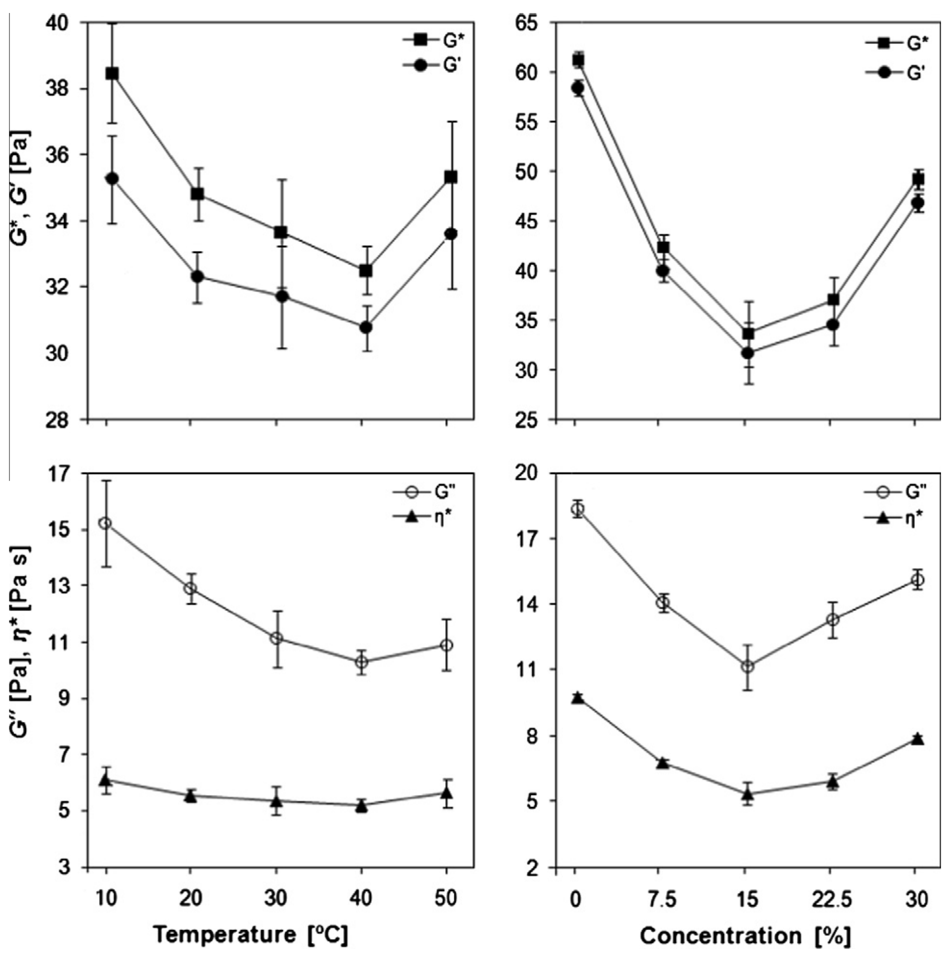

Fig. 7. Effect of temperature (at 15% concentration) and concentration (at 30 °C) on complex modulus (G^*), storage modulus (G'), loss modulus (G'') and complex viscosity (η^*) of K–PC mixtures at oscillation frequency of 1 Hz. Each standard deviation mark represents the related mean ± standard deviation ($P < 0.05$).

frequency. Complex modulus of K–PC samples showed lower dependence (increase) of frequency at higher frequency values.

Effect of temperature and concentration on the viscoelastic properties of K–PC mixtures is shown in Fig. 7. The addition of PC to ketchup resulted in a decrease in G^*, G', G'' and η^* values up to 40 °C and then an increase in these values at 50 °C, showing a plateau value between 0% and 30% concentrations. This plateau might have been due to the slippage and strong viscoelastic effects of PC at higher temperatures (Kuo et al., 2000). As for the effect of PC concentration, the addition of PC (casein source) to ketchup (prepared with 4% corn starch) resulted in a decrease in the dynamic shear parameters, G^*, G', G'' and η^* up to the 15% of PC concentration, showing a plateau value between 0% and 30% concentrations (Fig. 7). Similar plateau value was observed by Noisuwan et al. (2009) for G^* of the normal rice starch gels containing NaCAS (sodium caseinate) at the concentrations between 2.5–10% and WPI (whey protein isolate) at the concentrations between 2.5% and 7.5%. They have reported that the reason for the formation of plateau value was not yet fully understood; therefore, further investigation is needed. On the other hand, it should be noted that there was no effect of NaCAS on the viscosity of 4% corn starch in pH 7 phosphate buffer (Kelly et al., 1995). They explained this occurrence with respect to decrease in swelling volume of the starch granules, which would compensate for the increase in the viscosity of continuous phase with the increase in NaCAS concentration. Present study also showed a delay in the increase in dynamic shear parameters of ketchup (including corn starch at 4%, Fig. 1) with the addition of PC (caseinate source). Furthermore, in their study on the viscoelastic properties of mixed gels of corn starch and WPI, Shim and Mulvaney (2001) reported that WPI acted as an inactive diluent of the corn starch fraction at lower solids contents (15% total solid). Accordingly, in our study, the mean total solid content of the K–PC mixtures was near to this level (16.28%, Table 2).

3.4.3. Applicability of Cox–Merz rule

Cox–Merz rule indicates that the dynamic shear viscosity is nearly equal to the steady shear viscosity when frequency is equal to shear rate. This rule has been studied for many polymers, solution, and complex food systems (Da Silva and Rao, 1992; Tiziani and Vodovotz, 2005; Yaşar et al., 2009). In order to examine the applicability of the Cox–Merz rule (Eq. (20)), the apparent viscosity, η and complex viscosity η^* of K–PC mixtures were plotted against shear rate, $\dot{\gamma}$ and angular frequency (ω), respectively (Fig. 8). It was observed that the magnitudes of η^* were higher than those of η, indicating that the Cox–Merz rule was not applicable to K–PC mixtures. Bistany and Kokini (1983) determined steady and dynamic shear rheological properties of commercial tomato ketchup samples and found that the Cox–Merz rule was not applicable. Accordingly, it was reported that this behavior was in good agreement with those found in waxy maize starch dispersions (Chamberlain and Rao, 1999; Da Silva et al., 1998), pectin dispersion (Lopes Da Silva et al., 1993) and cooked rice flour dispersion (Chun and Yoo, 2004). Da Silva et al. (1998) explained that the failure in starch dispersions to follow Cox–Merz rule could be attributed to the fact that heterogeneous nature undergoes aggregation. In addition, the departures from the Cox–Merz rule with η^* values, have been reported to occur in structured polymer systems when aggregation takes place among polymer chains (Lapasin and Pricl, 1995) and are generally attributed to structure decay due to effect of strain deformation applied to the system (Chamberlain and Rao, 1999). As shown in Fig. 8, at concentration of 15%, η^* overlapped η; however, the difference between the two values (η^* and η) increased with the increase in the concentration of PC from 15% to 30%. It could be concluded from these results that the departures of K–PC mixtures from the Cox–Merz rule was concentration-dependent.

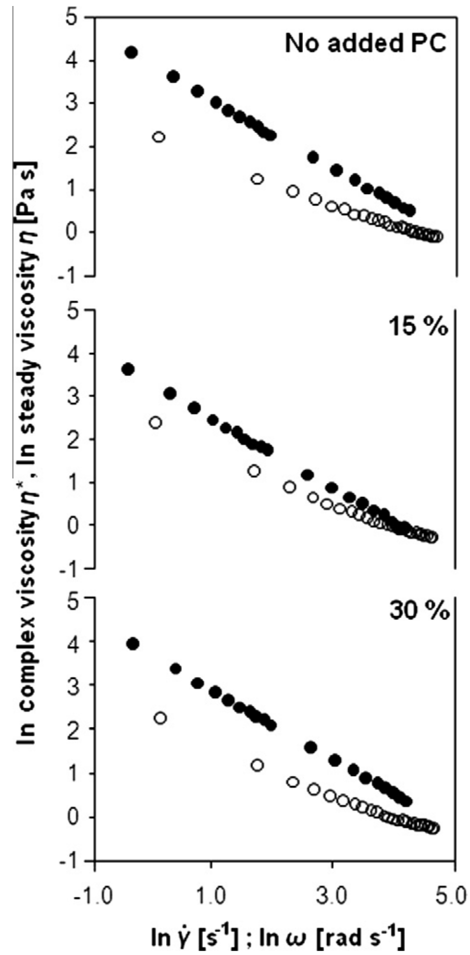

Fig. 8. Comparison of oscillatory and continuous shear viscosities (Cox–Merz rule) of the ketchup and K–PC mixtures at 30 °C. Open symbol: η, closed symbol: η^*.

4. Conclusions

The ketchup–processed cheese (K–PC) mixtures at different concentrations (0–30%) exhibited a shear-thinning behavior with low yield stress values (σ_0). The effect of temperature on apparent viscosity (η) of K–PC mixtures is clearly explained by the Arrhenius relationship with high correlations (R^2). Mathematical models were developed for the estimation of η_{50} of K–PC mixtures as a function of PC concentration and temperature. Judging from the R^2 values, an exponential model appears to be a better choice than a power-law model with respect to effect of the temperature and concentration ranges studied on the K–PC mixtures. On the other hand, the multiple regression analysis showed that the statistically fitted model of Eq. (7) could be proposed to analyze the combined effect of temperature and concentration on the η_{50} values of K–PC samples. Based on the frequency sweep data of storage (G') and loss (G'') moduli as a function of frequency, the K–PC mixtures at concentrations of 0–30% exhibited the rheological behavior similar to weak gel-like macromolecular dispersions with G' much greater than G'' within the whole range of frequency applied. The Cox–Merz rule was not applicable to the K–PC mixtures and the departure of K–PC mixtures from the rule was determined to be concentration-dependent.

In this study, the compositional properties of ketchups could be changed by the usage of processed cheese (PC) at particular combinations, which could give rise to alterations in their rheological and sensory properties. Such modifications would be of great economical importance to food industry. PC can be used to improve these properties when appropriate levels of this product are taken into consideration. Ketchup mixed with processed cheese (K–PC) is a newly developed product in this study and has not been produced yet in the food industry. There is no published data informing the rheological and sensory properties of this product. Therefore, information obtained in this study may be useful in practical industrial food product process monitoring and development.

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