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ORIGINAL PAPER

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Chemical, sensory and rheological properties of some commercial German and Egyptian tomato ketchups

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Abstract The rheological behaviour of eight tomato ketchups measured in the shear rate range from 0.1 to 100 1/s and with oscillatory tests was studied over a wide range of temperatures (0–50 °C) using a Physica UDS 200 rheometer. The results indicated that these tomato ketchups behave as non-Newtonian fluids semi-solid and have a definite yield stress. The relationship between η_{eff} and temperature of all the tomato ketchup brands under investigation was examined. Significantly higher correlation was found between η_{eff} and temperature. The η_{eff} values decrease with an increase in temperature. Oscillatory test data revealed weak gel-like (dispersion structure) behaviour of the ketchup: the magnitudes of G' were higher than those of G'', and both increased with oscillatory frequency. The effect of temperature on the viscosity can be described by means of an Arrhenius-type equation. The flow activation energy for viscous flow depends on the chemical composition; the flow activation energy increases with the total solids contents. Chemical, physical and sensory tests for tomato ketchups were made.

Keywords Tomato ketchup · Chemical composition · Rheological parameters · Flow behaviour · Oscillatory test · Flow activation energy

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Introduction

Ketchup is a descriptive term for a number of different products, which consist of various pulp, strained and seasoned fruits; the variety made from tomatoes being the most popular condiment. Good quality ketchup is judged by flavour, consistency, uniformity and attractiveness of colour. Tomato ketchup is a clean, sound product made from properly prepared strained tomatoes with spices, salt, sugar and vinegar with or without starch, onions and garlic and contains not less than 12% of tomato solids. It is the most important product of tomato and is consumed extensively. A major part of the tomato processed is used for making ketchup [1]. Many newly developed tomato products with or without other vegetable juices are now appearing on the market, and among these new products with "high service content" tomato ketchups have been probably the first to find favour with the consumer and they still represent a large share of the market [2]. Even though ketchup is known worldwide, information on this product in the technical/scientific literature is limited [3]. Commercial ketchup can have an extremely variable composition; nearly all manufacturers have a formula of their own which differs in some respects from those of other manufacturers. These differences are mainly in the quantity, number and amount of spices or other flavouring agents used. Thus, it is difficult to establish the analytical parameters on which quality depends. Usually viscosity is considered an important physical property related to the quality of food products. Viscometric data are also essential for the design evaluation of food processing equipment such as pumps, piping, heat exchangers, evaporators, sterilizes, filters and mixers. Many foods of commercial importance, such as tomato paste and tomato ketchup, are concentrated dispersions of insoluble matter in aqueous media. Their rheological behaviour, especially the yield point, is important in the handling, storage, processing and transport of concentrated suspensions in industry [4]. The viscosity of fluid foods is an important parameter of their texture. It determines to a great extent the overall feel in the mouth and influences the intensity of the flavour [5]. Therefore, for many years, the viscosity of liquid and semi-solid foods has been of interest to researchers and industrialists. Correlation between sensory and instrumental values of texture parameters can be used for industrial quality control to keep the sensory viscosity within a range assuring good consumer acceptance [6, 7]. A complete outline of the physicochemical and sensory characterization of ketchup has been reported previously [8]. The yield point values of ketchup were correlated with the pectin content [9]. Ketchups are time-independent, non-Newtonian fluids that show a small thixotropy [10]. The different brands examined differed essentially only in viscosity and yield point values. The quality of ketchup is strongly dependent on its preservation. The most typical use of ketchup is in “fast-food” restaurants, where it is normally stored at room temperature after the opening of the container; the classic black ring which is formed in the bottle neck is a definite sign of the result of a Maillard-type degradation, which implies other important quality changes [2]. All the test modes discussed so far involve subjecting the foodstuff to a step change in $\dot{\gamma}$ or τ and measuring the stress as a function of time. A useful procedure in the study of food rheology is to subject the same sample to a periodic deformation. If the rheological behaviour is studied through a dynamic test, the stress is made to vary sinusoidally with time at a determined frequency (ω). Oscillation is a nondestructive technique for investigating the structure of foods. It is an ideal method for measuring structural formation changes. From the application of this technique, which is especially valuable for small values of time, several rheological parameters were defined [11, 12]. On the other hand [11] steady shear and dynamic shear rheological properties of commercial tomato ketchup samples have been determined and it was found that the Cox–Merz rule was not applicable. The present work was done to determine the rheological behaviour of tomato ketchups in steady and dynamic shear, in relation to the chemical composition, temperature and sensory characteristics.

Materials and methods

Materials

Eight brands of commercial tomato ketchups were purchased in local German and Egyptian supermarkets, five were obtained from Germany (Lidl, Kraft, Heinz, Werder, Reichelt) and three were obtained from Egypt (GSF Egypt, Heinz Egypt, Americana). The tomato ketchups were examined in the first week after production and were tested soon after their bottles had been opened.

Methods

Analytical methods

Moisture content, total solids, total soluble solids, ash, ascorbic acid and starch were determined according to the methods in Ref. [13]. The pH was measured with a Schott CG840 pH meter. Titratable acidity was determined by titration with 0.1 N NaOH solution using phenolphthalein as the indicator according to the method in Ref. [13]. The total and reducing sugar content was determined by the Shaffer and Hartman method as described in Ref. [13]. Total pectic substances contents were determined by the method of Carre and Hayness, which was described in Ref. [14]. The pulp content was determined according to the method in Ref. [15]. The colour index of the ketchup was determined by the method in Ref. [16]. Carotenoids were determined according to the method in Ref. [17], while lycopene was determined according to the method in Ref. [18]. The specific heat (C_p) was determined according to the method in Ref. [19]. The density was determined with a pycnometer at 5 and 30 °C according to the method in Ref. [13].

Rheological measurements

Rotational and oscillatory measurements were performed using a Physica UDS 200 rheometer equipped with an electronically commutated synchronous motor allowing rheological testing in controlled-stress and controlled-strain modes.

The instrument allows the individual creation of complex real time tests containing a large number of different intervals in controlled-stress and controlled-strain modes, both in rotational and in oscillatory modes. The direct strain oscillation option based on a real position control as described earlier was used for oscillatory testing.

Precise temperature control was done by a Peltier cylinder TEZ150P temperature system that assures minimal temperature gradients across the measuring gap by a patent-protected design. The data were analysed by using Universal Software US200.

The Herschel–Bulkley model describes the flow curve of a material with a yield point and shear thinning or shear thickening behaviour at stresses above the yield in comparison with the Bingham or Casson equations with a higher correlation coefficient:

$$\tau = \tau_0 + K\dot{\gamma}^n. \tag{1}$$

Effective viscosity

The effective viscosity was calculated using Eq. (2) as described in Ref. [20]:

$$\eta_{\text{eff}}(\dot{\gamma}) = \frac{\tau_0}{\dot{\gamma}} + K\dot{\gamma}^{n-1}. \tag{2}$$

Hysteresis area

The hysteresis area evaluation method calculates the area between two curves, commonly the up and down curve of a shear rate sweep. This area is given in units of pascals per second.

Oscillatory measurement analysis

The storage modulus G', the loss modulus G'' and the angular frequency ω were described by Eqs. (3) and (4):

$$G' = K'_1(\omega)^x, \tag{3}$$

$$G'' = K''_2(\omega)^y. \tag{4}$$

Plots of logω versus logG' and logG'' dynamic rheological data were subjected to linear regression and the magnitudes of the intercepts, slopes, and R^2 were tabled according to the methods in Refs. [21, 22].

Flow activation energy and the effect of temperature on viscosity

The flow activation energy was calculated using the Arrhenius-type equation as mentioned in Refs. [15, 23, 24]:

$$\eta = \eta_\infty \exp\left(E_a/RT\right). \quad (5)$$

Sensory evaluation

Sensory tests were carried out by a properly well trained panel of 20 testers. They were selected if their individual scores in ten different tests showed a reproducibility of 90%. Samples of the different products in arbitrarily identified glasses were ranked in order of acceptability for consistency (texture), colour, taste, odour and overall acceptability by each panellist separately.

Statistical analysis

The data for the sensory tests of all the tomato ketchup were subjected to analysis of the variance followed by least significant digit analysis according to the method in Ref. [25].

Results and discussion

Technological characteristics, such as chemical composition, rheological, physical and sensory properties, play an important role in the formation of the processing steps which are necessary for the production of tomato ketchup. This part deals with some of these aspects, in order to obtain some useful data for the differentiation between the tomato ketchups tested: Lidl, Kraft, Werder, Heinz and Reichelt from Germany and Americana, Heinz and GSF from Egypt. These kinds represent the most widely available tomato ketchups that are used in Germany and Egypt.

Chemical and physical properties of tomato ketchup

The results recorded in Table 1 show some chemical and physical properties of the tomato ketchups.

Total solids, moisture and ash

The solids content is an important factor for the production of tomato ketchup. It is well known that the higher the total solids the better will be the quality of the end product. As shown in Table 1 there is a slight difference in the total solids content between ketchup samples. The Americana ketchup had the highest total solids content, 33.35%, while the Kraft ketchup showed the lowest content, 24.36%. The results are in agreement with those obtained by Canovas and Peleg [26], who found the total solids in Heinz tomato ketchup to be 32.2 % and in Stop and Shop tomato ketchup to be 34.4%. Also the same data of Table 1 represent the ash content of the tomato ketchup. The lowest content was 2.186% for the Heinz ketchup from Egypt, while the highest content was 3.94%

Table 1 Some chemical and physical properties of tomato ketchup. Each value is the average of three replicates plus/minus the standard error. The chemical composition is on a wet weight basis.

Components	Lidl	Kraft	Werder	Heinz	Reichelt	Americana Egypt	Heinz Egypt	GSF Egypt
Total solids (%)	28.26±0.040	24.36±0.075	24.38±0.190	32.49±0.100	26.21±0.880	33.35±0.142	31.31±0.022	32.54±0.087
Moisture (%)	71.58±0.040	75.64±0.075	75.62±0.190	67.51±0.100	73.79±0.880	66.65±0.142	68.69±0.022	67.46±0.087
Ash (%)	3.610±0.001	3.060±0.001	2.548±0.0001	3.940±0.002	3.374±0.0008	2.938±0.005	2.186±0.0026	2.420±0.006
Ascorbic acid (mg/100 g)	27.14±0.137	26.97±0.308	23.39±0.095	21.30±0.008	24.12±0.510	28.99±0.063	27.11±0.041	29.89±0.033
pH values	3.663±0.003	3.713±0.003	3.843±0.003	3.403±0.003	3.413±0.003	3.476±0.003	3.683±0.003	3.713±0.012
Titratable acidity (as anhydrous lactic acid) (%)	1.407±0.066	1.283±0.006	0.829±0.004	1.640±0.009	1.619±0.031	1.544±0.0001	1.606±0.0005	1.559±0.0017
Starch (%)	0.831±0.002	0.727±0.002	3.246±0.004	0.593±0.011	3.924±0.017	4.513±0.015	0.863±0.012	2.391±0.013
Total sugars (%)	15.5460±0.017	11.9748±0.015	12.0460±0.104	16.9706±0.089	14.2137±0.071	17.8370±0.048	15.3846±0.110	17.7929±0.127
Reducing sugars (%)	10.2731±0.011	8.3590±0.017	8.1996±0.012	12.5689±0.037	9.1154±0.044	11.9992±0.025	10.1496±0.042	12.6050±0.038
Nonreducing sugars (%)	5.2729	3.6158	3.8464	4.4017	5.0983	5.8378	5.2350	5.1879
Total pectic substances (%)	6.6104	5.9242	5.8246	7.9330	5.5262	6.4849	6.0108	6.8045
Water-soluble pectin (%)	0.9356±0.013	1.1506±0.063	1.1536±0.017	1.6482±0.024	1.0928±0.015	1.2820±0.018	1.1243±0.016	1.4741±0.013
Ammonium oxalate soluble pectin (%)	4.1036±0.022	3.5478±0.025	3.2971±0.038	4.4624±0.021	3.2696±0.052	3.4246±0.037	3.7264±0.041	3.8682±0.036
Acid-soluble pectin (%)	1.5712±0.009	1.2258±0.016	1.3739±0.021	1.8224±0.015	1.1638±0.018	1.7783±0.014	1.1601±0.023	1.4622±0.019
Pulp content (v/v) (%)	56.53±0.546	58.87±1.922	80.46±0.067	71.13±1.235	63.80±0.529	74.47±0.176	76.47±0.176	66.93±0.874
Colour index (optical density at 420 nm)	0.867±0.002	0.848±0.007	0.888±0.003	0.612±0.002	0.819±0.0003	0.912±0.0005	0.953±0.003	0.986±0.0025
Carotenoids (mg/l)	1.415±0.022	1.289±0.034	1.612±0.037	0.934±0.056	1.053±0.002	1.095±0.0031	1.651±0.0074	1.674±0.0552
Lycopene (mg/100 g)	8.9729±0.032	7.710±0.011	9.137±0.033	7.013±0.008	8.219±0.034	8.352±0.0203	11.169±0.020	11.249±0.019
Specific heat capacity (kJ/kg K)	3.0674±0.003	3.1873±0.001	3.1867±0.002	2.9517±0.002	3.1321±0.002	2.9278±0.003	2.9848±0.003	2.9503±0.002
Density at 5 °C (kg/m^3)	1118.64±0.000	1116.21±0.052	1113.28±0.000	1150.42±0.033	1119.27±0.000	1158.58±0.008	1150.93±0.003	1160.67±0.007
Density at 30 °C (kg/m^3)	1109.64±0.037	1105.25±0.027	1102.42±0.003	1140.45±0.011	1109.69±0.004	1149.52±0.005	1143.39±0.001	1150.75±0.001

for the Heinz ketchup from Germany. The results are in agreement with those obtained by the France Centre de Recherches Foch [27], who found the ash content to be 3.4, 2.8 and 4.2 for tomato ketchup.

Titratable acidity and pH value

pH and acidity are important factors influencing the quality of tomato ketchup. The pH values ranged between 3.40 for Heinz and 3.84 for Werder ketchups. The values obtained are in accordance with that obtained by Rani and Banins [9], who found that the pH for tomato ketchup ranged between 3.55 and 3.87, and by Porretta and Birzi [2], who found the pH for tomato ketchup to be 3.78 and 3.76. The acidity values obtained from the ketchups tested ranged between 0.83% and 1.64% for Werder and Heinz ketchups, respectively. Also the results are in agreement with those obtained by Porretta and Birzi [2].

Ascorbic acid (vitamin C)

Tomato and tomato products are considered as a good source of vitamin C. The results given in Table 1 show that the ketchup samples under investigation contained the following vitamin C levels: 27.14, 26.97, 23.39, 21.30, 24.12, 28.99, 27.11 and 29.89 mg/100 g. The results are in agreement with those of Orzaez et al. [28], who found the vitamin C content ranged between 8.11and 60.04 mg/100 g.

Total sugars

Sugars are one of the most important quality parameters of tomato ketchup, because they contribute to the flavour, quality, platability and discoloration of tomato ketchup. The data given in Table 1 show that the total sugar contents of the ketchups tested were within the range 11.97–17.79% for the Kraft and GSF Egypt ketchups, respectively, while the reducing sugar content ranged from 8.36% to 12.61% for the Kraft and GSF Egypt ketchups. The data obtained are in agreement with the data observed by Pearson [14], the France Centre de Recherches Foch [27] and Vitacel [29], who found mean values and ranges including sucrose 9.3 and 4.2–12.7 g/100 g, glucose 6.1 and 3.7–10.8 g/100 g and fructose 5.7 and 3.6–11.0 g/100 g.

Pectic substances and pulp content

Pectic substances are the main factor which has a great influence on the quality, stability, process ability and viscosity of tomato ketchup. The total pectic content of ketchup was the sum of the pectin fractions extract, the water extract, the ammonium oxalate extract and the acid extract. The results obtained presented in Table 1 show the total pectin for the ketchups. The ammonium oxalate extract was the highest, while the water-soluble pectin showed the lowest content. The data obtained were in accordance with the data found by Sharoba [30], who found that the ammonium oxalate extract was the highest in tomato products. The pulp content was also in the range from 80.46 to 56.53 v/v for Werder and Lidl ketchups, respectively.

Colour index, lycopene and carotenoid content

The colour index (optical density at 420 nm) for the ketchups was between 0.612 and 0.986 for the Heinz and GSF Egypt ketchups, respectively. Epidemiological studies have shown that increased consumption of fruits, including tomatoes, is associated with a reduced risk of lung and other epithelial cancers. It has been suggested that the high carotenoid levels in tomatoes and fruits are responsible for this reduced risk [31]. Also increased consumption of tomatoes and tomato products has been associated with decreased cancer risk. One fat-soluble compound identified in tomatoes which may be responsible for this association is lycopene [32].

The carotenoid contents presented in Table 1 are in the range 0.93–1.67 mg/l. The results are in agreement with those obtained by Tavares and Rodriguez [33]; on the other hand, the lycopene content ranged between 7.71 and 11.25 mg/100 g. These results are in agreement with those obtained by Wilberg and Rodriguez [34].

Density and specific heat capacity

Knowledge of the physical properties of food is fundamental when analysing the unit operations present in the food industry. The study of these food properties and their responses to process conditions is necessary because they influence the treatment received during the processing and also because they are good indicators of other properties and qualities of food. This allows a better control of both product and processing, with benefits for the producer, industry and the consumer. The transport phenomena of momentum, heat and mass can be applied with efficiency in food systems if engineering data are available [35]. Unfortunately, such engineering property data are scarce. Data such as density (ρ), and its variation with temperature, and specific heat capacity are very important for the food industry in general and in particular for fruit derivatives since they are necessary for the design and the optimisation of several processing operations (pumping, evaporation, heat transfer). The densities of tomato ketchup at 5 and 30 °C are shown in Table 1. GSF Egypt tomato ketchup had the highest density (1160.67 kg/m^3), while the Werder tomato ketchup showed the lowest level (1113.28 kg/m^3). These results are in agreement with those obtained by Ramos and Ibarz [36], who found that the density decreased with an increase in temperature and increased with an increase in soluble solids concentration.

The densities of Lidl ketchup are 1,118.64 and 1,109.64 kg/m^3 at 5 and 10 °C, respectively.

During the manufacture of some commercial products, juice or ketchup is concentrated. It is necessary to know the specific heat changes due to different factors, as a function of moisture content, since, for the purpose of many engineering calculations, the variations due to temperature are small and an average value of the specific heat is used for limited temperature ranges [37]. The specific heat values varied from 2.93 to 3.19 kJ/kg K. These results agree with the results obtained by Alvarado [19], who found that the specific heat for tomato (3.94, 3.48, 3.18 and 2.93 kJ/kg K) depended on the moisture content (94.5%, 8.6%, 74.8% and 64.1%), respectively. The specific heat capacity is required in cooling, freezing and heat processes, and for the calculation of energy demand. Specific heat is used in the estimation of the Prandtl number ($Pr=\eta \cdot C_p/\lambda$), which is important in the process calculation.

Rheological properties of tomato ketchups

Shear rate examination

The most important single factor determining the quality of commercially processed tomato ketchup is its viscosity. Rheological properties of tomato ketchups were studied over a wide range of temperature at 0, 10, 20, 30, 40 and 50 °C. Tomato ketchup showed non-Newtonian fluid character. It showed semi-solid behaviour at all temperatures assayed. In pseudoplastic materials the apparent viscosity decreases as the rate of shear at which the material is tested increases. This semi-solid behaviour is the result of a complex interaction among the pulp, soluble pectin, organic acids, soluble solids and the high volume concentration of particles [4].

Herschel–Bulkley model used

The steady flow curves obtained were well described by the Herschel–Bulkley model. The experimental values of the shear stress and the shear rate were fitted by Eq. (1). The rheological parameters τ_0, K and n were calculated, using Physica US200 software, are shown in Table 2. The yield point (τ_0) was higher for Reichelt and Heinz Egypt ketchups, and lower for Heinz, Americana and GSF brands. The τ_0 values at 20 °C were 12.39, 11.91, 13.23, 10.74, 14.76, 6.41, 20.69 and 6.81 Pa for all the tomato ketchups under study. τ_0 decreased when the temperature increased for the different tomato ketchup brands under investigation. These data are in agreement with those previously reported by other investigators [38, 39].

On the other hand, the K value was higher for Heinz (30.23 Pa s^n) and lower for Reichelt (13.15 Pa s^n) ketchups at 0 °C. These data are in agreement with those previously reported by other investigators [26]. The reason for such differences in the flow behaviour constants between tomato ketchup brands might be referred to the variations in their content of total solids, pectic substances and the particle size and shape. Chemical analysis of tomato ketchup brands (Table 1) indicated that Heinz tomato ketchup has the highest amount of total pectic substances, 7.93%, and total solids, 32.49%. These results are in agreement with those obtained by Sharoba [30], who reported that the higher K values could be referred to the presence of more suspended total pectic substances in the tomato products. The consistency index K increased with increasing total solids and decreased with increasing temperature.

Table 2 Arrhenius-type constants relating the effect of temperature and viscosity at 100 rpm on tomato ketchup.

Products	E_a (kJ/mol)	η_∞ (mPa s)	R^2	Temperature range (°C)
Lidl	9.336	2.828	0.995	0–50
Kraft	7.711	3.558	0.992	0–50
Werder	9.055	3.059	0.999	0–50
Heinz	7.124	3.790	0.997	0–50
Reichelt	10.873	2.240	0.975	0–50
Americana Egypt	10.649	2.635	0.999	0–50
Heinz Egypt	10.195	2.690	0.985	0–50
GSF Egypt	9.162	2.765	0.999	0–50

The flow index values n for the tomato ketchups are given in Table 2, with n<1 indicating that the rheological behaviour is pseudoplastic. The n values ranged between 0.25 and 0.42. These results could be confirmed with the data obtained by Young et al. [39], who indicated that the n value was 0.36 for tomato ketchup at 25 °C, and by Canovas and Peleg [26], who indicated that the n values obtained from two tomato ketchups (Heinz and Stop & Shop) ranged between 0.38 and 0.40. It is observed from these results that K and n decreased as the temperature rose. At a given temperature, K increased with the increase in total solids. These results could be confirmed with the data obtained by Ibarz et al. [24], who reported that temperature was found to have a large effect on the consistency index but had little effect on the behaviour index. The rheological parameters are very important values; from the engineering standpoint they are required to calculate an important dimensionless value, which is known as the generalized Reynolds number. To Solve the problems of fluid flows and pumping we need the Reynolds number [40]. Besides, the calculation of the heat transfer coefficient for non-Newtonian fluids depends upon the consistency of the fluid as indicated by Charm [41].

The coefficient of correlation r for all tomato ketchup samples ranged form 0.994 to 0.999.

Thixotropic behaviour

The characterization of the time-dependent flow properties of ketchup is important for food processing and handling, process design and control, product develop-

Table 3 Herschel–Bulkley parameters of some selected commercial Tomato ketchups.

Product	T (°C)	τ_0 (Pa)	K (Pa s^n)	n	A_{TH} (Pa/s)	r	Standard deviation (Pa)	η_{eff} (100 1/s) (Pa s)
Lidl	0	12.3068	20.0285	0.3197	58.1471	0.9985	1.0504	0.9961
	10	15.7275	17.5870	0.3172	57.2791	0.9991	0.6950	0.9151
	20	12.3860	16.4536	0.2936	50.7233	0.9994	0.4677	0.7599
	30	11.7691	15.1366	0.2841	21.8698	0.9997	0.2820	0.6777
	40	9.4902	13.5721	0.2825	20.3319	0.9997	0.2508	0.5934
	50	9.0160	12.0232	0.2944	84.2759	0.9998	0.2050	0.5566
Kraft	0	10.2800	20.6487	0.3195	142.9456	0.9991	0.9003	1.0021
	10	13.0214	16.3841	0.3258	21.7734	0.9992	0.6494	0.8648
	20	11.9059	15.1682	0.3165	10.6336	0.9997	0.3698	0.7706
	30	11.8486	14.2565	0.3143	42.5832	0.9997	0.3075	0.7247
	40	9.1167	10.9722	0.3221	23.3525	0.9998	0.2041	0.5748
	50	9.6065	9.8657	0.3323	137.5546	0.9997	0.2376	0.5518
Werder	0	15.9199	18.5343	0.3679	−357.5409	0.9999	0.04122	1.1679
	10	15.0714	15.6712	0.3651	−278.0301	0.9999	0.1738	0.9927
	20	13.2298	14.2858	0.3531	−213.8128	0.9999	0.2067	0.8586
	30	12.1083	13.0206	0.3481	−190.1649	0.9999	0.1391	0.7680
	40	11.3622	11.4883	0.3513	−152.0508	0.9999	0.0876	0.6929
	50	10.6891	10.1207	0.3556	−100.8229	0.9999	0.0505	0.6274
Heinz	0	2.6142	30.2300	0.2702	349.7060	0.9991	0.9485	1.0753
	10	6.1703	23.9665	0.2712	219.4178	0.9991	0.7446	0.8973
	20	10.7426	20.4536	0.2750	172.5254	0.9989	0.3698	0.8331
	30	9.1715	18.5896	0.2697	148.6840	0.9998	0.2739	0.7354
	40	10.3718	15.5825	0.2868	193.5472	0.9999	0.2041	0.6875
	50	10.9494	11.9643	0.3147	250.4545	0.9999	0.2376	0.6192
Reichelt	0	27.6880	13.1533	0.3831	146.8294	0.9994	0.6447	1.0447
	10	24.3318	14.0371	0.3447	123.3966	0.9994	0.5482	0.9299
	20	14.7636	12.3765	0.3156	54.7101	0.9999	0.1487	0.6771
	30	12.2438	11.6158	0.3141	25.5546	0.9999	0.1317	0.6159
	40	11.9710	10.4172	0.3266	46.0923	0.9998	0.2228	0.5885
	50	10.1615	9.4036	0.3268	32.7503	0.9997	0.2132	0.5252
Americana Egypt	0	6.5122	21.2910	0.4157	−365.9452	0.9996	0.9983	1.5091
	10	6.1268	18.8290	0.4023	−307.8464	0.9998	0.6427	1.2618
	20	6.4094	16.4216	0.3998	−258.4437	0.9998	0.4675	1.0991
	30	6.3150	13.9206	0.3999	−210.2129	0.9999	0.3628	0.9411
	40	6.4040	11.8069	0.4042	−179.5318	0.9998	0.3292	0.8235
	50	5.9523	10.6568	0.4018	−139.0691	0.9998	0.3264	0.7374
Heinz Egypt	0	26.3161	17.5841	0.3794	625.0226	0.9986	1.26334	1.2720
	10	23.7951	16.6321	0.3587	422.1681	0.9977	1.3722	1.1055
	20	20.6927	15.5263	0.3402	228.5369	0.9973	1.2633	0.9507
	30	19.4517	12.8961	0.3437	96.0905	0.9963	1.2454	0.8224
	40	19.2523	13.6668	0.3157	46.3696	0.9942	1.4109	0.7773
	50	12.4338	10.7888	0.3232	85.5568	0.9970	0.8365	0.6023
GSF Egypt	0	3.3556	18.4351	0.3292	165.8373	0.9990	0.8425	0.8729
	10	5.8053	17.6516	0.3019	87.0963	0.9984	0.8645	0.7668
	20	6.8057	16.9099	0.2789	38.0513	0.9984	0.7351	0.6790
	30	7.6497	14.8182	0.2692	17.0361	0.9991	0.4576	0.5885
	40	7.9699	13.6992	0.2601	35.8265	0.9994	0.3217	0.5335
	50	7.6914	12.5435	0.2501	40.3726	0.9995	0.2563	0.4738

ment, structure and flow relationships, and physical parameters and sensory evaluation correlation. Thixotropy values are also tabulated in Table 3. The values lead to the conclusion that Lidl, Kraft, Rechelt, Heinz, Heinz Egypt and GSF Egypt tomato ketchups exhibit thixotropic properties but Werder and Americana Egypt tomato ketchups exhibit rheopectic properties which could be referred to the high percentage of native starch. As the temperature is increased, the intermolecular distances increase and therefore the viscosity will decrease for these main reasons. The viscosity is a function of temperature and the dissolved solid concentration [42].

Effective viscosity

The effective viscosity was calculated for the Herschel–Bulkley model by using Eq. (2) as mentioned by Senge [20]. The results are given in Table 3.

The relationship between η_{eff} and temperature of all the tomato ketchup brands under investigation was examined. Significantly higher correlation was found between η_{eff} and temperature. η_{eff} decreases with an increase in temperature.

Flow activation energy and the effect of temperature on viscosity of tomato ketchup

The flow activation energy has been related to some fundamental thermodynamic properties of Newtonian fluids. For example E_a has been found to be approximately one third or one quarter of the heat of vaporization, depending on the shape and bonding of the liquid molecules. Empirical equations have been suggested for the estimation of the flow activation energy as a function of the viscosity and the temperature of various classes of liquids [43]. The flow activation energy decreased significantly when suspended particles were present in the product, as in cloudy juices and fruit purees. In pseudoplastic fruit products, the flow activation energy was directly proportional to the flow behaviour index, i.e., the more pseudoplastic the product, the less the effect of temperature on its apparent viscosity.

The flow activation energies of the pseudoplastic products (tomato ketchup) as reported in Table 4 were calculated at a constant shear rate (100 1/s). The viscosity decreases with temperature; this effect of temperature on the flow behaviour of fluid foods can be described by the Arrhenius relationship [26, 44, 45].

The Arrhenius constants for the temperature range 0–50 °C (η_∞ and E_a) together with the regression coefficients are listed in Table 4. For the flow activation energy, the values range from 7.12 to 10.87 kJ/mol and depend on the chemical composition. The activation energy increases with the soluble solids contents: Americana Egypt tomato ketchup total solids 33.35% and E_a=10.56 kJ/mol, and Kraft tomato ketchup total solids 24.36% and E_a=7.71 kJ/ mol. These results are in agreement with those obtained by Rani and Banins [9], who reported activation energies of laboratory ketchups of 3.36 and 4.88 kcal/mol for commercial ketchup samples. Also these results have trends in accordance with results obtained for different tomato products with similar characteristics by Harper and El Sahrigi [46], who reported E_a=3.83 kcal/mol K for a tomato juice concentrate of 30% solids using high shear rates of 500–800 1/s. The E_a value for tomato concentrates of 30–36% solids was 2.3±0.3 kcal/mol K [47]. Furthermore, the calculation of E_a may be useful in estimating the effect of homogenization where it would be hypothesized that the homogenized concentrate would have a higher E_a than the non-homogenized control owing to an increase in the number of insoluble particles, a decrease in particle size and a decrease in viscosity.

Oscillatory tests

The oscillatory test, also called the dynamic rheological experiment, can be used to determine viscoelastic properties of food. The storage modulus G' expresses the magnitude of the energy that is stored in the material or that is recoverable per cycle of deformation. G'' is a measure of the energy that is lost as viscous dissipation

Table 4 Dynamic shear data of some selected tomato ketchups ($G'$and G'' versus frequency, rad/s).

Product	T (°C)	G′			G″			Product	T (°C)	G′			G″		
		Constant K′ (Pa)	Constant n′	R^2	Constant K″ (Pa)	Constant n″	R^2			Constant K′ (Pa)	Constant x	R^2	Constant K″ (Pa)	Constant y	R^2
Lidl	0	307.36	0.1691	0.997	67.915	0.3463	0.998	Reichelt	0	476.73	0.1354	0.999	84.4310	0.2496	0.999
	10	299.44	0.1467	0.999	56.772	0.3304	0.999		10	395.98	0.1070	0.998	67.5040	0.2208	0.999
	20	292.52	0.1209	0.999	52.074	0.3146	0.999		20	380.35	0.1032	0.999	58.0750	0.2397	0.998
	30	272.88	0.1183	0.996	41.486	0.3042	0.999		30	339.21	0.1143	0.996	51.0240	0.2257	0.999
	40	267.93	0.1158	0.995	41.222	0.2844	0.998		40	319.34	0.1219	0.994	45.6410	0.2435	0.998
	50	233.40	0.0999	0.995	40.369	0.2586	0.998		50	317.09	0.0906	0.998	46.6270	0.2235	0.997
Kraft	0	259.85	0.1508	0.998	57.622	0.3399	0.995	American Egypt	0	129.14	0.1818	0.999	25.703	0.3132	0.998
	10	255.35	0.1233	0.997	51.782	0.3280	0.998		10	123.41	0.1554	0.998	22.532	0.3142	0.998
	20	250.82	0.1225	0.999	46.731	0.3081	0.995		20	121.54	0.1454	0.994	19.040	0.3076	0.999
	30	247.17	0.1080	0.997	43.489	0.2880	0.997		30	114.56	0.1150	0.998	18.651	0.3054	0.998
	40	233.55	0.1021	0.996	37.741	0.2695	0.997		40	106.66	0.1154	0.999	16.594	0.3060	0.997
	50	230.49	0.1014	0.994	31.326	0.2583	0.999		50	100.14	0.1081	0.996	16.701	0.3001	0.996
Werder	0	208.28	0.1523	0.998	38.974	0.2727	0.998	Heinz Egypt	0	486.48	0.1329	0.999	89.521	0.2995	0.999
	10	195.25	0.1467	0.997	35.749	0.2596	0.998		10	448.73	0.1264	0.999	75.446	0.2857	0.999
	20	184.90	0.1445	0.995	34.526	0.2447	0.997		20	398.21	0.1241	0.998	59.291	0.2779	0.999
	30	180.21	0.1329	0.996	31.780	0.2311	0.996		30	376.41	0.1119	0.997	57.196	0.2685	0.999
	40	177.42	0.1211	0.995	29.480	0.2262	0.998		40	364.83	0.1044	0.999	45.452	0.2559	0.999
	50	171.53	0.1142	0.999	26.800	0.2217	0.997		50	339.67	0.0953	0.998	42.598	0.2385	0.999
Heinz	0	323.52	0.158	0.999	66.122	0.3337	0.999	GSF Egypt	0	381.04	0.1689	0.997	79.666	0.3183	0.999
	10	313.49	0.1401	0.999	54.888	0.3287	0.999		10	345.54	0.1526	0.998	72.905	0.3178	0.999
	20	309.19	0.1156	0.997	49.472	0.3226	0.999		20	328.99	0.1392	0.999	61.716	0.3106	0.999
	30	297.17	0.1063	0.998	47.421	0.3067	0.998		30	312.51	0.1390	0.996	52.056	0.3070	0.998
	40	289.82	0.1022	0.995	41.898	0.2934	0.997		40	307.56	0.1158	0.998	47.186	0.3016	0.999
	50	286.39	0.0835	0.998	35.227	0.2895	0.998		50	293.09	0.1129	0.997	46.686	0.2978	0.998

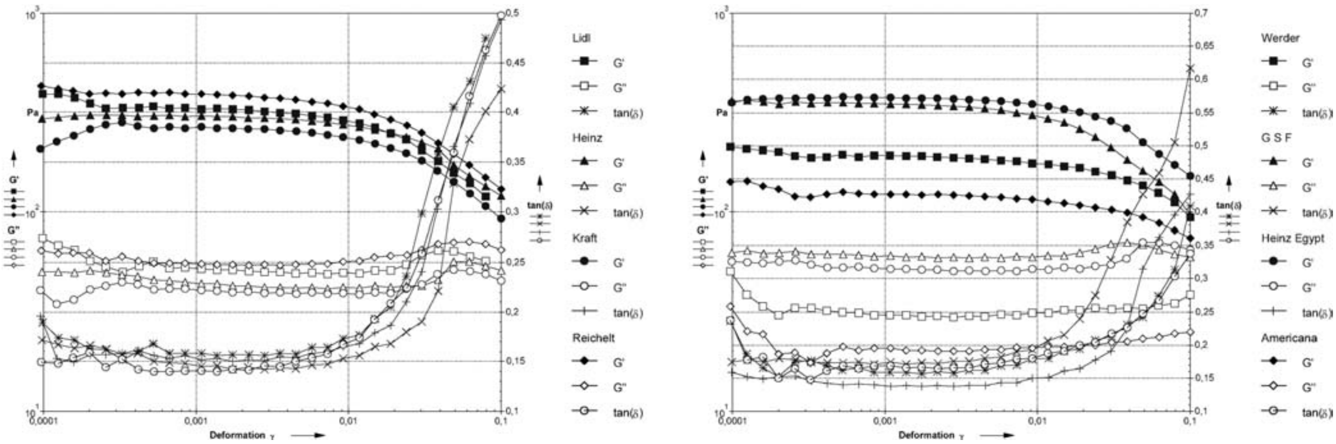

Fig. 1 Amplitude sweeps for tomato ketchups at 20 °C. The storage modulus (G') and the loss modulus (G'') curves are shown as a function of the deformation (γ).

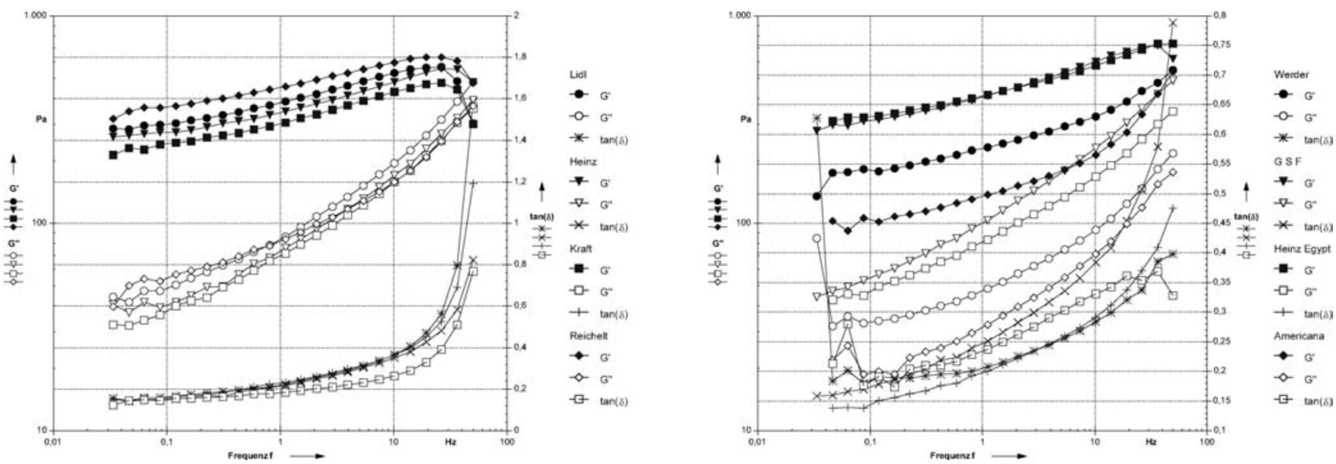

Fig. 2 Frequency sweeps: G' and G'' for tomato ketchups as a function of the frequency at20 °C.

per cycle of deformation. Therefore, for a perfectly elastic solid, all the energy is stored, i.e. G'' is zero and the stress and the 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°.

Amplitude sweeps

The amplitude sweep should achieve the following three aims:

1. Determination of the limit of the linear viscoelastic range (LVE range). The limit of the range is exceeded at the point at which the first of the two curves (G' or G'' function) begins to leave the constant plateau value significantly (e.g. showing a decreasing G' value). The permitted bandwidth can be defined by the user.
2. Characterization of the material structure. Does the sample show structure formation with $G'>G''$ or liquid character with $G''>G'$? All the ketchup samples show $G'>G''$ in the LVE range, which means they all have a semisolid character at very low deformation.
3. Evaluation of the structural strength as the G' value in the LVE range (sometimes called "rigidity").

The experimental values of the amplitude sweep measurement obtained for all the tomato ketchups blends at 20 °C are shown in Fig. 1. The value of G' was higher than that of G'', which showed that the tomato ketchups were more elastic than viscous.

Frequency sweep

The oscillatory test was carried out in the frequency range 10^{-3}–100 Hz and at 0, 10, 20, 30, 40 and 50 °C. The frequency sweep for the tomato ketchups at 20 °C is shown in Fig. 2. Plots of logω versus log$G'$and logG'' dynamic rheological data were subjected to linear regression and the magnitudes of the intercepts, slopes and

Table 5 Sensory properties of tomato ketchup. The values represent the rankings of 20 panellists (mean plus/minus standard error).

Products	Sensory attributes				
	Consistency (texture)	Colour	Taste	Odour	Overall acceptability
	(25)	(25)	(25)	(25)	(100)
Lidl	18.00±1.05[a]	19.39±0.96[a]	18.39±0.88[b]	17.72±0.99[a]	77.61±3.18[a]
Kraft	19.11±0.73[a]	18.17±1.39[a]	16.39±1.14[a,b]	16.39±0.91[a]	76.06±2.88[a]
Werder	19.06±0.99[a]	19.39±1.18[a]	15.56±1.33[a]	18.50±1.13[a,b]	76.16±3.42[a]
Heinz	17.39±0.99[a]	18.33±1.04[a]	14.11±0.74[a]	16.28±1.19[a]	70.44±2.00[a]
Reichelt	18.28±1.47[a]	18.39±1.30[a]	18.39±1.16[b]	19.17±1.20[b]	73.89±2.80[a]
Least significant digit analysis at $p \leq 0.05$	2.9734	3.2746	2.9653	3.0186	8.0273
Americana Egypt	20.62±0.74[b]	20.23±0.53[b]	15.92±1.36[a]	15.85±1.06[a]	79.15±2.28[b]
Heinz Egypt	15.38±1.16[a]	17.23±1.06[a]	16.62±1.23[a]	16.92±1.09[a]	71.00±3.07[a]
GSF Egypt	20.92±0.59[b]	20.77±0.68[b]	17.46±1.01[a]	18.00±0.78[a]	80.62±2.29[b]
LSD at $p \leq 0.05$	2.4076	2.1929	3.3491	2.7379	7.1463

[a,b]There is no significant difference ($p \geq 0.05$) between any two means that have the same superscripts, within the same acceptability attribute

R^2 are summarized in Table 4. When the deformation was less than 0.001 the ketchups showed ideal elastic behaviour like viscoelastic materials. If the storage and the loss moduli as well as the loss angle are plotted versus angular frequency ω, the viscoelastic behaviour of the sample can be described very well by Eqs. (3) and (4) [48].

The frequency sweep measurements agree with results obtained previously. In particular this means that, within the applied frequency range, the storage modulus was much larger than the loss modulus for all the tomato ketchups, indicating dominant elastic properties (Fig. 2). In such dispersions the fluid properties are more important and only a part of the energy input is stored. The results of the oscillation measurements are now evaluated systematically, analogous to the rheological basic tests without the appearance of rheopectic behaviour.

In every case it was found that tomato ketchup does not show gel structure formation. The composition as the interactions between the physical and chemical properties is reflected in the different levels of G', G'' and tanδ. The results of the oscillatory tests are specifically different from the results of the shear rate examination

$$\dot{\gamma} = 100\ 1/\text{s}.$$

Loss angle δ (phase angle) values

Another popular material function used to describe viscoelastic behaviour is the tangent of the phase shift or phase angle (called tanδ), which is also a function of frequency:

$$\tan\delta = G''/G'. \tag{6}$$

Observations of polymer systems give the following numerical ranges for tan δ: very high for dilute solutions, 0.2–0.3 for amorphous polymers, low (near 0.01) for glassy crystalline polymers and gels [50]. The values of tanδ for all the tomato ketchups showed that tanδ ranged between 0.27–0.18, 0.29–0.17, 0.24–0.19, 0.25–0.16, 0.21–0.17, 0.3–0.2, 0.23–0.16 and 0.27–0.19 for Lidl, Kraft, Werder, Heinz, Reichelt, Americana, Heinz Egypt and GSF Egypt tomato ketchups, respectively. Significant correlation was found between tanδ and temperature. The tanδ values decreased with an increase in temperature.

Sensory evaluation of tomato ketchup

As in all foods, the organoleptic tests are generally the final guide of the quality from the consumer's point of view [51]. Thus, it is beneficial to make a comparison between tomato ketchups. There was no significant difference for the tomato ketchups in consistency, colour, odour, taste and overall acceptability. On the other hand, the scores showed significant differences between Heinz Egypt ketchup and the other products. The highest consistency scores were for GSF Egypt ketchup (20.92) and the lowest consistency scores were for Heinz Egypt ketchup (15.38). The colour scores of the GSF Egypt ketchup and the Americana ketchup were higher than for the other tomato ketchup products. The overall acceptability for the Heinz and Heinz Egypt tomato ketchups was lower than those of the other ketchup products (70.44 and 71.0, respectively). Also the results of the sensory evaluation scores are shown in Table 5.

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