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The rheological properties of ketchup as a function of different hydrocolloids and temperature

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Summary The flow properties of ketchup were assessed upon addition of commonly used food thickeners: guar, xanthan and CMC gum at three different concentrations (0.5%, 0.75% and 1%) and four temperatures (25, 35, 45 and 55 °C). The ketchup without supplementation served as a control. All ketchup formulations exhibited non-Newtonian, pseudoplastic behaviour at all temperatures and hydrocolloid levels. The Power-law and Herschel-Buckley model were successfully applied to fit the shear stress versus shear rate data. The flow behaviour indices, n and n', varied in the range of 0.189–0.228 and 0.216–0.263, respectively. The consistency coefficients, k and k', were in the range of 8.42–27.22 and 6.56–20.10 Pa s^n, respectively. The addition of hydrocolloids increased the yield point (τ_0) and apparent viscosity of the ketchup in comparison to that of the control. The Arrhenius equation was successfully used to describe the effects of temperature on the apparent viscosity of the prepared formulations. The E_a value appeared in the range between 5492.6 and 21475.8 J mol^{-1}.

Keywords Ketchup, polysaccharides, rheology, temperature.

Introduction

Tomato is one of the most important vegetable products mainly marketed in a processed form i.e. pastes, concentrates or ketchup (Mazaheri Tehrani & Ghandi, 2007). Ketchup is a descriptive term for a number of different products, which consist of various pulps, strained and seasoned fruits; the variety made from tomatoes being the most popular condiment. Tomato ketchup is a heterogeneous, spiced product, produced basically from either cold or hot extracted tomatoes; or directly from concentrates, purees or tomato paste (Sahin & Ozdemir, 2004).

Many newly developed tomato products with or without other vegetable juices are now present on the Iranian market. Among these new products with 'high service content' tomato ketchups have been probably the first to find favour with consumers and they still occupy a large share of the market. The most typical use of ketchup is in 'fast-food' restaurants, where it is normally stored at room temperature. Many foods of commercial importance, such as tomato paste and tomato ketchup, are concentrated dispersions of insoluble matter in aqueous media.

Knowledge of the rheological properties of fluid and semisolid foodstuffs is important in the design of flow processes in the quality control, storage and the processing stability, and in understanding and designing texture (Vercet *et al.*, 2002; Mazaheri Tehrani & Ghandi, 2007). The viscosity of tomato ketchup is a major quality component for consumer acceptance. Usually viscosity is considered an important physical property related to the quality of food products. Therefore, reliable and accurate rheological data are necessary for designing and optimization of various food processing equipment such as pumps, piping, heat exchangers, evaporators, sterilises, filters and mixers (Crandall & Nelson, 1975; Tanglertpaibul & Rao, 1987; Stoforos & Reid, 1992; Vercet *et al.*, 2002).

Ketchups are time-independent, non-Newtonian fluids that show a small thixotropy (Bottiglieri *et al.*, 1991). Tomato ketchup obtains its viscosity from naturally occurring pectic substances in fruits. Their rheological behaviour is important during handling, storage, processing and transport of concentrated suspensions in industry. Other factors such as enzymatic degradations, pectin/protein interaction, pulp content, homogeniza-

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tion process and concentration may also affect the consistency of tomato products (Crandall & Nelson, 1975; Tanglertpaibul & Rao, 1987; Stoforos & Reid, 1992; Vercet *et al*., 2002; Mazaheri Tehrani & Ghandi, 2007). These inconsistencies may be alleviated by addition of different hydrocolloids (Sahin & Ozdemir, 2004).

Hydrocolloids are water-soluble, high molecular weight polysaccharides that serve a variety of functions in food systems including enhancing viscosity, creating gel-structures, film formation, control of crystallization, inhibition of syneresis, improving texture, encapsulation of flavours and lengthening the physical stability (Dziezak, 1991; Glicksman, 1991; Garti & Reichman, 1993; Dickinson, 2003). Generally, gums and stabilisers have non-Newtonian rheology and they impart non-Newtonian character to the emulsions even when the amount of the dispersed phase is low (Ford *et al*., 1997). For consumers' acceptability, the long-term stability of sauces is also very important. Thus, hydrocolloids are widely used in the food industry. The ketchup is usually kept in the bottles outside of refrigerator in stores in Iran. Thus different temperatures might affect its rheological properties. This storage approach makes frequently results in a loss of ketchup consistency and serum separation, both of which are not accepted well by consumers. Hydrocolloids can be added to improve consistency and decrease the serum loss of the ketchup (Singh Gujral *et al*., 2002; Sahin & Ozdemir, 2007) but the effect of temperature on the ketchup rheology made with addition of hydrocolloids are yet unknown. Thus, the aims of this study were (i) to assess the flow behaviour and viscosity of ketchup as affected by addition of different hydrocolloids (xanthan, guar gum, CMC) at varying concentrations, (ii) to determine the temperature dependency of such created mixtures and (iii) to establish the best model for describing the flow behaviour of ketchup produced in Iran.

Materials and methods

Materials

Semi-hot break double concentrated tomato paste, with a total soluble solids (TSS) content of 30%, was obtained from a pilot plant vacuum evaporation of tomato juice at the Department of Food Science and Technology (Ferdowsi University, Mashad, Iran). Other ingredients typically used in ketchup preparation (sugar, salt, vinegar, onion, garlic and spices) were purchased from local markets in Mashhad (Iran). Three different commercial hydrocolloids used in this study were guar gum (Food grade xanthan gum, Sigma-Aldrich Co., St Louis MO, USA), xanthan gum (Food grade xanthan gum, Sigma-Aldrich Co.) and CMC (Incom Inc., Mersin, Turkey). The tomato ketchup was prepared in accordance with our formulations, using the ingredients shown in Table 1.

Table 1 Recipe used for the preparation of formulated tomato ketchups

Ingredients formulation	Formulation
Tomato paste (g)	5000
Sugar (g)	500
Salt (g)	60
Vinegar (mL)	175
Onion (g)	25
Garlic (g)	15
Cinnamon (g)	1.5
Clove (g)	1.25
Black pepper fruit (g)	1.5
Paprika extract (ml)	1
Hydrocolloids[a]	

[a] Hydrocolloids were added into ketchups at the concentration of 0, 0.5, 0.75 and 1 g/100 g.

Preparation of tomato ketchup

The concentrated tomato paste was diluted to 12% TSS in accordance to the formulation. This mixture was placed into an open pan and spices (onion, garlic, cloves, cinnamon and black pepper fruits) were added. The mixture was then heated on a hot plate, set at a moderate temperature, and stirred continuously until the mixture reached the desired temperature of 80 °C. The hydrocolloids were preblended with the sugar and salt and then added to the ketchup and stirred for 2 min at 4000×g (JA-12, Beckman Coulter, Fullerton, CA, USA) with an electric hand blender during the final stages of cooking. Heating was continued until the mixture was concentrated to the TSS content of 24%. Then, vinegar and paprika extract were added to the mixture, and the ketchup was heated until a TSS of 26.5% was obtained. The final TSS of all ketchup samples was 28%. The final levels of each hydrocolloid by weight in ketchup samples were 0.5, 0.75 or 1%. While still hot, ketchup samples were poured into glass jars, sealed with rubber seal screw caps, and then stored at ambient temperature (20–22 °C) for 24 h before the analyses. The ketchup without hydrocolloids was deemed as the control.

Rheological measurements

Rheological evaluations were carried out on the ketchup samples after 1 day of storage at ambient temperature using a rotational viscometer (Bohlin Model Visco 88, Bohlin Instruments, Cirencester, UK) equipped with a heating circulator (Julabo, Model F12-MC, Julabo Labortechnik, Seelbach, Germany). Appropriate measuring bob and cups (C14, C25 and C30) were used during viscosity measurements according to the viscosity of dispersion. The prepared samples were loaded into the cup and allowed to equilibrate for 10 min at desired temperature (25, 35, 45 or 55 °C) and subjected to a programmed logarithmic shear rate ramp increasing from 0 to 300 s^{-1} during 3 min followed by a logarithmically decreasing rate of shear from 300 to 0 s^{-1} in 3 min.

The power law (Sahin & Ozdemir, 2004) and Herschel–Bulkley (Sharoba *et al.*, 2005) equations were found to be an adequate model to describe the flow behaviour of the ketchup. Flow behaviour was described by the fitting of the power law (i) and Herschel–Bulkley (ii) model to experimental data (shear stress-shear rate):

$$\tau = \kappa\dot{\gamma}^{n} \tag{1}$$

$$\tau = \tau_0 + k'\dot{\gamma}^{n} \tag{2}$$

where τ is the shear stress (Pa); ($\dot{\gamma}$) is the shear rate (s^{-1}); k and k' are the consistency coefficients (Pa s^n); n and n' are the flow behaviour index (dimensionless); and τ_0 is the yield point (Pa s). The temperature dependency was evaluated by fitting the Arrhenius-type model to experimental data using the consistency index as an indication of the viscous nature of food (Sengul *et al.*, 2005):

$$k = k_0\,e^{E_a/RT} \tag{3}$$

where k_0 is the proportionality constant (or consistency coefficient at a reference temperature, Pa s^n), E_a the activation energy (J mol^{-1}), R the universal law gas constant (J mol^{-1} K), and T the absolute temperature (K).

Statistical analysis

The experiments were organised as a randomised full factorial design with hydrocolloids (three levels), hydrocolloids concentration (four levels) and temperature (four levels) as the main effects. The whole design was replicated twice. The results were analysed using a general linear model (GLM) procedure of the MINITAB ver. 14.2. The level of significance was preset at $P < 0.05$.

Results and discussion

Flow behaviour

Both consistency coefficients (k and k') and yield point were significantly ($P < 0.05$, $P < 0.01$ and $P < 0.0001$, respectively) affected by all main factors (type and concentration of hydrocolloids, and temperature) and all interactions of these factors in the present study (Table 2). The consistency coefficient (k, k') and flow behaviour index (n, n') obtained by fitting of the power law and Herschel–Bulkley models to the experimental shear stress-shear rate data, as a function of temperature are given in Table 3. The power law equation was found to be an adequate model to describe the flow behaviour of the samples in this study. Viscosity functions data showed that all ketchups under examination were non-Newtonian fluids, since the values for flow behaviour indices, n, were below 1, which was indicative of the pseudoplastic (shear thinning) nature of tomato ketchups (Singh Gujral *et al.*, 2002; Sahin & Ozdemir, 2004; Bayoda *et al.*, 2008). The coefficients of determination (R^2) obtained were high and varied from 0.995 to 0.999 for power law and 0.990 to 0.993 for the Herschel–Bulkley models. The flow behaviour indices (n) of the power law model ranged between 0.189 and 0.228 while the same parameters were between 0.216 and 0.263 for the Herschel–Bulkley model.

As estimated by the power law model, the addition of each gum decreased the flow behaviour index values except for guar gum at 0.75% concentration but this decrease was insignificant (Table 3). But no such trend was predicted by the Herschel–Bulkley model and addition of hydrocolloids sometimes increased and sometimes decreased the n' values (Table 3). The smaller the n values the greater the departure from the Newtonian behaviour (Chhinnan *et al.*, 1985). Therefore, the ketchup with the level of 1% of guar gum was more pseudoplastic at 55 °C (Table 3). For a provision of a high viscosity and good mouth feel a hydrocolloids characterised by a low n-value would be required (Marcotte *et al.*, 2001).

Table 2 Adjusted mean squares from analysis of variance of rheological properties of ketchups[a]

Source of variation	DF	τ_0 (Pa)	*P*-value	k' (Pa s^n)	*P*-value	k (Pa s^n)	*P*-value
Hydrocolloid (H)	2	39.228	< 0.0001	39.538	< 0.0001	108.428	< 0.0001
Concentration (C)	3	155.299	< 0.0001	198.621	< 0.0001	351.86	< 0.0001
Temperature (T)	3	37.37	< 0.0001	141.489	< 0.0001	281.115	< 0.0001
H×C	6	6.542	< 0.0001	4.938	< 0.0001	12.6	< 0.0001
H×T	6	1.816	0.001	2.130	< 0.0001	5.487	< 0.0001
C×T	9	2.032	< 0.0001	10.111	< 0.0001	21.48	< 0.0001
H×C×T	18	1.087	0.003	0.746	< 0.0001	0.809	< 0.0001
Error	48	0.395		0.197		0.145	

[a] k and k' (consistency coefficient, Pa s^n) and τ_0 (yield point, Pa) were obtained by fitting the power law and Herschel–Bulkley models, respectively, to the data.

Table 3 Effect of hydrocolloid concentration and temperature on yield point (τ_o), consistency coefficient (k, k') and flow behaviour index (n, n') from the power law and Herschel–Bulkley model of formulated ketchups[a]

Hydrocolloid/ concentration (%)	Temperature (°C)	Power law model			Herschel–Bulkley			
		k (Pa s^n)	n	R^2	τ_o (Pa)	k' (Pa s^n)	n'	r^2
Control								
	25	19.34	0.228	0.999	4.41	16.18	0.250	0.991
	35	11.38	0.225	0.995	2.18	9.89	0.244	0.992
	45	9.53	0.219	0.998	2.39	7.82	0.244	0.992
	55	8.42	0.213	0.999	2.57	6.56	0.244	0.993
Xanthan gum								
0.5	25	23.82	0.218	0.998	9.37	16.70	0.257	0.991
	35	22.04	0.214	0.998	7.79	16.22	0.249	0.992
	45	19.85	0.212	0.999	6.42	14.83	0.242	0.992
	55	17.84	0.208	0.997	6.11	13.23	0.243	0.990
0.75	25	24.64	0.211	0.999	10.04	17.33	0.255	0.991
	35	23.18	0.209	0.999	9.98	16.41	0.255	0.992
	45	21.43	0.205	0.998	7.12	16.06	0.238	0.993
	55	18.96	0.199	0.998	7.45	13.36	0.239	0.993
1.0	25	26.73	0.204	0.999	11.87	18.38	0.250	0.992
	35	25.62	0.203	0.999	11.39	17.19	0.252	0.992
	45	23.31	0.198	0.996	8.93	16.68	0.244	0.992
	55	20.97	0.199	0.998	7.68	15.24	0.238	0.991
Guar gum								
0.5	25	22.54	0.215	0.998	9.05	16.00	0.256	0.991
	35	17.04	0.208	0.995	5.88	12.71	0.243	0.992
	45	15.99	0.206	0.997	6.01	11.73	0.244	0.992
	55	14.26	0.204	0.998	3.78	11.45	0.229	0.992
0.75	25	23.87	0.231	0.999	7.39	18.54	0.263	0.993
	35	18.88	0.227	0.999	4.67	15.46	0.251	0.991
	45	16.44	0.219	0.997	5.04	12.53	0.249	0.990
	55	15.77	0.218	0.999	5.00	11.86	0.248	0.991
1.0	25	24.63	0.206	0.999	9.33	17.84	0.256	0.992
	35	19.72	0.198	0.998	7.56	14.11	0.238	0.992
	45	17.68	0.194	0.999	4.11	14.31	0.216	0.992
	55	16.98	0.189	0.997	5.38	12.60	0.219	0.993
CMC								
0.5	25	24.42	0.221	0.998	8.59	18.24	0.258	0.992
	35	23.16	0.219	0.995	8.62	17.03	0.258	0.991
	45	20.87	0.208	0.997	6.42	16.16	0.240	0.993
	55	18.64	0.201	0.998	6.90	13.43	0.240	0.993
0.75	25	25.98	0.216	0.999	9.92	18.81	0.255	0.993
	35	24.58	0.212	0.999	9.45	17.17	0.255	0.993
	45	23.12	0.208	0.997	8.36	16.98	0.246	0.992
	55	20.44	0.199	0.999	7.58	14.81	0.237	0.993
1.0	25	27.22	0.218	0.999	9.87	20.10	0.255	0.992
	35	26.10	0.215	0.998	10.34	18.31	0.256	0.992
	45	24.28	0.204	0.999	9.42	17.12	0.244	0.991
	55	22.13	0.196	0.997	8.12	16.11	0.235	0.991
SEM		0.27	0.01		0.44	0.32	0.003	

The values of consistency coefficient, k, ranged from 8.42 to 27.22 Pa s^n. The addition of different hydrocolloids and increase in their concentrations resulted in higher k values at all temperatures tested (Table 3). The increase in the consistency coefficient was the highest with the addition of CMC followed by the addition of xanthan and guar gums. The k' values ranged from 6.56 to 20.1 Pa s^n and addition of CMC had the highest and guar gum had the lowest effect on consistency coefficient evaluated by the Herschel–Bulkley model (Tables 3). Both indices as predicted by models were positively and significantly ($P < 0.05$) affected by the increase in hydrocolloid concentration (Table 3).

Similar results for the flow behaviour indices and consistency coefficients have been reported previously by Dervisoglu & Kokini (1986), Rani & Bains (1987), Bottiglieri *et al.* (1991), Sahin & Ozdemir (2004) and Sharoba *et al.* (2005). Singh Gujral *et al.* (2002) also found that the addition of different hydrocolloids increased the consistency of tomato ketchup. They mentioned that among the hydrocolloids used guar, xanthan and CMC had the highest effect on the consistency coefficients.

Marcotte *et al.* (2001) investigated the effects of concentration and temperature on the rheological behaviour of some food hydrocolloids (carrageenan, pectin, gelatin, starch, and xanthan). They found in general that an increase in concentration of hydrocolloids was accompanied by an increase in pseudoplasticity. In their study, the consistency coefficients increased similarly to our observations with the concentration of hydrocolloids. The yield point (τ_0) was higher for ketchups with xanthan gum and CMC but lower after addition of guar gum (Table 3). τ_0 was also positively related to the gum concentration; however, this trend was not apparent for guar gum (Table 3).

The relationship between apparent viscosity (η_a) and shear rate of tomato ketchups with added hydrocolloids was plotted in Fig. 1. It is evident from the figures that the η_a of all samples decreased with increasing shear rate with apparent direct dependency of the gum concentration. Ketchups with addition of hydrocolloids at a level of 1% had the highest consistency. The higher solid content generally causes an increase in the viscosity resulting from mainly molecular movements and interfacial film formation (Bhattacharya *et al*., 1992; Maskan & Gogus, 2000). Gomez-Diaz & Navaza (2003) explained such increase of *k* values by increasing water binding capacity, which was related to an increase of hydrocolloids concentration. The addition of guar gum had a greater effect on the increase of viscosity than CMC and xanthan gum supplementation. Xanthan gum also caused a significant ($P < 0.05$) increase in the apparent viscosity of the tomato ketchup. Its branching nature provided its unusual rheological characteristics, better than CMC. The least increase in the apparent viscosity with the addition of CMC could be resulted from its lower molecular weight and DS. Increasing the apparent viscosity with additional xanthan gum is in agreement with other findings (Garti *et al*., 1997; Schorsch *et al*., 1997; Alexander, 1999; Casas *et al*., 2000).

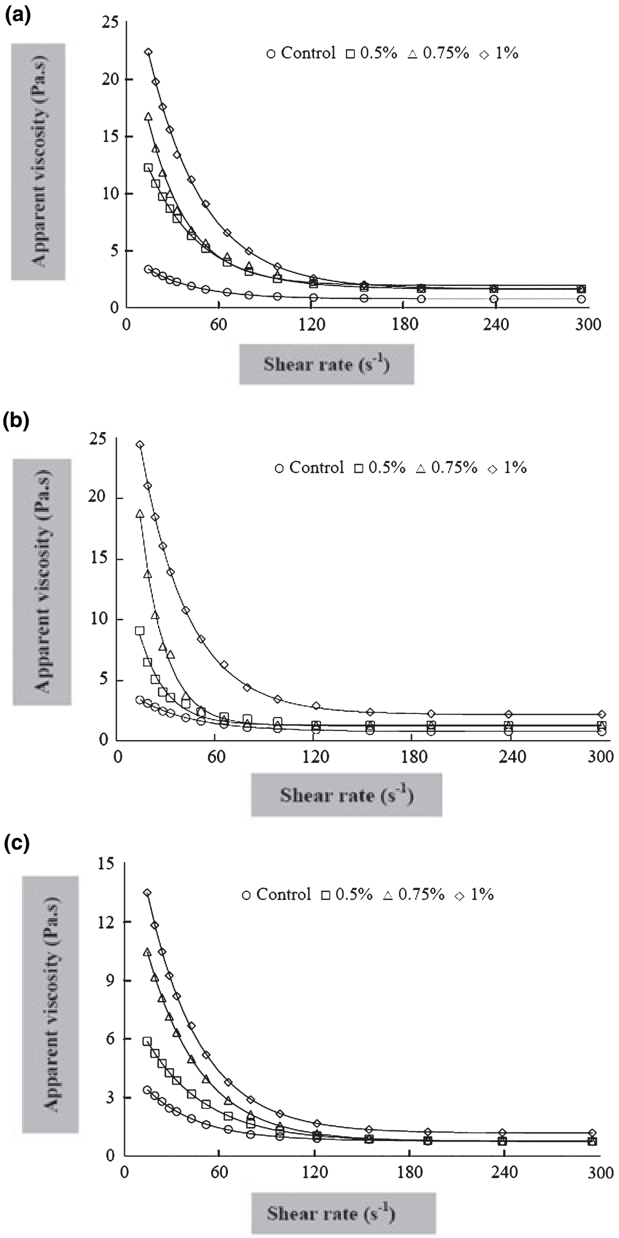

Figure 1 The apparent viscosity of ketchup at different shear rates as affected by three different concentrations of xanthan gum (a), guar gum (b) or CMC (c) at different concentrations (0.5%, 0.75%, and 1%) at 25 °C.

Effect of temperature

Table 4 shows the effect of temperature on rheological properties of ketchup containing different gums. A decrease in consistency coefficients was observed with the increasing temperature indicating a decrease in apparent viscosity at higher temperatures (Fig. 2). Similar results were also reported by Sharoba *et al.* (2005). These results also confirmed the observation obtained by Ibarz *et al.* (1996), who reported that temperature had a large effect on the consistency coefficient.

The flow behaviour index also showed a declining trend with the temperature, which indicates that the

Table 4 Effect of different hydrocolloids on Arrhenius-type equation parameters of formulated ketchup[a]

Level of gum (%)	k_0 (Pa s^n)	E_a (KJ mol^{-1})	R^2
Control	0.0025	21.47	0.94
Xanthan gum			
0.5	1.00	7.72	0.99
0.75	1.49	6.85	0.96
1	1.86	6.51	0.95
Guar gum			
0.5	0.186	11.52	0.94
0.75	0.24	11.09	0.95
1	0.41	9.84	0.93
CMC			
0.5	1.26	7.25	0.99
0.75	2.07	6.18	0.98
1	2.87	5.49	0.97

[a] k_0 (Pa s^n) and E_a (J mol^{-1}) parameters were obtained by fitting Arrhenius model to the experimental data.

ketchups tended to have higher pseudoplasticity at higher temperatures (Table 4). In pseudoplastic fruit products, the flow activation energy is directly proportional to the flow behaviour index, i.e. the more pseudoplastic the product, the less the effect of temperature on its apparent viscosity (Sharoba *et al.*, 2005). Sharoba *et al.* (2005) reported that an increase in temperature decreased the flow behaviour index of some commercial ketchup. Razavi *et al.* (2007) also reported that the flow behaviour index of sesame paste/date syrup blends also showed a decreasing trend with the temperature.

The temperature dependence of the viscosity of ketchup was assessed by applying the Arrhenius-type model (Barbosa Canovas & Peleg, 1983; Singh & Eipeson, 2000). The parameters obtained by fitting the consistency coefficient (k) data as a function of temperature are provided in Table 4. High R^2 values showed that the apparent viscosity of ketchups in relation to the temperature obeyed the Arrhenius type behaviour. The E_a values decreased for all samples containing the hydrocolloids in comparison to the control. Therefore, the control had the greatest temperature dependency and the ketchup containing 1% CMC, the least. Increasing hydrocolloid concentration in ketchup resulted in a decline of the activation energy. However, the effect of gums on increasing of k_0 (as a viscosity index) was more pronounced upon addition of CMC. Other reports showed that the activation energy increases with the soluble solids content (Harper & El-Sahrigi, 1965; Rani & Bains, 1987; Sharoba *et al.*, 2005). Marcotte *et al.* (2001) described the temperature effect on apparent viscosity of some food hydrocolloids with Arrhenius model and concluded that xanthan gum gave the lowest E_a values, whereas intermediate values of activation energy was obtained for starch, pectin and gelatin. In general, the higher the activation energy, the greater the effect of temperature on the viscosity (Mohd. Nurul *et al.*, 1999).

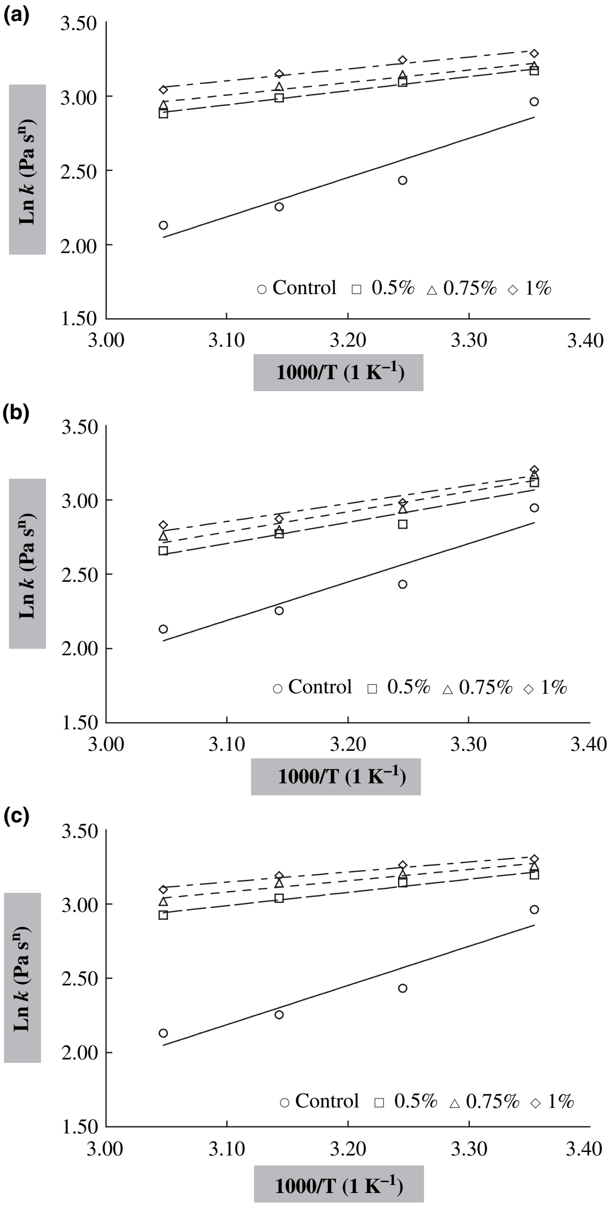

Figure 2 Consistency index as a function of temperature of ketchup samples stabilised by addition of (a) xanthan, (b) guar, or (c) CMC at different concentrations (0.5%, 0.75% and 1%).

Conclusions

The results of this study indicated that ketchup supplemented with studied hydrocolloids (xanthan, guar, CMC) behave as non-Newtonian, shear thinning fluid in temperature range of 25–55 °C. The power law model was more reliable estimation of the rheological behaviour of the ketchups than the Herschel–Bulkley model. Increasing the gum concentration increased the apparent viscosity in comparison to the control; however, the effect of guar gum on viscosity was greater than those of xanthan and CMC gums. The consistency indices increased with the concentration of all three hydrocolloids showing that addition of these gums stabilises the consistency of the ketchup. The activation energy in general is found to decrease using gum substitute as compared with the control sample. Ketchup containing 1% CMC had the lowest temperature dependency meaning that had the highest stabilising effect on ketchup.

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